

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9647/01

Paper 1 Multiple Choice

29 August 2016
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluids.

Write your name, index number and tutorial class on the Answer Sheet in the spaces provided unless this has been done for you.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **17** printed pages and **1** blank page.



Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 3.00 g of an impure sample of calcium carbonate was heated strongly until there was no change in mass. 200 cm³ of carbon dioxide, measured at room conditions, was obtained.

What is the percentage purity of calcium carbonate?

- A** 27.8 % **B** 29.8 % **C** 30.4 % **D** 35.8 %

- 2 *Use of the Data Booklet is relevant to this question.*

Which underlined element in the following species has the +6 oxidation number?

- A** ReOC_l₄
B H₂P₂O₇²⁻
C TiCl₄
D SbCl₅²⁻

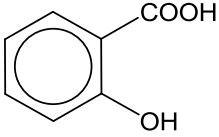
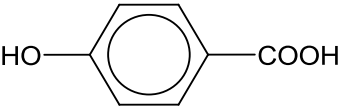
- 3 *Use of the Data Booklet is relevant to this question.*

Deuterium, ²₁D, is an isotope of hydrogen.

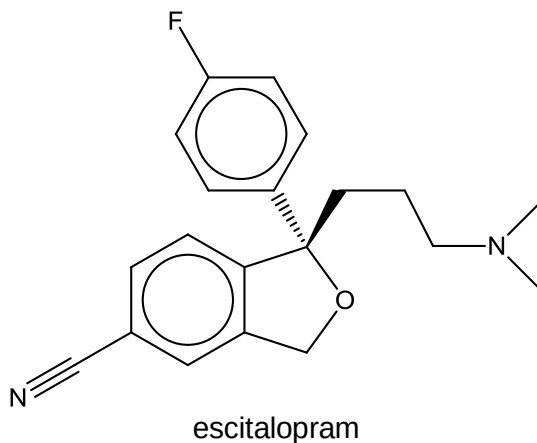
Which of the following species has more electrons than protons, and more neutrons than protons?

- A** D₃O⁺ **B** ND₄⁺
C OD⁻ **D** A/D₄⁻

- 4 In which of the following pairs does the first compound have a higher melting point than the second compound?

	first compound	second compound
A	Mg ₃ N ₂	Al ₂ O ₃
B	NH ₂ OH	H ₂ O
C	CH ₃ OCH ₃	(CH ₃) ₂ NH
D		

- 5 Which of the following bonds is **not** present in the following molecule?



- A a σ bond formed by sp^3-sp^2 overlap between two C atoms
 B a σ bond formed by $sp-sp$ overlap between C and N atoms
 C a σ bond formed by sp^2-sp^2 overlap between two C atoms
 D a σ bond formed by sp^3-sp^2 overlap between C and N atoms
- 6 Which of the following sets of compounds and ions is arranged in **increasing** bond angles?
- A $\text{NO}_2^+ < \text{CO}_3^{2-} < \text{SO}_4^{2-}$
 B $\text{IF}_4^- < \text{N}_2\text{O}_4 < \text{N}_3^-$
 C $\text{ICl}_2^- < \text{H}_2\text{S} < \text{NO}_2$
 D $\text{SCl}_2 < \text{C}_2\text{H}_2 < \text{CH}_2\text{Cl}_2$
- 7 0.50 g of a volatile liquid was placed in a syringe with a frictionless piston. The syringe was slowly warmed up till 91.0°C at atmospheric pressure. The volume occupied in the syringe was 200.0 cm^3 when all the liquid was vaporised.

Assuming the vapour behaves as an ideal gas, what is the relative molecular mass of the liquid?

- A 18.7 B 74.9 C 93.5 D 149.8

- 8 The enthalpy change when solid calcium chloride dissolves in water is -120 kJ mol^{-1} . 250 g of water is placed in an insulated cup containing 11.1 g of calcium chloride.

If the solution has the same specific heat capacity as liquid water, what is the rise in temperature of the solution?

- A $\frac{11.1 \times 120}{250 \times 4.18} \text{ K}$ B $\frac{11.1 \times 120 \times 10^3}{111 \times 250 \times 4.18} \text{ K}$
 C $\frac{250 \times 4.18}{11.1 \times 120 \times 10^3} \text{ K}$ D $\frac{11.1 \times 120}{111 \times 250 \times 4.18} \text{ K}$

- 9 Use of the Data Booklet is relevant to this question.

The standard half-cells of four metals Mg, P, Q and R and their respective cations in solution were connected in pairs and the potential difference recorded.

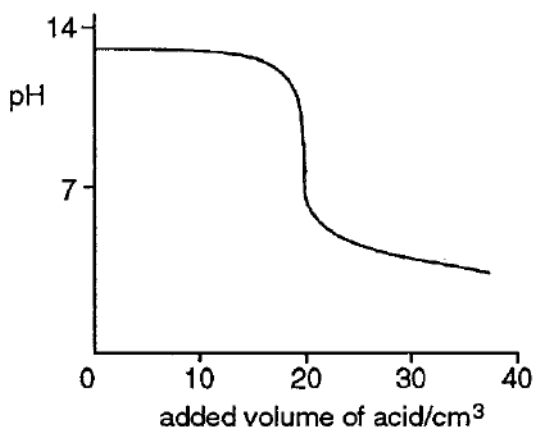
The results obtained are as shown.

positive electrode	negative electrode	e.m.f. /V
P	Mg	+1.60
Q	Mg	+2.22
Q	R	+2.55

Which of the following is the **decreasing** order of reducing power for the four metals?

- A $R > \text{Mg} > P > Q$
 B $R > \text{Mg} > Q > P$
 C $Q > P > \text{Mg} > R$
 D $P > Q > \text{Mg} > R$
- 10 Which of the following statements is always true for a chemical reaction that has reached chemical equilibrium?
- A The yield of the product(s) is greater than 50%.
 B The rate of the forward reaction is greater than the backward reaction.
 C The amounts of reactants and products do not change.
 D Both forward and backward reactions have stopped.

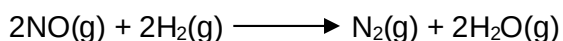
- 11 The graph shows the change in pH when 0.10 mol dm^{-3} acid is gradually added to $V \text{ cm}^3$ of 0.10 mol dm^{-3} alkali.



Which of the following combinations could have given these results?

	V	alkali	acid
A	10	$\text{Sr}(\text{OH})_2$	$\text{CH}_3\text{CO}_2\text{H}$
B	20	$\text{Ba}(\text{OH})_2$	HCl
C	10	$\text{Ca}(\text{OH})_2$	H_2SO_4
D	20	NaOH	$\text{HO}_2\text{C}-\text{CO}_2\text{H}$

- 12 Nitrogen oxide reacts with hydrogen gas as shown in the equation below.



The reaction was determined to be second order with respect to NO and first order with respect to H_2 . In an experiment, 2.0 mol dm^{-3} of excess NO was used to react with H_2 , the concentration of H_2 decreased to 6.25% of its original value in 24 minutes.

How many minutes will it take for the concentration of H_2 to decrease to 6.25% of its original value if the experiment was repeated using an excess of 4.0 mol dm^{-3} of NO?

- A** 1.5 **B** 4.5 **C** 6.0 **D** 9.0

- 13 **Figure 1** shows the melting points of eight consecutive elements whereas **Figure 2** shows the third ionisation energies of another set of eight consecutive elements, inclusive of element **Z** in **Figure 1**.

Which of the options in **Figure 2** correspond to element **Z** in **Figure 1**?

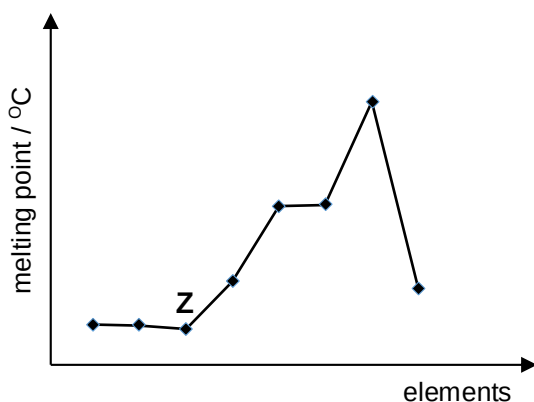


Figure 1

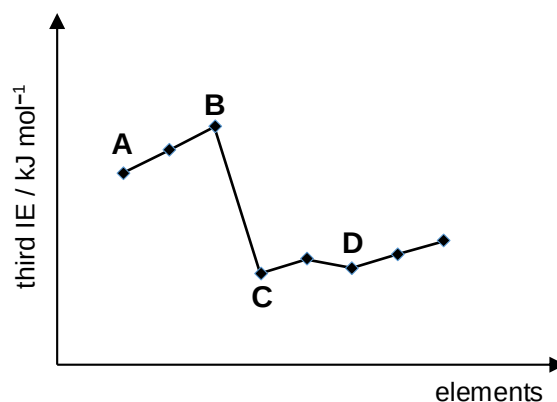


Figure 2

- 14 An equimolar amount of MgCl_2 , PCl_5 and KCl were separately added to three beakers, each containing 50 cm^3 of water.

Which option correctly shows the resultant solutions arranged in **increasing** pH?

- A MgCl_2 , PCl_5 , KCl
 - B PCl_5 , MgCl_2 , KCl
 - C KCl , MgCl_2 , PCl_5
 - D PCl_5 , KCl , MgCl_2
- 15 Which of the following properties would **not** be expected for Group II elements or their compounds?
- A Barium sulfate has a higher temperature of decomposition than magnesium sulfate.
 - B Barium oxide in water produces a solution which reacts with dilute hydrochloric acid to give a solution with a pH of approximately 7.
 - C Beryllium forms compounds with the least covalent character.
 - D Upon heating the nitrates of Group II elements, the volume of nitrogen dioxide evolved is four times as great as the volume of oxygen.

- 16** Interhalogen compounds contain atoms of two or more different halogens. The interhalogen ICl was reacted with excess aqueous sodium hydroxide for a period of time.

What is the relative proportion of each ion present in the solution after this reaction?

	Cl^-	I^-	IO^-	IO_3^-
A	1	1	0	0
B	1	0	1	0
C	1	2	3	1
D	3	2	0	1

- 17** Which statement about hydrogen halides is **incorrect**?

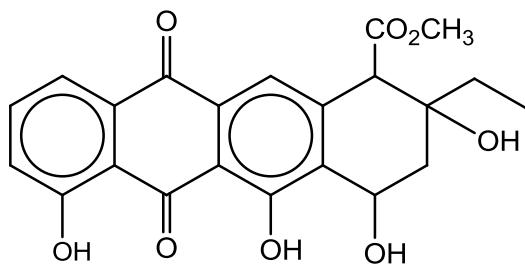
- A** The acidity of hydrogen halides increases down the group.
- B** The reducing power of hydrogen halides increases down the group.
- C** The halogens, with the exception of fluorine, react with hydrogen to form hydrogen halides which have permanent dipole – permanent dipole interactions.
- D** The thermal stability of hydrogen halides increases down the group due to a larger electron cloud that is more polarisable.

- 18** *Use of the Data Booklet is relevant to this question.*

Which of the following is **not** true about the first row transition metals and their compounds?

- A** $\text{Fe}(\text{CN})_6^{3-}$ does not oxidise I^- .
- B** $\text{Fe}_2(\text{CO}_3)_3$ can be prepared by reacting $\text{FeCl}_3(\text{aq})$ with $\text{Na}_2\text{CO}_3(\text{aq})$.
- C** On addition of $\text{H}_2\text{O}_2(\text{aq})$ to hot acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, a green solution is formed.
- D** On addition of $\text{Co}(\text{NO}_3)_3$ to water, a gas that relights a glowing splint is produced.

- 19 Aklavinone is a tetracycline antibiotic.



aklavinone

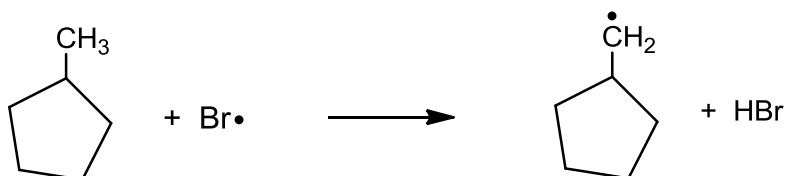
Which combination of the number of chiral centres and of the number of sp^2 and sp^3 hybridised carbon atoms does it possess?

	number of chiral centres	number of sp^2 hybridised carbon	number of sp^3 hybridised carbon
A	3	14	8
B	3	15	7
C	5	14	8
D	5	15	7

- 20 Methylcyclopentane reacts with bromine in the presence of UV light.

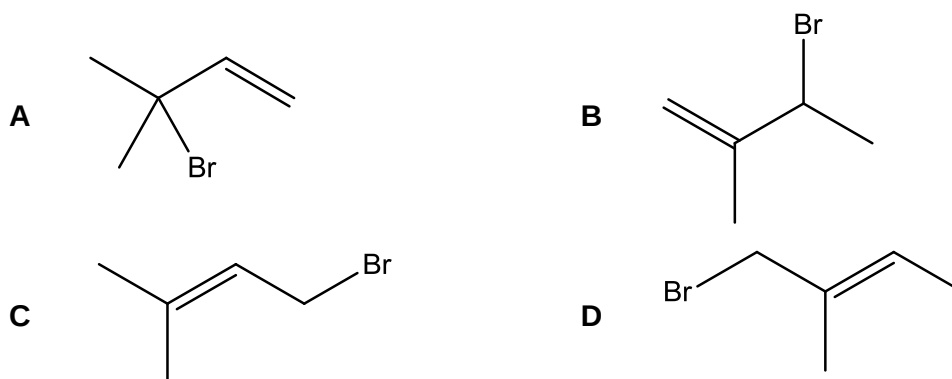
Which statement is true about this reaction?

- A** A possible rate determining step for this reaction is

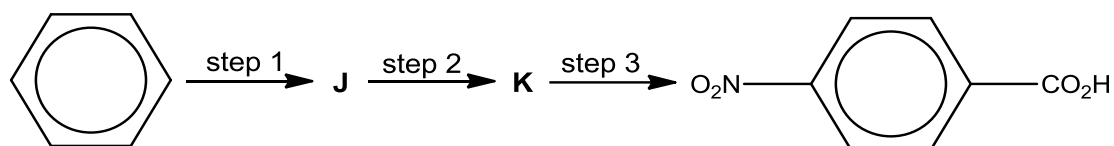


- B** There are three possible monosubstituted products.
C Methylcyclopentane will react slower with chlorine than bromine in the presence of UV light.
D A by-product formed in this reaction is hydrogen.

- 21 Which is the main product formed when one mole of 2-methylbuta-1,3-diene is allowed to react with one mole of HBr at room temperature for a prolonged period of time?



- 22 Which of the following could be the reagents and conditions for the three steps used in the synthesis shown below.



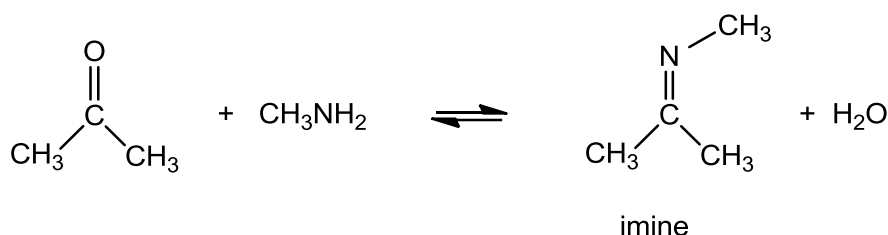
	step 1	step 2	step 3
A	concentrated HNO ₃ and concentrated H ₂ SO ₄ , heat	CH ₃ Cl and AlCl ₃	KMnO ₄ and H ₂ SO ₄ , heat
B	CH ₃ (CH ₂) ₂ Cl and AlCl ₃	K ₂ Cr ₂ O ₇ and H ₂ SO ₄ , heat	concentrated HNO ₃ and concentrated H ₂ SO ₄ , heat
C	CH ₃ Cl and AlCl ₃	concentrated HNO ₃ and concentrated H ₂ SO ₄ , heat	K ₂ Cr ₂ O ₇ and H ₂ SO ₄ , heat
D	CH ₃ (CH ₂) ₂ Cl and AlCl ₃	concentrated HNO ₃ and concentrated H ₂ SO ₄ , heat	KMnO ₄ and H ₂ SO ₄ , heat

- 23 A student investigated four different fuels. Each fuel was used separately to raise the temperature of 1 dm³ of water from 20 °C to 100 °C. Each fuel undergoes complete combustion. All other conditions were kept the same in each experiment.

Which fuel will produce the smallest amount of carbon dioxide in these experiments?

	fuel	standard enthalpy change of combustion/ kJ mol ⁻¹
A	ethane	1560
B	ethanol	1367
C	methanol	715
D	propane	2220

- 24** The main reason that phenol is a better Brønsted acid than cyclohexanol is
- A** that it is a better proton donor.
 - B** the cyclohexyl group is an electron donating group by induction, which destabilises the anion formed during the dissociation.
 - C** phenol is able to stabilise the anion formed during the dissociation by resonance, where the electrons are delocalised in the phenyl ring.
 - D** the phenyl group is an electron withdrawing group by induction, which stabilises the anion formed during the dissociation.
- 25** Propanone reacts with methylamine to form an imine as shown in the equation.

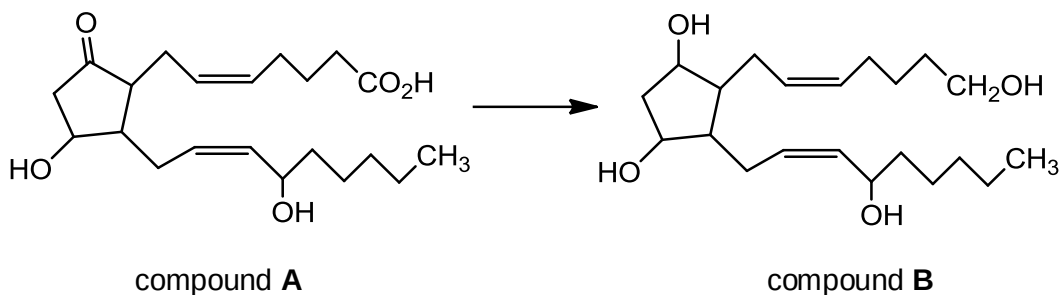


Similarly, propanone also reacts with hydroxylamine, NH_2OH , to form an oxime.

Which of the following best describes the type of reaction that has occurred and the structural formula of the oxime?

	type of reaction	structural formula of the oxime
A	nucleophilic addition	$ \begin{array}{c} \text{N} - \text{H} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array} $
B	nucleophilic addition	$ \begin{array}{c} \text{N} - \text{OH} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array} $
C	condensation	$ \begin{array}{c} \text{N} - \text{H} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array} $
D	condensation	$ \begin{array}{c} \text{N} - \text{OH} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array} $

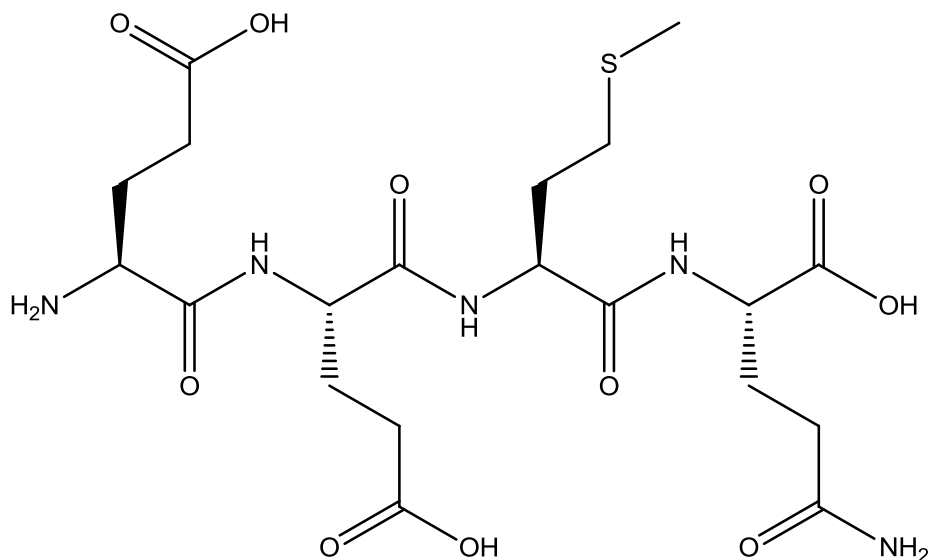
- 26 Compound **A** is an example of a prostaglandin, which belongs to a group of physiologically active lipid compounds having diverse hormone-like effects in animals.



Which reagent will convert compound **A** to compound **B** efficiently?

A NaBH_4 C H_2/Pt	B $\text{LiAlH}_4/\text{dry ether}$ D $\text{Sn}/\text{concentrated HCl}$
- 27 Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, is found in sour milk.
- Which of the following equations represent a possible reaction with lactic acid?
- A** $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}(\text{OCH}_3)\text{CO}_2\text{H} + \text{H}_2\text{O}$
- B** $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CH}(\text{OCOCH}_3)\text{CO}_2\text{H}$
- C** $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}(\text{Cl})\text{CO}_2\text{H} + \text{POCl}_3 + \text{HCl}$
- D** $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H} + 4\text{I}_2 + 7\text{NaOH} \rightarrow (\text{CO}_2^-\text{Na}^+)_2 + \text{CHI}_3 + 5\text{NaI} + 6\text{H}_2\text{O}$

28

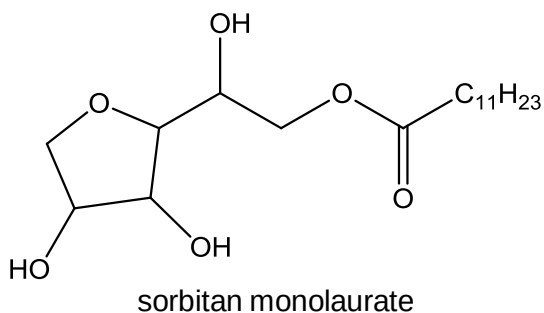


The tetrapeptide above is a fragment of SNAP-25, a substrate of Botulinum toxin (Botox).

How many moles of NaOH will react with 1 mole of the tetrapeptide when it is heated under reflux with aqueous sodium hydroxide until no further reaction occurs?

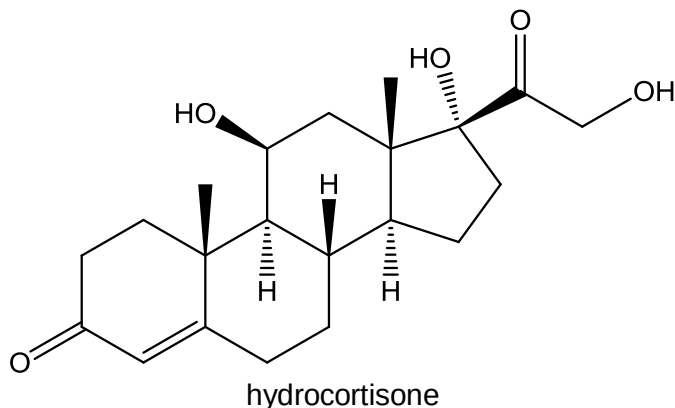
- A** 3 **B** 5 **C** 6 **D** 7

- 29 The demand for 'natural' shampoos and detergents has led to the development of more biodegradable detergents such as sorbitan monolaurate, which is made from plants.



Which of the following statements about sorbitan monolaurate is correct?

- A It is optically inactive.
 - B It can react with concentrated sulfuric acid on heating.
 - C There will be an orange precipitate formed upon adding 2,4–dinitrophenylhydrazine to the compound.
 - D There will be no colour change on heating the compound with acidified potassium dichromate(VI) solution.
- 30 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.



Which of the following statements about hydrocortisone is correct?

- A When treated with an excess of hot concentrated acidified KMnO_4 , it forms a compound containing seven carbonyl groups.
- B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.
- C When treated with cold dilute KMnO_4 , it forms a compound containing two additional hydroxy groups.
- D When treated with NaBH_4 in the presence of methanol, it forms a compound containing seven hydroxy groups.

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

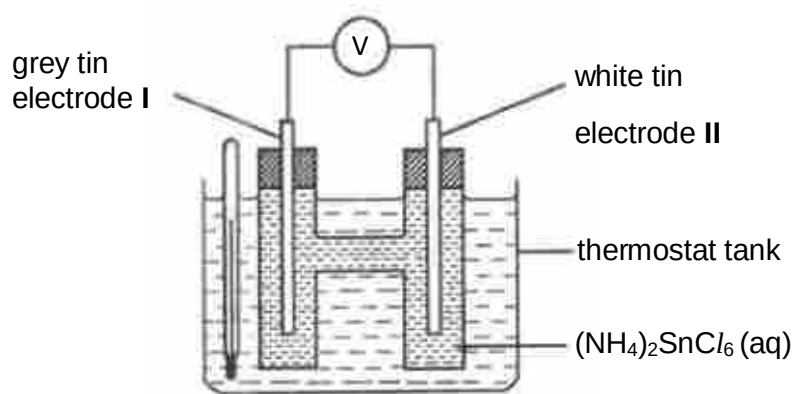
No other combination of statements is used as a correct response.

- 31** Epsom salt is a sedative for the nervous system. Its active ingredient is magnesium sulfate which is soluble in water. The corresponding barium sulfate is insoluble in water.

What factors account for the difference in solubility between magnesium sulfate and barium sulfate?

- 1** Magnesium sulfate has a higher solubility product than barium sulfate.
- 2** Magnesium ions have a higher enthalpy of hydration than barium ions.
- 3** Magnesium sulfate has a larger magnitude of lattice energy than barium sulfate.

- 32** The diagram shows a set-up used to find the transition temperature at which white tin and grey tin are in equilibrium. This was found to be 15 °C. Above 15 °C, grey tin from electrode **I** dissolves and is deposited on electrode **II** as white tin.



Which of the following statements about the set-up are true?

- 1** At 15 °C, no current flows.
- 2** Below 15 °C, electrons flow through the external circuit from **I** to **II**.
- 3** The conversion of white tin to grey tin is an endothermic process.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

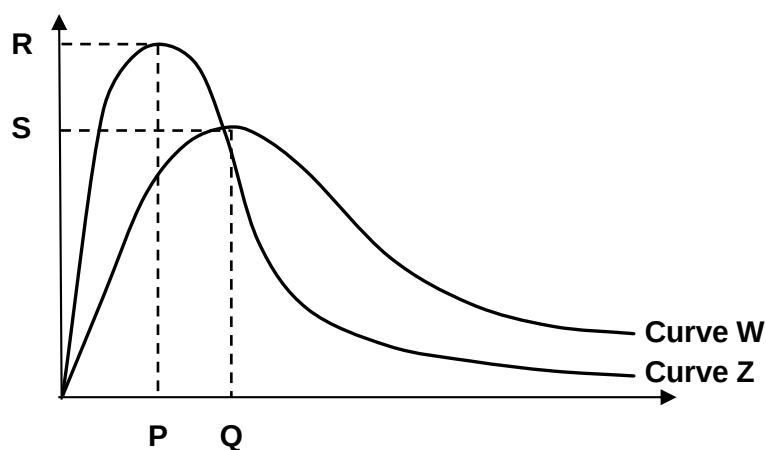
33 The pK_a values of some ammonium ions at 298 K are given below.

ammonium ion	pK_a
$CH_3NH_3^+$	10.66
$(CH_3)_3NH^+$	9.81

Based on the data given, which of the following statements are correct?

- 1 The pH of 0.1 mol dm^{-3} of $(CH_3)_3NH^+Cl^-$ is 5.4.
- 2 $(CH_3)_3N$ is more basic than CH_3NH_2 due to the presence of more electron donating alkyl groups.
- 3 1 mol of $(CH_3)_3N$ requires more HCl for complete neutralisation than 1 mol of CH_3NH_2 .

34 Curve **Z** represents the distribution of energies of the gaseous molecules for an uncatalysed reaction.



Which of the following statements are **false**?

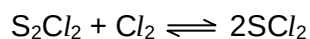
- 1 Curve **W** will be the distribution curve obtained when the reaction is catalysed and **Q** represents the most probable energy of the molecules.
- 2 Curve **W** will be the distribution curve obtained at a higher temperature and **S** represents the most probable energy of the molecules.
- 3 Curve **Z** will be the distribution curve obtained when the reaction is uncatalysed and **P** represents the most probable energy of the molecules.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 35** Sulfur burns in chlorine gas to form disulfur dichloride, S_2Cl_2 . In excess chlorine gas, the following equilibrium is established.



Which statements regarding S_2Cl_2 and its equilibrium with SCl_2 are **correct**?

- 1** S_2Cl_2 dissolves in water to give a solution with pH greater than 7.
- 2** S_2Cl_2 is a liquid at room temperature.
- 3** The sulfur atoms have a bent geometry in both S_2Cl_2 and SCl_2 .

- 36** *Use of the Data Booklet is relevant to this question.*

Which of the following statements are true for green aqueous solution of $V_2(SO_4)_3$?

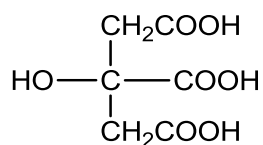
- 1** Zn metal can reduce $V^{3+}(aq)$ to $V^{2+}(aq)$.
- 2** The solution appears green as the d-orbitals are split by the presence of the sulfate ions.
- 3** $V^{3+}(aq)$ can serve as a homogeneous catalyst in the reaction between iodide ions and peroxodisulfate ions.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

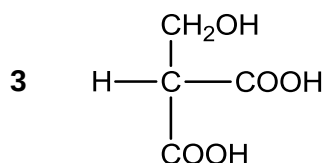
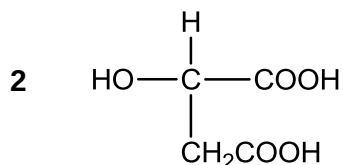
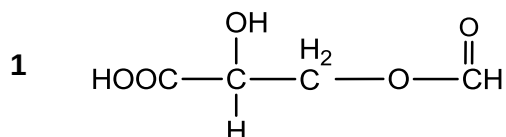
- 37** Unripe fruits often contain polycarboxylic acids. These are acids with more than one carboxylic acid group in their molecule. One such acid is citric acid shown below.



Another polycarboxylic acid present in unripe fruit is a colourless crystalline solid, **W**, which has molecular formula of $\text{C}_4\text{H}_6\text{O}_5$.

A sample of **W** of mass 1.97 g was dissolved in water and the resulting solution titrated with 1.00 mol dm^{-3} NaOH. 29.4 cm^3 of 1.00 mol dm^{-3} NaOH was required for complete neutralisation.

What could **W** be?



- 38** Which of the following statements are always true of the isoelectronic point, pI, of an amino acid?

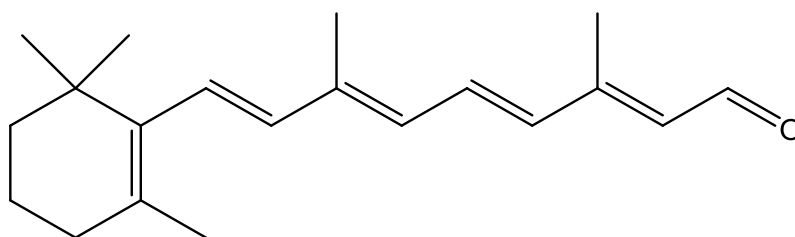
- 1** It is the pH where the zwitterionic form of the amino acid is most dominant.
- 2** It is the pH where the amino acid does not migrate when placed in an electric field.
- 3** It is the average of the first two pK_a values.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

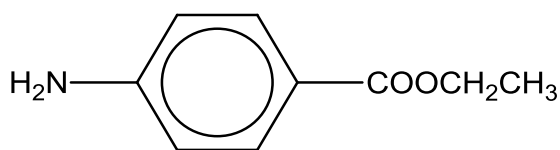
- 39** The rod cells in the retina at the back of the eye contain an alcohol called retinol which is responsible for their sensitivity to light. Retinol is oxidised by an enzyme-catalysed reaction to retinal with the following structure:



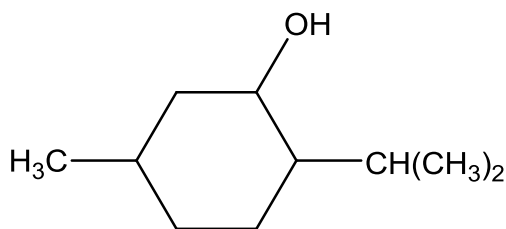
retinal

Which of the following statements about retinal are correct?

- 1** It can react with NH_2NH_2 .
 - 2** The molecular formula of retinal is $\text{C}_{20}\text{H}_{28}\text{O}$.
 - 3** Oxidative cleavage of retinal gives two different organic products.
- 40** Benzocaine and menthol are local anaesthetics used in sunburn ointments and skin lotions. Their structures are shown below:



benzocaine



menthol

Which of the following reagents and conditions can be used to distinguish between the two compounds?

- 1** aqueous bromine, dark
- 2** iodine in aqueous sodium hydroxide, heat
- 3** acidified aqueous potassium manganate(VII), heat

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Answers:

1	2	3	4	5	6	7	8	9	10
A	A	D	B	D	B	B	B	A	C
11	12	13	14	15	16	17	18	19	20
A	C	A	B	C	D	D	B	B	A
21	22	23	24	25	26	27	28	29	30
A	D	A	C	D	B	D	D	B	C
31	32	33	34	35	36	37	38	39	40
C	D	D	B	C	D	C	B	A	B

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9647/02

Paper 2 Structured Questions

16 August 2016
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

For Examiner's Use	
Question no.	Marks
1	
2	
3	
4	
5	
6	
7	
TOTAL	

This document consists of **15** printed pages and **1** blank page.



1 Planning (P)

The solubility of a metal hydroxide, $M(OH)_2$ at a particular temperature is defined as the mass of metal hydroxide that dissolve in 100 g of water.

A saturated solution of the metal hydroxide is one in which no more solid can dissolve at this fixed temperature. At 25°C, the solubility of metal hydroxide is approximately less than 2g /100g of water.

You are to plan an experiment using the method of gravimetric analysis to achieve these objectives:

1. determine the solubility product, K_{sp} of the metal hydroxide accurately;
2. determine how the solubility of the metal hydroxide in sodium hydroxide is affected by the concentration of hydroxide ions.

- (a) (i) Write an equation with state symbols to show the dissolution of the metal hydroxide in water.

..... [1]

- (ii) Suggest and explain how the solubility of the metal hydroxide varies with the concentration of hydroxide ions.

.....
 [1]

- (b) You are provided with:

- pure solid metal hydroxide
- 2.0 mol dm⁻³ of sodium hydroxide
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of a saturated metal hydroxide solution
- the preparation of a suitable range of diluted sodium hydroxide solutions
- an outline of how the results could be used to calculate the solubility of metal hydroxide and its K_{sp} and show how the solubility of metal hydroxide in sodium hydroxide varies with the concentration of hydroxide ions
- the risks involved and safety precautions taken

.....

- (c) Suggest another experimental method to determine how the solubility of metal hydroxide changes with the presence of sodium hydroxide. Suggest the results to be collected.

.....

[2]

[Total: 12]

- 2 **A**, **B** and **C** are three organic molecules which share the same molecular formula, $C_8H_9NO_2$.

You are to make use of the data about the reactions of **A**, **B** and **C** given in the table below to deduce their identities.

reaction	reagent used	A	B	C
1	$KMnO_4(aq)$, $H_2SO_4(aq)$ heat	purple colour remains	purple MnO_4^- decolourised	purple MnO_4^- decolourised
2	excess $Br_2(aq)$	white solid formed with $M_r = 308.8$	no visible reaction	white solid formed with $M_r = 308.8$
3	$NaOH(aq)$ at room temperature	dissolves to give a colourless solution	dissolves to give a colourless solution	does not dissolve at all
4	$Na_2CO_3(aq)$	no visible reaction	effervescence seen	no visible reaction
5	$HCl(aq)$ at room temperature	does not dissolve at all	dissolves to give a colourless solution	dissolves to give a colourless solution

- (a) (i) Deduce the molecular formula of the white solid formed from **A** in reaction 2.
 [1]
- (ii) What type of reaction takes place in reaction 2 for **A**?
 [1]
- (iii) Hence list the possible functional groups present in **A** based on reaction 2 alone.
 [2]
- (b) (i) List the functional groups that are being tested for in reaction 3.
 [2]

- (ii) Identify the gas that is being produced in reaction 4 for **B** and how you would confirm its identity.

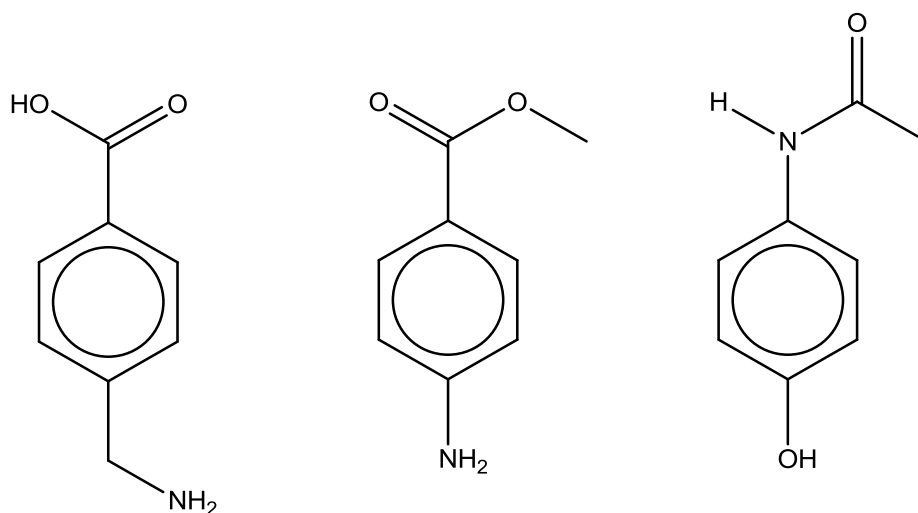
.....

..... [2]

- (iii) Which of the functional groups you have named in **b(i)** is confirmed by reaction 4?

..... [1]

- (c) You now have enough information to determine the identities of **A**, **B** and **C**. Below are three possible structures of **A**, **B** and **C** (not in order).

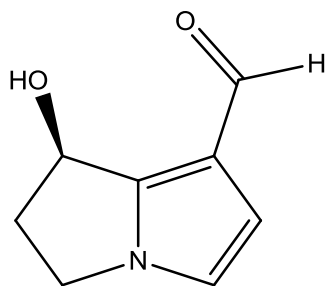


Draw the structural formula of the three compounds in the boxes below.

A	
B	
C	

[3]

- (d) Hydroxydanaidal is an insect pheromone synthesised by male tiger moths from heliotrine in plants. It is an isomer of the three organic molecules above and is made up of two five-membered rings.



hydroxydanaidal

In order for a ring to be aromatic, it has to fulfil the following criteria:

- The ring must have $4n+2$ electrons in the delocalised p-orbital cloud (where n is a positive integer).
- The ring must be planar.
- Every atom in the ring must be able to participate in delocalising the electrons.

- (i) Given that the N atom is sp^2 hybridised, what is the number of p electrons in the right ring of hydroxydanaidal?

..... [1]

- (ii) Hence state if the right ring is aromatic.

..... [1]

- (iii) Suggest reagents and conditions for a reaction that that will distinguish hydroxydanaidal from the three isomers **A**, **B** and **C**.

..... [1]

[Total: 15]

- 3 Group VII elements can form oxoanions of XO_n^- which are strong oxidising agents. One such example is bromate(V) anion, BrO_3^- which can oxidise iodide to form iodine, and itself reduced to bromide.

(a) Write a balanced ionic equation for the reaction between bromate(V) and iodide.

..... [1]

(b) A student wished to analyse the amount of iodine and the bromide ions produced from the above reaction and hence he carried out the following procedures.

- 1) Add 25.0 cm^3 of $0.150 \text{ mol dm}^{-3}$ potassium bromate(V) solution to excess potassium iodide (3 grams) and 5 cm^3 of $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in a 250 cm^3 conical flask.
- 2) Add sufficient chloroform, CHCl_3 , to the above solution immediately and transfer the mixture to a separating funnel.
- 3) Separate the organic and aqueous layers and add barium nitrate solution to the aqueous layer in a beaker.
- 4) Filter the above mixture and add silver nitrate to the filtrate in the conical flask.
- 5) To the resultant mixture in the conical flask in step 4, add sufficient concentrated ammonia and filter once again.

(i) What is the purpose of adding chloroform in step 2?

.....
 [1]

(ii) What is the reason for adding barium nitrate in step 3?

.....
 [1]

(iii) A mixture of two precipitates will be formed when silver nitrate is added into step 4. Suggest the identities of the precipitates.

..... [1]

(iv) Describe clearly what the student will observe in step 5 after he added in concentrated ammonia and performed a filtration. Explain the chemistry behind his method.

.....

 [3]

(c) Explain why fluorine does not form oxoanions such as FO_3^- .

.....

.....

..... [1]

[Total: 8]

4 Compound **X** and compound **Y** are oxides formed from period 3 elements.

When water is added to both oxides, only **X** dissolves but not **Y**. However, **Y** will dissolve when it is added to the aqueous solution of **X** and NaOH (aq) separately.

It is known that aqueous solution of **X** can react with solid potassium hydroxide in a ratio of 1:3.

Identify compound **X** and **Y**, and explain the above reactions with the aid of balanced equations.

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.....

.....

.....

.....

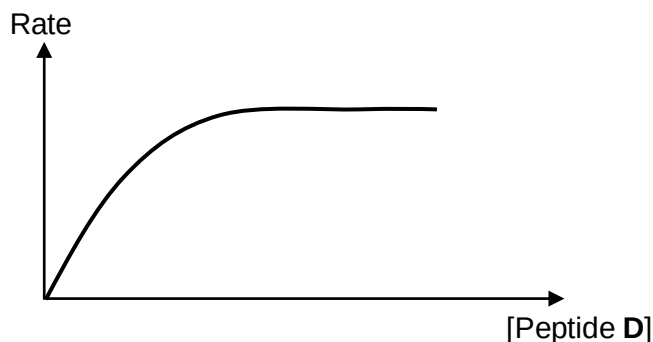
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[Total: 7]

- 5 Chymotrypsin is a digestive enzyme found in the small intestines that can hydrolyse peptide bonds within proteins. It is also used as a form of treatment for sports injuries to reduce pain and inflammation. The three main amino acids involved in the catalytic activity are histidine, aspartic acid and serine.

- (a) The graph shows the results of an investigation of the initial rate of hydrolysis of peptide **D** by the enzyme chymotrypsin. In the experiments, the initial concentration of peptide **D** was varied but that of chymotrypsin was kept constant.

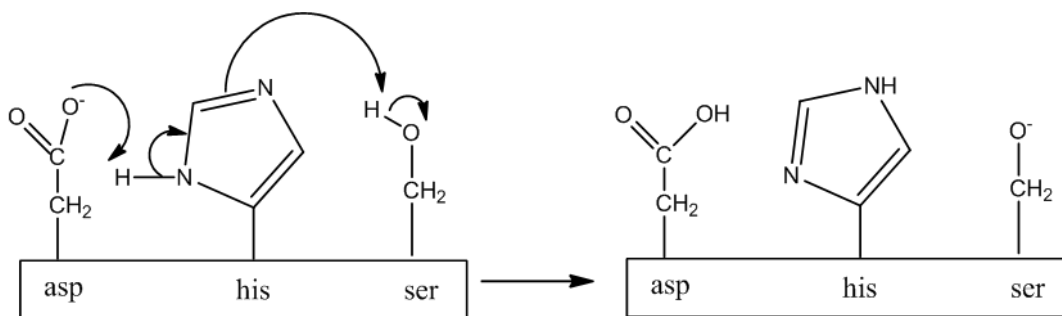


Explain the difference in the rate of hydrolysis at high and low concentrations of peptide **D**.

.....

 [2]

- (b) The first step of the mechanism of the action of chymotrypsin is shown:



- (i) In an aqueous external environment, suggest and explain whether the three amino acids are orientated inward or outward of the compact structure.

.....

 [2]

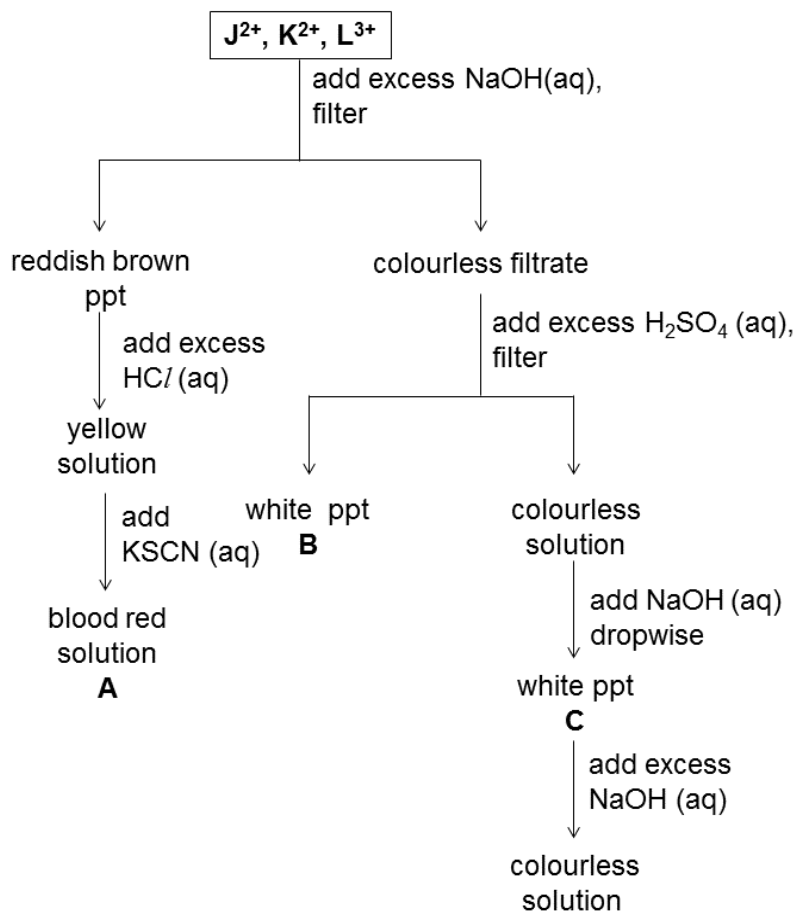
- (ii) State the roles of histidine in the mechanism shown above.
..... [1]
- (iii) Explain with reference to the mechanism, how a low pH might affect the enzymatic activity of chymotrypsin.
.....
..... [2]
- (iv) Draw the structural formula of a tripeptide with the sequence *ser-his-asp*, showing the form which it would exist at pH 4.5 given the pK_a of the R-group in his = 6.04 and pK_a of the R-group in asp = 3.90.

[2]

[Total: 9]

6 Three unknown cations J^{2+} , K^{2+} and L^{3+} are analysed according to the flowchart below.

J, **K** and **L** can be any one of the following: Al, Mn, Fe, Co, Ni, Pb, Zn, Sc.



(a) Identify the three cations and the three unknowns **A**, **B** and **C**.

[6]

cations

J^{2+} :

K^{2+} :

L^{3+} :

unknowns

A:

B:

C:

- (b) Vanadium(II) chloride, VCl_2 is prepared by the thermal decomposition of vanadium(III) chloride, VCl_3 .

(i) Write the electronic configuration of a vanadium atom.

..... [1]

(ii) Hence explain why the third ionisation energy of vanadium is higher than the second ionisation energy.

.....

.....

..... [1]

(iii) Predict, with reason, which of the chlorides of vanadium, VCl_2 or VCl_3 will have a higher melting point.

.....

.....

..... [1]

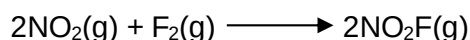
[Total: 9]

- 7 Nitryl fluoride, NO_2F is a colourless gas which acts as a strong oxidising agent and fluorinating agent.

(a) Draw a dot-and-cross diagram of NO_2F .

[1]

- (b) It is known that NO_2F can be produced from nitrogen dioxide and fluorine according to the equation below.



The rate equation for the reaction was also found to be $\text{Rate} = k[\text{NO}_2][\text{F}_2]$.

(i) Propose a two-step mechanism consistent with the above equation, indicating the rate determining step.

.....

..... [2]

- (ii) Given that the reaction is exothermic, sketch a labelled energy profile diagram for the complete reaction path including the formation of the intermediate species.

[3]

- (c) When NO_2 and excess F_2 were mixed together, $[\text{NO}_2\text{F}]$ varies with time, as shown in the table below. The initial $[\text{NO}_2]$ used is $0.400 \text{ mol dm}^{-3}$.

t / min	$[\text{NO}_2\text{F}] / \text{mol dm}^{-3}$	$\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t} / \text{mol dm}^{-3} \text{ min}^{-1}$	$[\text{NO}_2] / \text{mol dm}^{-3}$
0.25	0.150	0.60	0.250
0.50	0.245		
0.75	0.300		
1.00	0.340		
1.25	0.360		
1.50	0.375	0.06	0.025

- (i) Explain why it is necessary to use excess fluorine in this experiment to confirm the order with respect to nitrogen dioxide.

.....

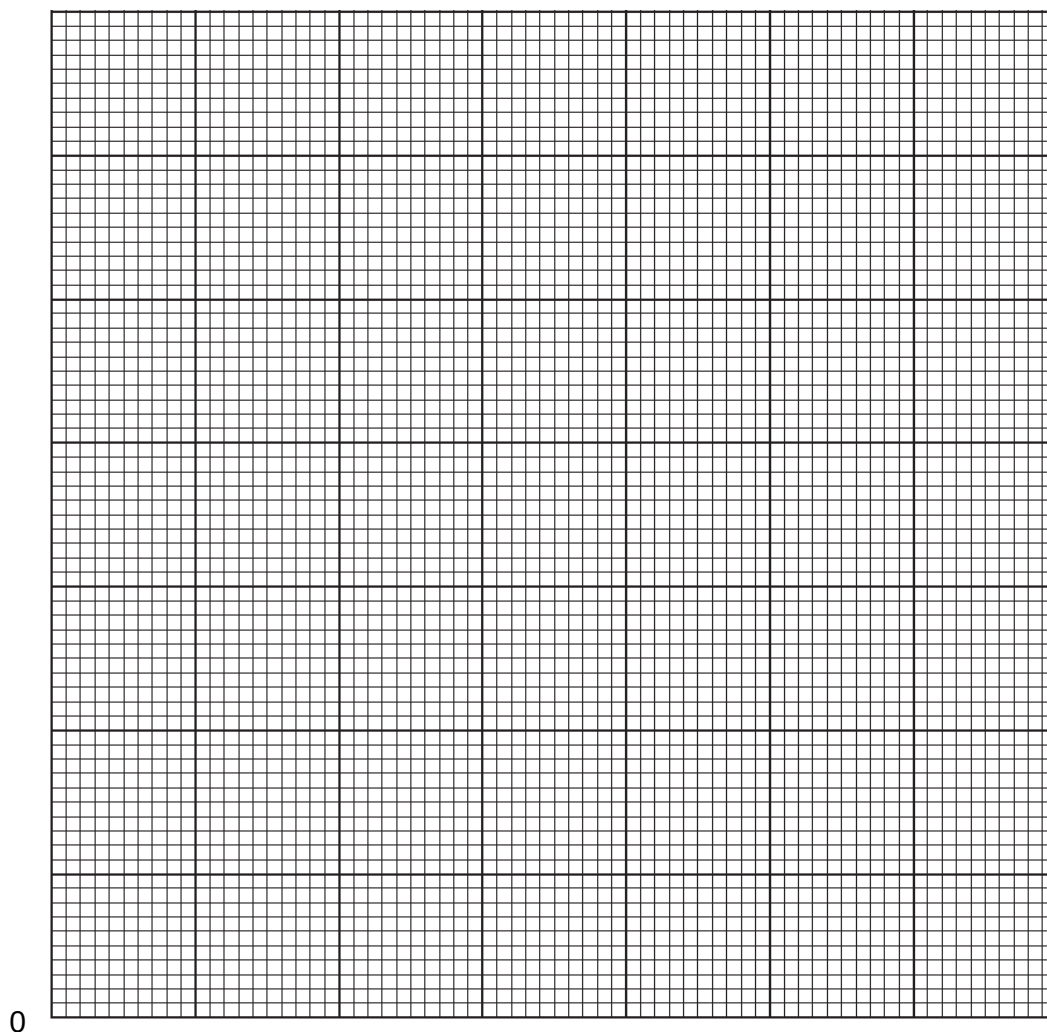
..... [1]

- (ii) The rate at a particular time can be approximated using:

$$\text{rate} = \frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$$

Complete the table above by calculating $\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$ (to 2 decimal places) and the $[\text{NO}_2]$ left (to 3 decimal places) at the respective timings. [2]

- (iii) Hence, plot a graph of $\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$ against $[\text{NO}_2]$ to confirm and explain that the reaction is first order with respect to NO_2 .



.....

[3]

[Total: 12]

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9647/03

Paper 3

23 August 2016
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions. Start each question on a new sheet of writing paper.
A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind a cover sheet.
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **15** printed pages and **1** blank page.



- 1** Besides reducing carbon dioxide emission, CO_2 levels in the atmosphere can be lowered through a process known as carbon capture and sequestration (CCS). One form of naturally occurring CCS is the conversion of CO_2 into plant biomass during photosynthesis.

Scientists have also devised chemical methods of CCS. The processes for isolating carbon dioxide and for storing it has been the focus of some research.

- (a)** Amine gas treating has been studied as a reaction for the first part of the CCS process. This method uses aqueous solutions of various alkylamines to capture carbon dioxide from the waste gases of industrial productions.
- (i)** Monoethanolamine (MEA) and dimethylethanolamine (DMEA) are two alkylamines that are commonly used in amine gas treating.

base	$\text{p}K_{\text{b}}$
$\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (DMEA)	3.73
$\text{HOCH}_2\text{CH}_2\text{NH}_2$ (MEA)	4.52
$\text{C}_6\text{H}_5\text{NH}_2$	9.13

Explain the difference in $\text{p}K_{\text{b}}$ values in the table. [3]

- (ii)** The aqueous solution containing 32% MEA by weight can neutralise up to 0.5 mol CO_2 per mole of the amine. Assume that density of the solution is 1 kg dm^{-3} .

Calculate the pH of 32% MEA solution. [3]

- (b) (i)** Another alkylamine, dimethylpiperazine (DMP), has the molecular formula $\text{C}_6\text{H}_{14}\text{N}_2$.

1 mole of DMP can be formed from 2 moles of N-methyl-2-chloroethylamine under suitable conditions.

1. State the conditions needed for this reaction.
2. Write a balanced equation for the conversion of N-methyl-2-chloroethylamine into DMP, showing the structural formulae of N-methyl-2-chloroethylamine and DMP. [2]

- (ii)** Under room conditions, N-methyl-2-chloroethylamine reacts with

1. $\text{ClCH}_2\text{CO}_2\text{H}$ and
2. $\text{CH}_3\text{COC}l$

Name the type of reaction that occur and suggest the structure of the compound formed in each reaction. [3]

- (c) CO₂ that is captured from amine gas treating needs to be sequestered so that it does not return into the atmosphere.

Carbon sequestration has been attempted using mineral carbonation. In this method, liquid CO₂ is buried under a volcanic rock known as basalt. Over a period of time, CO₂ reacts with metal oxides in the rock to form MgCO₃ and CaCO₃. This method allows a large amount of CO₂ in the atmosphere to be trapped as solid thus reducing its effect as a greenhouse gas.

- (i) In volcanic areas, underground temperatures rises with increasing depth. Two types of carbonates found in these areas are rhodochrosite MnCO₃ and calcite CaCO₃.

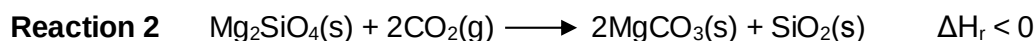
By quoting suitable data from the Data Booklet, explain whether MnCO₃ or CaCO₃ decomposes more readily in the presence of geothermal heat. [3]

- (ii) Magnesite, MgCO₃, forms an equilibrium with CO₂ when it is trapped underground in high temperature.



Suggest how mineral carbonation can be maintained despite high temperature and justify your answer. [2]

- (iii) Fosterite, Mg₂SiO₄, is a component of basalt that reacts with CO₂ in the following reaction.



$$\text{enthalpy change of combustion of Mg(s)} = -607 \text{ kJ mol}^{-1}$$

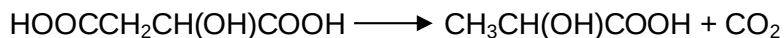
$$\text{enthalpy change of formation of Mg}_2\text{SiO}_4(\text{s}) = -59.5 \text{ kJ mol}^{-1}$$

$$\text{enthalpy change of formation of SiO}_2(\text{s}) = -911 \text{ kJ mol}^{-1}$$

Using the information above and relevant data from the *Data Booklet*, draw an energy level diagram and hence calculate the enthalpy change of **reaction 2**. [4]

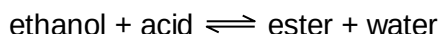
[Total: 20]

- 2 (a) The primary fermentation of grape juice produces wine and carbon dioxide. Sometimes, a secondary fermentation takes place a few months after the primary fermentation is finished and the wine has been bottled. This secondary fermentation converts 2-hydroxybutanedioic acid (malic acid) in the wine into 2-hydroxypropanoic acid (lactic acid). There are two benefits: the carbon dioxide produced can be used to make the wine sparkling; the conversion of the malic acid into lactic acid decreases the acidity of the wine.



A typical concentration of malic acid in wine is 0.05 mol dm^{-3} .

- (i) Calculate the volume of carbon dioxide produced at room temperature and pressure conditions when 1.0 dm^3 of wine undergoes secondary fermentation. [1]
 - (ii) A typical wine bottle has a capacity of 1.5 dm^3 . Using the ideal gas equation, calculate the pressure the carbon dioxide produced would exert inside the air gap of the bottle containing 1.3 dm^3 of wine at room temperature. [1]
 - (iii) In fact, the pressure inside the bottle is much less under these conditions. Explain why this differs from the pressure you calculated in (a)(ii). [1]
- (b) Another way by which the acidity in wine can be decreased is by an acid-catalysed ester formation:

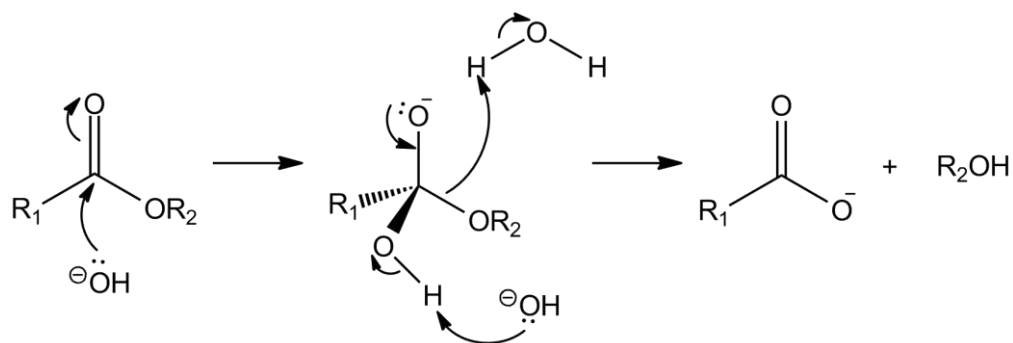


Wine consists of ethanol and water. A 1.0 dm^3 of wine typically contains 10% of ethanol by mass and a 0.10 mol dm^{-3} concentration organic acid, assuming density of wine is 1 g cm^{-3} .

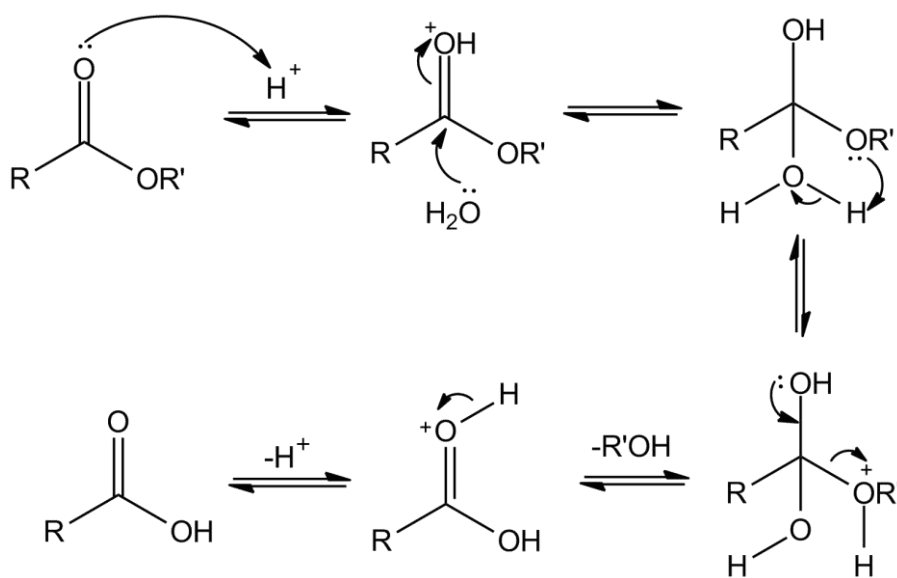
- (i) Calculate the value for the equilibrium constant K_c for the ester formation, given that 17.4% of acid is converted to ester. [3]
 - (ii) Maturation is the process where the wine evolves to a state of readiness for bottling or drinking. Before the wine is ready to be kept in a dark and cool environment at an ambient temperature below 20°C in barrels for storage, they will equilibrate to form ester. Suggest two reasons why wine needs several months to mature before this reaction takes place significantly. [2]
- (c) Describe a laboratory test to distinguish between 2-hydroxybutanedioic acid (malic acid) and 2-hydroxypropanoic acid (lactic acid). State the reagents and conditions you would use and any observations that you would make for each compound. Write the equation for any reaction that occurs. [3]

(d) Typically, esters can be hydrolysed in dilute acid or alkali.

The mechanism of both hydrolysis methods are shown as follow:



alkaline hydrolysis



acidic hydrolysis

In alkaline hydrolysis, the hydroxide anion attacks the electron deficient carboxyl carbon.

In acid hydrolysis, the acid protonates the carboxyl oxygen to render the carboxyl carbon more electrophilic towards nucleophilic attack by water.

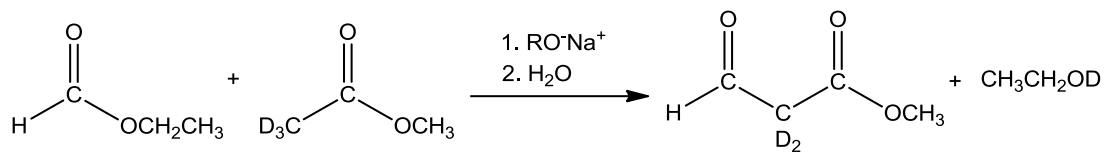
(i) What is the role of

1. OH^- in step 1 of alkaline hydrolysis
2. H^+ in acidic hydrolysis respectively? [2]

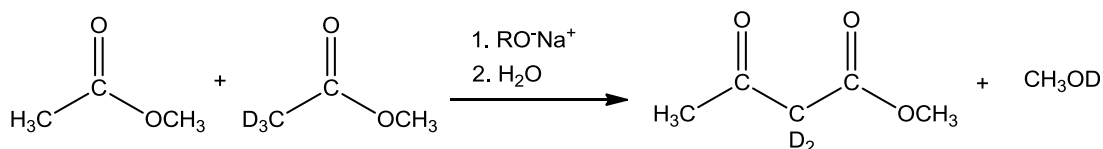
(ii) What is the role of water in acid hydrolysis? [1]

(iii) Outline the two advantages of alkaline hydrolysis. [2]

- (e) Claisen condensation is a carbon–carbon bond forming reaction that can occur between two esters in the presence of a strong base, resulting in a β -keto ester. In the mixture of methyl ethanoate and ethyl methanoate, the following Claisen condensation products are formed.

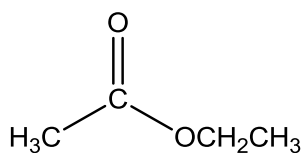


and

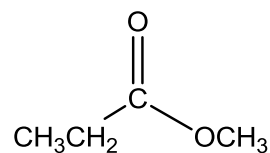


(Deuterium, ^2_1D , is an isotope of hydrogen.)

Predict the structures of β -keto esters formed when ethyl ethanoate is mixed with methyl propanoate under suitable reaction conditions.



ethyl ethanoate



methyl propanoate

[4]

[Total: 20]

- 3 (a) The characteristic properties of transition metals include coloured ions, complex formation, variable oxidation states and catalytic activity.

Transition metals are used extensively as heterogeneous catalysts in industrial processes. An example is the use of iron as a catalyst in the Haber process to manufacture ammonia.

- (i) Explain what is meant by the term *heterogeneous*. [1]
- (ii) State, in the correct order, three essential steps for the mechanism of heterogeneous catalysis. [2]
- (iii) The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its efficiency as a heterogeneous catalyst.

Suggest a reason why transition metals which adsorb weakly are usually not good heterogeneous catalysts. [1]

- (iv) A catalyst containing molybdenum(VI) was analysed for its molybdenum content by reducing a sample to the molybdenum(III) state. When titrated with acidified potassium manganate(VII), the molybdenum(III) was oxidised back to molybdenum(VI).

A 0.330 g sample of the catalyst, after reduction, required 27.50 cm³ of 0.0200 mol dm⁻³ potassium manganate(VII) to convert the molybdenum(III) into molybdenum(VI).

Calculate the percentage by mass of molybdenum in the catalyst. [2]

- (b) (i) The chemistry of the transition metal, tungsten, has certain similarities to that of sulfur. Both elements reach their maximum +6 oxidation states when combined with the electronegative element, oxygen.

Most tungsten occurs naturally in the tungsten anion, WO₄²⁻, analogous to the sulfate ion, SO₄²⁻. A common mineral is Scheelite which is calcium tungstate, CaWO₄.

Draw the structure showing the bonding in the WO₄²⁻ ion and give the O–W–O bond angle. [2]

- (ii) Tungsten(VI) oxide, WO₃, is used in electrochromic windows which change colour when an electrical voltage is applied.

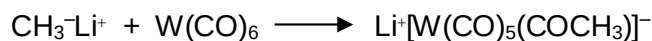
In electrochromic windows, a voltage is applied between a transparent layer of tungsten(VI) oxide and a source of ions such as a lithium salt, and the following reaction takes place during which some of the lithium ions are incorporated into the structure of the oxide:



The product, Li_xWO₃, is known as a tungsten bronze and its colour depends on the value of x. The value of x can vary from 0 to 1; a typical value giving blue-black colour is when x = 0.3.

Calculate the average oxidation state of the tungsten when x = 0.3. [1]

- (iii) A complex of tungsten, W(CO)_6 , has zero oxidation state for tungsten. It reacts with CH_3^-Li^+ as shown by the following equation:



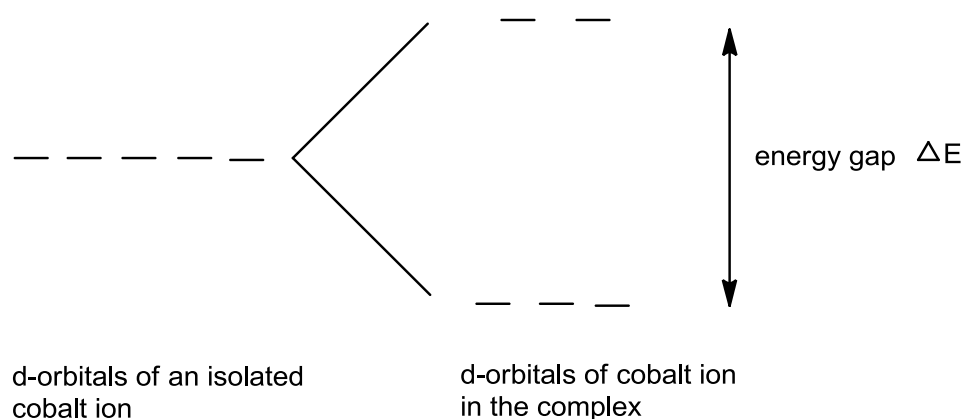
The reaction is nucleophilic addition where CH_3^- is a nucleophile.

Illustrate the shape of $[\text{W(CO)}_5(\text{COCH}_3)]^-$ by drawing the displayed formula of the anionic complex. [1]

- (c) CoF_6^{3-} and $\text{Co(NH}_3)_6^{3+}$ are two octahedral complexes which are blue and yellow in colour respectively.

The colours of the two complexes are different due to different ligands which cause splitting of the five 3d orbitals by different amount.

The following diagram shows how the five d-orbitals are split in an octahedral environment.



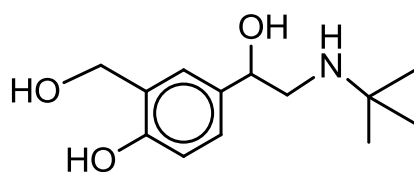
In the 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In the 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary before the higher energy d-orbitals are used.

CoF_6^{3-} is a 'high spin' complex while $\text{Co(NH}_3)_6^{3+}$ is a 'low spin' complex.

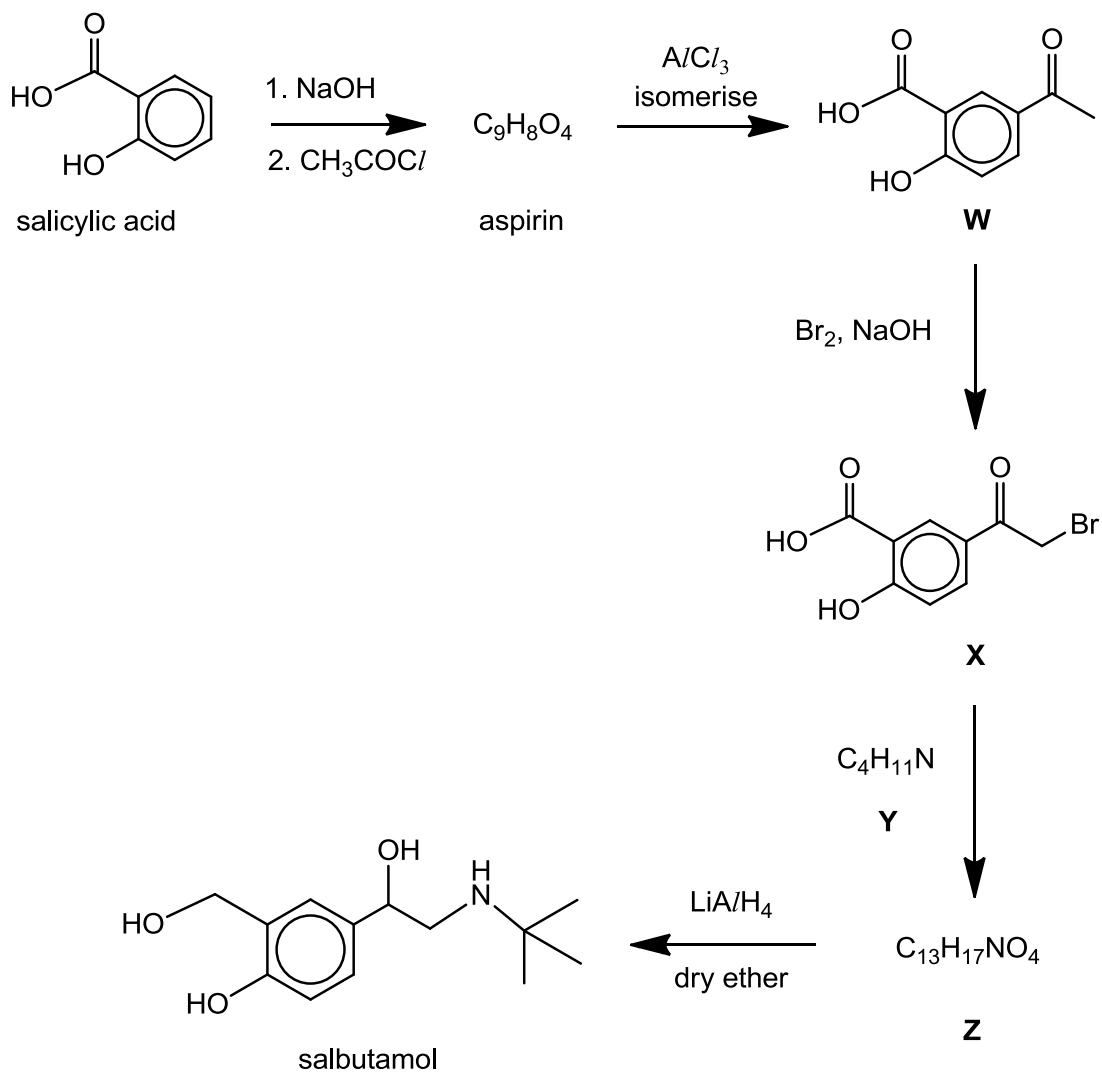
- (i) Draw two diagrams like the one above to show the electronic configurations of cobalt ions in CoF_6^{3-} and $\text{Co(NH}_3)_6^{3+}$ respectively. [2]
- (ii) Hence, explain which of the two complexes will have a larger energy gap, ΔE . [1]
- (iii) Explain why electrons usually prefer to occupy orbitals singly, rather than in pairs. [1]

- (d) Salbutamol is an anti-asthma drug which is prepared from aspirin, which in turn is prepared from salicylic acid.



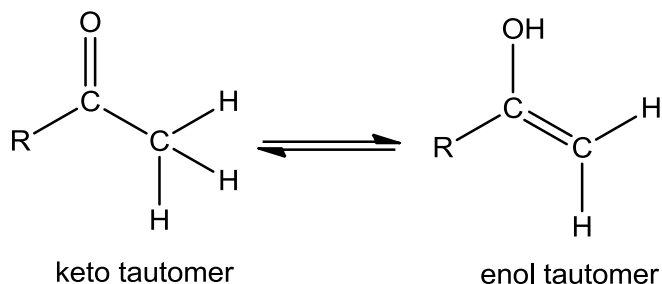
salbutamol

The following reaction scheme shows the synthesis of salbutamol from salicylic acid.



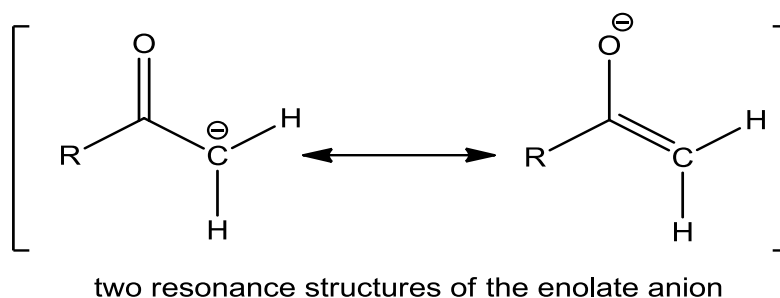
- (i) Draw the structures of aspirin, product **Z** and reagent **Y**. [3]

- (ii) A carbonyl compound with a hydrogen atom on its α -carbon rapidly equilibrates with its corresponding enol form as shown.



This rapid inter-conversion between the keto and enol form is a special kind of isomerism known as tautomerism.

In the presence of strong bases, the hydrogen atom on its α -carbon is abstracted to form a resonance-stabilised enolate anion as shown below:



Resonance structures differ only in the position of their electrons.

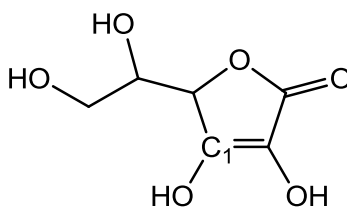
The mechanism for the reaction from product **W** to form product **X** using Br_2 and NaOH involves the intermediate, enolate anion. The two steps are:

- The first step involves an acid-base reaction between the hydroxide ion and the methyl group to give the enolate anion.
- Using its resonance structure with the $\text{C}=\text{C}$ bond, the enolate anion undergoes electrophilic attack by Br_2 to give product **X**.

Based on the information given, describe the mechanism for the reaction to form product **X** from product **W**. In your answer, show any relevant charges, lone pairs of electrons and arrows to show movement of electrons. [3]

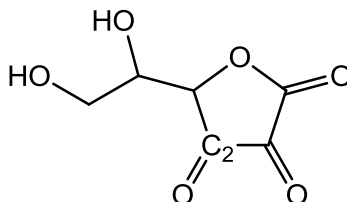
[Total: 20]

- 4 This question concerns ascorbic acid (vitamin C, $C_6H_8O_6$) and its chemistry. The structure of ascorbic acid is provided below.



ascorbic acid

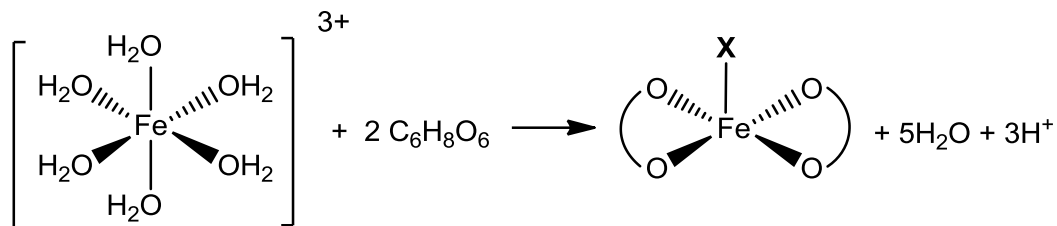
- (a) Ascorbic acid can be used in the synthesis of other compounds, with the use of $Si(CH_3)_3Cl$ as a protecting group for the alcohol groups.
- (i) In water, $Si(CH_3)_3Cl$ hydrolyses at a much faster rate than $C(CH_3)_3Cl$.
Explain the difference in the ease of hydrolysis. [2]
- (ii) State and describe the mechanism for the hydrolysis of $C(CH_3)_3Cl$ in water. You should include in your answer:
- Dipoles of relevant covalent bonds
 - Curly arrows
 - Label for the slow step [3]
- (b) Dehydroascorbic acid (DHA), $C_6H_6O_6$, with its structure shown below, is the oxidised product of ascorbic acid.



dehydroascorbic acid

- (i) State the oxidation number of:
- the carbon labelled C_1 in ascorbic acid.
 - the carbon labelled C_2 in DHA. [2]
- (ii) Write a balanced half equation, showing their structural formulae, for the reduction of DHA to ascorbic acid. [1]
- (iii) The electrode potential of ascorbic acid at pH 2 is +0.281 V. Explain how the electrode potential value changes as the pH increases. [2]
- (c) Electrolysis of an aqueous solution of $Fe(\text{ascorbate})_2$ buffered at pH 2 was carried out, with 22.4 cm^3 of hydrogen gas obtained at room temperature and pressure. Ascorbate is the conjugate base of ascorbic acid.
- (i) Using information from the *Data Booklet*, determine the minimum voltage required to run this electrolysis. [2]
- (ii) Calculate the mass of the product obtained at the anode. [2]

- (d) To 50 cm³ of an aqueous solution of ascorbic acid, 200 cm³ of ethanol was added. Some FeCl₃ was dissolved in this solution and the solid, Fe(ascorbate)₂X with an *M_r* of 422.8, was filtered off. The equation is as follows:



Note:  represents the ascorbate ligand

- (i) Suggest the role of ethanol in the preparation of the precipitate. [1]
- (ii) Determine the identity of the ion X. [1]
- (iii) The formation of Fe(ascorbate)₂X from Fe(H₂O)₆³⁺ involves a ligand substitution between H₂O and the ascorbate ion as shown in the equation above.

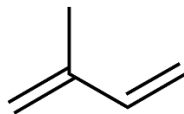
Explain the sign of the entropy change for the formation of Fe(ascorbate)₂X.

Hence given that the formation is exothermic, deduce the sign of the standard Gibbs free energy change. [4]

[Total: 20]

5 The use of the *Data Booklet* is relevant to this question.

- (a) 2-methylbuta-1,3-diene, also known as isoprene, is produced by many plants and serves as a building block for monoterpenes when two isoprene units combine without any rearrangement of the carbon skeleton. Monoterpenes all have molecular formula of $C_{10}H_{16}$.



isoprene

Compounds **A** and **B** are geometric isomers of a monoterpene commonly used in perfumes for their sweet herbal scent. Compounds **A** and **B** react with cold dilute alkaline potassium manganate(VII) to produce stereoisomers of $C_{10}H_{22}O_6$.

Compounds **A** and **B** react with hot concentrated acidified potassium manganate(VII) to produce compounds **C**, $C_3H_4O_3$, **D**, $C_3H_4O_4$, **E**, C_3H_6O and a gas **F**. Both **C** and **E** give a yellow precipitate with aqueous alkaline iodine. A 1.04 g sample of **D** reacted with excess sodium metal to produce 240 cm^3 of gas.

Use the information to suggest, with explanation, identities of **A** to **F**. [9]

- (b) Fehling's solution is often used as a distinguishing test in the qualitative analyses of organic compounds. It is prepared by mixing two separate solutions, known as Fehling's A and Fehling's B. Fehling's A is aqueous copper(II) sulfate while Fehling's B is an aqueous solution of potassium sodium tartrate made in sodium hydroxide.

Tartaric acid, H_4T , can exist as a tetraanion, T^{4-} , in a strongly alkaline medium. In Fehling's B, it exists as the H_2T^{2-} anion.

The standard electrode potentials, $E^\ominus$, of several species are shown in the table below.

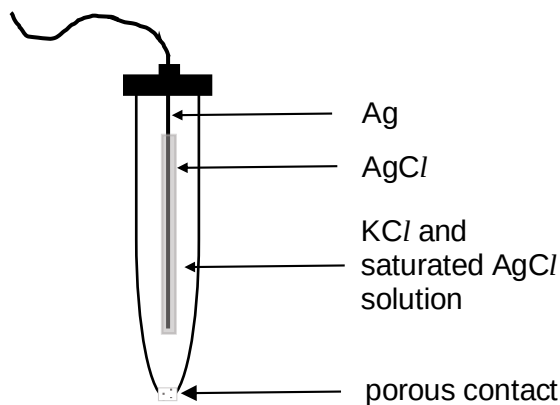
	Electrode reaction	$E^\ominus/V$
1	$Cu_2O + H_2O + 2e^- \rightleftharpoons 2Cu + 2OH^-$	-0.36
2	$2Cu^{2+} + H_2O + 2e^- \rightleftharpoons Cu_2O + 2H^+$	+0.20
3	$[Cu(HT)_2]^{4-} + 2H_2O + 2e^- \rightleftharpoons Cu + 2H_2T^{2-} + 2OH^-$	+0.25
4	$HCO_2H + 2H^+ + 2e^- \rightleftharpoons HCHO + H_2O$	-0.03
5	$CO_2 + 4H^+ + 4e^- \rightleftharpoons HCHO + H_2O$	-0.07
6	$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	-0.11

Adding Fehling's solution to methanal causes a reaction to take place.

- (i) By selecting appropriate electrode reactions from the *Data Booklet* or the table above, construct a balanced equation for this reaction. [1]
- (ii) Use your answer in part (i) to calculate the $E^\ominus_{\text{cell}}$ for this reaction. [1]
- (iii) Describe the observations for this reaction. [1]

- (c) Electrode potential values are often quoted with reference to the standard hydrogen electrode (SHE). It is however, seldom used because it is difficult to regulate the pressure of hydrogen gas at 1 atm.

One of the more commonly used reference electrodes in electrochemistry is the silver/silver chloride electrode (SSCE). It is made of a silver wire that is coated with a thin layer of silver(I) chloride, immersed in a potassium chloride solution saturated with silver(I) chloride.



schematic of a silver/silver chloride electrode

One of the advantages of using the SSCE is that it can be directly immersed into the other half-cell, thereby negating the use of a salt bridge.

- (i) Suggest the purpose of having the porous contact. [1]

The solution in the SSCE is colourless in spite of the presence of a d-block element.

- (ii) Explain how the colour in transition metal compounds arise. [2]

- (iii) Write the full electronic configuration of Ag^+ and hence explain why it is **not** coloured. [2]

- (d) Adding a reagent that selectively brings one of the ions out of a solution as a precipitate while leaving the other ion in the solution is a technique known as selective precipitation.

Data about the solubilities in water and solubility products of silver(I) hydroxide and copper(II) hydroxide at 298 K are given below. Only the numerical values of the solubility products are given.

hydroxide	solubility/ mol dm ⁻³	solubility product
AgOH	1.23×10^{-4}	1.52×10^{-8}
Cu(OH) ₂	1.77×10^{-7}	2.20×10^{-20}

As a general standard, two ions are selectively separated when a maximum 0.01% of the precipitated compound still remains as the aqueous ions.

Determine if selective precipitation can be performed on a solution containing 0.200 mol dm⁻³ Ag⁺ and 0.200 mol dm⁻³ Cu²⁺ with the addition of solid potassium hydroxide. [3]

[Total: 20]

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9647/02

Paper 2 Structured Questions

16 August 2016
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

For Examiner's Use	
Question no.	Marks
1	
2	
3	
4	
5	
6	
7	
TOTAL	

This document consists of **12** printed pages.



1 Planning (P)

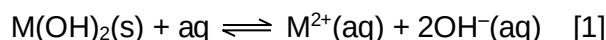
The solubility of a metal hydroxide, $M(OH)_2$ at a particular temperature is defined as the mass of metal hydroxide that dissolve in 100 g of water.

A saturated solution of the metal hydroxide is one in which no more solid can dissolve at this fixed temperature. At 25°C, the solubility of metal hydroxide is approximately less than 2g /100g of water.

You are to plan an experiment using the method of gravimetric analysis to achieve these objectives:

1. determine the solubility product, K_{sp} of the metal hydroxide accurately;
2. determine how the solubility of the metal hydroxide in sodium hydroxide is affected by the concentration of hydroxide ions.

- (a) (i) Write an equation with state symbols to show the dissolution of metal hydroxide in water. [1]



- (ii) Suggest and explain how the solubility of the metal hydroxide varies with the concentration of hydroxide ions. [1]

The solubility of metal hydroxide **decreases** when the concentration of sodium hydroxide **increases** as there is **common ion effect or explanation of eqm shifting to the left when concentration of hydroxide increases (LCP)**.

- (b) You are provided with:
- pure solid metal hydroxide
 - 2.0 mol dm⁻³ of sodium hydroxide
 - the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of a saturated metal hydroxide solution
- the preparation of a suitable range of diluted sodium hydroxide solutions
- an outline of how the results could be used to calculate the solubility of metal hydroxide and its K_{sp} and show how the solubility of metal hydroxide in sodium hydroxide varies with the concentration of hydroxide ions
- the risks involved and safety precautions taken [8]

Method 1:

1. Using a 50 cm³ burette/ 100 cm³ measuring cylinder/ 50 cm³ pipette, place 100 cm³ of distilled water into a pre-weighted 250 cm³ dry and clean conical flask/beaker (M1 g) placed in a thermostated water bath controlled at a fixed temperature. Weigh again with the distilled water inside to obtain the total mass of the distilled water and beaker, M2 g.

2. Add about 2-4g (> solubility and depending on volume of solution used) mass of solid metal hydroxide to the solution and stir with a glass rod. Stir the mixture continuously until no more solid dissolves to ensure a saturated solution is obtained.

Let the mass of metal hydroxide be M3 g.

3. Allow reaction mixture to stand/ leave for a long time to reach equilibrium.
4. Pre-weigh the dry filter paper, M4 g. Filter the mixture with the use of a filter paper and filter funnel into a beaker. Discard the filtrate. Weigh the mass of the filter paper and solid, M5 g.
5. Wash the residue with some cold water and dry the filter paper with residue in an oven/IR lamp. Temperature should be pre-set to 60°C (lower than the decomposition temperature and to prevent the filter paper from burning). Let the filter paper cool down in a dessicator. Weigh the filter paper and its contents.
6. Repeat the process of heating, cooling and weighing till constant mass of the filter paper and its contents is obtained.

Mass of dissolved solute = $M3 - (M5 - M4) = X$ g

(mass of solid $M(OH)_2$ added - mass of residue)

Mass of solvent = $M2 - M1 = Y$ g

Solubility of metal hydroxide in 100g of water = $X / Y \times 100$ (g/100g of water)

OR

Method 2:

1. Measure about 100 cm³ (any volume) of water using a measuring cylinder and place it in a dry and clean beaker placed in a thermostated water bath.
2. Add about 2g (> solubility and depending on volume of solution used) mass of solid metal hydroxide to the solution and stir with a glass rod. Stir the mixture continuously until no more solid dissolves to ensure a saturated solution is obtained.
3. Allow reaction mixture to stand/ leave for a long time to reach equilibrium.
4. Using an electronic weighing balance, measure and record the mass of an empty, dry crucible/beaker. This is recorded as M1 g.
5. Using a dry filter funnel and filter paper, filter the suspension and collect the saturated filtrate in the crucible. Measure the mass of the filtrate and crucible. The mass obtained is M2 g.
6. Using a Bunsen burner, heat the solution until all the liquid is evaporated off and constant mass is obtained, cool it and re-weigh the beaker with its contents (M3 g).

Mass of dissolved solute = $(M3 - M1) = X$ g

Mass of solvent = $(M2 - M1) = Y$ g

Solubility of metal hydroxide in 100g of water = $100 \times X/Y$

6. Repeat the experiment with another mass of metal hydroxide to get reliable results.

7. Conversion of solubility in g/ 100 g of water to mol dm⁻³ assume density of water = 1g cm⁻³

Calculate the K_{sp} of metal hydroxide as $K_{sp} = [M^{2+}][OH^-]^2$.

Results:



Equilibrium concentration
(mol dm⁻³)

x

 $2x$

In a saturated solution,

$$K_{sp} = [x][2x]^2 = 4x^3$$

Preparation of standard solutions of sodium hydroxide

Volume of NaOH / cm ³	Volume of water / cm ³	Initial concentration of NaOH (mol dm ⁻³)	Final concentration of NaOH (mol dm ⁻³)
50	100	2	1
50	100	1	0.5

7. Prepare at least three standard solutions of sodium hydroxide of different concentration (2 mol dm^{-3} , 1 mol dm^{-3} and 0.5 mol dm^{-3}).
8. Use of a burette to transfer 50 cm^3 of the 2 mol dm^{-3} sodium hydroxide solution into a 100 cm^3 volumetric flask. Measuring cylinder is not accepted.
9. Top up to the mark with distilled water. Stopper, invert and shake to obtain a homogeneous solution of 1 mol dm^{-3} sodium hydroxide.
10. Repeat steps 1-3 using 50 cm^3 of the 1 mol dm^{-3} sodium hydroxide to obtain a stock solution of 0.5 mol dm^{-3} sodium hydroxide.

OR vary the volume of water and sodium hydroxide used (keeping total volume constant), use the same concentration of sodium hydroxide to obtain diluted solutions

To investigate how the solubility of metal hydroxide varies with the concentration of sodium hydroxide:

11. Repeat steps 1- 6 using the other three standard solutions of sodium hydroxide of concentration (2 mol dm^{-3} , 1 mol dm^{-3} and 0.5 mol dm^{-3}).
12. Calculate the solubility of metal hydroxide for the three concentrations of sodium hydroxide and tabulate how the solubility of metal hydroxide change with concentration of sodium hydroxide.

Solubility of metal hydroxide in sodium hydroxide = $g / 100g$ of solvent

13. Observe the trend that when concentrations of sodium hydroxide used decreases, the solubility of metal hydroxide increases.

Risk and safety precaution

Metal hydroxide and sodium hydroxide is corrosive and toxic in nature. Minimise contact by using gloves and goggles.

OR

Use oven/heat resistant gloves or tongs to handle the hot beaker/crucible.

OR Cool hot crucible before handling OR wear gloves when heating.

- (c) Suggest another experimental method to determine how the solubility of metal hydroxide changes with the presence of sodium hydroxide. Suggest the results to be collected. [2]

Titrimetric method. Prepare a saturated solution of metal hydroxide in sodium hydroxide of known concentration and titrate the solution with standard HCl solution.

Results to be collected are: Initial burette reading/ final burette reading / titre volume
[Total: 12]

- 2 **A**, **B** and **C** are three organic molecules which share the same molecular formula, $C_8H_9NO_2$.

You are to make use of the data about the reactions of **A**, **B** and **C** given in the table below to deduce their identities.

reaction	reagent used	A	B	C
1	$KMnO_4(aq)$, $H_2SO_4(aq)$ heat	purple colour remains	purple MnO_4^- decolourised	purple MnO_4^- decolourised
2	excess $Br_2(aq)$	white solid formed with $M_r = 308.8$	no visible reaction	white solid formed with $M_r = 308.8$
3	$NaOH(aq)$ at room temperature	dissolves to give a colourless solution	dissolves to give a colourless solution	does not dissolve at all
4	$Na_2CO_3(aq)$	no visible reaction	effervescence seen	no visible reaction
5	$HCl(aq)$ at room temperature	does not dissolve at all	dissolves to give a colourless solution	dissolves to give a colourless solution

- (a) (i) Deduce the molecular formula of the white solid formed from **A** in reaction 2. [1]



- (ii) What type of reaction takes place in reaction 2 for **A**? [1]

Electrophilic substitution

- (iii) Hence, list the possible functional groups present in **A** based on reaction 2 alone. [2]

Phenol, phenylamine

- (b) (i) List the functional groups that are being tested for in reaction 3. [2]

phenol and carboxylic acid

- (ii) Identify the gas that is being produced in reaction 4 for **B** and how you would confirm its identity. [2]

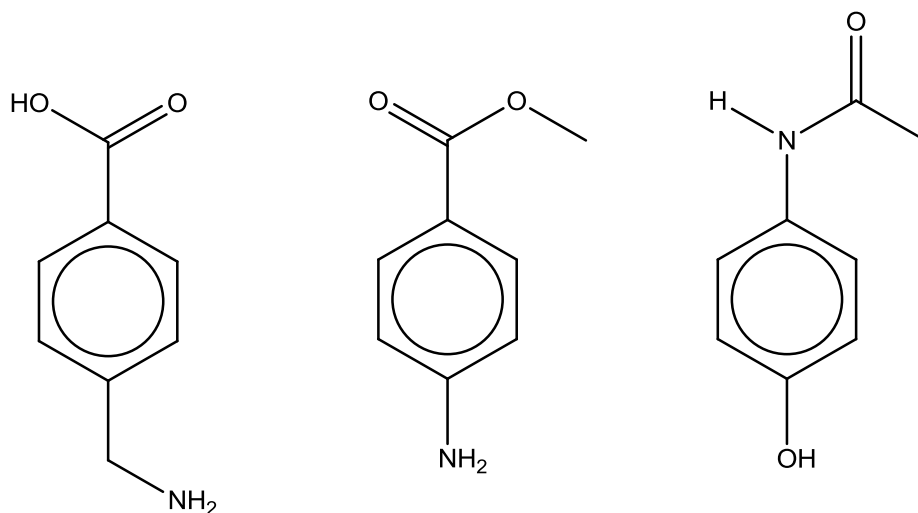
CO₂.

Pass the gas through a solution of Ca(OH)₂. It should form a white precipitate.

- (iii) Which of the functional groups you have named in **b(i)** is confirmed by reaction 4? [1]

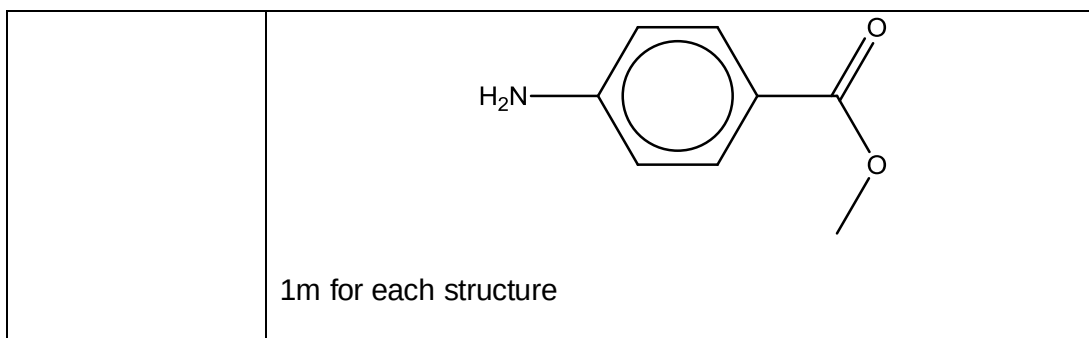
Carboxylic acid

- (c) You now have enough information to determine the identities of **A**, **B** and **C**. Below are three possible structures of **A**, **B** and **C** (not in order).

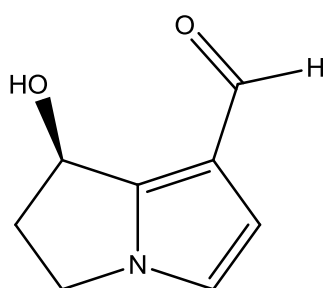


Draw the structural formula of the three compounds in the boxes below. [3]

A	
B	
C	



- (d) Hydroxydanaidal is an insect pheromone synthesised by male tiger moths from heliotrine in plants. It is an isomer of the three organic molecules above and is made up of two five-membered rings.



hydroxydanaidal

In order for a ring to be aromatic, it has to fulfil the following criteria:

- The ring must have $4n+2$ electrons in the delocalised p-orbital cloud (where n is a positive integer)
- The ring must be planar
- Every atom in the ring must be able to participate in delocalising the electrons.

- (i) Given that the N atom is sp^2 hybridised, what is the number of p electrons in the right ring of hydroxydanaidal? [1]

6 [1]

- (ii) Hence, state if the right ring is aromatic. [1]

Yes.

- (iii) Suggest reagents and conditions for a reaction that that will distinguish hydroxydanaidal from the three isomers **A**, **B** and **C**. [1]

Add Tollens' reagent and warm/heat.

Add 2,4-DNPH or Brady's Reagent.

If student stated in (ii) that it is not aromatic then accept:

Add Fehling's solution and warm/heat as ecf

[Total: 15]

- 3 Group VII elements can form oxoanions of XO_n^- which are strong oxidising agents. One such example is bromate(V) anion, BrO_3^- which can oxidise iodide to form iodine, and itself reduced to bromide.

(a) Write a balanced ionic equation for the reaction between bromate(V) and iodide. [1]



(b) A student wished to analyse the amount of iodine and the bromide ions produced from the above reaction and hence he carried out the following procedures.

- 1) Add 25.0 cm^3 of $0.150 \text{ mol dm}^{-3}$ potassium bromate(V) solution to excess potassium iodide (3 grams) and 5 cm^3 of 1 mol dm^{-3} H_2SO_4 in a 250 cm^3 conical flask.
- 2) Add sufficient chloroform, CHCl_3 , to the above solution immediately and transfer the mixture to a separating funnel.
- 3) Separate the organic and aqueous layers and add barium nitrate solution to the aqueous layer in a beaker.
- 4) Filter the above mixture and add silver nitrate to the filtrate in the conical flask.
- 5) To the resultant mixture in the conical flask in step 4, add sufficient concentrated ammonia and filter once again.

(i) What is the purpose of adding chloroform in step 2? [1]

It is to extract iodine into the organic layer as iodine is more soluble in CHCl_3 due to the formation of effective interaction (induced dipole - induced dipole).

(ii) What is the reason for adding barium nitrate in step 3? [1]

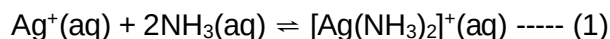
It is to remove sulfate as barium sulfate so that it will not interfere with the reaction when silver nitrate is added.

(iii) A mixture of two precipitates will be formed when silver nitrate is added into step 4. Suggest the identities of the precipitates. [1]

AgBr and AgI

(iv) Describe clearly what the student will observe in step 5 after he added in concentrated ammonia and performed a filtration. Explain the chemistry behind his method. [3]

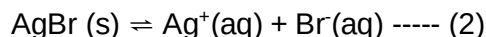
Cream ppt of AgBr dissolves to give a colourless filtrate and yellow ppt of AgI is obtained as the residue.



When concentrated NH_3 is added, the soluble complex of $[\text{Ag}(\text{NH}_3)_2]^+$ is

formed, lowering the concentration of Ag^+ .

Hence the eqm (2) position shifts to the RHS, causing AgBr to dissolve.



OR

The ionic product $[\text{Ag}^+][\text{Br}^-]$ become smaller than K_{sp} .

However the K_{sp} values of AgI(s) is extremely low such that its ionic product $[\text{Ag}^+][\text{I}^-]$ still exceed its K_{sp} [1], hence AgI remains insoluble even when concentrated NH_3 is added.

(c) Explain why fluorine does not form oxoanions such as FO_3^- . [1]

1. F does not have 3d orbitals that are energetically accessible for electrons to occupy / for expansion of octet to occur.
2. Fluorine is too / highly electronegative to have a positive oxidation number OR cannot form dative bonds (if student include answer 1)
3. Fluorine is a small atom such that 3 oxygen atoms around it would result in too much electronic repulsion / steric hindrance.

[Total: 8]

4 Compound **X** and compound **Y** are oxides formed from period 3 elements.

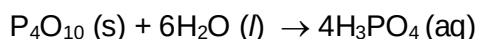
When water is added to both oxides, only **X** dissolves but not **Y**. However, **Y** will dissolve when it is added to the aqueous solution of **X** and NaOH (aq) separately.

It is known that aqueous solution of **X** can react with solid potassium hydroxide in a ratio of 1:3.

Identify compound **X** and **Y**, and explain the above reactions with the aid of balanced equations.

Compound **X**: P_4O_{10} / phosphorus (V) oxide / phosphorus pentoxide
Compound **Y**: Al_2O_3 / aluminium oxide

Only **X** is soluble in water but not **Y**:

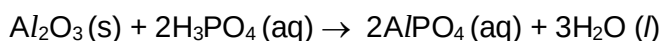


ECF from identity of compound **X** for P_2O_5

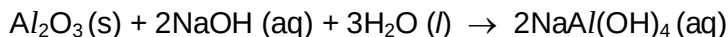
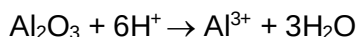
Al_2O_3 has high lattice energy / strong ionic bonds and hence is not able to dissolve in water.

Y will dissolve when added to the aqueous solution of **X** and NaOH (aq) separately:

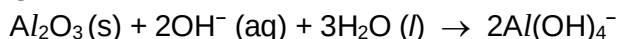
Al_2O_3 is amphoteric and will react with both acids and alkalis.



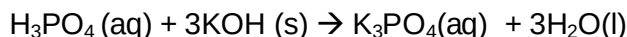
OR



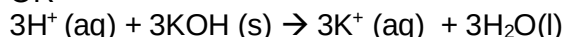
OR



Reactions of solutions of X with potassium hydroxide:

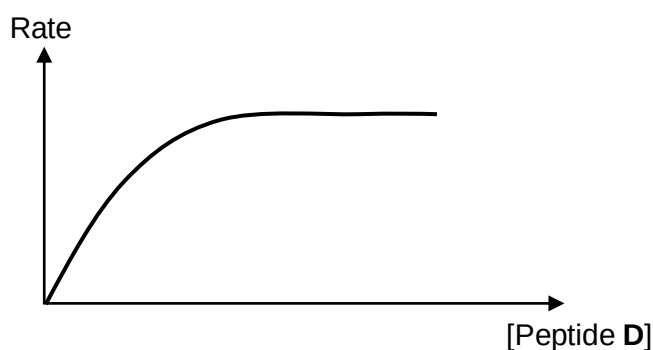


OR



[Total: 7]

- 5 Chymotrypsin is a digestive enzyme found in the small intestines that can hydrolyse peptide bonds within proteins. It is also used as a form of treatment for sports injuries to reduce pain and inflammation. The three main amino acids involved in the catalytic activity are histidine, aspartic acid and serine.
- (a) The graph shows the results of an investigation of the initial rate of hydrolysis of peptide **D** by the enzyme chymotrypsin. In the experiments, the initial concentration of peptide **D** was varied but that of chymotrypsin was kept constant.

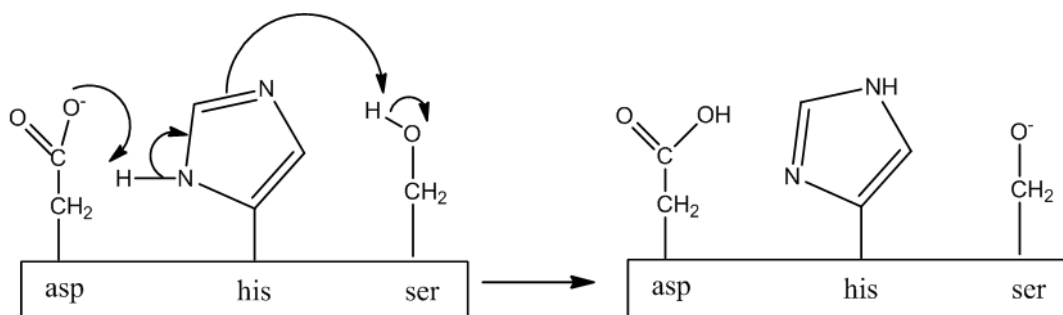


Explain the difference in the rate of hydrolysis at high and low concentrations of peptide **D**. [2]

At low concentration of peptide D, substrates do not saturate or occupy all the available active sites. Rate of reaction will be directly proportional to [substrate] or first order reaction with respect to substrate.

At high concentration of peptide D, substrates saturate or occupy all the available active sites. Rate of reaction will be independent of [substrate] Or zero order reaction with respect to substrate.

- (b) The first step of the mechanism of the action of chymotrypsin is shown:



- (i) In an aqueous external environment, suggest and explain whether the three amino acids are orientated inward or outward of the compact structure. [2]

Three amino acids are orientated outward of the compact structure as they contain the polar hydroxyl and amine group which are able to form hydrogen bonds/ ion-dipole with water molecules/ catalytic activity as there is binding to substrate .

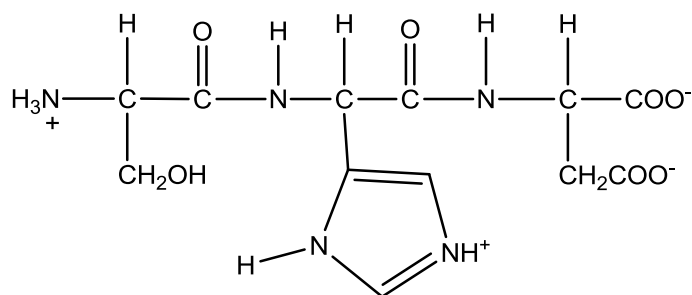
- (ii) State the roles of histidine in the mechanism shown above. [1]

It is both an acid (proton donor) and a base (proton acceptor). Or protonate and deprotonate.

- (iii) Explain with reference to the mechanism, how a low pH might affect the enzymatic activity of chymotrypsin. [2]

At low pH, excess H^+ will react with the basic amine group of histidine OR it will react with the COO^- group of asp OR ionic bonds are disrupted, hence this will lead to changes in enzyme shape and cause denaturation/ lose enzymatic activity/ mechanism will not work.

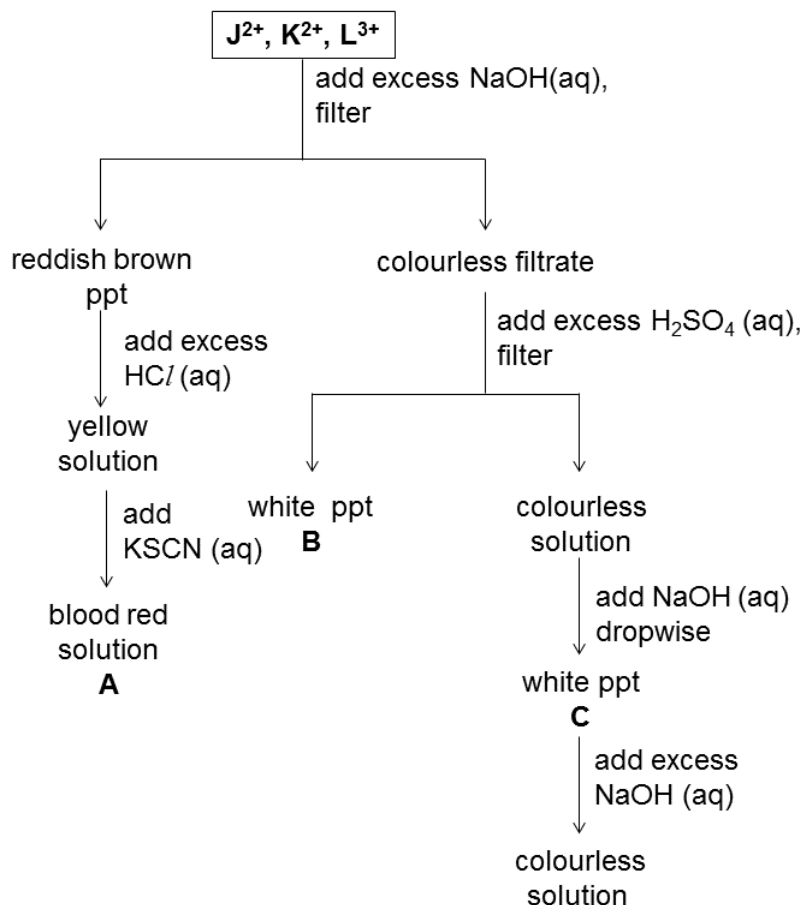
- (iv) Draw the structural formula of a tripeptide with the sequence *ser-his-asp*, showing the form which it would exist at pH 4.5 given the pK_a of the R-group of his = 6.04 and pK_a of the R-group of asp = 3.90. [2]



[Total: 9]

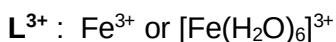
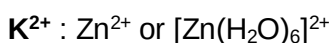
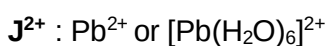
6 Three unknown cations J^{2+} , K^{2+} and L^{3+} are analysed according to the flowchart below.

J, **K** and **L** can be any one of the following: Al, Mn, Fe, Co, Ni, Pb, Zn, Sc.

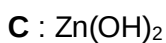


(a) Identify the three cations and the three unknowns **A**, **B** and **C**. [6]

Cations



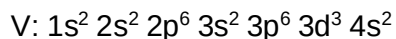
Unknowns



Identity of J and K can be switched.

(b) Vanadium (II) chloride, VCl_2 is prepared by the thermal decomposition of vanadium (III) chloride, VCl_3 .

(i) Write the electronic configuration of the vanadium atom. [1]



- (ii) Hence, explain why the third ionisation energy of vanadium is higher than the second ionisation. [1]

The second electron removed is from the 4s orbital whereas the third electron is removed from the 3d orbital. The third electron removed is from an inner principal quantum shell, which experiences greater nuclear attraction and hence, requires more energy to remove.

- (iii) Predict, with reason, which of the chlorides of vanadium, VCl_2 or VCl_3 will have a higher melting point. [1]

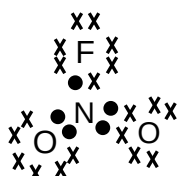
$$\text{Lattice energy} \propto \left| \frac{q_+ q_-}{r_+ + r_-} \right|$$

VCl_3 will have a higher melting point. As V^{3+} has a smaller ionic radius and a higher charge, VCl_3 will have a more exothermic lattice energy requiring more energy to melt. [1]

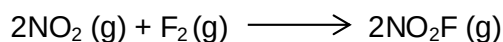
[Total: 9]

- 7 Nitryl fluoride, NO_2F is a colourless gas which acts as a strong oxidising agent and fluorinating agent.

- (a) Draw a dot-and-cross diagram of NO_2F . [1]

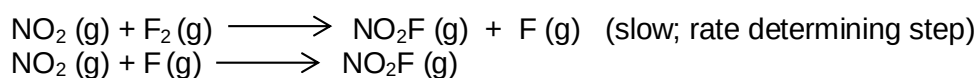


- (b) It is known that NO_2F can be produced from nitrogen dioxide and fluorine according to the equation below.

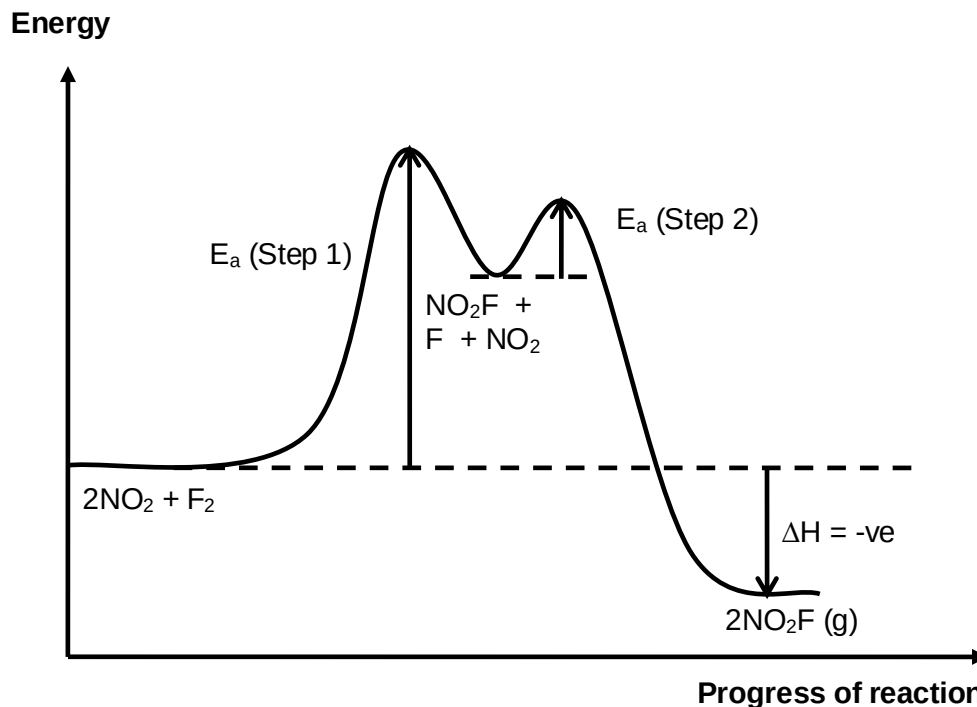


The rate equation for the reaction was also found to be $\text{Rate} = k[\text{NO}_2][\text{F}_2]$.

- (i) Propose a two-step mechanism consistent with the above equation, indicating the rate determining step. [2]



- (ii) Given that the reaction is exothermic, sketch a labelled energy profile diagram for the complete reaction path including the formation of the intermediate species. [3]



- (c) When NO_2 and excess F_2 were mixed together, $[\text{NO}_2\text{F}]$ varies with time, as shown in the table below. The initial $[\text{NO}_2]$ used is $0.400 \text{ mol dm}^{-3}$.

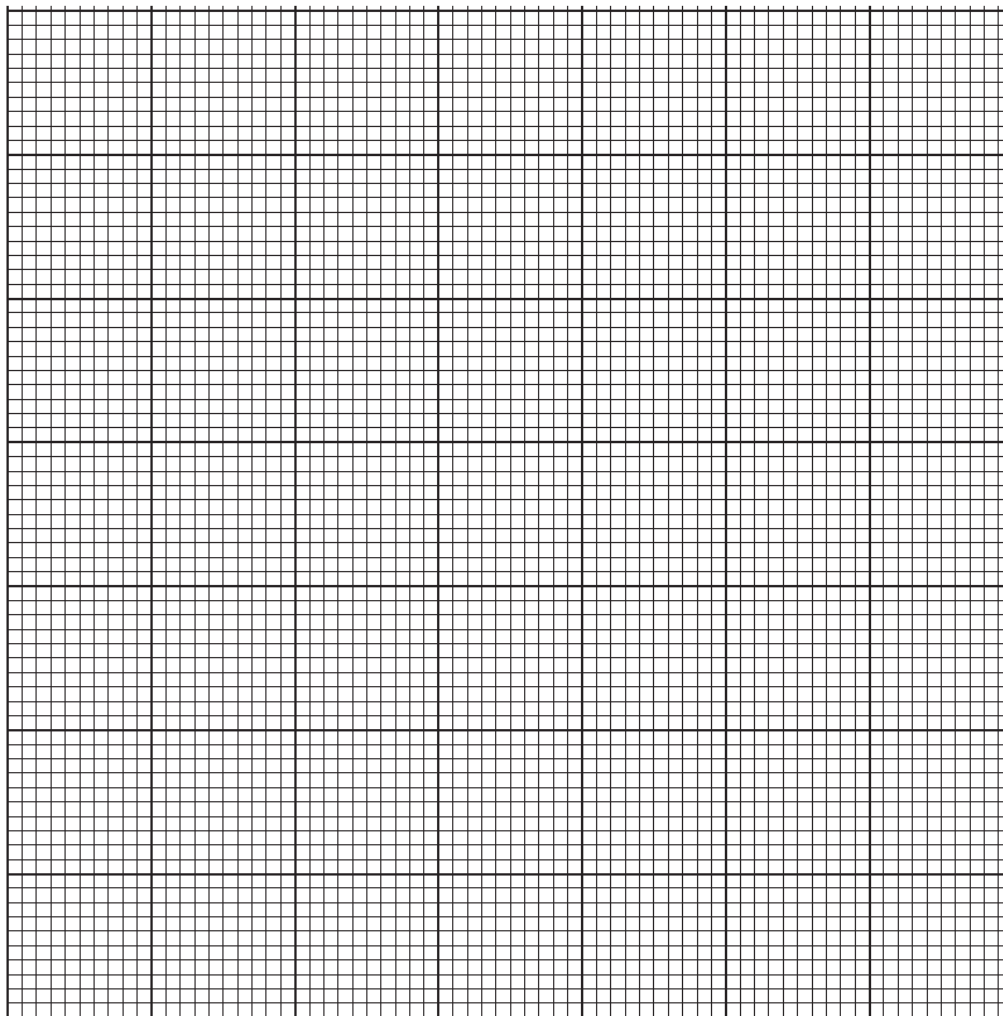
t / min	$[\text{NO}_2\text{F}] / \text{mol dm}^{-3}$	$\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t} / \text{mol dm}^{-3} \text{ min}^{-1}$	$[\text{NO}_2] / \text{mol dm}^{-3}$
0.25	0.150	0.60	0.250
0.50	0.245	0.38	0.155
0.75	0.300	0.22	0.100
1.00	0.340	0.16	0.060
1.25	0.360	0.08	0.040
1.50	0.375	0.06	0.025

- (i) Explain why it is necessary to use excess fluorine in this experiment to confirm the order with respect to nitrogen dioxide. [1]

This is to keep the concentration of fluorine relatively constant during the experiment so that the rate depends only on the concentration of NO_2 . / pseudo first order wrt NO_2 .

- (ii) The rate at a particular time can be approximated using rate = $\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$. Complete the table above by calculating $\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$ (to 2 decimal places) and the $[\text{NO}_2]$ left (to 3 decimal places) at the respective timings. [2]

- (iii) Hence, plot a graph of $\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$ against $[\text{NO}_2]$ to confirm and explain that the reaction is first order with respect to NO_2 . [3]

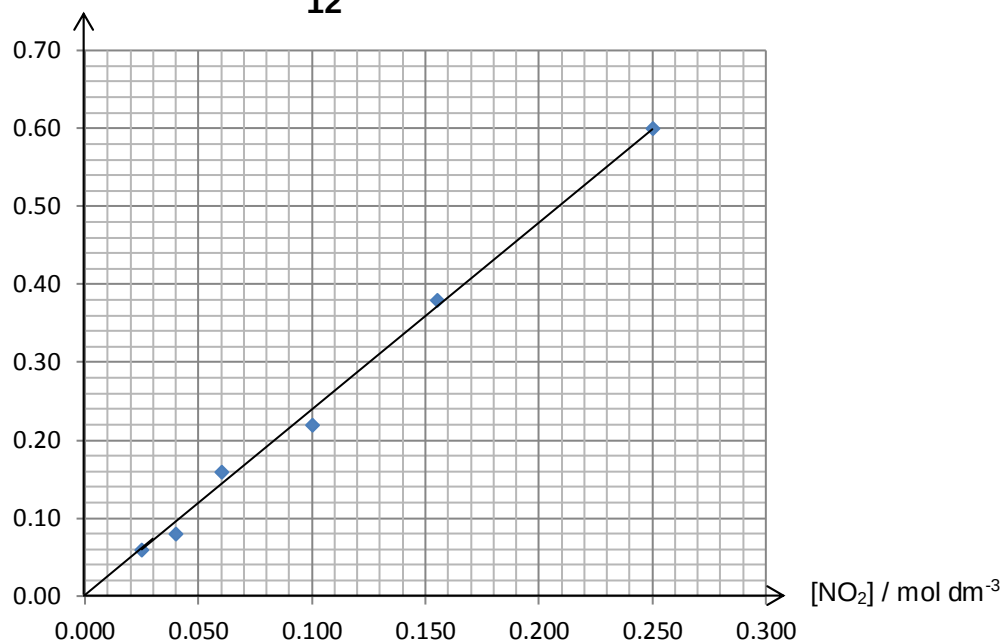


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.....

$$\frac{\Delta[\text{NO}_2\text{F}]}{\Delta t} / \text{mol dm}^{-3} \text{min}^{-1}$$

12



As a straight line graph passing through the origin is obtained, OR the rate is directly proportional to the concentration of NO_2 , hence the reaction is first order with respect to NO_2 .

[Total: 12]

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9647/03

Paper 3

23 August 2016
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions. Start each question on a new sheet of writing paper.
A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind a cover sheet.
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **15** printed pages and **1** blank page.

9647/03/Prelim/16
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ANGLO-CHINESE JUNIOR COLLEGE
Department of Chemistry

[Turn over]

- 1 Besides reducing carbon dioxide emission, CO₂ levels in the atmosphere can be lowered through a process known as carbon capture and sequestration (CCS). One form of naturally occurring CCS is the conversion of CO₂ into plant biomass during photosynthesis.

Scientists have also devised chemical methods of CCS. The processes for isolating carbon dioxide and for storing it has been the focus of some research.

- (a) Amine gas treating has been studied as a reaction for the first part of the CCS process. This method uses aqueous solutions of various alkylamines to capture carbon dioxide from the waste gases of industrial productions.
- (i) Monoethanolamine (MEA) and dimethylethanolamine (DMEA) are two alkylamines that are commonly used in amine gas treating.

base	pK _b
HOCH ₂ CH ₂ N(CH ₃) ₂ (DMEA)	3.73
HOCH ₂ CH ₂ NH ₂ (MEA)	4.52
C ₆ H ₅ NH ₂	9.13

Explain the difference in pK_b values in the table. [3]

Basic strength:



C₆H₅NH₂ is the weakest base as the lone pair of electron on the N atom is delocalised into the phenyl group. This makes the lone pair less available to accept H⁺.

DMEA is a stronger base than MEA because it has two additional electron donating methyl groups which increases the electron density on the N atom and improves its ability to accept proton.

- (ii) The aqueous solution containing 32% MEA by weight can neutralise up to 0.5 mol CO₂ per mole of the amine. Assume that density of the solution is 1 kg dm⁻³.

Calculate the pH of 32% MEA solution. [3]

$$\begin{aligned} n(\text{MEA}) \text{ in } 1 \text{ dm}^3 \text{ of } 32\% \text{ solution} \\ &= 320 \div [16.0 + 14.0 + 2(12.0) + 7(1.0)] \\ &= 5.246 \text{ mol} \end{aligned}$$

$$\text{Concentration MEA solution} = 5.246 \text{ mol dm}^{-3}$$

$$K_b = 10^{-4.52} = 3.162 \times 10^{-5} \text{ mol dm}^{-3}$$

Let [OH⁻] be y mol dm⁻³

$$K_b = \frac{[\text{HOCH}_2\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{HOCH}_2\text{CH}_2\text{NH}_2]}$$

$$3.162 \times 10^{-5} = \frac{y^2}{5.246}$$

$$y = 0.01288 \text{ mol dm}^{-3}$$

$$\text{pOH} = 1.89$$

$$\text{pH} = 12.1$$

- (b) (i) Another alkylamine, dimethylpiperazine (DMP), has the molecular formula $C_6H_{14}N_2$.

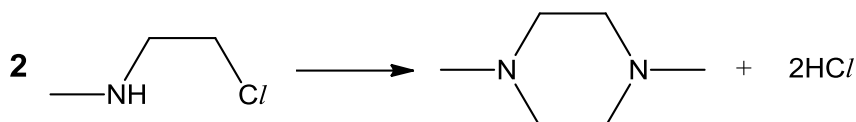
1 mole of DMP can be formed from 2 moles of N-methyl-2-chloroethylamine under suitable conditions.

1. State the conditions needed for this reaction.
2. Write the balance equation for the conversion of N-methyl-2-chloroethylamine into DMP, showing the structural formulae of N-methyl-2-chloroethylamine and DMP.

[2]

1. Ethanol, heat under pressure / in a sealed tube

2.

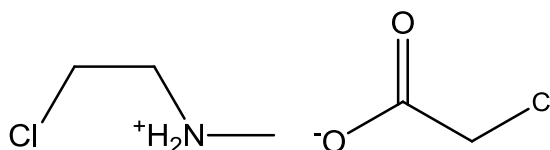


- (ii) Under room conditions, N-methyl-2-chloroethylamine reacts with

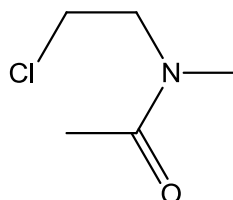
1. $\text{ClCH}_2\text{CO}_2\text{H}$ and
2. CH_3COCl

Name the type of reaction that occur and suggest the structure of the compound formed in each reaction.
[3]

1. Acid-base reaction



2. Condensation reaction / Nucleophilic substitution



- (c) CO_2 that is captured from amine gas treating needs to be sequestered so that it does not return into the atmosphere.

Carbon sequestration has been attempted using mineral carbonation. In this method, liquid CO_2 is buried under a volcanic rock known as basalt. Over a period of time, CO_2 reacts with metal oxides in the rock to form MgCO_3 and CaCO_3 . This method allows a large amount of CO_2 in the atmosphere to be trapped as solid thus reducing its effect as a greenhouse gas.

- (i) In volcanic areas, underground temperatures rises with increasing depth. Two types of carbonates found in these areas are rhodochrosite MnCO_3 and calcite CaCO_3 .

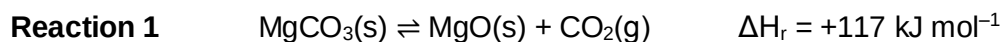
By quoting suitable data from the Data Booklet, explain whether MnCO_3 or CaCO_3 decomposes more readily in the presence of geothermal heat. [3]

Ion	Radii / nm
Ca^{2+}	0.099
Mn^{2+}	0.080

MnCO_3 is expected to decompose more readily than CaCO_3 .

This is because Mn^{2+} has smaller ionic radius than Ca^{2+} . This causes the charge density and polarising power of Mn^{2+} to be greater than that of Ca^{2+} thus polarising the C-O bond / distorting the electron cloud in the C-O bond of the anion in MnCO_3 to a greater extent.

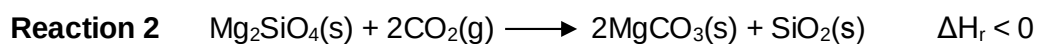
- (ii) Magnesite, MgCO_3 , forms an equilibrium with CO_2 when it is trapped underground in high temperature.



Suggest how mineral carbonation can be maintained despite high temperature and justify your answer. [2]

High partial pressure of CO_2 must be maintained so that the backward reaction is favoured to lower the number of moles of gaseous particles.

- (iii) Fosterite, Mg_2SiO_4 , is a component of basalt that reacts with CO_2 in the following reaction.



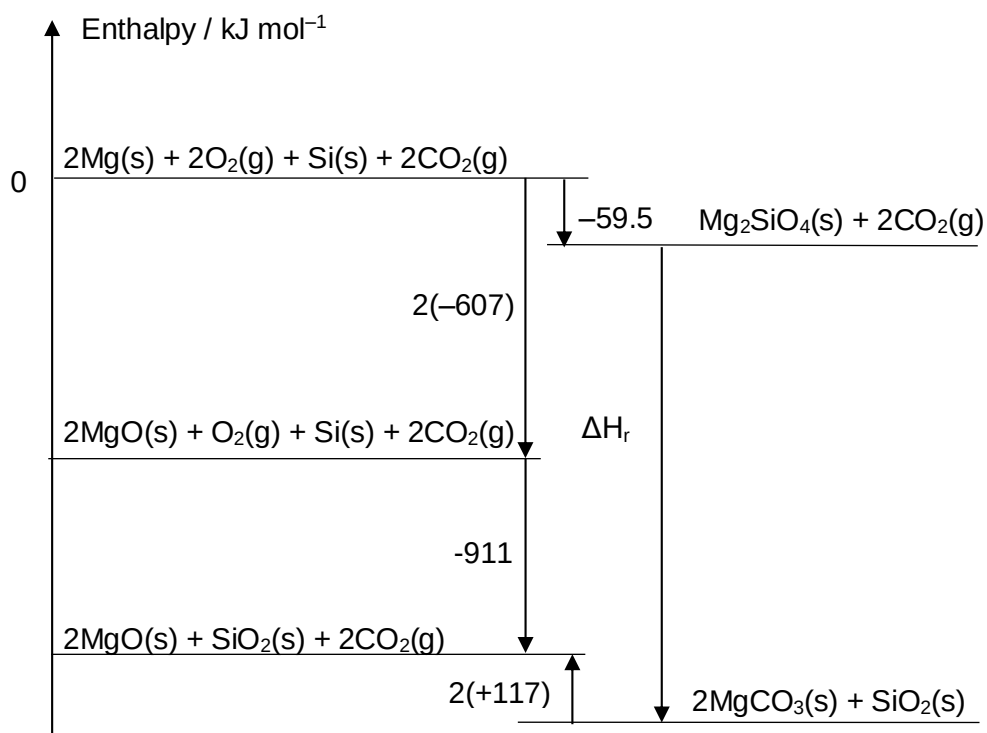
enthalpy change of combustion of $\text{Mg}(\text{s}) = -607 \text{ kJ mol}^{-1}$

enthalpy change of formation of $\text{Mg}_2\text{SiO}_4(\text{s}) = -59.5 \text{ kJ mol}^{-1}$

enthalpy change of formation of $\text{SiO}_2(\text{s}) = -911 \text{ kJ mol}^{-1}$

Using the information above and relevant data from the *Data Booklet*, draw an energy level diagram and hence calculate the enthalpy change of **reaction 2**.

[4]



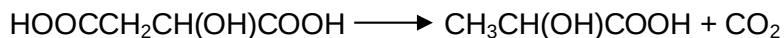
$$\Delta H_r = 2(-117) + 2(-607) + 59.5 - 911$$

$$\Delta H_r = -2299.5$$

$$\Delta H_r = -2300 \text{ kJ mol}^{-1} \text{ (correct to 3 s.f.)}$$

[Total: 20]

- 2 (a) The primary fermentation of grape juice produces wine and carbon dioxide. Sometimes, a secondary fermentation takes place a few months after the primary fermentation is finished and the wine has been bottled. This secondary fermentation converts 2-hydroxybutanedioic acid (malic acid) in the wine into 2-hydroxypropanoic acid (lactic acid). There are two benefits: the carbon dioxide produced can be used to make the wine sparkling; the conversion of the malic acid into lactic acid decreases the acidity of the wine.



A typical concentration of malic acid in wine is 0.05 mol dm^{-3} .

- (i) Calculate the volume of carbon dioxide produced at room temperature and pressure conditions when 1.0 dm^3 of wine undergoes secondary fermentation. [1]

Amount of CO_2 = amount of malic acid = $0.05 \times 1.0 = 0.05 \text{ mol}$

Volume of carbon dioxide produced = $0.05 \times 24 = \underline{1.20 \text{ dm}^3}$ (correct to 3 s.f.)

- (ii) A typical wine bottle has a capacity of 1.5 dm^3 . Using the ideal gas equation, calculate the pressure the carbon dioxide produced would exert inside the air gap of the bottle containing 1.3 dm^3 of wine at room temperature. [1]

$$PV = nRT$$

$$P = (0.065)(8.31)(298)/(0.2 \times 10^{-3}) = \underline{8.05 \times 10^5 \text{ Pa}}$$
 (correct to 3 s.f.)

- (iii) In fact, the pressure inside the bottle is much less under these conditions. Explain why this differs from the pressure you calculated in (a)(ii). [1]

This is due to the fact that CO_2 is not an ideal gas and as such, it will not obey the ideal gas equation. CO_2 is a relatively massive non-polar molecule, thus its molecular volume is not considered to be negligible as compared to the total volume of the gas at such a high pressure.

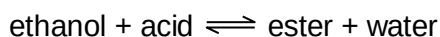
OR

Intermolecular interactions between CO_2 molecules are not negligible at such a high pressure too. Thus, CO_2 deviate more from ideality.

OR

Carbon dioxide can dissolve in aqueous solution. Thus less CO_2 will occupy in the empty space.

- (b) Another way by which the acidity in wine can be decreased is by acid-catalysed ester formation:



Wine consists of ethanol and water. A 1.0 dm^3 of wine typically contains 10% of ethanol by mass and a 0.10 mol dm^{-3} concentration organic acid, assuming density of wine is 1 g cm^{-3} .

- (i) Calculate the value for the equilibrium constant K_c for the ester formation,

given that 17.4% of acid is converted to ester.

[3]

	ethanol	+	acid	$\rightleftharpoons$	ester	+	water
I/mol	100/46		0.1		0		
C	-0.0174		-0.0174		+0.0174		
E/mol	2.1565		0.0826		0.0174		

$$K_c = 0.0977$$

- (ii) Maturation is the process where the wine evolves to a state of readiness for bottling or drinking. Before the wine is ready to be kept in a dark and cool environment at an ambient temperature below 20 °C in barrels for storage, they will equilibrate to form ester. Suggest two reasons why wine needs several months to mature before this reaction takes place significantly.

[2]

The reaction is slow due to low temperature.

Concentration of acid is low thus leading to slow rate of reaction.

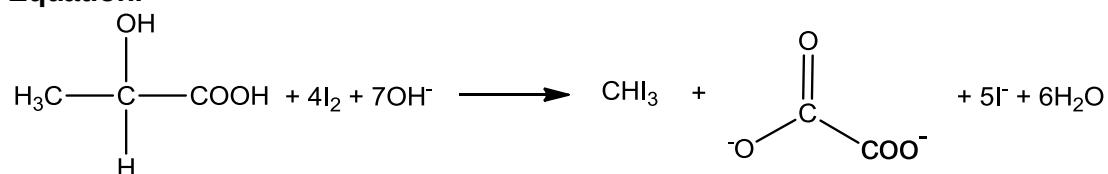
- (c) Describe a laboratory test to distinguish between 2-hydroxybutanedioic acid (malic acid) and 2-hydroxypropanoic acid (lactic acid). State the reagents and conditions you would use and any observations that you would make for each compound. Write equation for any reaction that occurs.

[3]

Reagents & Conditions: aqueous I_2 , NaOH (aq), warm to 60 °C

Observations: 2-hydroxypropanoic acid will give yellow ppt. while 2-hydroxybutanedioic acid will not.

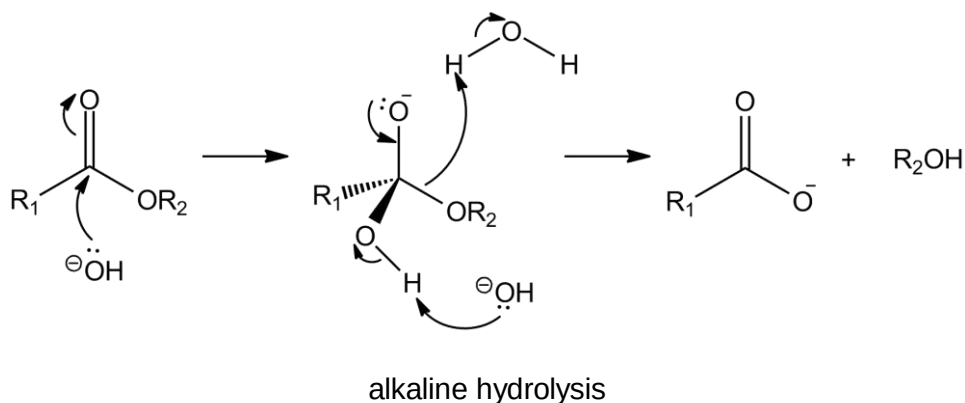
Equation:

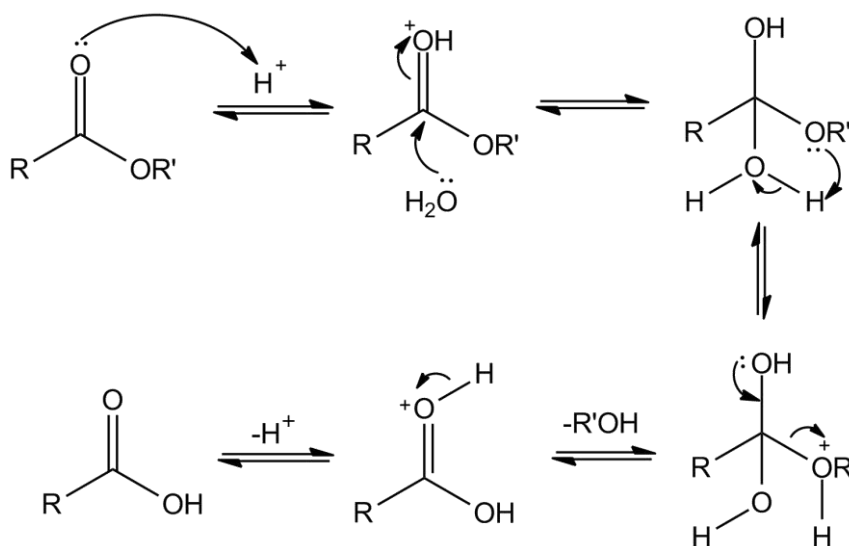


[1]

- (d) Typically, esters can be hydrolysed in dilute acid or alkali.

The mechanism of both hydrolysis methods are shown as follow:





acidic hydrolysis

In alkaline hydrolysis, the hydroxide anion attacks the electron deficient carboxyl carbon.

In acid hydrolysis, the acid protonates the carboxyl oxygen to render the carboxyl carbon more electrophilic towards nucleophilic attack by water.

(i) What is the role of

1. OH^- in step 1 of alkaline hydrolysis
 2. H^+ in acidic hydrolysis respectively?
- [2]

OH^- is acting as a nucleophile.

H^+ is acting as a catalyst.

(ii) What is the role of water in acid hydrolysis? [1]

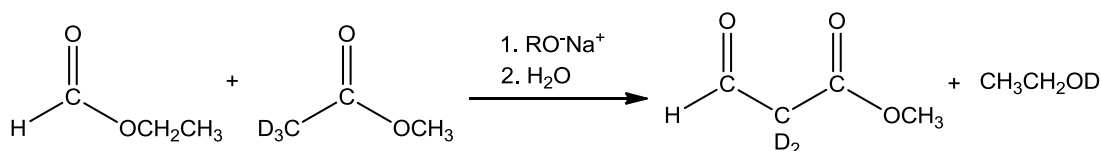
Water is acting as a nucleophile.

(iii) Outline the two advantages of alkaline hydrolysis. [2]

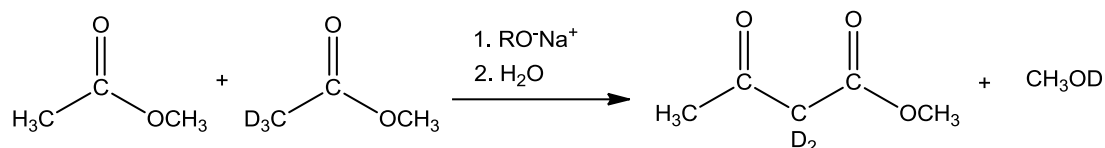
The reaction is irreversible or complete which means that there will be high yield.

The products are easier to separate as one of the products is ionic (aqueous layer) and will be found in a different phase from the organic reactants.

(e) Claisen condensation is a carbon-carbon bond forming reaction that can occur between two esters in the presence of a strong base, resulting in a β -keto ester. In the mixture of methyl ethanoate and ethyl methanoate, the following Claisen condensation products are formed.

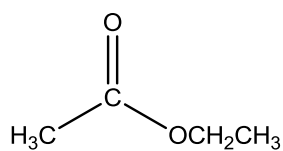


and

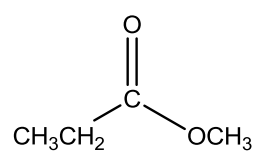


(Deuterium, ^2_1D , is an isotope of hydrogen.)

Predict the structures of β -keto esters formed when ethyl ethanoate is mixed with methyl propanoate under suitable reaction conditions.

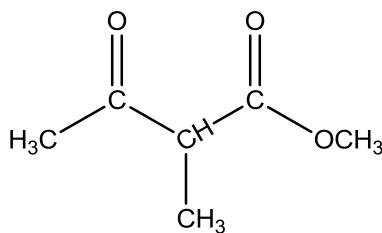
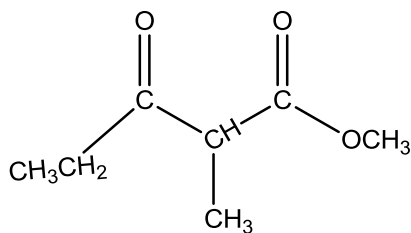
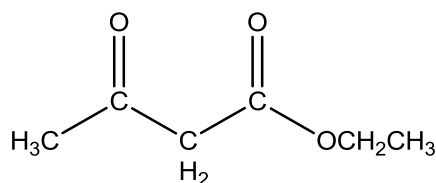
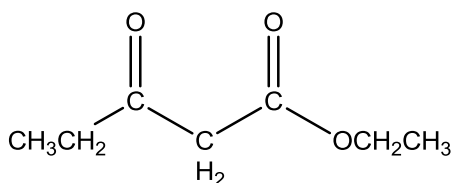


ethyl ethanoate



methyl propanoate

[4]



[Total:20]

- 3 (a) The characteristic properties of transition metals include coloured ions, complex formation, variable oxidation states and catalytic activity.

Transition metals are used extensively as heterogeneous catalysts in industrial processes. An example is the use of iron as a catalyst in the Haber process to manufacture ammonia.

- (i) Explain what is meant by the term *heterogeneous*? [1]

Reactants and catalyst are in different phase.

- (ii) State, in the correct order, three essential steps for the mechanism of heterogeneous catalysis. [2]

- 1) Surface adsorption/adsorption of reactant molecules on surface of catalyst
- 2) Reaction between reactant molecules Allow :bonds in reactants weakened
- 3) Products desorbed from the surface

- (iii) The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its efficiency as a heterogeneous catalyst.

Suggest a reason why transition metals which adsorb weakly are usually not good heterogeneous catalysts. [1]

Reactants not brought together or
No increase in reactant concentration on catalyst surface or
Reactants not held long enough for a reaction to occur or
Reactant bonds not weakened

- (iv) A catalyst containing molybdenum(VI) was analysed for its molybdenum content by reducing a sample to the molybdenum(III) state.

When titrated with acidified potassium manganate(VII), the molybdenum(III) was oxidised back to molybdenum(VI).

A 0.330 g sample of the catalyst, after reduction, required 27.50 cm³ of 0.0200 mol dm⁻³ potassium manganate(VII) to convert the molybdenum(III) into molybdenum(VI).

Calculate the percentage by mass of molybdenum in the catalyst. [2]

1 mole of molybdenum(III) compound loses 3 moles of electrons on oxidation while 1 mole of manganate(VII) accept 5 moles of electrons in acidic medium.

Amount of MnO₄⁻ in 27.50 cm³ = $27.5 \times 10^{-3} \times 0.02 = 5.50 \times 10^{-4}$ mol

Amount of Mo = $\frac{5}{3} \times 5.50 \times 10^{-4} = 9.17 \times 10^{-4}$ mol

Mass of Mo = $95.9 \times 9.17 \times 10^{-4} = 8.80 \times 10^{-2}$ g

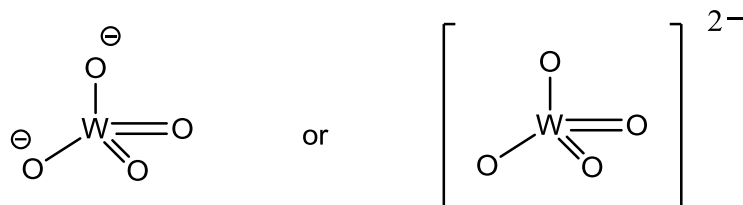
% Mo = $(8.80 \times 10^{-2} / 0.330) \times 100 = 26.7 \%$

- (b) (i) The chemistry of the transition metal, tungsten, has certain similarities to that of sulfur. Both elements reach their maximum +6 oxidation states when

combined with the electronegative element, oxygen.

Most tungsten occurs naturally in the tungsten anion, WO_4^{2-} , analogous to the sulfate ion, SO_4^{2-} . A common mineral is Scheelite which is calcium tungstate, CaWO_4 .

Draw the structure showing the bonding in the WO_4^{2-} ion and give the O–W–O bond angle. [2]



Bond angle: 109.5°

- (ii) Tungsten(VI) oxide, WO_3 , is used in electrochromic windows which change colour when an electrical voltage is applied.

In electrochromic windows, a voltage is applied between a transparent layer of tungsten(VI) oxide and a source of ions such as a lithium salt, and the following reaction takes place during which some of the lithium ions are incorporated into the structure of the oxide:



The product, Li_xWO_3 , is known as a tungsten bronze and its colour depends on the value of x . The value of x can vary from 0 to 1; a typical value giving blue-black colour is when $x = 0.3$.

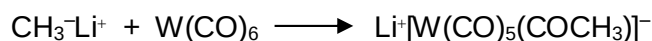
Calculate the average oxidation state of the tungsten when $x = 0.3$. [1]

Let oxidation state of the tungsten be m

$$0.3 + m + (-2)3 = 0$$

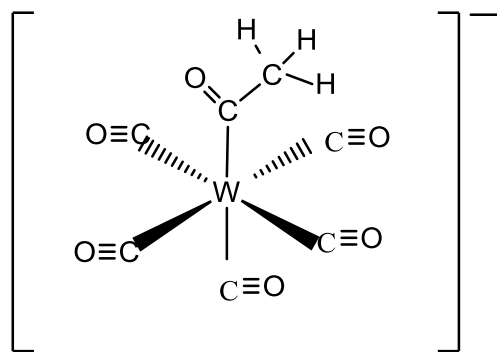
$$m = \underline{+5.7}$$

- (iii) A complex of tungsten, $\text{W}(\text{CO})_6$, has zero oxidation state for tungsten. It reacts with CH_3^-Li^+ as shown by the following equation:



The reaction is nucleophilic addition where CH_3^- is a nucleophile.

Illustrate the shape of $[\text{W}(\text{CO})_5(\text{COCH}_3)]^-$ by drawing the displayed formula of the anionic complex. [1]

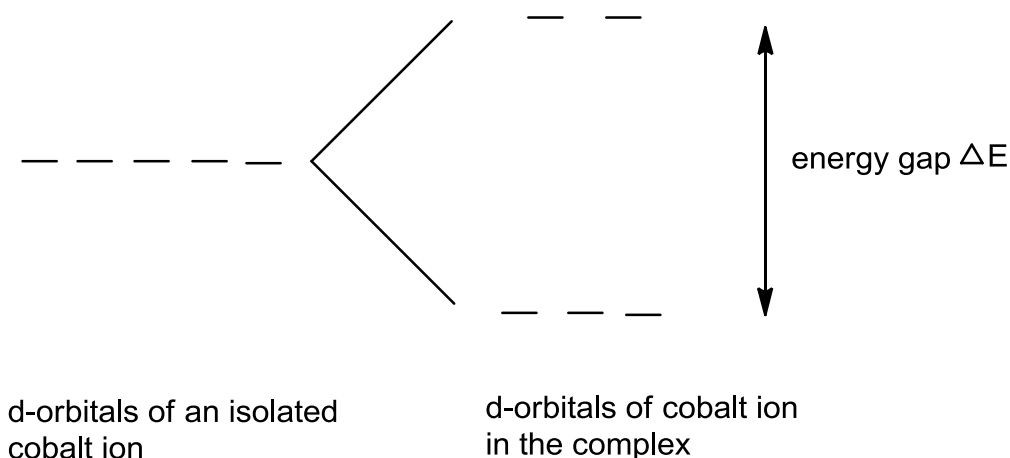


**Note: all covalent bonds must be shown as it is a displayed formula.
Octahedral shape illustrated with wedge and dash bonds.**

- (c) CoF_6^{3-} and $\text{Co}(\text{NH}_3)_6^{3+}$ are two octahedral complexes which are blue and yellow in colour respectively.

The colours of the two complexes are different due to different ligands which cause splitting of the five 3d orbitals by different amount.

The following diagram shows how the five d-orbitals are split in an octahedral environment.

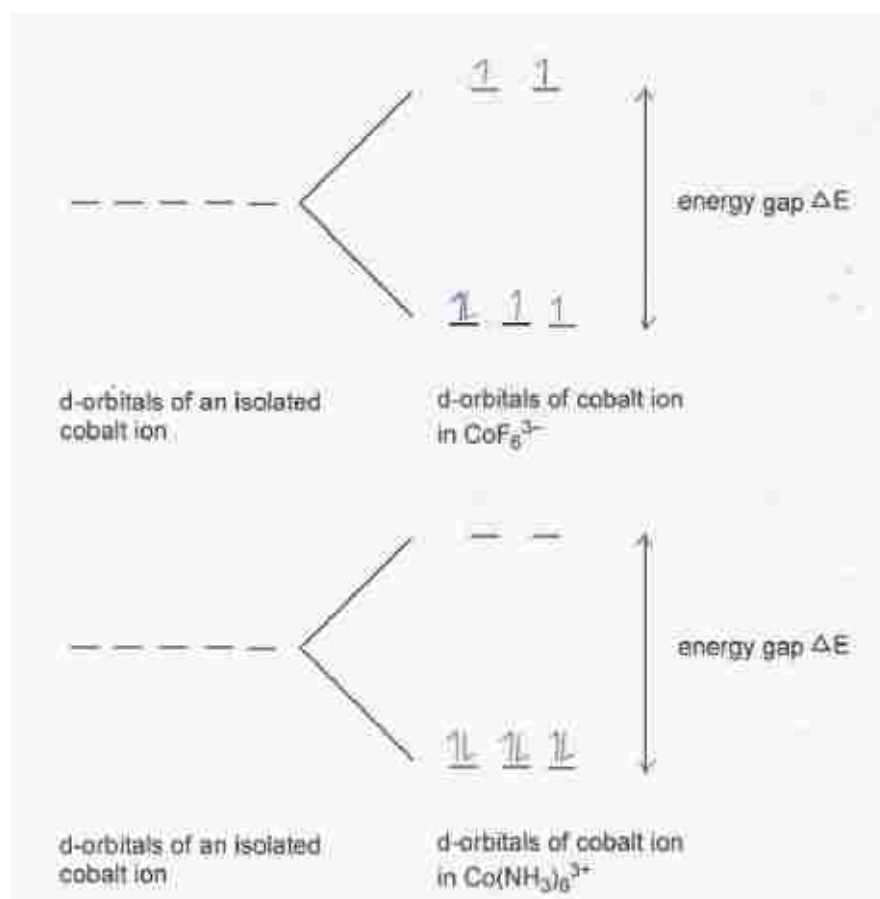


In the 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In the 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary before the higher energy d-orbitals are used.

CoF_6^{3-} is a 'high spin' complex while $\text{Co}(\text{NH}_3)_6^{3+}$ is a 'low spin' complex.

- (i) Draw two diagrams like the one above to show the electronic configurations of cobalt ions in CoF_6^{3-} and $\text{Co}(\text{NH}_3)_6^{3+}$ respectively. [2]



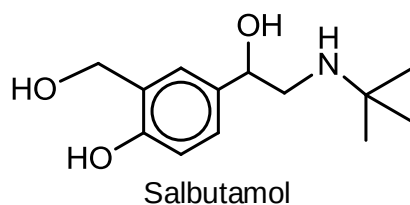
- (ii) Hence, explain which of the two complexes will have a larger energy gap, ΔE . [1]

Co(NH₃)₆³⁺ since ΔE is large so pairing of electrons at lower level is preferred rather than promotion of electrons to a higher level.

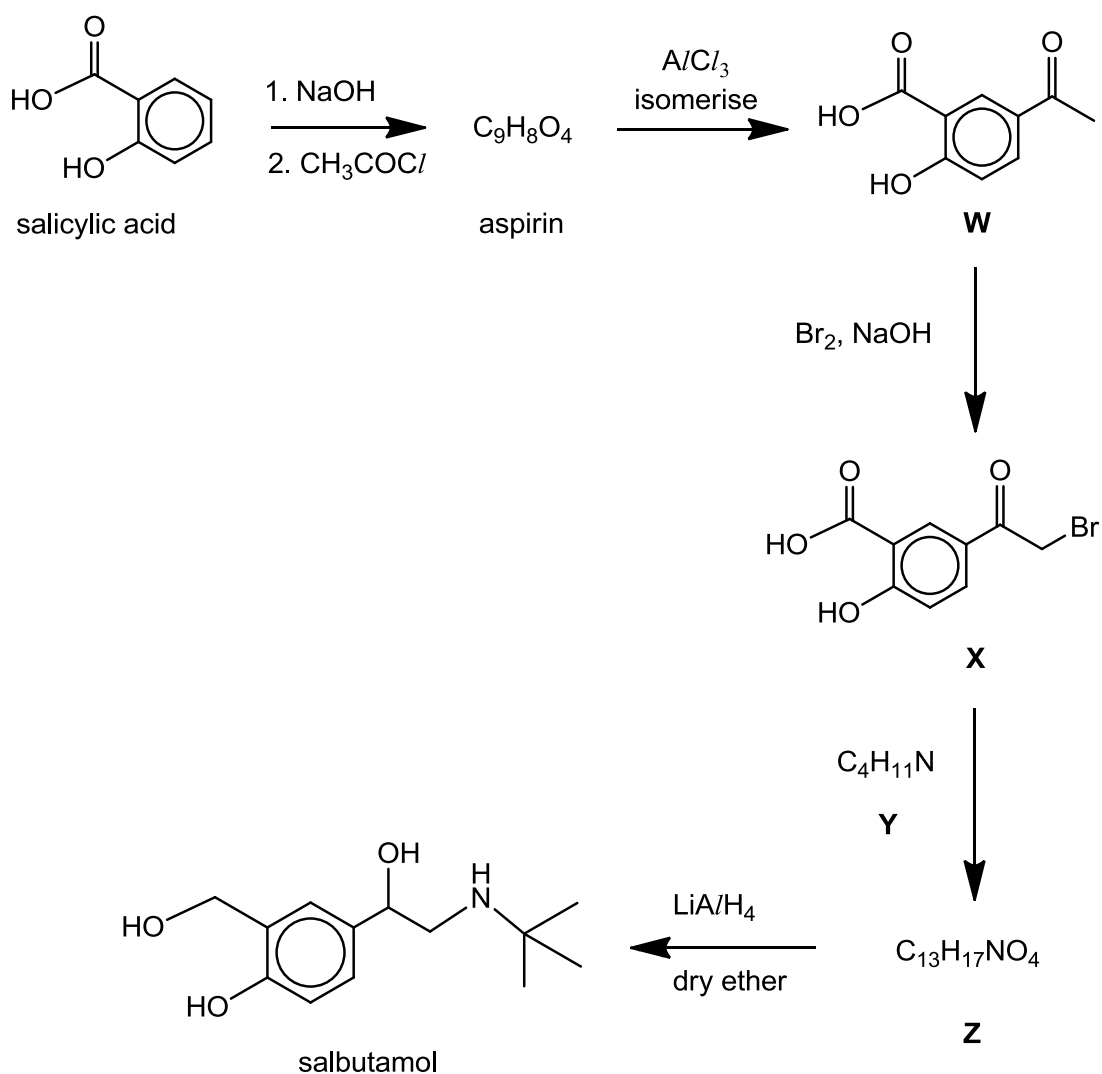
- (iii) Explain why electrons usually prefer to occupy orbitals singly, rather than in pairs. [1]

There will be electrostatic repulsion between electrons if they are paired up.

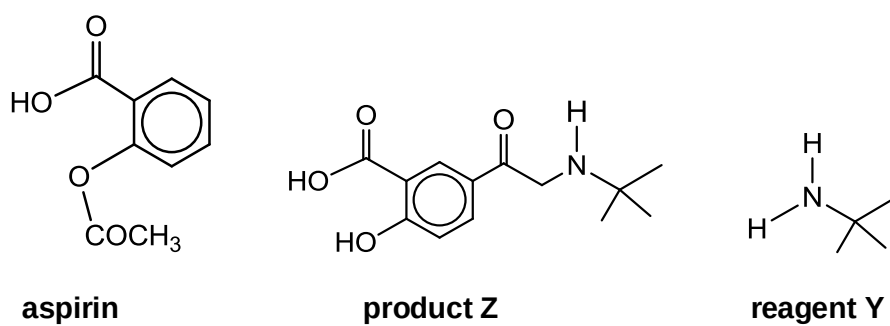
- (d) Salbutamol is an anti-asthma drug which is prepared from aspirin, which in turn is prepared from salicylic acid.



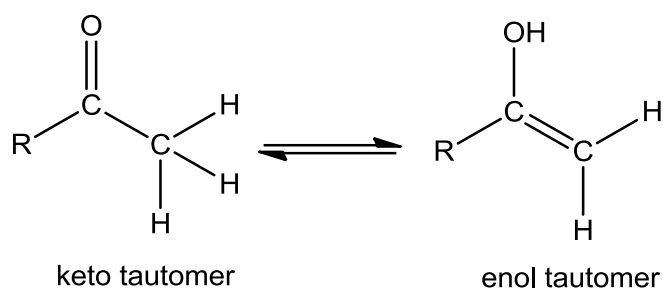
The following reaction scheme shows the synthesis of Salbutamol from salicylic acid.



(i) Draw the structures of aspirin, product **Z** and reagent **Y**. [3]

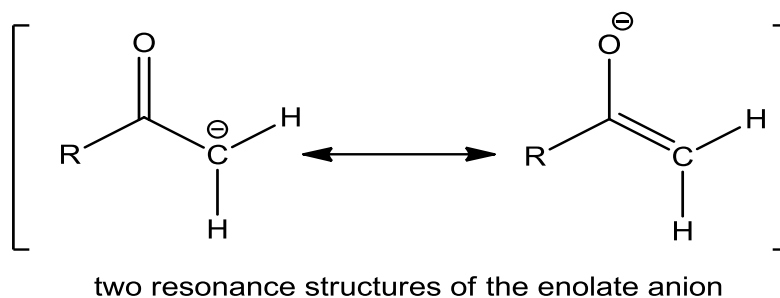


(ii) A carbonyl compound with a hydrogen atom on its α carbon rapidly equilibrates with its corresponding enol form as shown.



This rapid inter-conversion between the keto and enol form is a special kind of isomerism known as tautomerism.

In the presence of strong bases, the hydrogen atom on its α -carbon is abstracted to form a resonance-stabilised enolate anion as shown below:

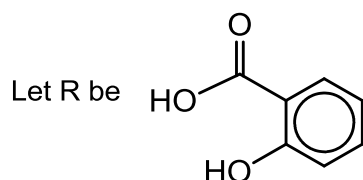


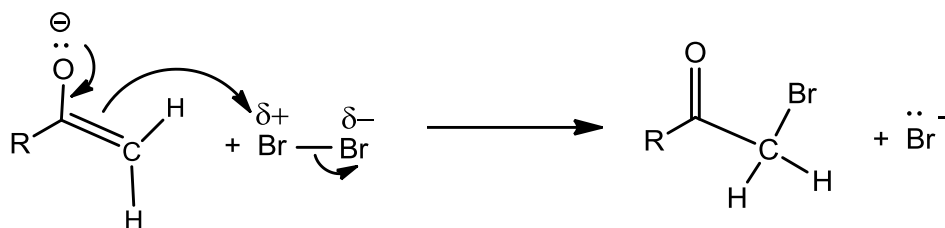
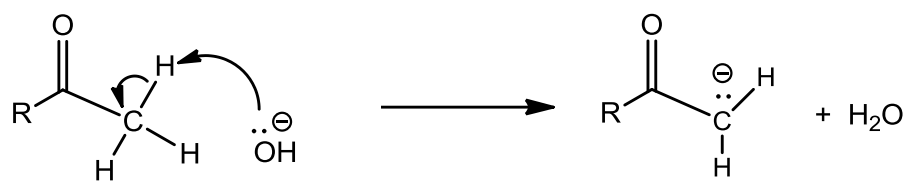
Resonance structures differ only in the position of their electrons.

The mechanism for the reaction from product **W** to form product **X** using Br_2 and NaOH involves the intermediate, enolate anion. The two steps are:

- The first step involves an acid-base reaction between the hydroxide ion and the methyl group to give the enolate anion.
- Using its resonance structure with the $\text{C}=\text{C}$ bond, the enolate anion undergoes electrophilic attack by Br_2 to give product **X**.

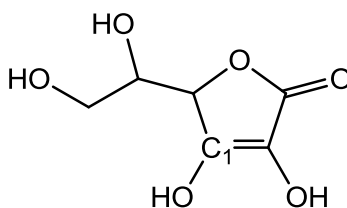
Based on the information given, describe the mechanism for the reaction to form product **X** from product **W**. In your answer, show any relevant charges, lone pairs of electrons and arrows to show movement of electrons. [3]





[Total: 20]

- 4 This question concerns ascorbic acid (vitamin C, $C_6H_8O_6$) and its chemistry. The structure of ascorbic acid is provided below.



ascorbic acid

- (a) Ascorbic acid can be used in the synthesis of other compounds, with the use of $Si(CH_3)_3Cl$ as a protecting group for the alcohol groups.

- (i) In water, $Si(CH_3)_3Cl$ hydrolyses at a much faster rate than $C(CH_3)_3Cl$.

Explain the difference in the ease of hydrolysis.

[2]

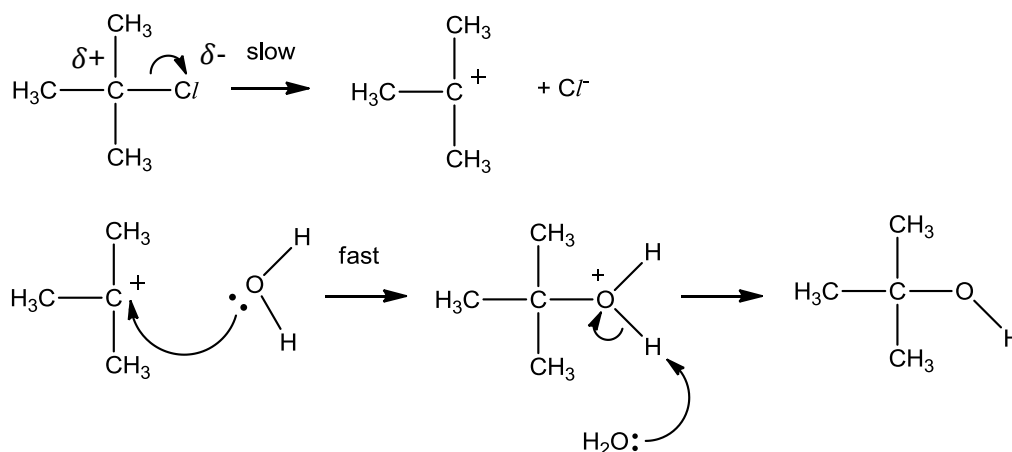
Si has empty 3d orbitals that can accept a lone pair of electrons from water while there are no empty orbitals available to accept lone pair for C, requiring the formation of a carbocation prior to nucleophilic attack by water.

- (ii) State and describe the mechanism for the hydrolysis of $C(CH_3)_3Cl$ in water. You should include in your answer:

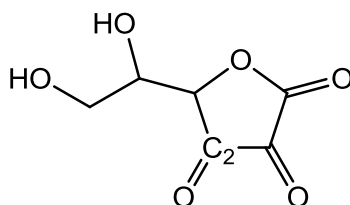
- Dipoles of relevant covalent bonds
- Curly arrows
- Label for the slow step

[3]

S_N1 / unimolecular nucleophilic substitution



- (b) Dehydroascorbic acid (DHA), $C_6H_6O_6$, with its structure shown below, is the oxidised product of ascorbic acid.



Dehydroascorbic acid

- (i) State the oxidation number of:
- the carbon labelled C₁ in ascorbic acid.
 - the carbon labelled C₂ in DHA.

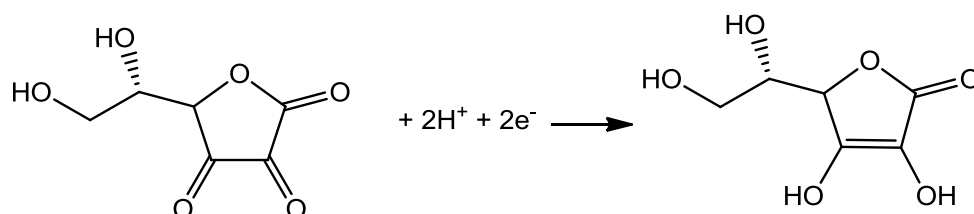
[2]

Ascorbic acid: +1

DHA: +2

- (ii) Write a balanced half equation, showing their structural formulae, for the reduction of DHA to ascorbic acid.

[1]



- (iii) The electrode potential of ascorbic acid at pH 2 is +0.281 V. Explain how the electrode potential value changes as the pH increases.

[2]

With an increase in pH, there is a decrease in the concentration of H⁺. Thus the position of equilibrium for the reaction in (ii) shifts to the left, favouring the tendency for oxidation of ascorbic acid. Hence the electrode potential becomes less positive / more negative with a rise in pH.

- (c) Electrolysis of an aqueous solution of Fe(ascorbate)₂ buffered at pH 2 was carried out, with 22.4 cm³ of hydrogen gas obtained at room temperature and pressure, Ascorbate is the conjugate base of ascorbic acid.

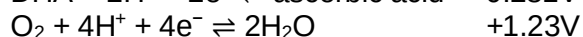
- (i) Using information from the *Data Booklet*, determine the minimum voltage required to run this electrolysis.

[2]

Cathode



Anode



E_{cell} is to be calculated correctly based on correctly selected electrode potentials

$$E_{\text{cell}} = -0.00 - (+0.281) = -0.281\text{V}$$

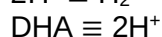
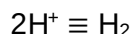
A minimum of 0.281V is required to run the electrolysis.

- (ii) Calculate the mass of the product obtained at the anode.

[2]

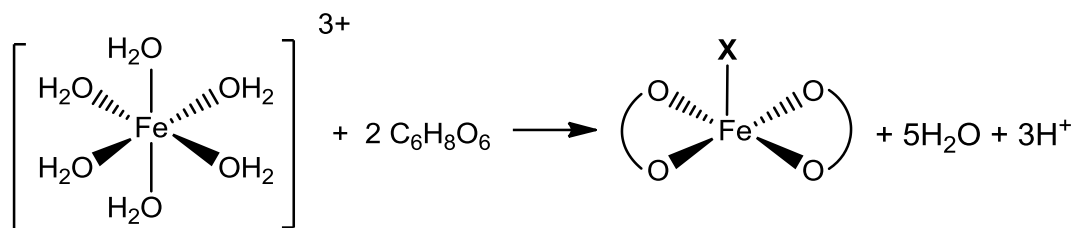
The oxidation of ascorbic acid is easier at the anode than water. Identifies DHA as the product at the anode in words or working

$$\text{Amount of H}_2 = \frac{22.4}{24000} = 9.333 \times 10^{-4} \text{ mol}$$



$$\text{Mass of DHA} = 9.333 \times 10^{-4} \times 174 = 0.162 \text{ g}$$

- (d) To 50 cm³ of an aqueous solution of ascorbic acid, 200 cm³ of ethanol was added. Some FeCl₃ was dissolved in this solution and the solid, Fe(ascorbate)₂X with an M_r of 422.8, was filtered off. The equation is as follows:



Note:  represents the ascorbate ligand

- (i) Suggest the role of ethanol in the preparation of the precipitate. [1]

It serves to reduce the solubility of the compound in solution / encourages precipitation.

- (ii) Determine the identity of the ion X. [1]

Either by inspection of the equation

OR

$$422.8 - 55.8 - 2(175) = 17$$

Hydroxide / OH⁻

- (iii) The formation of Fe(ascorbate)₂X from Fe(H₂O)₆³⁺ involves a ligand substitution between H₂O and the ascorbate ion as shown above.

Explain the sign of the entropy change for the formation of Fe(ascorbate)₂X.

Hence given that the formation is exothermic, deduce the sign of the standard Gibbs free energy change. [4]

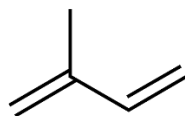
Being bidentate, each ascorbate ion replaces 2 water molecules coordinated to Fe³⁺ OR increase in the number of species/particles. There is an increase in the entropy during the formation of Fe(ascorbate)₂X. Hence ΔS > 0.

As ΔG = ΔH - TΔS and ΔH < 0,
ΔG will have a negative sign.

[Total: 20]

5 The use of the *Data Booklet* is relevant to this question.

- (a) 2-methylbuta-1,3-diene, also known as isoprene, is produced by many plants and serves as a building block for monoterpenes when two isoprene units combine without any rearrangement of the carbon skeleton. Monoterpenes all have molecular formula of $C_{10}H_{16}$.



isoprene

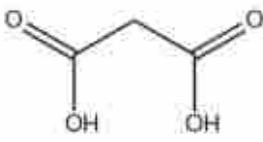
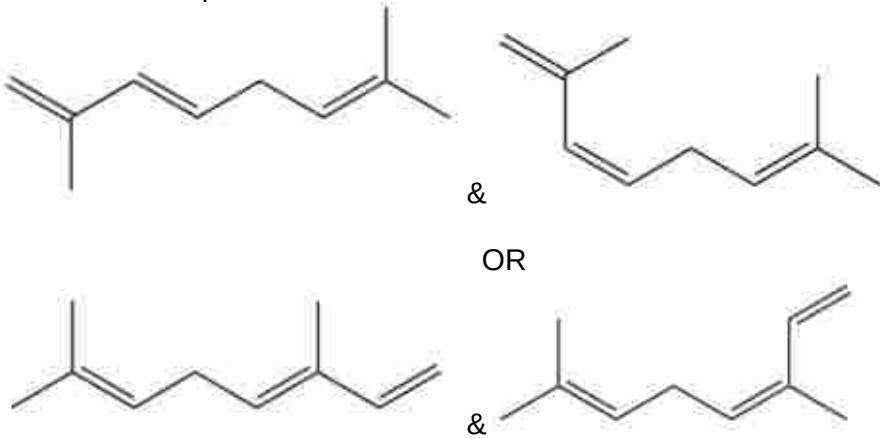
Compounds **A** and **B** are geometric isomers of a monoterpene commonly used in perfumes for their sweet herbal scent. Compounds **A** and **B** react with cold dilute alkaline potassium manganate(VII) to produce stereoisomers of $C_{10}H_{22}O_6$.

Compounds **A** and **B** react with hot concentrated acidified potassium manganate(VII) to produce compounds **C**, $C_3H_4O_3$, **D**, $C_3H_4O_4$, **E**, C_3H_6O and a gas **F**. Both **C** and **E** give a yellow precipitate with aqueous alkaline iodine. A 1.04 g sample of **D** reacted with excess sodium metal to produce 240 cm^3 of gas.

Use the information to suggest, with explanation, identities of **A** to **F**.

[9]

Statements	Explanations/Inferences/Deductions
1. A and B react with cold dil. $KMnO_4/OH^-$ to produce $C_{10}H_{22}O_6$.	A and B underwent mild oxidation. An increase of 6 $-OH$ groups suggests 3 alkenes.
2. A and B react with hot conc. $KMnO_4/H^+$ to produce C , $C_3H_4O_3$, D , $C_3H_4O_4$, E , C_3H_6O and a gas F .	A and B underwent vigorous oxidation. F is CO_2 . $\Rightarrow$ a terminal alkene is present on A and B .
3a. C and E give yellow ppt. with $I_2(aq)OH^-$.	C and E contain CH_3CO- group. (Do not accept $CH_3CH(OH)-$ since these are products of vigorous oxidation.) $\therefore$ C is 2-oxopropanoic acid. $\therefore$ E is propanone.
3b. 1.04 g of D produces 240 cm^3 of gas with Na.	$\eta(\text{D}) = 1.04 \div 104 = 0.0100\text{ mol}$ Gas is H_2 , $\eta(H_2) = 240 \div 24000 = 0.0100\text{ mol}$ Since $1\text{ D} \equiv 1\text{ H}_2 \Rightarrow \text{D}$ has 2 acidic protons. i.e. 2 carboxylic acid groups. $\therefore$ D is propane-1,3-dioic acid.
4. Alternative to	Since C , D and E are oxidised products of alkene

deducing C, D and E.	cleavage, they either possess ketone and/or carboxylic acid functional groups. Based on molecular formula of C, the 3 O atoms can be attributed to (1) 3 ketones OR (2) 1 carboxylic acid and 1 ketone. Since there are only 3 C atoms, option (1) is invalid. ∴ C is a ketoacid ⇒ 2-oxopropanoic acid. Based on molecular formula of D, the 4 O atoms can be attributed to (1) 2 carboxylic acid groups OR (2) 1 carboxylic acid group and 2 ketones OR (3) 4 ketones. Since there are only 3 C atoms, options (2) and (3) are invalid. ∴ D has to be a 3 C dicarboxylic acid. ⇒ propane-1,3-dioic acid. Based on molecular formula of E, the 1 O atom can only be a ketone functional group. ∴ E is propanone.	
C 	D 	E 
Therefore, acceptable structure for A and B: 		

- (b) Fehling's solution is often used as a distinguishing test in the qualitative analyses of organic compounds. It is prepared by mixing two separate solutions, known as Fehling's A and Fehling's B. Fehling's A is aqueous copper(II) sulfate while Fehling's B is an aqueous solution of potassium sodium tartrate made in sodium hydroxide.

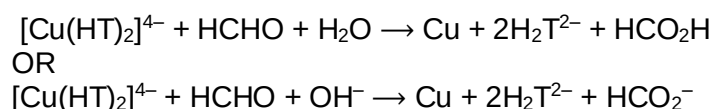
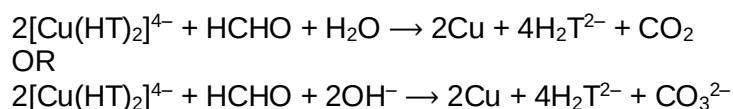
Tartaric acid, H_4T , can exist as a tetraanion, T^{4-} , in a strongly alkaline medium. In Fehling's B, it exists as the H_2T^{2-} anion.

The standard electrode potentials, $E^\ominus$, of several species are shown in the table below.

	Electrode reaction	$E^\ominus / \text{V}$
1	$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Cu} + 2\text{OH}^-$	-0.36
2	$2\text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cu}_2\text{O} + 2\text{H}^+$	+0.20
3	$[\text{Cu}(\text{HT})_2]^{4-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cu} + 2\text{H}_2\text{T}^{2-} + 2\text{OH}^-$	+0.25
4	$\text{HCO}_2\text{H} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCHO} + \text{H}_2\text{O}$	-0.03
5	$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{HCHO} + \text{H}_2\text{O}$	-0.07
6	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCO}_2\text{H}$	-0.11

Adding Fehling's solution to methanal causes a reaction to take place.

- (i) By selecting appropriate electrode reactions from the *Data Booklet* or the table above, construct a balanced equation for this reaction. [1]



- (ii) Use your answer in part (i) to calculate the $E^\ominus_{\text{cell}}$ for this reaction. [1]

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{cat}} - E^\ominus_{\text{an}} \\ &= +0.25 - (-0.07) \\ &= \underline{+0.32 \text{ V}} \end{aligned}$$

OR

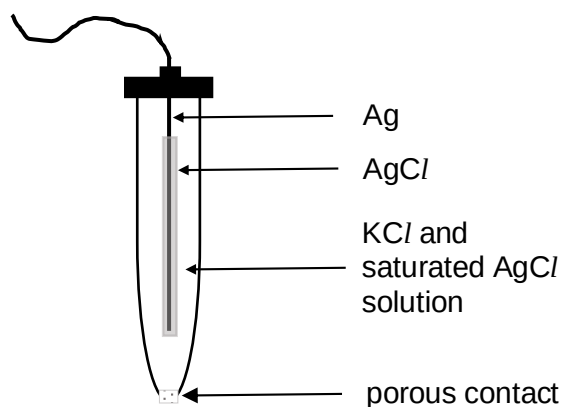
$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{cat}} - E^\ominus_{\text{an}} \\ &= +0.25 - (-0.03) \\ &= \underline{+0.28 \text{ V}} \end{aligned}$$

- (iii) Describe the observations for this reaction. [1]

Blue coloured solution decolourises with the formation of a reddish-brown/ pink coloured mirror/solid/precipitate.

- (c) Electrode potential values are often quoted with reference to the standard hydrogen electrode (SHE). It is however, seldom used because it is difficult to regulate the pressure of hydrogen gas at 1 atm.

One of the more commonly used reference electrodes in electrochemistry is the silver/silver chloride electrode (SSCE). It is made of a silver wire that is coated with a thin layer of silver(I) chloride, immersed in a potassium chloride solution saturated with silver(I) chloride.



schematic of a silver/silver chloride electrode

One of the advantages of using the SSCE is that it can be directly immersed into the other half-cell, thereby negating the use of a salt bridge.

- (i) Suggest the purpose of having the porous contact. [1]

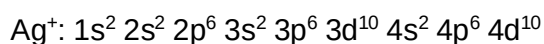
The porous contact allows for the exchange of ions between the two half-cells.

The solution in the SSCE is colourless in spite of the presence of a d-block element.

- (ii) Explain how the colour in transition metal compounds arise. [2]

When ligands approach transition metal atom/ion, the degenerate d orbitals split into two non-degenerate energy levels (accept comparison of similar vs different energy; i.e. no need "degenerate" if student can explain). d-d* transition occurs when an electron from the lower energy level absorbs certain wavelength of visible light and gets promoted to the higher energy level. Colour seen is complementary to the wavelengths of light absorbed.

- (iii) Write the full electronic configuration of Ag^+ and hence explain why it is not coloured. [2]



As Ag^+ has a full d subshell, d-d* transition is not possible from the lower energy level to the higher energy level OR no wavelengths in visible light are absorbed and all are transmitted, making Ag^+ colourless.

- (d) Adding a reagent that selectively brings one of the ions out of a solution as a precipitate while leaving the other ion in the solution is a technique known as selective precipitation.

Data about the solubilities in water and solubility products of silver(I) hydroxide and copper(II) hydroxide at 298 K are given below. Only the numerical values of the solubility products are given.

hydroxide	solubility/mol dm ⁻³	solubility product
AgOH	1.23×10^{-4}	1.52×10^{-8}
$\text{Cu}(\text{OH})_2$	1.77×10^{-7}	2.20×10^{-20}

As a general standard, two ions are selectively separated when a maximum 0.01% of the precipitated compound still remains as the aqueous ions.

Determine if selective precipitation can be performed on a solution containing $0.200 \text{ mol dm}^{-3} \text{ Ag}^+$ and $0.200 \text{ mol dm}^{-3} \text{ Cu}^{2+}$ with the addition of solid potassium hydroxide. [3]

Since solubility of $\text{Cu}(\text{OH})_2$ is lower than AgOH , it will be precipitated first.

To maximally precipitate $\text{Cu}(\text{OH})_2$, AgOH has to be saturated.

$$[\text{OH}^-] \text{ when AgOH is sat.} = \frac{1.52 \times 10^{-8}}{0.200} = 7.60 \times 10^{-8} \text{ mol dm}^{-3}$$

$$[\text{Cu}^{2+}] \text{ when AgOH is sat.} = \frac{2.20 \times 10^{-20}}{(7.60 \times 10^{-8})^2} = 3.81 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\%[\text{Cu}^{2+}] \text{ remaining} = \frac{3.81 \times 10^{-6}}{0.200} \times 100\% = 0.001905\% \approx 0.00191\% < 0.01\%$$

Therefore Cu^{2+} can be selectively precipitated from Ag^+ .



ANDERSON JUNIOR COLLEGE
2016 JC2 PRELIMINARY EXAMINATIONS

CHEMISTRY

9647/03

Higher 2

21 September 2016

Paper 3 Free Response

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Paper
 Data Booklet
 Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

Start each question on a fresh sheet of paper.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

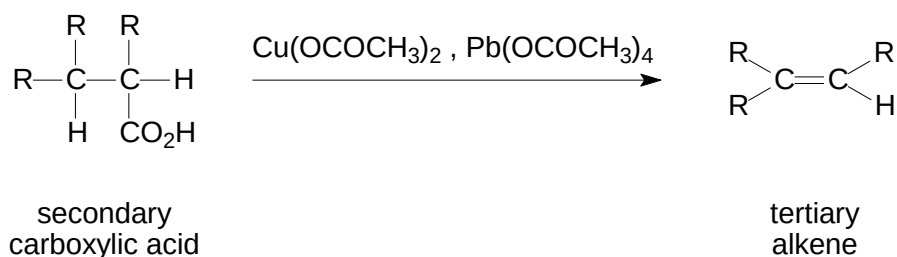
This document consists of **12** printed pages.

- 1 (a) Transition elements show typical properties that distinguish them from s-block elements such as calcium. The following table gives data about some physical properties of the elements calcium, iron and copper.

property	calcium	iron	copper
relative atomic mass	40.1	55.8	63.5
atomic radius (metallic) / nm	0.197	0.126	0.128
ionic radius (2+) / nm	0.099	0.076	0.069
melting point / °C	839	1535	1085
density / g cm ⁻³	1.54	7.86	8.92
electrical conductivity / $\times 10^6$ S cm ⁻¹	0.298	0.100	0.596

- (i) Explain why the atomic radii of iron and copper are similar to each other. [2]
- (ii) The melting point of iron is significantly higher than that of calcium. Explain this in terms of the type and strength of bonding in each metal. [3]
- (iii) Using relevant data from the table, explain why the densities of iron and copper are significantly greater than that of calcium. (No calculations are required.) [2]
- (b) Cu(I) ions are unstable and readily undergo disproportionation in aqueous solution.
- Write an ionic equation showing the disproportionation of Cu⁺(aq) ions, and choose relevant $E^\ominus$ values from the *Data Booklet* to calculate $E_{\text{cell}}^\ominus$ for the reaction. [2]
- (c) Cu(I) is stable in insoluble salts and in some complexes. Complexes of Cu(I) are colourless whereas complexes of Cu(II) are coloured. Use these facts to explain the following observations, writing equations for all reactions.
- (i) The addition of KI(aq) to CuSO₄(aq) produces a white precipitate, CuI, and a brown solution. The brown solution turns colourless when aqueous sodium thiosulfate, Na₂S₂O₃, is added, and the white precipitate remains. [2]
- (ii) On boiling with copper foil, the colour of a solution of CuCl₂ in concentrated hydrochloric acid changes from blue to colourless. The colourless solution contains a linear complex ion of copper and chlorine.
- After filtering off the excess copper metal and diluting the solution with water, a white precipitate is formed, which contains 35.9 % of chlorine by mass. [3]

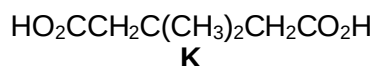
- (d) Some copper compounds have found a use as reagents for unusual organic reactions. An example is the use of a mixture of copper(II) ethanoate and lead(IV) ethanoate for the conversion of carboxylic acids into alkenes containing one less carbon atom. This reaction is known as oxidative decarboxylation.



When a secondary carboxylic acid **G**, $\text{C}_9\text{H}_{16}\text{O}_2$, was treated in this way, alkene **H**, C_8H_{14} , was formed. On treatment with hot acidified concentrated KMnO_4 , **H** produced a single compound **J**, $\text{C}_8\text{H}_{14}\text{O}_3$.

Compound **J** evolved CO_2 with $\text{Na}_2\text{CO}_3(\text{aq})$, gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and gave a yellow precipitate with alkaline aqueous iodine.

When the yellow precipitate had been filtered off, acidification of the aqueous solution produced 3,3-dimethylpentan-1,5-dioic acid, **K**.

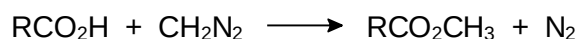


Use the information above to deduce the structures for compounds **G**, **H** and **J**, explaining all the reactions involved.

[6]

[Total: 20]

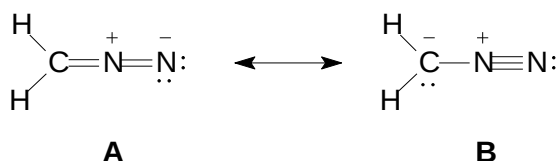
- 2 (a) One frequently used method for preparing methyl esters is by reaction of carboxylic acids with diazomethane, CH_2N_2 .



The reaction of a carboxylic acid with diazomethane occurs via a two-step mechanism.

- Protonation of diazomethane by the carboxylic acid to yield methyldiazonium ion, CH_3N_2^+ , and carboxylate ion in the first step.
- Reaction of the carboxylate ion with CH_3N_2^+ to form N_2 in the second step.

- (i) **A** and **B** are two possible resonance structures of diazomethane, CH_2N_2 .



Suggest which resonance structure of diazomethane, **A** or **B**, is likely to be involved in the first step of the mechanism.

[1]

- (ii) Using your answer from (a)(i), suggest the mechanism for the reaction between RCO_2H and diazomethane. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

- (b) (i) Write an equation for the complete combustion of methyl ethanoate, $\text{CH}_3\text{CO}_2\text{CH}_3$.

[1]

- (ii) Define the term *standard enthalpy change of formation*.

[2]

- (iii) Use the standard enthalpy changes of combustion, $\Delta H_c^\ominus$ in **Table 2.1** to calculate the standard enthalpy change of formation of methyl ethanoate.

Table 2.1

	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$
carbon	−393.5
hydrogen	−285.8
methyl ethanoate	−1592.1

[3]

(c) Describe one simple chemical test to distinguish between $\text{HCO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CO}_2\text{CH}_3$. State clearly how each compound behaves in the test. [3]

(d) Consecutive elements **W**, **X**, **Y** and **Z** are in the third period of the Periodic Table. Element **Y** has the highest first ionisation energy and the lowest melting point of these four elements.

(i) Describe what you would see when elements **W** and **Z** are separately burned in air or oxygen. [2]

(ii) The oxides of elements **X** and **Y** can be obtained when the elements are burned in excess oxygen. The oxides of **X** and **Y** have melting points of 1720°C and 580°C respectively.

Briefly relate these melting points to the structure of and bonding in each of these oxides. [2]

(iii) Describe the reactions, if any, of the oxides of elements **X** and **Y** with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. [3]

[Total: 20]

- 3 (a) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy such as digital cameras and MP3 players. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is LaNi_5H_6 and the other is $\text{NiO}(\text{OH})$. The electrolyte is aqueous KOH . During discharge, an electrochemical reaction takes place to produce $\text{LaNi}_5(\text{s})$ and $\text{Ni}(\text{OH})_2(\text{s})$ and releases electrical energy.

- (i) Construct the two half–equations for the reactions that take place at each electrode during **discharge**. Indicate the polarity of the electrodes in your answer. [2]

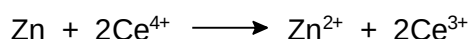
- (ii) During **recharge**, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (a)(i), write the overall equation for the reaction that occurs during **recharge**. [1]

- (iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation for the formation of one product at the electrode of the Ni–MH battery. [1]

- (b) Zinc–cerium battery is another type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.



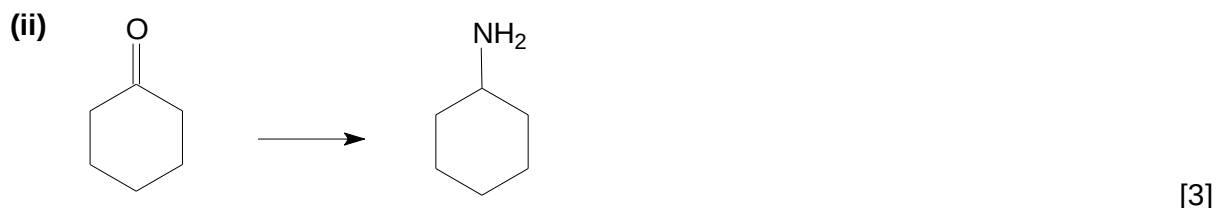
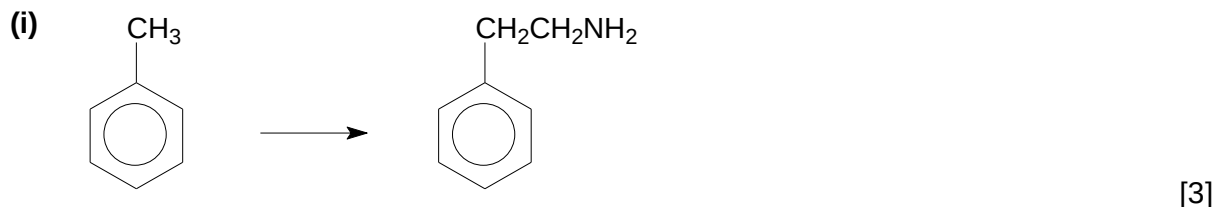
- (i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the cerium half–cell, using relevant data from the *Data Booklet*. [1]

- (ii) Using relevant data from the *Data Booklet*, deduce if the $\text{Ce}^{4+}/\text{Ce}^{3+}$ half–cell can be replaced with Br_2/Br^- half–cell. [1]

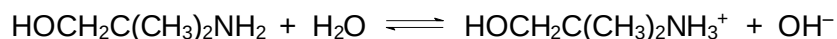
- (c) Amines can be made from a variety of compounds.

Suggest, **in no more than three steps**, how each of the following transformations can be achieved.

For each transformation, draw the structures of the intermediate compounds and indicate reagents and conditions for each of the steps.



- (d) The buffer of 2-amino-2-methylpropan-1-ol (AMP) has been shown to be well suited for the determination of the activity of enzymes like alkaline phosphatase and lactate dehydrogenase. It hydrolyses in water with a pK_b value of 4.3.



- (i) A 100 cm^3 solution containing $0.500 \text{ mol dm}^{-3}$ of $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2$ is mixed with a 100 cm^3 solution containing $0.800 \text{ mol dm}^{-3}$ $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+$.

Calculate the pH of the buffer solution formed.

[2]

- (ii) State the ratio of $\frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]}$ when the pH of the buffer solution is 9.7.

Hence calculate the mass of solid NaOH to be added to the buffer solution in (d)(i) to achieve this ratio.

[2]

- (e) Proteins are long-chain molecules made by linking together amino acids.

Myoglobin is one such protein that stores and releases oxygen in vertebrate muscle cells. The table below shows some of the amino acids in a molecule of myoglobin.

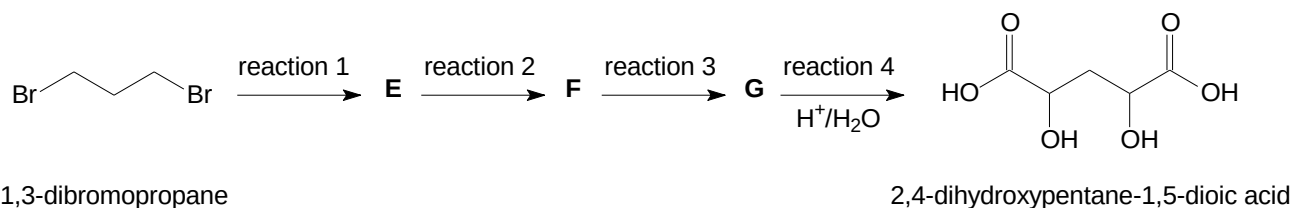
amino acid	aspartic acid	serine	alanine	lysine
abbreviation	asp	ser	ala	lys
formula of side chain	$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{CH}_2\text{OH}$	$-\text{CH}_3$	$-(\text{CH}_2)_4\text{NH}_2$

- (i) Given that asp-lys-ala is a particular **section** of the protein chain of myoglobin, draw the displayed formula for this **section** at pH 7. [1]
- (ii) Describe **two** types of side-chain interaction that would occur between the amino acids residues of myoglobin. Illustrate your answer with suitable pairs of amino acids from the table above. [2]
- (iii) Casein is the predominant protein found in milk. The conversion of milk to cheese is a denaturation process involving the addition of the *Lactobacillus* bacterium which produces lactic acid.

Explain this phenomenon by considering the types of side-chain interaction that are affected during the denaturation of casein. [1]

[Total: 20]

- 4 (a) 1,3-dibromopropane is the starting material for a four-step reaction sequence which produces 2,4-dihydroxypentane-1,5-dioic acid. The four reactions are shown.



Compound **F** has the molecular formula $C_3H_4O_2$. On treatment with Tollens' reagent, it gives a silver mirror.

- (i) Draw the structures of **E** and **F**. [2]

- (ii) When preparing compound **F** from **E** it is important that the product is distilled off rather than continually refluxed.

State which unwanted product is avoided by distilling off compound **F**.

[1]

- (iii) In an experiment, 9.0 g of 1,3-dibromopropane was converted into compound **F** with an overall yield of 67 %. Calculate the mass of **F** that was obtained.

[2]

- (iv) Compound **G** is converted into the final product by reaction with dilute acid. Suggest the structure of **G**.

[1]

- (b) The oxides of Group I and II metals have many uses. Beryllium oxide, BeO , is used in many high-performance semiconductor parts for applications such as radio equipment, while sodium oxide, Na_2O , is a significant component of glasses and windows.

- (i) Using the given data and other relevant data from the *Data Booklet*, construct an energy level diagram and use it to calculate the lattice energy of beryllium oxide. Label each energy level in your diagram and draw arrows representing the energy terms involved. Use symbols or numbers to represent these energy terms.

enthalpy change of formation of beryllium oxide	-609 kJ mol^{-1}
enthalpy change of atomisation of beryllium	$+324 \text{ kJ mol}^{-1}$
first electron affinity of oxygen	-141 kJ mol^{-1}
second electron affinity of oxygen	$+798 \text{ kJ mol}^{-1}$

[3]

- (ii) The theoretical lattice energy of beryllium oxide is $-4293 \text{ kJ mol}^{-1}$. Suggest a reason why this value is different from your answer in (b)(i).

[1]

- (iii) Explain how you would expect the numerical magnitude of the lattice energy of beryllium oxide to compare with that of sodium oxide.

[2]

- (iv) Explain the reaction(s) that occur(s) when chlorine gas is bubbled into a flask containing water, at room temperature, to which sodium oxide has been added. Write equation(s) where appropriate.

[2]

- (c) Soluble chromates(VI) in the soil are toxic at low concentrations for plants.

In water treatment to remove the chromate(VI) ions, $\text{CrO}_4^{2-}(\text{aq})$, from a sample of soil water, aqueous acidified iron(II) sulfate is first added to the water sample to convert the chromate(VI) ions to chromium(III) ions, $\text{Cr}^{3+}(\text{aq})$. This is followed by adding aqueous sodium carbonate to the resultant solution to produce effervescence and an insoluble compound.

- (i) Construct an equation for the reaction between aqueous acidified iron(II) sulfate and chromate(VI) ions.

[1]

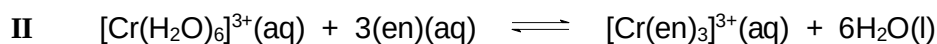
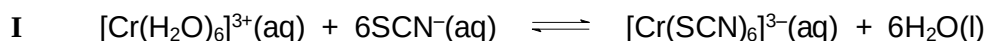
- (ii) Identify the insoluble compound formed upon adding aqueous sodium carbonate.

With the aid of an appropriate ionic equation, explain its formation.

[2]

- (d) Chromium(III) ions coordinate with both monodentate and polydentate ligands.

Consider the following complex formation reactions with thiocyanate, SCN^- , and ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, ligands:



where (en) is ethylenediamine

- (i) Explain what is meant by *entropy*.

[1]

- (ii) Explain how you would expect the entropy change, $\Delta S_r^\ominus$, for reaction II to compare with that for reaction I.

[2]

[Total: 20]

5 Nitrogen forms numerous oxides, two of which are dinitrogen monoxide, N_2O , and dinitrogen tetroxide, N_2O_4 .

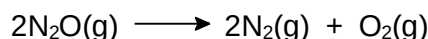
- (a) Dinitrogen monoxide, N_2O , is a non-toxic gas that is used commercially as the propellant in cans of whipped cream.

Given that N_2O is a linear molecule, draw a 'dot-and-cross' diagram showing the electrons (outer shells only) in N_2O .

You should distinguish carefully between electrons originating from each of the nitrogen atoms.

[1]

- (b) At 1200 K and in the presence of a gold wire, N_2O decomposes as follows.



The kinetics of this reaction can be followed by measuring the total pressure, P , as it changes with time, t . In one such experiment, the total pressure changes as follows.

total pressure, P / kPa	25.0	27.5	30.0	32.5	34.0	35.0
time, t / s	0	1030	2360	4230	5870	7420
partial pressure, p , of N_2O / kPa	25.0					

- (i) What is the total pressure when the reaction is complete? [1]

- (ii) Show that the partial pressure of N_2O at any time, t , is equal to $(75.0 - 2P)$ kPa. [2]

- (iii) Hence calculate the partial pressures of N_2O after 1030 s, 2360 s, 4230 s, 5870 s and 7420 s. [1]

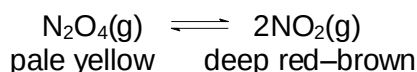
- (iv) Using your answers from (b)(iii) and the data above, plot these data on suitable axes and use your graph to determine the order of reaction with respect to N_2O .

You should show all your working and draw clearly any construction lines on your graph.

[3]

- (v) The rate of reaction is expressed in kPa s^{-1} . Write the rate equation for the reaction, and calculate a value for the rate constant. Include units in your answer. [3]

At a temperature of 27 °C, gaseous N₂O₄ and NO₂ are in dynamic equilibrium according to the following equation.



- (c)** When 4.60 g of N₂O₄ is placed in an evacuated 1.48 dm³ flask at 27 °C, the equilibrium pressure is 1.00 atm (101 kPa).
- (i)** Calculate the number of moles of N₂O₄ at the start. [1]
 - (ii)** Calculate the number of moles of gas at equilibrium, assuming the gases behave ideally. [1]
 - (iii)** Hence calculate the percentage of the N₂O₄ that has been dissociated. [2]
 - (iv)** Write an expression for the equilibrium constant, K_p , for the reaction and show it has a value of 0.17 atm at 27 °C. [3]
- (d)** When the equilibrium mixture from **(c)** at 27 °C is suddenly compressed in a gas syringe, the mixture immediately darkens and then slowly becomes paler. Suggest why the mixture behaves in this way. [2]

[Total: 20]



ANDERSON JUNIOR COLLEGE
2016 JC2 PRELIMINARY EXAMINATIONS

CHEMISTRY

9647/01

Higher 2

22 September 2016

Paper 1 Multiple Choice

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC / FIN number, **including** the reference letter.

Shade the NRIC / FIN number.

Exam Title: JC2 Prelim

Exam Details: H2 Chemistry / Paper 1

Date: 22/09/2016

This document consists of **18** printed pages.

Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1** Antimony (Sb) can be produced in a two-stage process from its ore stibnite, Sb_2S_3 .

The ore is first roasted in oxygen, producing Sb_4O_6 and SO_2 .

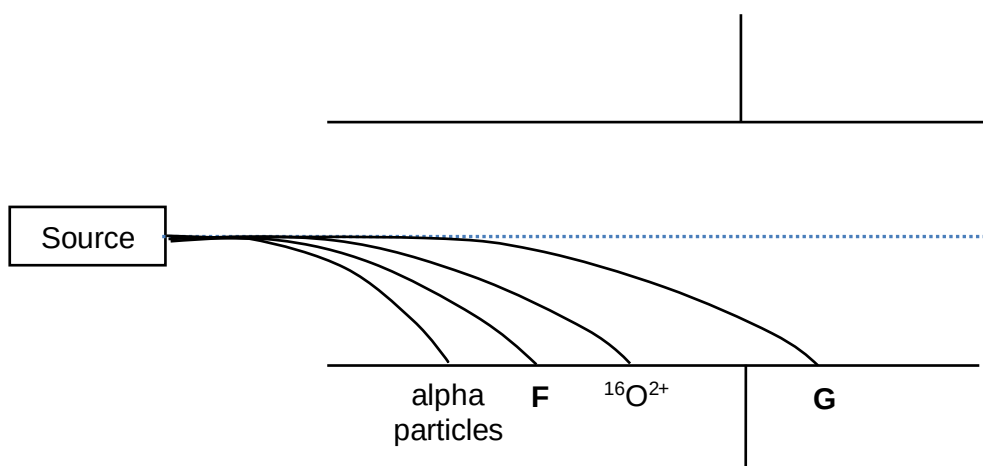
The Sb_4O_6 is then reduced by carbon, producing Sb and CO_2 .

What volume of CO_2 , measured at room temperature and pressure, is produced from 20 moles of Sb_2S_3 ?

- A** 360 dm^3 **B** 670 dm^3 **C** 720 dm^3 **D** 1440 dm^3

- 2** Alpha particles, ${}^4\text{He}^{2+}$, are commonly emitted by large radioactive nuclei.

The path of a mixture of ${}^{16}\text{O}^{2+}$ ions, alpha particles and two unknown ions, **F** and **G**, upon entering an electric field is shown below.



Which of the following represent **F** and **G**?

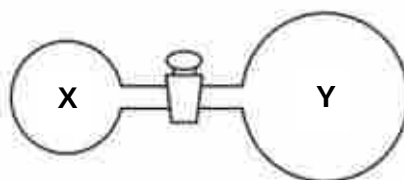
	F	G
A	${}^1\text{H}^+$	${}^9\text{Be}^{2+}$
B	${}^{12}\text{C}^{2+}$	${}^{27}\text{Al}^{3+}$
C	${}^9\text{Be}^{2+}$	${}^{14}\text{N}^{3+}$
D	${}^{12}\text{C}^+$	${}^1\text{H}^+$

- 3 In a research on the atomic nucleus, scientists have been comparing the stability of isotopes with the same neutron : proton ratio.

Which isotope has the same neutron : proton ratio as ^{10}B ?

- A ^{32}P B ^{32}S C ^{40}Ar D ^{40}K

- 4 Two glass vessels **X** and **Y** are connected by a closed valve.



X contains helium at $20\text{ }^{\circ}\text{C}$ at a pressure of $1 \times 10^5\text{ Pa}$. **Y** has been evacuated, and has three times the volume of **X**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to $100\text{ }^{\circ}\text{C}$.

What is the final pressure in the system?

- A $3.18 \times 10^4\text{ Pa}$
 B $4.24 \times 10^4\text{ Pa}$
 C $1.25 \times 10^5\text{ Pa}$
 D $5.09 \times 10^5\text{ Pa}$
- 5 The interhalogen compound BrF_3 is a volatile liquid which autoionises.



The electrical conductivity of BrF_3 decreases with increasing temperature.

Which statement is correct?

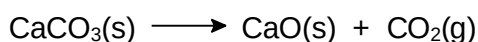
- A The autoionisation process is endothermic and the shape of the cation is linear.
 B The autoionisation process is endothermic and the shape of the cation is non-linear.
 C The autoionisation process is exothermic and the shape of the cation is linear.
 D The autoionisation process is exothermic and the shape of the cation is non-linear.

- 6 In an experiment, it was found that complete combustion of 10.0 g of an alcohol, **J**, raised the temperature of 100 g of water in a container from 25 °C to 75 °C.

Given that the process is only 65% efficient and the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, what is the total heat energy released per gram of **J** burnt?

- A** 2.09 kJ g⁻¹ **B** 3.22 kJ g⁻¹ **C** 13.5 kJ g⁻¹ **D** 20.8 kJ g⁻¹

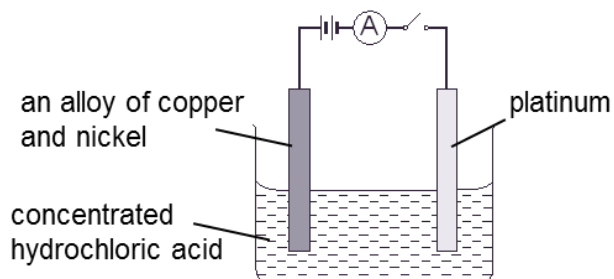
- 7 Limestone is a sedimentary rock largely made up of different crystal forms of calcium carbonate. At high temperatures, calcium carbonate decomposes to form calcium oxide and carbon dioxide.



What are the correct signs of ΔH and ΔS for this decomposition?

	ΔH	ΔS
A	–	–
B	–	+
C	+	–
D	+	+

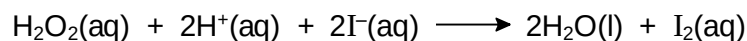
- 8 The circuit shown in the diagram was set up.



Which electrode reactions will occur on closing the switch?

	anode reaction	cathode reaction
A	neither nickel nor copper is dissolved	hydrogen is evolved
B	copper is dissolved preferentially	copper is deposited
C	nickel is dissolved preferentially	hydrogen is evolved
D	nickel and copper are both dissolved	copper is deposited

- 9 The reaction of hydrogen peroxide with iodide ions in acidic solution can be monitored by an initial rate method.



The following results were obtained for a series of experiments with different volumes of each reagent used.

experiment number	volume of $\text{H}_2\text{O}_2(\text{aq}) / \text{cm}^3$	volume of $\text{H}^+(\text{aq}) / \text{cm}^3$	volume of $\text{I}^-(\text{aq}) / \text{cm}^3$	volume of water / cm^3	time taken / s
1	40	40	20	0	33
2	20	40	20	20	66
3	40	20	30	10	22
4	20	40	30	10	44

What could be the mechanism of this reaction?

- A** $\text{H}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{OH}^+$ (fast)
 $\text{OH}^+ + 2\text{I}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{I}_2$ (slow)
- B** $\text{H}_2\text{O}_2 + \text{I}^- \longrightarrow \text{H}_2\text{O} + \text{IO}^-$ (slow)
 $\text{H}^+ + \text{IO}^- \longrightarrow \text{HIO}$ (fast)
 $\text{HIO} + \text{H}^+ + \text{I}^- \longrightarrow \text{I}_2 + \text{H}_2\text{O}$ (fast)
- C** $2\text{H}^+ + 2\text{I}^- \longrightarrow 2\text{HI}$ (fast)
 $2\text{HI} + \text{H}_2\text{O}_2 \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$ (slow)
- D** $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{HIO}$ (fast)
 $\text{HIO} + \text{I}^- \longrightarrow \text{I}_2 + \text{OH}^-$ (slow)
 $\text{OH}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O}$ (fast)

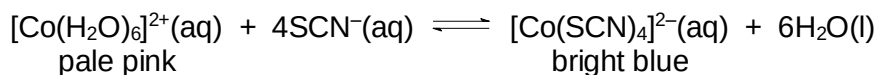
- 10 The same amount of electricity is passed through two electrolytic cells connected in series for 30 minutes. Cell 1 and Cell 2 contain aqueous solutions of $\text{Mn}(\text{NO}_3)_2$ and $\text{Au}(\text{NO}_3)_3$ respectively.

Given that 1.3 g of manganese is deposited on the cathode for Cell 1, what is the current used for electrolysis and the mass of the gold deposited on the cathode for Cell 2?

	current	mass of gold
A	1.3 A	3.1 g
B	1.3 A	4.7 g
C	2.5 A	3.1 g
D	2.5 A	4.7 g

- 11 Cobalt forms many coloured complexes with ligands such as H_2O and SCN^- .

A 100 cm^3 solution of $\text{Co}^{2+}(\text{aq})$ turns from pink to bright blue when 10 cm^3 of $\text{KSCN}(\text{aq})$ is added to the solution.



At equilibrium, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{SCN})_4]^{2-}$ are found to be present in a mole ratio of 1:10.

Given that $\lg K_c$ for the equilibrium is 3.00, which of the statements is **incorrect**?

- A The units of K_c is $\text{mol}^{-4}\text{ dm}^{12}$.
- B At equilibrium, $[\text{SCN}^-] = 3.16 \times 10^{-1}\text{ mol dm}^{-3}$.
- C $[\text{Co}(\text{SCN})_4]^{2-}$ is more stable than $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
- D Dilution of the reaction mixture decreases the proportion of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ at equilibrium.

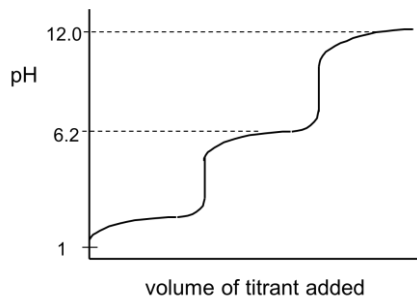
- 12 In which reaction is the underlined substance acting as a base?

- A $\text{HNO}_3 + \underline{\text{H}_2\text{SO}_4} \longrightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$
- B $\text{HSiO}_3^- + \underline{\text{HCN}} \longrightarrow \text{CN}^- + \text{H}_2\text{O} + \text{SiO}_2$
- C $\text{HNO}_2 + \underline{\text{HCO}_3^-} \longrightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{NO}_2^-$
- D $\text{C}_6\text{H}_5\text{O}^- + \underline{\text{CH}_2\text{ClCO}_2\text{H}} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_2\text{ClCO}_2^-$

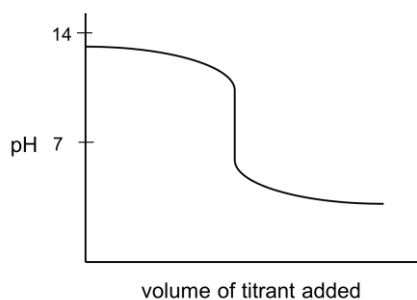
- 13** The change of colour for an indicator occurs over a limited range of pH that falls between ± 1.00 of the pK_a value of the indicator.

Which is the **most** suitable indicator that can be used to determine the end point of the corresponding titration?

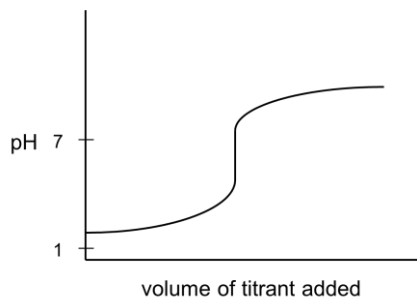
A alizarin yellow
($pK_a = 11.0$)



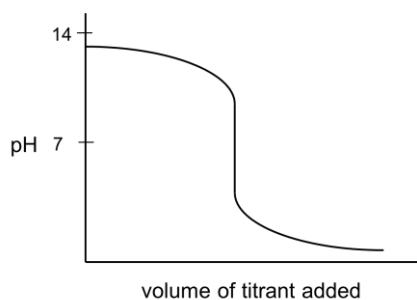
B bromothymol blue
($pK_a = 7.1$)



C methyl yellow
($pK_a = 3.3$)

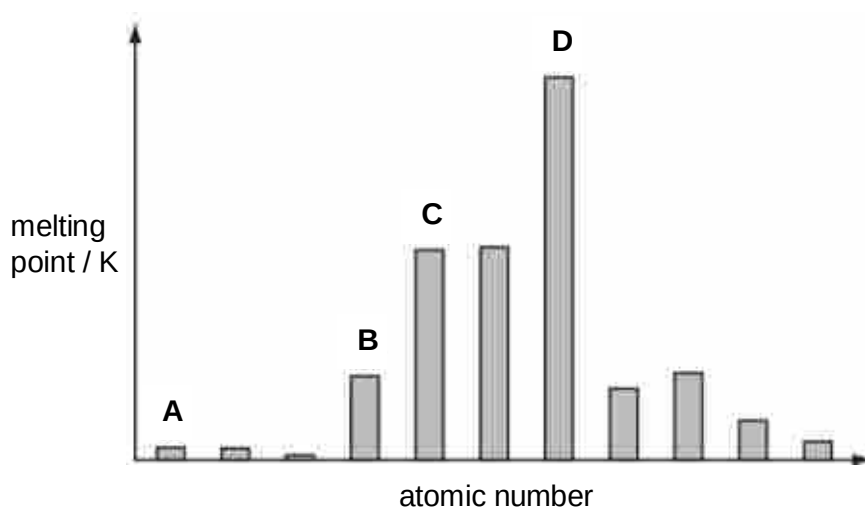


D thymol blue
($pK_a = 1.6$)



- 14 The bar chart shows the melting points of a series of consecutive elements arranged in order of increasing atomic number. The elements sodium to chlorine form part of this series.

Which bar represents sodium?



- 15 Which oxide does **not** react with dilute sodium hydroxide to produce a salt?

A Al_2O_3 B P_4O_{10} C SO_2 D SiO_2

- 16 The three minerals below are obtained from mines around the world. Each one behaves as a mixture of two carbonate compounds. They can be used as fire retardants because they decompose in the heat, producing CO_2 . This gas smothers the fire.

Barytomite	$\text{BaCa}(\text{CO}_3)_2$
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Huntite	$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$

What is the order of effectiveness as fire retardant, from best to worst?

	best → worst		
A	dolomite	barytomite	huntite
B	dolomite	huntite	barytomite
C	huntite	barytomite	dolomite
D	huntite	dolomite	barytomite

- 17** Iodine is far less soluble in water than it is in aqueous potassium iodide, where it forms the complex ion I_3^- . For this reason, reactions involving aqueous iodine are often carried out in potassium iodide solution.

Which equation describes the quantitative determination of iodine in the presence of excess potassium iodide?

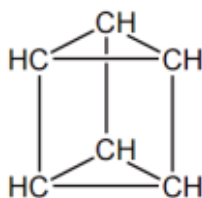
- A** $\text{I}_2 + 2\text{SO}_4^{2-} \longrightarrow 2\text{I}^- + \text{S}_2\text{O}_8^{2-}$
B $2\text{I}^- + 2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{I}_2 + \text{S}_4\text{O}_6^{2-}$
C $\text{I}_3^- + 2\text{SO}_4^{2-} \longrightarrow 3\text{I}^- + \text{S}_2\text{O}_8^{2-}$
D $\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$

- 18** Astatine, At, is below iodine in Group VII of the Periodic Table.

Which statement is most likely to be correct?

- A** AgAt(s) reacts with excess dilute aqueous ammonia to form a solution of a soluble complex.
B At_2 and KCl(aq) react to form KAt(aq) and Cl_2 .
C KAt(aq) and dilute sulfuric acid react to form white fumes of HAt(g) .
D NaAt(s) and concentrated sulfuric acid react to form At_2 .

- 19** In 1869 Ladenburg suggested a structure for benzene, C_6H_6 , in which one hydrogen atom is attached to each carbon atom.



Ladenburg structure

A compound $\text{C}_6\text{H}_4\text{Cl}_2$ could be formed with the same carbon skeleton as the Ladenburg structure.

How many structural isomers would this compound have?

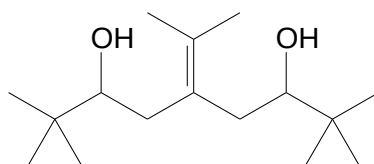
- A** 3 **B** 4 **C** 5 **D** 6

- 20 High-energy irradiation in the stratosphere produces radicals from chlorofluoroalkanes, commonly known as CFCs.

Which radical could result from this irradiation of $\text{CHFClCF}_2\text{Cl}$?

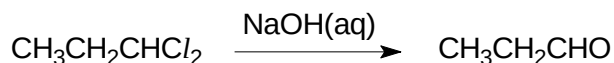
- A $\text{CHFCl}\dot{\text{C}}\text{FCl}$
 B $\dot{\text{C}}\text{HClCF}_2\text{Cl}$
 C $\dot{\text{C}}\text{HFClCF}_2\text{Cl}$
 D $\dot{\text{C}}\text{FClCF}_2\text{Cl}$

- 21 Compound **L** has the following structure.



What is the total number of geometrical isomers that can be formed from the product of the reaction of compound **L** with excess concentrated sulfuric acid at 170 °C?

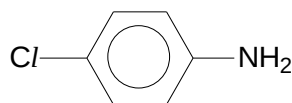
- A 8 B 7 C 4 D 3
- 22 1,1-dichloropropane reacts with excess hot aqueous sodium hydroxide in a series of steps to give propanal.



Which term describes the **second** step of this reaction?

- A addition
 B elimination
 C oxidation
 D substitution

- 23 4-chloroaniline is a pale yellow solid which is an important building block used for the production of pesticides, drugs and dyestuffs.

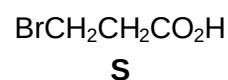
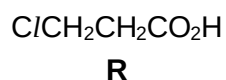
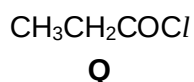
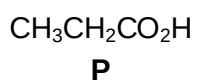


4-chloroaniline

Which of the following shows a suitable starting compound and sequence of steps to produce a good yield of 4-chloroaniline?

	starting compound	step 1	step 2
A		conc. HNO_3 , conc. H_2SO_4	Sn, conc. HCl followed by NaOH(aq)
B		dil. HNO_3	LiAlH_4
C		Cl_2 , AlCl_3	Sn, conc. HCl followed by NaOH(aq)
D		LiAlH_4	Cl_2 in CCl_4

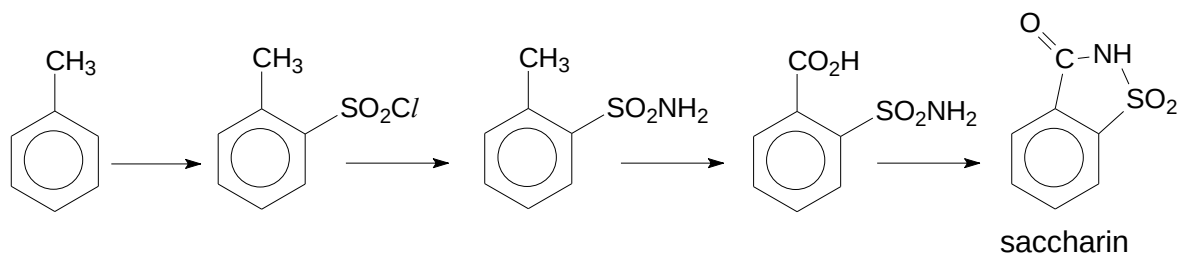
- 24 Why does hydrogen cyanide add to propanone but not to propene?
- A** Propanone is more susceptible to H^+ attack than propene.
- B** Propanone is more susceptible to CN^- attack than propene.
- C** The $\text{C}=\text{C}$ bond in propene is stronger than the $\text{C}=\text{O}$ bond in propanone.
- D** The two methyl groups in propanone exert a stronger electron donating effect than the single methyl group in propene.
- 25 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm^3 of water. The pH of each resultant solution is then measured.



Which of the following shows the correct order of **decreasing** pH of the solutions formed?

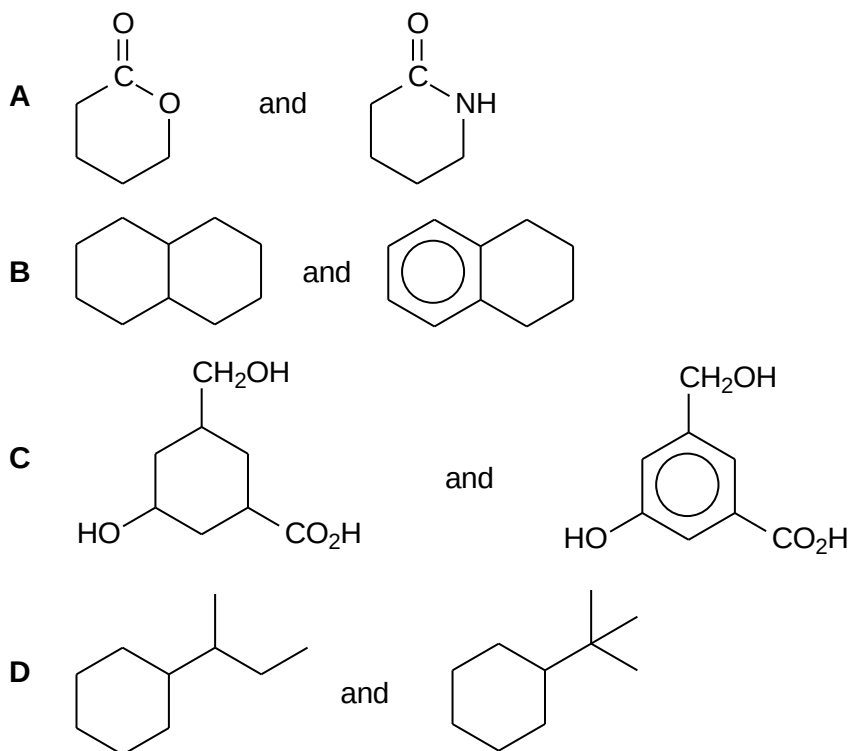
- A** P, R, S, Q
- B** P, S, R, Q
- C** Q, P, S, R
- D** Q, S, R, P

- 26 Saccharin is an artificial sweetening agent which can be synthesised from methylbenzene in the laboratory.

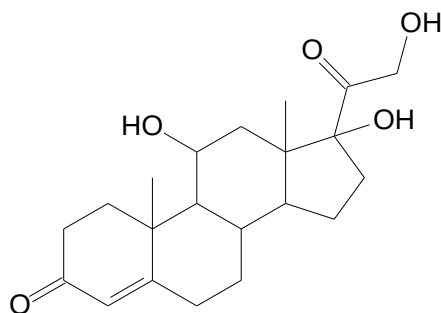


What type of reaction is **not** shown in this reaction scheme?

- A electrophilic substitution
 - B elimination
 - C nucleophilic substitution
 - D oxidation
- 27 Which pair of organic compounds **cannot** be distinguished by a chemical test?



- 28 Cortisol is a steroid hormone which is released in response to stress and low blood glucose. Its structure is shown in the diagram below.

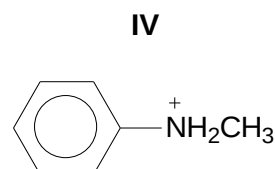
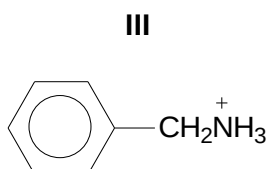
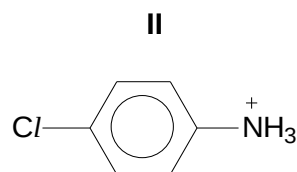
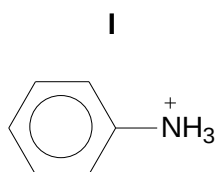


Cortisol is reduced with hydrogen in the presence of a platinum catalyst, and then oxidised by heating with acidified KMnO_4 . The product formed is further reacted with excess sodium to give an organic ion.

What is the charge on the organic ion produced?

- A 1- B 2- C 3- D 5-

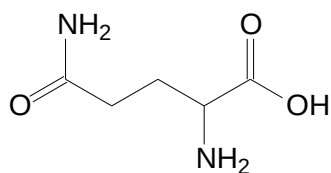
- 29 Consider the four species below.



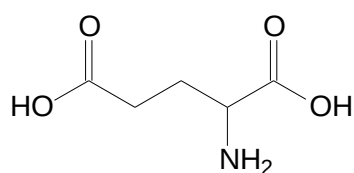
Which of the following shows the given species arranged in order of **decreasing** pK_a values?

- A III, IV, I, II
 B III, IV, II, I
 C IV, III, I, II
 D IV, II, III, I

- 30 The amino acids glutamine and glutamic acid can react with each other to form amide linkages.



glutamine



glutamic acid

What is the maximum number of different compounds, each containing one amide linkage, that can be formed from one molecule of glutamine and one molecule of glutamic acid?

- A 2
- B 3
- C 4
- D 5

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

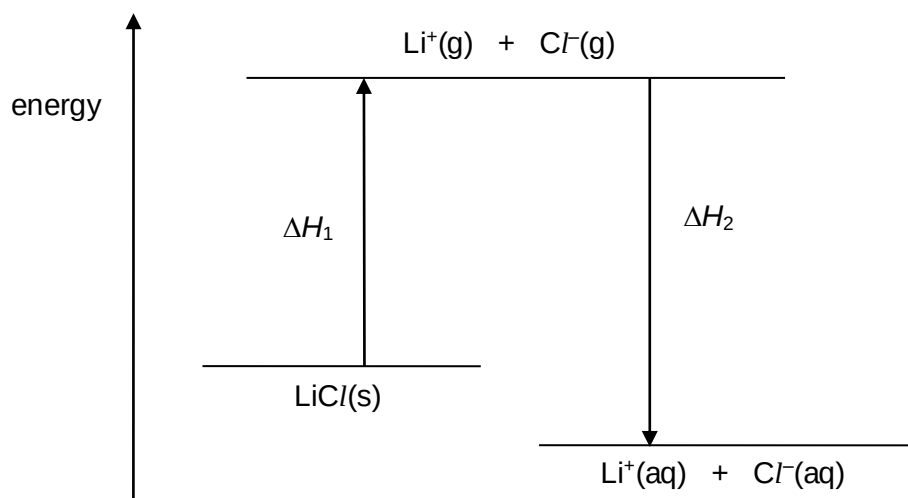
No other combination of statements is used as a correct response.

31 Which of the following ions has more electrons than protons and more protons than neutrons?

[$\text{H} = {}^1_1\text{H}$; $\text{D} = {}^2_1\text{H}$; $\text{C} = {}^{12}_6\text{C}$; $\text{O} = {}^{16}_8\text{O}$]

- 1** OH^-
- 2** HCO_3^-
- 3** DCO_3^-

32 An energy level diagram is shown below for the case of dissolving lithium chloride in water.



Which of the following about the enthalpy change of solution of lithium chloride is correct?

- 1** It is equal to $\Delta H_1 + \Delta H_2$.
- 2** It implies that dissolving lithium chloride is accompanied by an increase in temperature.
- 3** It is expected to be less exothermic than that of silver chloride.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

33 Why does raising the pressure of a fixed mass of gaseous reactants at a constant temperature cause an increase in the rate of reaction?

- 1** More collisions occur per second when the pressure is increased.
- 2** More molecules have energy greater than the activation energy at the higher pressure.
- 3** Raising the pressure lowers the activation energy.

34 *Use of the Data Booklet is relevant to this question.*

Which ions contain one or more unpaired electrons?

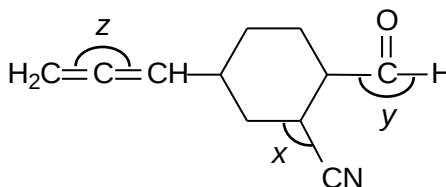
- 1** Cu^{2+}
- 2** Mn^{3+}
- 3** V^{3+}

35 When a hot glass rod is placed in a gas jar of hydrogen iodide, there is an immediate reaction as the hydrogen iodide decomposes.

Which statements about this reaction are correct?

- 1** Brown hydrogen iodide decolourises.
- 2** The hot rod provides the activation energy.
- 3** Purple fumes are observed.

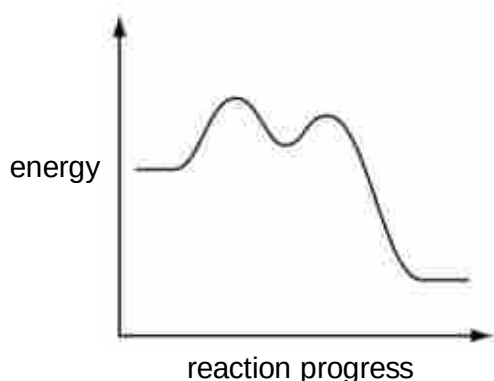
36 Which of the following statements are correct about compound **M**?



compound **M**

- 1** The bond angles in compound **M** increase in the order $x < y < z$.
- 2** There is only one sp hybridised carbon atom in compound **M**.
- 3** Compound **M** is planar.

37 A reaction pathway diagram is shown.



Which reactions would have this profile?

- 1 $(\text{CH}_3)_3\text{CBr} + \text{NaOH} \longrightarrow (\text{CH}_3)_3\text{COH} + \text{NaBr}$
- 2 $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$
- 3 $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Cl} + 2\text{NH}_3 \longrightarrow (\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$

38 Which of the following reactions will produce a racemic mixture?

- 1 $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$ heated under reflux with aqueous KOH.
- 2 CH_3CHO with HCN and a small amount of KOH.
- 3 $\text{CH}_3\text{CH}=\text{CHCH}_3$ with HBr dissolved in CCl_4 .

39 Compound **N** can react with alkaline aqueous iodine to form a yellow precipitate. When compound **N** reacts with hot acidified KMnO_4 , two products are obtained. Both products can also form a yellow precipitate with alkaline aqueous iodine.

What could be the identity of compound **N**?

- 1
- 2
- 3

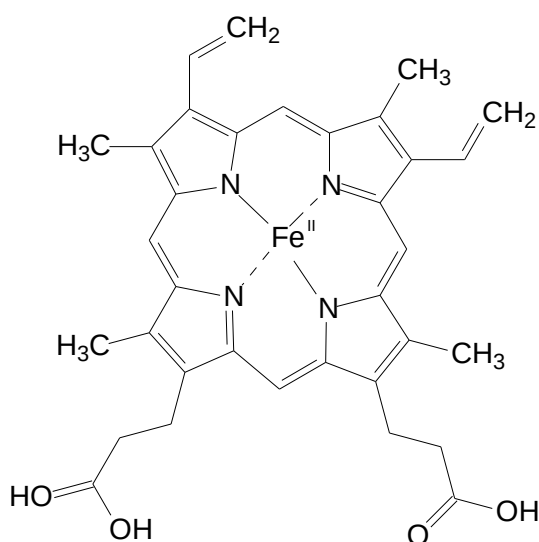
The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 40** Haemoglobin is a type of protein found in red blood cells. It transports oxygen from the lungs to body tissues. A haemoglobin molecule is a tetramer made up of four globular protein subunits. Each subunit is composed of a protein chain tightly associated with a non-protein haem group.

The diagram below shows the structure of a haem group.



Which of the following is correct about haemoglobin?

- 1 Haemoglobin has higher affinity for carbon monoxide than oxygen.
- 2 Each haemoglobin molecule can carry four oxygen molecules.
- 3 The polypeptide chains in haemoglobin are held together by hydrogen bonding only.



ANDERSON JUNIOR COLLEGE
2016 JC2 PRELIMINARY EXAMINATIONS

NAME: _____ **PDG:** ____/15 **Register No:** _____

CHEMISTRY

9647/02

Higher 2

16 September 2016

Paper 2 Structured Questions

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.

Write in dark blue or black pen.

You may use a pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use				
Paper 2	1		Total	/ 72
	2			
	3			
	4			
	5			
	6			

This document consists of **20** printed pages.

1 Planning (P)

Group II nitrates decompose on heating to form metal oxide, nitrogen(IV) oxide and oxygen.

Group II nitrates and their oxides are solids that can be easily weighed to determine the amount present. Nitrogen(IV) oxide is an acidic gas and can be absorbed by a known amount of excess strong alkali such as sodium hydroxide.



The amount of strong alkali remaining can then be determined by titrating against a standard solution of strong acid.

The oxygen produced from the decomposition can be trapped by a simple gas collection set-up to measure the volume collected.

You are to plan an experiment to confirm that the molar quantities of magnesium oxide, nitrogen(IV) oxide and oxygen produced agree with the equation for the thermal decomposition of magnesium nitrate.

- (a)** Write an equation for the thermal decomposition of magnesium nitrate. You should include state symbols in your equation.

..... [1]

- (b)** Suggest the capacity of the apparatus to be used to collect the oxygen gas.

Hence calculate the mass of magnesium nitrate to be heated to produce a stated volume of oxygen gas appropriate for the apparatus.

You should assume that one mole of any gas occupies 24.0 dm^3 under room conditions.

capacity of apparatus:

mass of magnesium nitrate to be heated: [2]

- (c) Use your answer to (b) to calculate the minimum volume of 1.00 mol dm^{-3} aqueous sodium hydroxide needed to absorb the nitrogen(IV) oxide produced from the thermal decomposition of magnesium nitrate.

volume of sodium hydroxide needed: [1]

- (d) You may assume that you are provided with:

- solid magnesium nitrate
- 1.00 mol dm^{-3} sodium hydroxide
- 0.20 mol dm^{-3} hydrochloric acid
- the apparatus and chemicals normally found in a school or college laboratory

Your plan should include:

- a diagram of the assembled apparatus capable of absorbing the nitrogen(IV) oxide and collecting the oxygen separately and in sequence;
- an outline of how the results would be obtained, including the essential details of the titration procedure;
- measures to ensure reliability of results;
- brief, but specific, details of how the results will be used to
 - determine the amounts in moles of reactant and all products at the end of complete thermal decomposition
 - confirm that the decomposition had occurred according to the molar ratios in the equation.

[Turn over

- 2 (a) Ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, may be regarded as a water molecule in which each of the hydrogen atoms has been replaced by an ethyl group.

At room temperature, boron trifluoride is a gas and ethoxyethane is a liquid. When boron trifluoride is mixed in a 1 : 1 molar ratio with ethoxyethane, a liquid with a boiling point of 127°C is formed.

- (i) Suggest what type of bond is formed between boron trifluoride and ethoxyethane, explaining your answer.

.....

 [2]

- (ii) Draw a diagram to illustrate the shape of and bonding in the product.

(You may represent the $-\text{CH}_2\text{CH}_3$ group with $-\text{R}$)

[1]

Often in the preparation of an organic compound the product is obtained as an aqueous solution. The chemist needs to separate the organic compound from water by using solvent extraction method. Organic compounds are more soluble in organic solvents than in water.

Ethoxyethane is a good solvent for many organic compounds. It is immiscible with water and has a low boiling point (35°C). When an aqueous solution containing an organic compound is shaken with ethoxyethane in a separating funnel, the compound distributes itself between the two layers, in accordance with its partition coefficient between ethoxyethane and water, until equilibrium is reached.

The partition coefficient, $K_{\text{partition}}$, of an organic compound, **J**, between ethoxyethane and water is given by the following expression.

$$K_{\text{partition}} = \frac{\text{concentration of J in ethoxyethane (organic layer)}}{\text{concentration of J in water (aqueous layer)}}$$

where the concentration of **J** can be expressed in g cm^{-3} .

The partition coefficient is a constant at a constant temperature.

(b) When 20 cm³ of ethoxyethane were shaken with 75 cm³ of an aqueous solution containing 5.00 g of **J**, it was found that 2.14 g of **J** were extracted into the ethoxyethane.

(i) Calculate the partition coefficient, $K_{\text{partition}}$, of **J** between ethoxyethane and water.

[1]

(ii) In another experiment

- 10 cm³ of ethoxyethane were shaken with 75 cm³ of an aqueous solution containing 5.00 g of **J** and the layers were separated.
- The aqueous layer was shaken with a second 10 cm³ portion of ethoxyethane and the layers were separated.
- The two organic layers were combined.

Use the value of $K_{\text{partition}}$ you calculated in **(b)(i)** to calculate the total mass of **J** extracted by this procedure.

[2]

(iii) Hence comment whether it is more efficient to use one 20 cm³ portion of ethoxyethane or two successive portions of 10 cm³ ethoxyethane for extraction.

..... [1]

(c) Anhydrous calcium chloride was then added to the combined organic layers obtained in **(b)(ii)**.

Suggest the reason for the addition of anhydrous calcium chloride.

..... [1]

[Total: 8]

- 3 Nitrogen and phosphorus are both Group V elements. Nitrogen exists in its elemental form as simple molecules, N_2 , while phosphorus occurs in one of the many forms, including 'white' phosphorus and 'red' phosphorus. Some data about these two forms of phosphorus are shown in **Table 1.1**.

Table 1.1

	'white' phosphorus	'red' phosphorus
appearance at room temperature	creamy white solid	red solid
melting point / °C	44	590
solubility in methylbenzene	soluble	insoluble

- (a) Suggest the type of structure and bonding in 'red' phosphorus. Explain your reasoning.

.....

 [2]

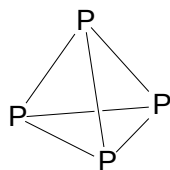
- (b) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

Suggest the type of hybridisation in N_2 and draw the arrangement of the hybrid orbital(s) around each nitrogen atom.

type of hybridisation

[2]

- (c) The corresponding form of phosphorus, P_2 , is not stable under standard conditions. Instead, 'white' phosphorus consists of molecules with a tetrahedral structure as shown.



'white' phosphorus

- (i) Unlike N_2 , P_2 is not stable under standard conditions. Suggest a reason for this.

.....
 [1]

- (ii) Using the data in **Table 1.2**, construct an appropriate energy cycle and use it to determine the enthalpy change for the conversion of 'white' phosphorus to the gaseous diatomic molecule, P_2 .

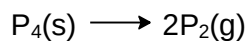


Table 1.2

P–P bond energy	200 kJ mol ⁻¹
P≡P bond energy	485 kJ mol ⁻¹
enthalpy change of vaporisation of $P_4(s)$	+12 kJ mol ⁻¹

[3]

- (iii) The formation of $P_2(g)$ from 'white' phosphorus is not spontaneous under standard conditions.

Suggest how the conditions would need to be changed to make it spontaneous. Explain your reasoning.

.....
.....
.....
..... [2]

- (d) Although nitrogen gas makes up about 79% of the atmosphere, it does not easily form compounds.

- (i) Explain why the conditions in a car engine lead to the production of oxides of nitrogen.

.....
..... [1]

- (ii) Give an equation for a reaction involved in the removal of nitrogen monoxide, NO, from a car's exhaust gases, in the catalytic converter.

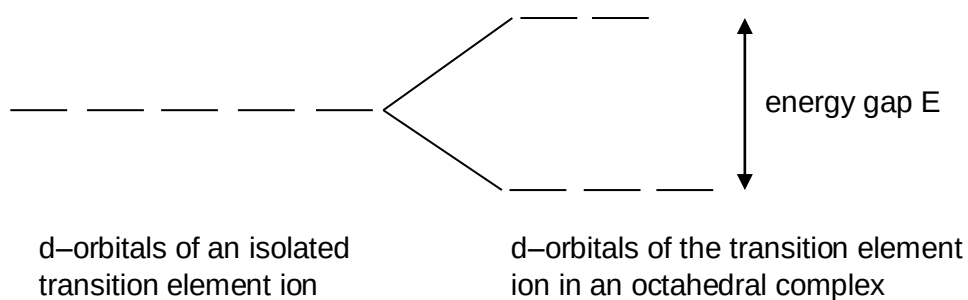
..... [1]

[Total: 12]

- 4 (a) (i) What is meant by the term *ligand* in the context of transition element chemistry?

.....
 [1]

- (ii) Although the five d-orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups, as shown in the following diagram.



Use this diagram as an aid in explaining the following.

- Transition element complexes are often coloured.

.....

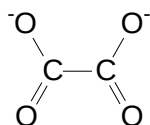
- The colour of a complex of a given transition element often changes when the ligands around it are changed.

.....

 [5]

- (b) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$, which contains the ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.

The structure of the ethanedioate ion is as follows.



- (i) Determine the oxidation number of carbon in this ion.
 [1]
- (ii) Determine the oxidation number of iron in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.
 [1]
- (iii) The iron atom in the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Draw a three-dimensional diagram to show the shape of this ion.

[2]

- (c) Kidney stones are usually made up of an inorganic salt of calcium with ethanedioate. Thus, people who are prone to kidney stones have to limit or avoid eating foods with high ethanedioate content such as spinach, peanuts and sweet potatoes.
- (i) Write the expression for the solubility product of calcium ethanedioate.
 [1]
- (ii) The value of K_{sp} for calcium ethanedioate is 2.3×10^{-9} . Calculate $[\text{C}_2\text{O}_4^{2-}]$ in a saturated solution of calcium ethanedioate.

[1]

- (iii) A solution **W** is saturated with both calcium ethanedioate and calcium chloride.

The concentration of ethanedioate ions in solution **W** is less than that calculated in (c)(ii). Explain why this is so.

.....
 [1]

- (d) By quoting relevant data from the *Data Booklet*, explain the following observations:

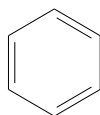
compound	pH of a 1.0 mol dm ⁻³ solution in water
NaCl	7.0
MgCl ₂	6.5
AlCl ₃	3.0

.....

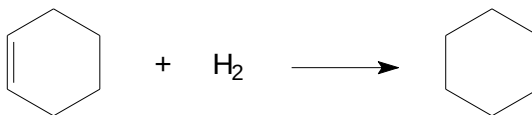
 [2]

[Total: 15]

- 5 (a) Kekulé proposed the following structure for benzene.



The enthalpy change of hydrogenation of cyclohexene, as shown, is -121 kJ mol^{-1} .



Based on this value for cyclohexene it is possible to calculate the enthalpy change of hydrogenation of benzene, based on Kekulé's structure, to be -363 kJ mol^{-1} .

Explain the difference between this calculated value and the actual value for the enthalpy change of hydrogenation of benzene of -209 kJ mol^{-1} .

.....
 [1]

- (b) Benzene undergoes electrophilic substitution reactions.

Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be formed from benzene. Give the reagents and conditions necessary for this process and identify the electrophile.

reagents

conditions

electrophile [2]

(c) Fig. 5.1 shows a reaction scheme starting from nitrobenzene.

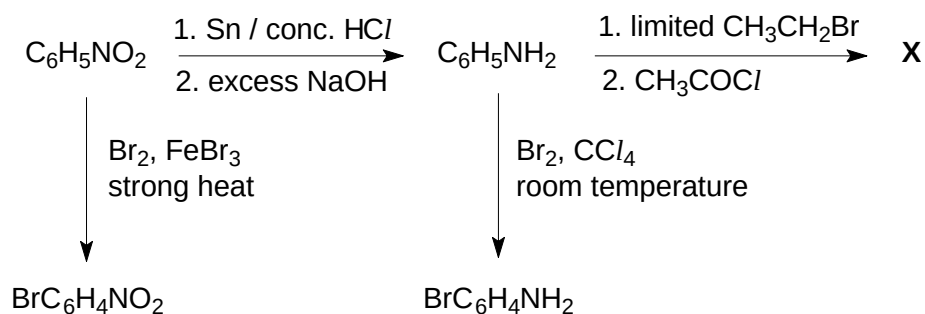


Fig. 5.1

- (i) Explain why the bromination of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, is possible with the milder conditions shown in Fig. 5.1.

.....

.....

..... [2]

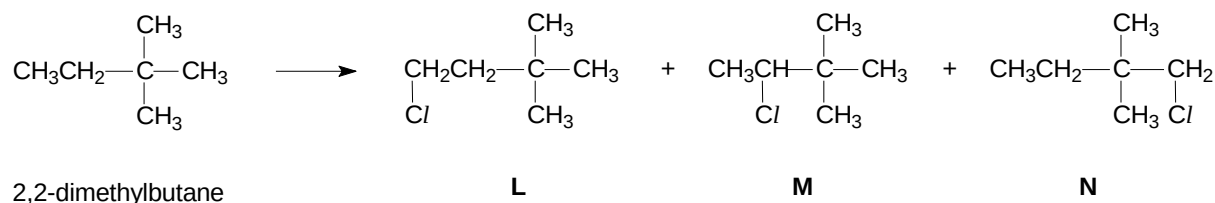
- (ii) Write an equation for the reaction between nitrobenzene and the reducing mixture, Sn / conc. HCl. Use [H] to represent the formula of the reducing agent in your equation.

..... [1]

- (iii) Draw the structural formula of X.

[1]

- (d) When heated with chlorine, the hydrocarbon 2,2-dimethylbutane produces compounds **L**, **M** and **N**.



It is observed that the rate of substitution of a hydrogen atom in 2,2-dimethylbutane by a chlorine atom is dependent on the type of hydrogen substituted – *primary*, *secondary* or *tertiary*.

The table below shows the relative rate of substitution by chlorine.

Reaction	Type of hydrogen substituted	Relative rate
$\text{RCH}_3 \longrightarrow \text{RCH}_2\text{Cl}$	<i>primary</i>	1
$\text{R}_2\text{CH}_2 \longrightarrow \text{R}_2\text{CHCl}$	<i>secondary</i>	7
$\text{R}_3\text{CH} \longrightarrow \text{R}_3\text{CCl}$	<i>tertiary</i>	21

Using the information from the table and by considering the number of hydrogen atoms of each type (*primary*, *secondary* or *tertiary*) within 2,2-dimethylbutane, predict the ratio of the three products **L**, **M** and **N**.

Explain how you arrived at your answer.

ratio of **L** to **M** to **N**:

explanation:

.....

..... [2]

[Total: 9]

- 6 (a) The interhalogen compound ICl reacts with alkenes in an addition reaction. ICl reacts faster with alkenes than the pure halogens.

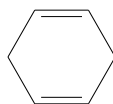
(i) Describe the mechanism of the reaction between ICl and propene.

[3]

(ii) Suggest why ICl reacts with alkenes faster than the pure halogens, Cl_2 , Br_2 and I_2 .

.....
 [1]

Cyclohexa-1,4-diene behaves as a typical alkene.



cyclohexa-1,4-diene

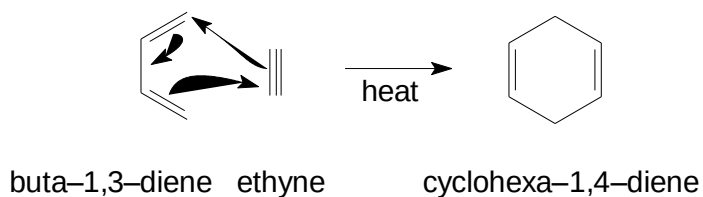
(b) State the total numbers of σ bonds and π bonds in a molecule of cyclohexa-1,4-diene.

number of σ bonds

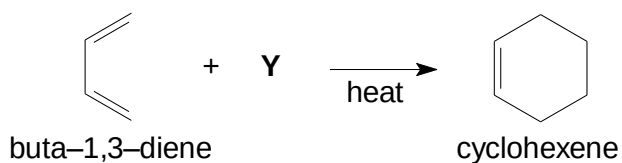
number of π bonds

[1]

- (c) Cyclohexa-1,4-diene can be made by heating buta-1,3-diene with ethyne in the Diels-Alder reaction. The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate the cyclohexa-1,4-diene in a single step.



- (i) In a similar type of reaction, cyclohexene can be formed from buta-1,3-diene and another alkene, Y.



Suggest the **name** of the alkene, Y, that would react with buta-1,3-diene to form cyclohexene in this type of reaction.

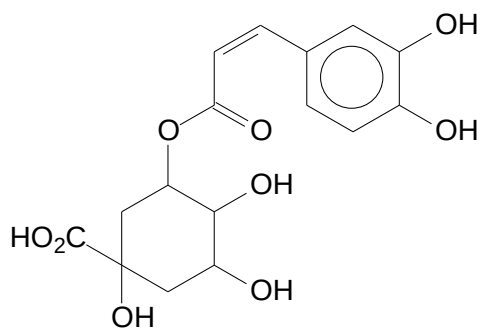
..... [1]

- (ii) In another similar reaction, penta-1,3-diene reacts with propene to form two products that are structural isomers.

Deduce the structures of these two isomers.

[2]

(d) Chlorogenic acid occurs naturally in coffee and an edible species of bamboo.

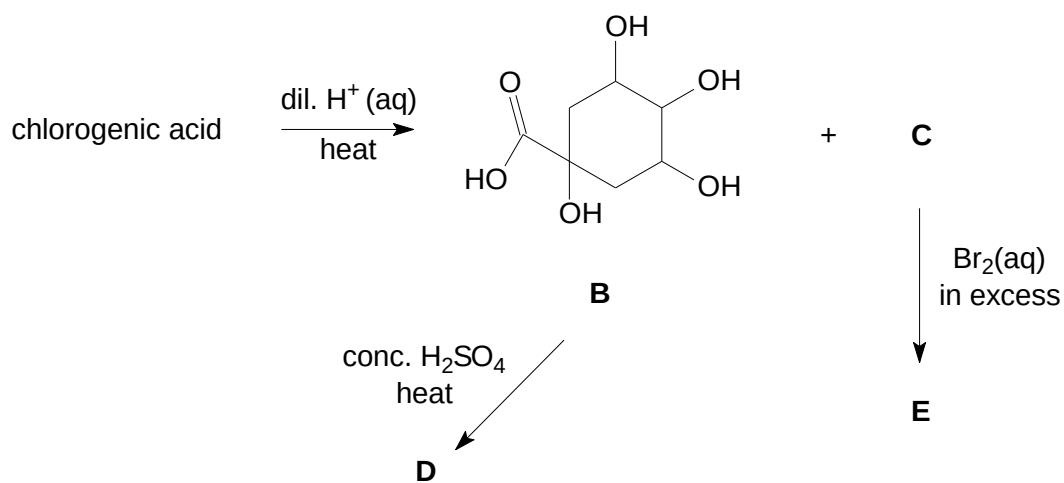


chlorogenic acid

(i) Draw the structural formula of the compound formed when chlorogenic acid is treated with an excess of sodium metal.

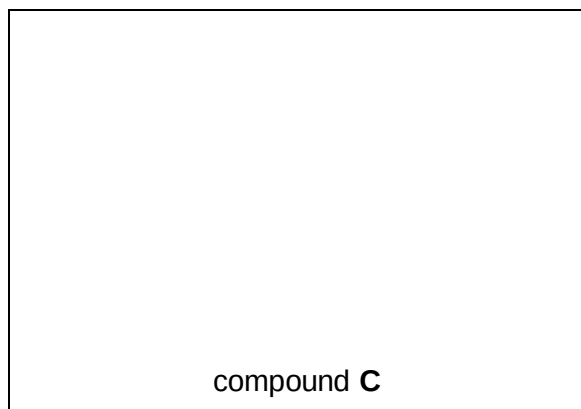
[1]

On heating with dilute acid, chlorogenic acid produces two compounds, **B** and **C**.



- (ii) State the *type of reaction* undergone by chlorogenic acid when **B** and **C** are formed. Draw the displayed formula of compound **C**.

type of reaction



[2]

When compound **B** is heated with concentrated H_2SO_4 , compound **D**, $\text{C}_7\text{H}_6\text{O}_3$, is formed.

CO_2 is evolved when compound **D** is treated with $\text{Na}_2\text{CO}_3(\text{aq})$. Compound **D** decolourises $\text{Br}_2(\text{aq})$ giving a white precipitate, but does not react with cold, alkaline KMnO_4 .

When compound **C** is treated with an excess of $\text{Br}_2(\text{aq})$, compound **E** is produced.

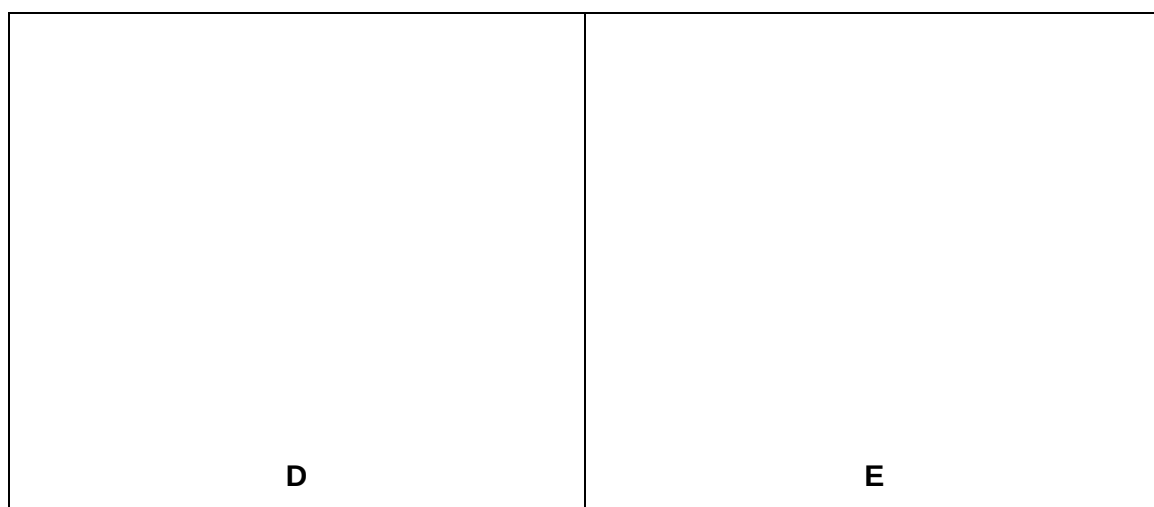
- (iii) Identify the functional group that would have been shown to be present in **D** if the test with cold, alkaline KMnO_4 had been positive.

..... [1]

- (iv) Name the functional groups in compound **D** that react with the following.

$\text{Na}_2\text{CO}_3(\text{aq})$ $\text{Br}_2(\text{aq})$ [2]

- (v) Suggest structures for compounds **D** and **E**.



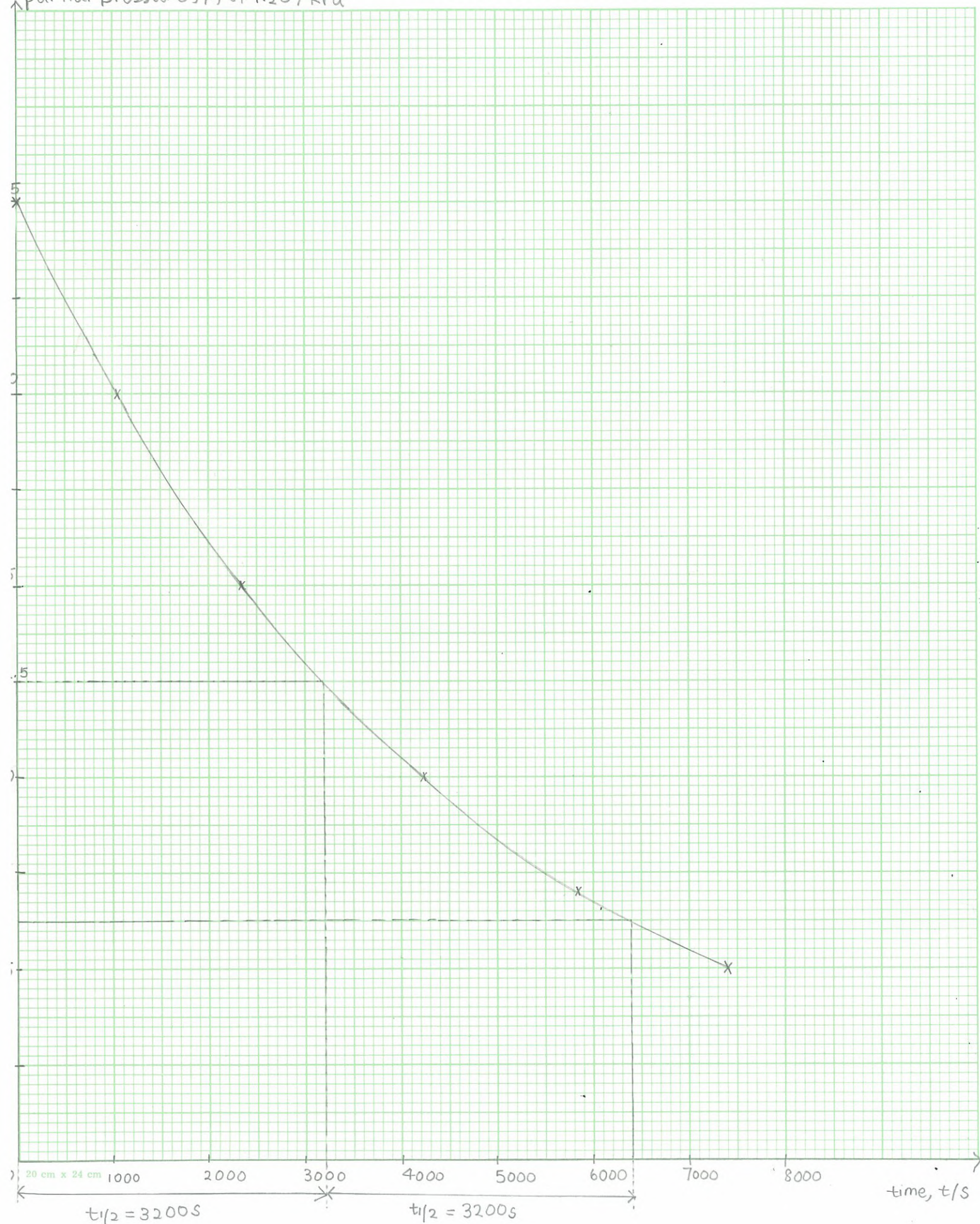
[2]

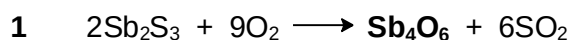
[Total: 16]

Name _____ Index No. _____

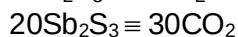
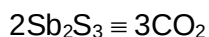
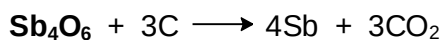
Subject _____ Class _____ Date _____

partial pressure, P , of N_2O / kPa





C



Volume of CO_2 produced at r.t.p. = $30 \times 24 = \underline{720 \text{ dm}^3}$

2 Angle of deflection, $\theta \propto \frac{\text{ionic charge}}{\text{mass}}$ (i.e. z/m ratio)

B

Arranging the species in order of **decreasing** angle of deflection, θ :

species	$^1\text{H}^+$	$^4\text{He}^{2+}$	$^9\text{Be}^{2+}$	$^{14}\text{N}^{3+}$	$^{12}\text{C}^{2+}$	$^{16}\text{O}^{2+}$	$^{27}\text{Al}^{3+}$	$^{12}\text{C}^+$
z/m	1.00	0.500	0.222	0.214	0.167	0.125	0.111	0.0833
identity			F	F	F		G	G

3

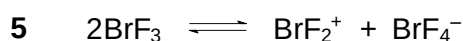
	no. of neutrons	no. of protons	ratio
^{10}B	5	5	1:1
^{32}P	17	15	
^{32}S	16	16	1:1
^{40}Ar	22	18	

B

4 Using $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$

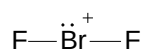
A

$$\begin{aligned}
 p_2 &= \frac{p_1 V_1 T_2}{V_2 T_1} \\
 &= \frac{1 \times 10^5 \times V_1 \times 373}{(3V_1 + V_1) \times 293} \\
 &= \frac{1 \times 10^5 \times 1 \times 373}{4 \times 293} \\
 &= \underline{3.18 \times 10^4 \text{ Pa}}
 \end{aligned}$$



D

Since the electrical conductivity of BrF_3 decreases (i.e. the position of equilibrium shifts left) when temperature increases, the **reverse endothermic** process is favoured to absorb the extra heat. Hence, the **forward** autoionisation process is **exothermic**.



Since there are 2 bond pairs and 2 lone pairs around the central Br atom, BrF_2^+ has a **bent** (non-linear) shape.

- 6 Total heat released = $(\frac{100}{65} \times 100 \times 4.18 \times 50) = 32.2 \text{ kJ}$ B
 Total heat released per gram = $\frac{1}{10} (32.154) = \underline{3.22 \text{ kJ g}^{-1}}$

- 7 Since $\Delta n_{\text{gas}} = +1 \text{ mol}$; $\Delta S > 0$. D
 Since $\Delta G < 0$ only at high temperatures, $\Delta H > 0$.
 (Since reaction involves breaking of C–O bond during thermal decomposition, $\Delta H > 0$.)

- 8 At the positive electrode (anode): C

species	$E^\ominus$
$\text{Cl}_2/\underline{\text{Cl}^-}$	+1.36
$\text{Cu}^{2+}/\underline{\text{Cu}}$	+0.34
$\text{Ni}^{2+}/\underline{\text{Ni}}$	–0.25

Since $E^\ominus(\text{Ni}^{2+}/\text{Ni})$ is the least positive, **Ni will be oxidised to Ni^{2+} .**

At the negative electrode (cathode):

species	$E^\ominus$
$\underline{\text{H}^+}/\text{H}_2$	0.00

H^+ will be reduced to H_2 .

- 9 Comparing expt. 1 and 2, B
 When volume of H_2O_2 is halved, time taken is doubled (i.e. rate is halved).
 $\Rightarrow$ **first order w.r.t. H_2O_2**

Comparing expt. 2 and 4,
 When volume of I^- increased 1.5 times, time taken decreased 1.5 times (i.e. rate increased 1.5 times).
 $\Rightarrow$ **first order w.r.t. I^-**

Comparing expt. 3 and 4,
 When volume of H_2O_2 is halved and volume of H^+ is doubled, time taken is doubled (i.e. rate is halved).
 Since reaction is first order w.r.t. H_2O_2 , increasing $[\text{H}^+]$ has no effect on the time taken.
 $\Rightarrow$ **zero order w.r.t. H^+**

Rate equation: **rate = $k [\text{H}_2\text{O}_2] [\text{I}^-]$**

$\Rightarrow$ one molecule of H_2O_2 and one I^- ion are involved in the slow step (r.d.s) of the mechanism

- 10 $\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$ C

$$n(\text{Mn}) = 1.3 / 54.9 = 0.0237 \text{ mol}$$

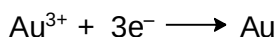
$$n(\text{e}^-) = 2 \times 0.0237 = 0.0474 \text{ mol}$$

Using $Q = n_e F$

$$Q = 0.0474 \times 96500 = 4574.1 \text{ C}$$

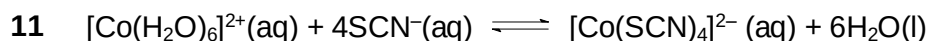
Using $Q = It$, $I = Q/t$

$$I = 4574.1 / (30 \times 60) = \underline{2.5 \text{ A}}$$



$$n(\text{Au}) = n(\text{e}^{-}) / 3 = 0.0474 / 3 = 0.0158 \text{ mol}$$

$$\text{mass of Au} = 0.0158 \times 197 = \underline{3.1 \text{ g}}$$



D

$$K_c = \frac{[\text{Co}(\text{SCN})_4]^{2-}]}{[\text{Co}(\text{H}_2\text{O})_6]^{2+}][\text{SCN}^{-}]^4}$$

$$\text{Units of } K_c = \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^4}$$

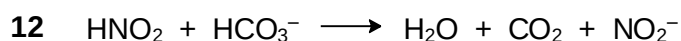
$$\text{Units of } K_c = \underline{\text{mol}^{-4} \text{ dm}^{12}} \quad \text{Hence, statement A is correct.}$$

$$10^3 = \frac{10}{1 \times [\text{SCN}^{-}]^4}$$

$$[\text{SCN}^{-}] = \underline{3.16 \times 10^{-1} \text{ mol dm}^{-3}} \quad \text{Hence, statement B is correct.}$$

Since K_c is more than 1, the position of equilibrium **lies to the right**. This indicates that $[\text{Co}(\text{SCN})_4]^{2-}$ is a more stable complex ion than $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Hence, statement C is correct.

Dilution of the reaction mixture decreases the concentration of ions in the solution. Hence, the **position of equilibrium shifts to the left** to increase the concentration of ions. This **increases** the proportion of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Hence, statement D is incorrect.



C

HCO_3^{-} acts as a *Bronsted base* which **accepts a proton** from HNO_2 , a *Bronsted acid*. The H_2CO_3 formed is unstable and decomposes to H_2O and CO_2 .

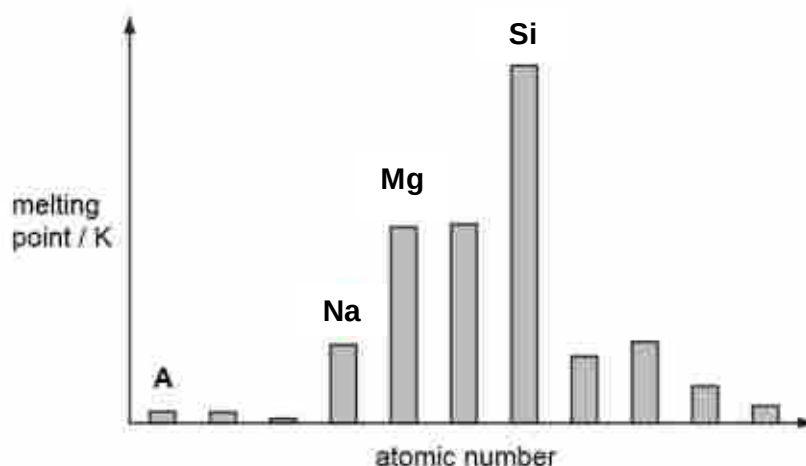
13 The working pH range of an indicator is between $\text{p}K_a - 1.00$ and $\text{p}K_a + 1.00$.

B

A suitable indicator will be one where the working pH range of the indicator lies within the range of rapid pH change at the end-point of the titration.

Hence, only the indicator in B fulfils the condition.

14



B

15	oxide	nature of oxide	reacts with dil. NaOH	remarks	D
	Al ₂ O ₃	amphoteric	yes	–	
	P ₄ O ₁₀	acidic	yes	–	
	SO ₂	acidic	yes	–	
	SiO ₂	acidic	no	only reacts with hot and concentrated strong alkalis to form silicates	

16 Each mineral behaves as a mixture of two carbonate compounds. D

mineral	formula	behaves as a mixture of
barytocalcite	BaCa(CO ₃) ₂	1 mol BaCO ₃ and 1 mol CaCO ₃
dolomite	CaMg(CO ₃) ₂	1 mol CaCO ₃ and 1 mol MgCO ₃
huntite	Mg ₃ Ca(CO ₃) ₄	3 mol MgCO ₃ and 1 mol CaCO ₃

The effectiveness of each of the three minerals as fire retardant is dependent on its **ease of thermal decomposition** to produce CO₂, which smothers the fire.

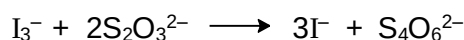
The ease of thermal decomposition of the minerals is dependent on the charge density and hence the polarising power of the respective Group II metal ions (Ba²⁺, Ca²⁺ and Mg²⁺).

The order of effectiveness as fire retardant, from best to worst, corresponds to the order of decreasing polarising power of the Group II metal ions: Mg²⁺, Ca²⁺, Ba²⁺.

Huntite is a more effective fire retardant than dolomite as huntite contains more MgCO₃ and hence it produces more CO₂ upon complete thermal decomposition.

17 I₂ undergoes a redox reaction with S₂O₃²⁻, forming I⁻ and S₄O₆²⁻. (Recall from 'Group VII') D

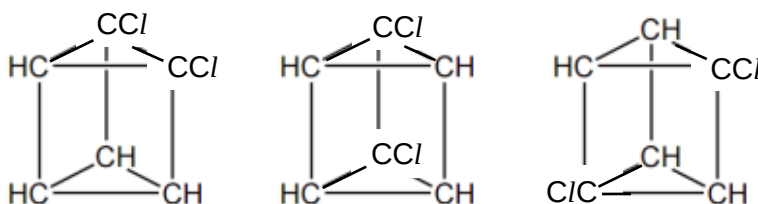
In the presence of excess KI, I₂ forms the complex ion I₃⁻. Hence, the overall equation is as shown:



18 Since At is below I in Group VII, D

- Similar to AgI, AgAt is likely to be **insoluble** in excess dilute aqueous NH₃
- At₂ is a weaker oxidising agent than Cl₂ and hence, At₂ is **unable** to oxidise Cl⁻ to form At⁻ and Cl₂
- KAt and **concentrated** sulfuric acid react to form **At₂** (HAt formed initially is oxidised by the sulfuric acid)

19 The compound C₆H₄Cl₂ has the following **three** structural isomers: A



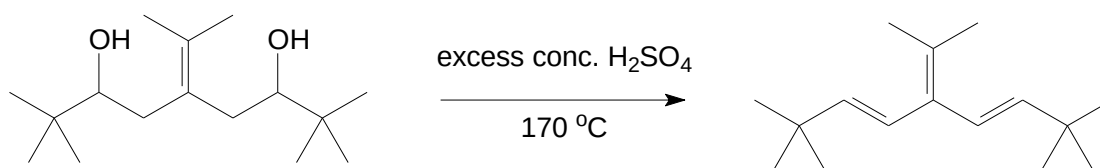
20

bond	bond energy / kJ mol ⁻¹
C–F	> 410
C–H	410
C–Cl	340

C

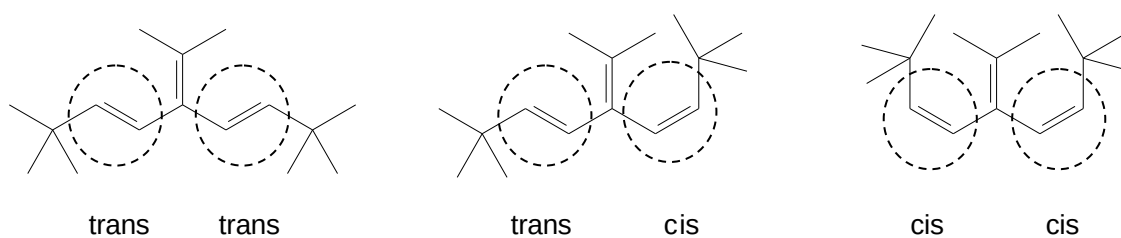
Irradiation of **CHFCICF₂Cl** results in **homolytic fission** of the weakest C–Cl bond, forming the **•CHFCF₂Cl** radical.

21

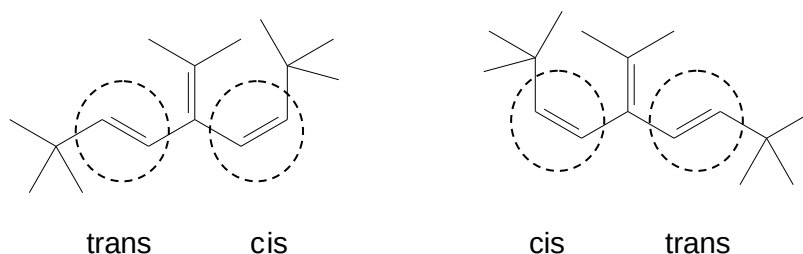


D

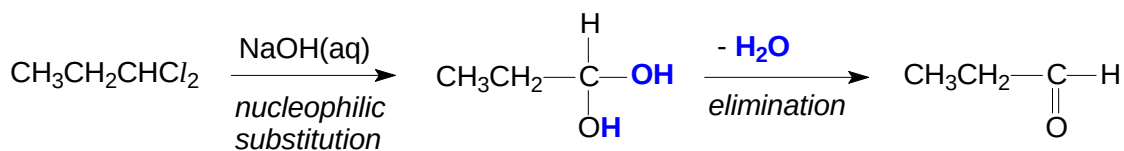
The **three** geometrical isomers of the product are as follows:



Note: The following two structures are equivalent.

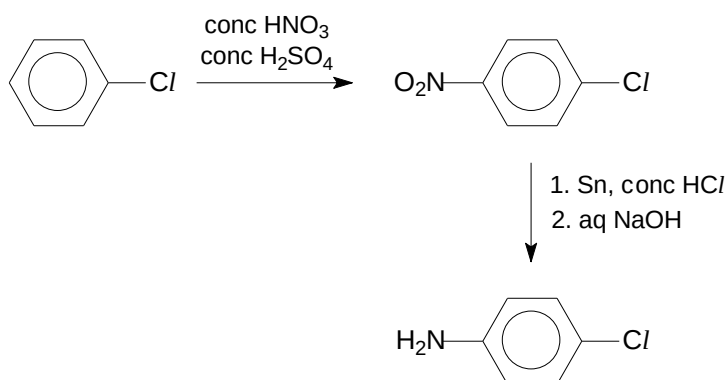


22



B

23



A

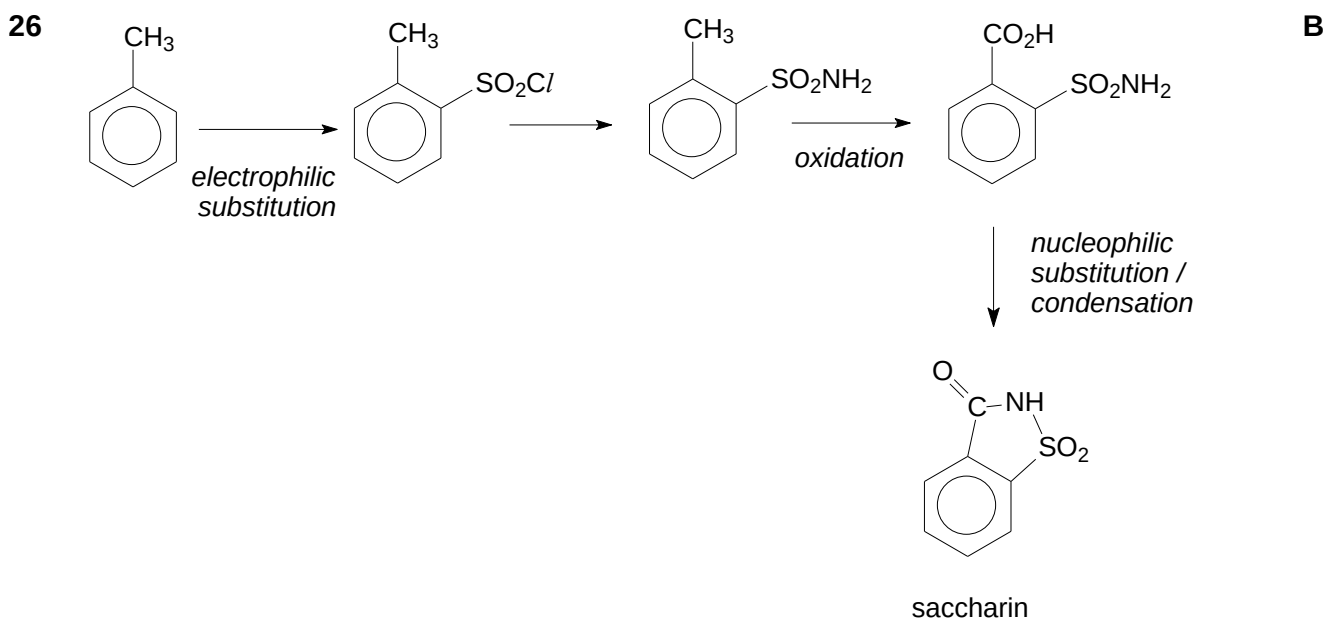
Note that –NO₂ is 3-directing and cannot be reduced using LiAlH₄.

- 24 The CN^- nucleophile attacks the **electron deficient** carbon in propanone in the **nucleophilic addition** mechanism. **B**
- 25 **Q hydrolyses** in water to produce a strongly acidic solution of $\text{CH}_3\text{CO}_2\text{H}$ and **HCl**. **B**
Hence, the resulting solution formed has the lowest pH.

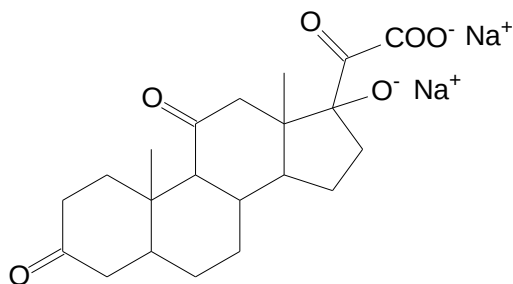
P, R and **S** are weak acids which ionise partially in water.

The presence of electronegative atoms (**Cl** and **Br**) on **R** and **S** exerts an electron-withdrawing effect on $\text{ClCH}_2\text{CH}_2\text{COO}^-$ and $\text{BrCH}_2\text{CH}_2\text{COO}^-$ respectively, which disperses the negative charge and stabilises the anion. Hence, the dissociation of $\text{CH}_3\text{CH}_2\text{COOH}$ to give H^+ ions is least favourable. The resulting solution from **P** has the highest pH.

Since **Cl** is more electronegative than **Br**, it exerts a stronger electron-withdrawing effect on $\text{ClCH}_2\text{CH}_2\text{COO}^-$ and hence $\text{ClCH}_2\text{CH}_2\text{COOH}$ is more acidic than $\text{BrCH}_2\text{CH}_2\text{CO}_2\text{H}$. Hence, the resulting solution from **R** has a lower pH than **S**.



- 27 **A:** aqueous KMnO_4 , dilute H_2SO_4 , heat **D**
For the compound on the left, purple solution decolourises.
(hydrolysis of ester + oxidation of primary alcohol)
For the compound on the right, purple solution remains.
- B:** aqueous KMnO_4 , dilute H_2SO_4 , heat
For the compound on the left, purple solution remains.
For the compound on the right, purple solution decolourises.
(side-chain oxidation on benzene ring)
- C:** aqueous Br_2 / neutral FeCl_3
For the compound on the left, orange solution remains / no violet colouration observed.
For the compound on the right, orange solution decolourises / violet colouration observed.



29 The four species given are conjugate acids of their corresponding amines.

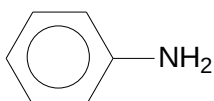
A

A low pK_a value for its conjugate acid will indicate a high pK_b value for the amine.

A decreasing pK_a value for the conjugate acids of the amines also indicates an increasing pK_b value for the amines.

Hence, the species can be arranged in the **order of decreasing basicity** of the corresponding amine.

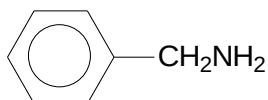
amine of I



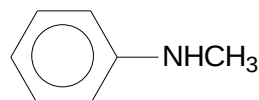
amine of II



amine of III



amine of IV



Amine of **III** is the most basic as the electron-donating alkyl group ($C_6H_5CH_2-$) increases the availability of lone pair on N.

Amines **I**, **II** and **IV** are less basic than that of **III** since the lone pair on N can be delocalised into the π electron cloud of the benzene ring, decreasing the availability of the lone pair.

Amine of **IV** is more basic than that of **I** and **II** as it is a secondary amine. The presence of the electron-donating alkyl group ($-CH_3$) increases the availability of the lone pair as compared to amines of **I** and **II**.

Amine of **II** is less basic than that of **I** as the presence of electron-withdrawing Cl decreasing the availability of the lone pair on N to a greater extent.

30 Possible combinations:

B

Glutamine Glutamic acid	$-\text{NH}_2$	$-\text{CO}_2\text{H}$
$-\text{NH}_2$	×	✓
$-\text{CO}_2\text{H}$ (1)	✓	×
$-\text{CO}_2\text{H}$ (2)	✓	×

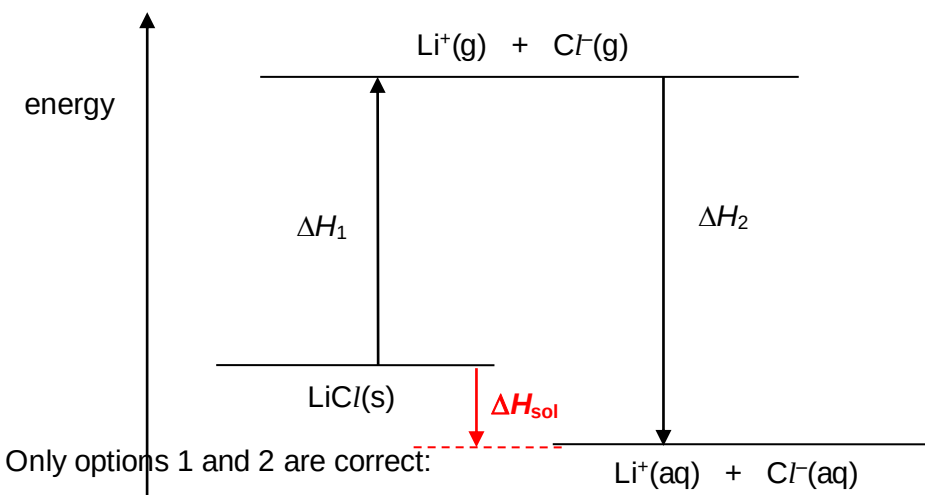
∴ 3 different compounds can be formed

31

	no. of protons	no. of electrons	no. of neutrons
OH^-	9	10	8
HCO_3^-	31	32	30
DCO_3^-	31	32	31

B

32



B

1. By Hess' law, $\Delta H_{\text{sol}}(\text{LiCl}) = \Delta H_1 + \Delta H_2$.
2. From the energy level diagram, $\text{LiCl(s)} \longrightarrow \text{Li}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ is an exothermic process. Hence, the process is accompanied by an increase in temperature.
3. Silver chloride is sparingly soluble while lithium chloride is soluble. Hence, $\Delta H_{\text{sol}}(\text{LiCl})$ is expected to be MORE exothermic than $\Delta H_{\text{sol}}(\text{AgCl})$.

33

1. When pressure is increased, the gaseous reactant particles become closer together. Hence, the frequency of effective collisions increases.
2. More molecules have energy greater than the E_a at a higher **temperature**.
3. Raising the pressure has no effect on the E_a . The E_a is lowered only in the presence of a catalyst.

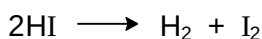
D

34

	electronic config.	no. of unpaired electrons
1. Cu^{2+}	$[\text{Ar}] 3d^9$	1
2. Mn^{3+}	$[\text{Ar}] 3d^4$	4
3. V^{3+}	$[\text{Ar}] 3d^2$	2

A

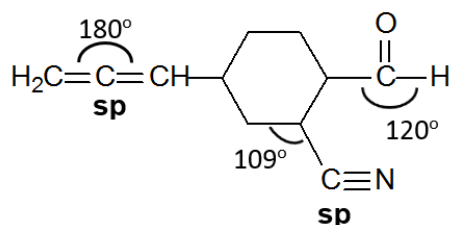
35



C

1. Gaseous hydrogen iodide appears as **white fumes** NOT brown
2. The hot rod provides the activation energy to break the H–I bond
3. The I_2 formed appears as purple fumes (violet black I_2 solids are also observed)

36



D

37 The reaction pathway diagram illustrates a **two-step** reaction mechanism.

D

1. Tertiary RX undergoes a two-step S_N1 mechanism
2. Primary RX undergoes a single step S_N2 mechanism
3. Same as option 2

38 The nucleophile (OH^- , CN^- , Br^-) can attack the carbocation / planar molecule from either side with equal probability in the S_N1 / nucleophilic addition / electrophilic addition mechanism.

C

A racemic mixture will not be formed in (1) since the product is not even chiral.

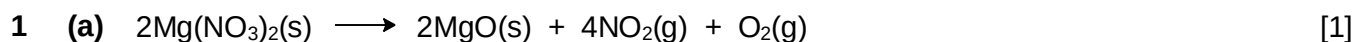
39 Compound 1 will undergo oxidative cleavage and compound 2 will undergo hydrolysis when reacted with hot acidified KMnO_4 .

B

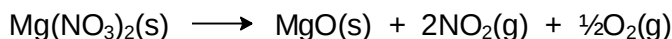
Compounds with the structure $\text{CH}_3-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-$ or $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$ will form a yellow ppt with alkaline aqueous iodine.

40 Option 1: Fe^{2+} in haemoglobin forms a stronger dative covalent bond with carbon monoxide than oxygen.
 Option 2: Each haemoglobin molecule contains 4 haem groups. One molecule of oxygen binds to the Fe^{2+} on each haem group.
 Option 3: The polypeptide chains in haemoglobin are held together by R group interactions.

B



OR



- (b) Correctly stated volume, with units, of apparatus to be used for gas collection.
E.g. 100 ml or 100 cm³ gas syringe [1]

AND

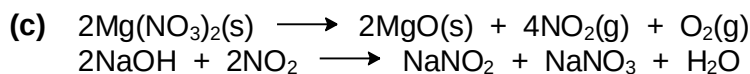
Correctly calculated mass of magnesium nitrate to produce a stated volume of O₂ gas that would be appropriate for the stated volume of apparatus.

E.g. for 60 cm³ of O₂,

$$n(\text{O}_2) = 60/24000 = 2.50 \times 10^{-3} \text{ mol}$$

$$n[\text{Mg}(\text{NO}_3)_2] = 2 \times n(\text{O}_2) = 5.00 \times 10^{-3} \text{ mol}$$

$$\text{mass of Mg}(\text{NO}_3)_2 = 5.00 \times 10^{-3} \times [24.3 + 2(14.0) + 6(16.0)] = \underline{0.742 \text{ g}}$$
 [1]



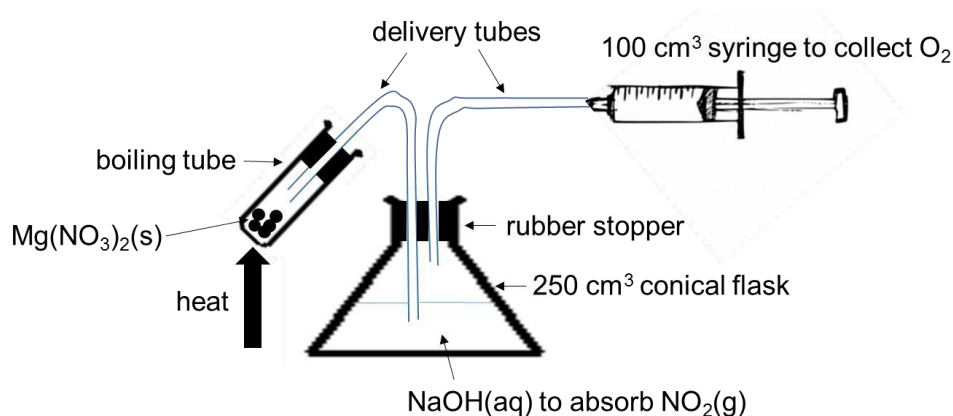
$$n(\text{NO}_2) = 2 \times n[\text{Mg}(\text{NO}_3)_2] = 2 \times 5.00 \times 10^{-3} = 0.0100 \text{ mol}$$

$$n(\text{NaOH}) = n(\text{NO}_2) = 0.0100 \text{ mol}$$

$$\text{min. volume of } 1.00 \text{ mol dm}^{-3} \text{ NaOH needed} = 0.0100 / 1.00 \times 1000 = \underline{10.00 \text{ cm}^3}$$
 [1]

- (d) A diagram of the assembled apparatus capable of absorbing the nitrogen(IV) oxide and collecting the oxygen separately and in sequence [2]

- Directly heated vessel (boiling tube) labelled magnesium nitrate with tube at exit
- Gas stream led into a liquid labelled (1.00 mol dm⁻³) NaOH which will absorb the nitrogen(IV) oxide / NO₂
- Collects a gas in a syringe or over a liquid, provided it is properly connected
- All parts of the apparatus are connected and air-tight AND nitrogen(IV) oxide absorption precedes oxygen collection



An outline of how the results would be obtained and measures to ensure reliability of results

[4]

1. Record the mass of the empty boiling tube.
2. Weigh accurately about 0.75 g of magnesium nitrate into a boiling tube.
3. Using a burette, add 20.00 cm³ of 1.00 mol dm⁻³ sodium hydroxide into the chamber collecting nitrogen(IV) oxide / NO₂.
4. Set up the apparatus according to the diagram above.
5. After ensuring that all the connections are properly sealed, start heating the magnesium nitrate in the boiling tube. Heat strongly for about 5 minutes, moving the boiling tube to ensure even heating of the solid. Continue heating until no further bubbling is seen in the sodium hydroxide solution and the syringe shows no further change in volume of oxygen gas collected.
6. Remove the delivery tube from the alkali before taking the boiling tube off the flame. *(To prevent back flow of liquid into the boiling tube due to cooling of air)*
7. Allow all the apparatus and chemicals to cool to room temperature before taking measurements.
8. Weigh the boiling tube and residue. Subtract the mass of the empty boiling tube to determine the mass of magnesium oxide produced.
9. Transfer all the sodium hydroxide solution into a 100 cm³ volumetric flask. Top up to the mark with distilled water. Stopper the flask and shake well to obtain a homogeneous solution.
10. Pipette 25.0 cm³ of the solution into a 250 cm³ conical flask for titration.
11. Add a few drops of methyl orange indicator. Titrate with the 0.20 mol dm⁻³ hydrochloric acid from the 50.00 cm³ burette until the solution turns from yellow to orange.
12. Repeat the titration until consistent results within ± 0.10 cm³ are obtained.
13. Record the volume of oxygen gas collected in the syringe.

Brief, but specific, details of how results will be used to determine the amounts in moles of reactant and all products at the end of complete thermal decomposition AND confirm that the decomposition had occurred according to the molar ratios in the equation

$$n(\text{MgO}) = \text{mass of MgO} / M_r \text{ of MgO} = x \text{ mol}$$

$$\begin{aligned} n(\text{NO}_2) &= n(\text{NaOH that reacted with NO}_2) \\ &= (20/1000 \times 1) - [(\text{vol. of HCl}/1000 \times 0.20) \times 100/25.0] = y \text{ mol} \end{aligned}$$

$$n(\text{O}_2) = \text{volume of O}_2/24000 = z \text{ mol}$$

}

[1]

Compare each of the values x , y and z with $n[\text{Mg}(\text{NO}_3)_2]$ used ($\approx 5.00 \times 10^{-3}$ mol) to check if the decomposition has occurred according to the molar ratios in the equation.

[1]

[Total: 12]

- 2 (a) (i) B atom in BF_3 molecule is electron-deficient as it has only 6 electrons around it. [2]
Hence, the B atom can accept another 2 electrons from the lone pair of O atom in ethoxyethane molecule. By forming a dative bond with the O atom of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, the B atom achieves the octet configuration.



(b) (i)
$$K_{\text{partition}} = \frac{\text{concentration of J in ethoxyethane (organic layer)}}{\text{concentration of J in water (aqueous layer)}}$$

$$= \frac{2.14 / 20}{(5 - 2.14) / 75} = \underline{2.81}$$
 [1]

- (ii) 1st extraction [2]

$$2.81 = (x / 10) / [(5 - x) / 75]$$

$$2.81 (5 - x) = 7.5 x$$

$$x = 1.36 \text{ g}$$

2nd extraction

Mass of **J** remaining in aqueous layer after 1st extraction = $5.00 - 1.36 = 3.64 \text{ g}$

$$2.81 = (y / 10) / [(3.64 - y) / 75]$$

$$2.81 (3.64 - y) = 7.5 y$$

$$y = 0.992 \text{ g}$$

$$\therefore \text{total mass of J extracted} = 1.36 + 0.992 = \underline{2.35 \text{ g}}$$

- (iii) It is more efficient to use two successive portions of 10 cm^3 ethoxyethane than one 20 cm^3 portion of ethoxyethane since total mass of **J** extracted is greater using two successive portions. [1]

- (c) Anhydrous calcium chloride (drying agent) was added to remove water present in the organic layer. [1]

[Total: 8]

- 3 (a) Giant covalent structure with strong covalent bonds between P atoms. [1]

Relatively high melting point **OR** insolubility in organic solvent (methylbenzene) [1]
suggests strong bonding throughout the structure.

- (b) type of hybridisation: sp [1]



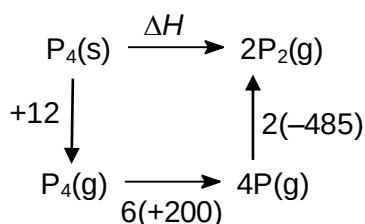
[1]

- (c) (i) Phosphorus-phosphorus triple bonds are much weaker than nitrogen-nitrogen triple bonds as phosphorus atoms are too big to come close enough together to form strong bonds. [1]

OR

Orbitals of P are larger and more diffused hence overlap of orbitals is less effective.

- (ii) [2]



$$\begin{aligned}
 \Delta H &= +12 + 6(+200) + 2(-485) \\
 &= \underline{+242 \text{ kJ mol}^{-1}}
 \end{aligned}$$

[1]

- (iii) Increase temperature [1]

$$\Delta G = \Delta H - T\Delta S$$

Since $\Delta H > 0$, $\Delta S > 0$ (as there is an increase in no. of moles of gas),
for ΔG to be negative (i.e. spontaneous), magnitude of $T\Delta S$ must be greater than that of ΔH . Hence, T must be large. [1]

- (d) (i) High temperature (needed for reaction between N_2 and O_2) [1]

- (ii) $2\text{NO} + 2\text{CO} \longrightarrow \text{N}_2 + 2\text{CO}_2$ [1]
OR $2\text{NO} + \text{C} \longrightarrow \text{N}_2 + \text{CO}_2$

[Total: 12]

- 4 (a) (i) A ligand is a neutral molecule or an anion which possesses at least one lone pair of electrons which can be used to form dative bonds with the central atom or ion. [1]

(ii) *Transition element complexes are often coloured:*

In the presence of ligands, the d orbitals of transition metal ion are split into two levels.

The energy gap E between the non-degenerate orbitals is small and corresponds to that in the visible light region. [1]

Energy is absorbed from the visible region when an electron is promoted from a lower level d orbital to a vacant higher level d orbital (d-d transition). [1]

The colour of the transition metal complex is the complement of the colour absorbed. [1]

The colour of a complex of a given transition element often changes when the ligands around it are changed:

The size / magnitude of the energy gap E depends on the ligand. [1]

(Since $E = hc / \lambda$),

When the ligand changes, E changes, λ (absorbed) also changes (hence colour of the complex changes). [1]

- (b) (i) Let O.N. of C in $C_2O_4^{2-}$ be x

$$2(x) + 4(-2) = -2$$

$$x = \underline{+3}$$

[1]

- (ii) Let O.N. of Fe in $[Fe(C_2O_4)_3]^{3-}$ be y

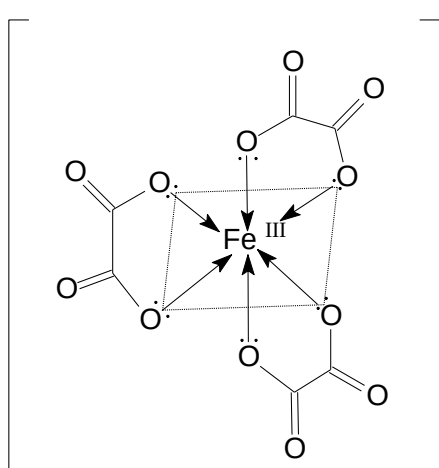
$$y + 3(-2) = -3$$

$$y = \underline{+3}$$

[1]

- (iii) [3-

[2]

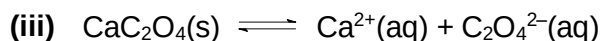


- (c) (i) $K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$

[1]

- (ii) $[C_2O_4^{2-}] = (2.3 \times 10^{-9})^{1/2} = \underline{4.80 \times 10^{-5} \text{ mol dm}^{-3}}$

[1]



Increase in $[\text{Ca}^{2+}]$ due to the presence of the common ion Ca^{2+} (from CaCl_2) in solution **W** shifts the position of the above equilibrium to the left. Hence, $[\text{C}_2\text{O}_4^{2-}]$ in solution **W** is less than that calculated in **(c)(i)**. [1]

(d)

cation	ionic radius / nm
Na^+	0.095
Mg^{2+}	0.065
Al^{3+}	0.050

[1]

The charge density of the cation increases from Na^+ to Mg^{2+} to Al^{3+} . Thus, the polarising power of the cation increases in the same order.

As a result, NaCl does not hydrolyse in water ($\text{pH} = 7$); MgCl_2 hydrolyses only to a small extent ($\text{pH} = 6.5$) and AlCl_3 hydrolyses to a larger extent ($\text{pH} = 3.0$). [1]

[Total: 15]

- 5 (a) The actual value for the enthalpy of hydrogenation of benzene is less exothermic as more energy is needed to break the bonds in benzene due to delocalisation of the π electrons. [1]

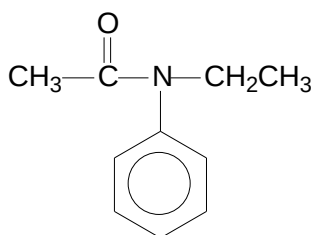
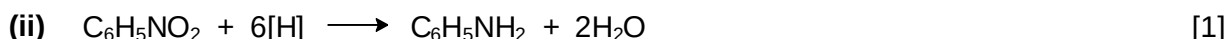
OR

Benzene is resonance-stabilised and hence has a lower energy level.

- (b) reagents: conc. HNO_3 + conc. H_2SO_4 } [1]
 conditions: $55 - 60^\circ\text{C}$ }
 electrophile: NO_2^+ [1]

- (c) (i) In phenylamine, the lone pair on the N atom is delocalised into the benzene ring, making the ring more electron-rich. [1]

Hence, the ring is more susceptible to (electrophilic) attack and hence does not require the strong electrophile Br^+ generated by the reaction between Br_2 and FeBr_3 . [1]



X

(d) 3 : 14 : 9

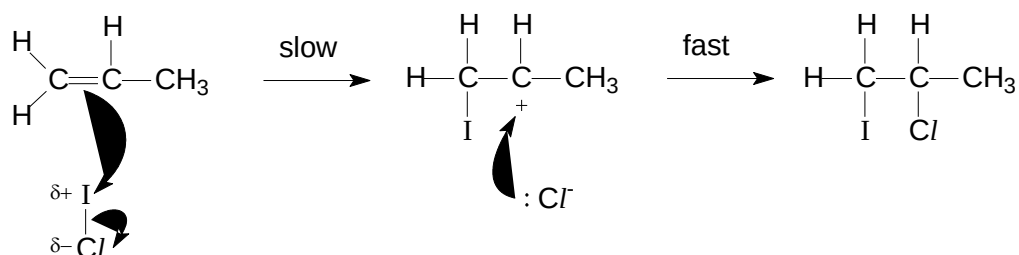
[1]

Relative rate suggests 1 : 7 : 1, but there are 3 primary to 2 secondary to 9 primary hydrogen atoms in **L**, **M** and **N** respectively. Hence, this ratio becomes 3 : 14 : 9.

[1]

[Total: 9]

6 (a) (i)



[3]

(ii) ICl is polar while pure halogens are not.

[1]

(b) number of σ bonds: 14
number of π bonds: 2 }

[1]

(c) (i) ethene

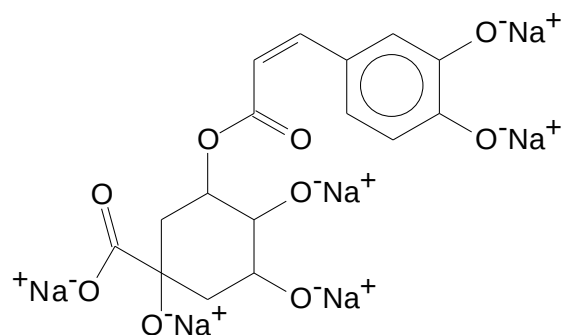
[1]

(ii)



[2]

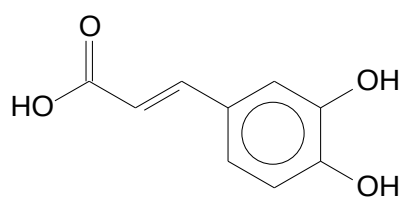
(d) (i)



[1]

(ii) (acid) hydrolysis

[1]



[1]

C

(iii) alkene **OR** C=C

[1]

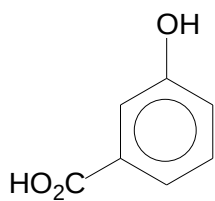
(iv) $\text{Na}_2\text{CO}_3(\text{aq})$: carboxylic acid
 $\text{Br}_2(\text{aq})$: phenol

[1]

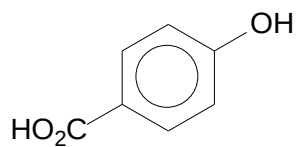
[1]

(v)

D:

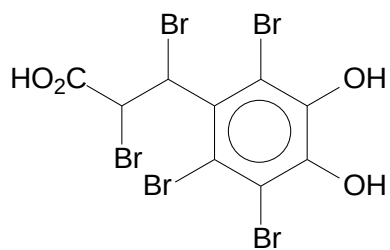


OR



[1]

E:



[1]

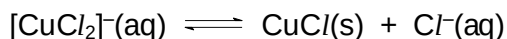
[Total: 16]

- 1 (a) (i) Nuclear charge / proton number increases from Fe to Cu. } [1]
- However, additional electrons are being added to the inner 3d subshell. As such, there is an increase in shielding effect caused by the increasing number of d electrons from Fe to Cu. } [1]
- Hence, effective nuclear charge remains fairly constant from Fe to Cu. [1]
- (ii) Fe uses both the 3d and 4s electrons while Ca only uses the 4s electrons for metallic bonding. [1]
- The ionic radius of Fe is also smaller than that of Ca, resulting in higher charge density. [1]
- This results in stronger metallic bonding between Fe ions and the valence electrons. [1]
- (iii) density = mass / volume } [1]
- Fe and Cu have greater atomic mass } [1]
- and smaller atomic radius. [1]
- (b) $2\text{Cu}^+(\text{aq}) \longrightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$ [1]
- State symbols not required*
- $E^\ominus(\text{Cu}^+/\text{Cu}) = +0.52 \text{ V}$
 $E^\ominus(\text{Cu}^{2+}/\text{Cu}^+) = +0.15 \text{ V}$
- $E_{\text{cell}}^\ominus = +0.52 - (+0.15) = \underline{+0.37 \text{ V}}$ [1]
- (c) (i) I^- and Cu^{2+} undergo a redox reaction to produce the white precipitate copper(I) iodide, CuI, and brown solution I_2 . } [1]
- $2\text{I}^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{CuI}(\text{s}) + \text{I}_2(\text{aq})$
- $\text{S}_2\text{O}_3^{2-}$ then reduces I_2 to I^- (colourless solution), itself oxidises to $\text{S}_4\text{O}_6^{2-}$ (redox reaction). } [1]
- $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \longrightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$
- State symbols not required*
- (ii) Cu and Cu^{2+} undergo a redox reaction (or comproportionation) to form a colourless Cu(I) complex, $[\text{CuCl}_2]^-$. } [1]
- $\text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \longrightarrow 2[\text{CuCl}_2]^- (\text{aq})$

Element	Cu	Cl
% by mass	64.1	35.9
A_r	63.5	35.5
No. of moles	$64.1/63.5$ $= 1.009$	$35.9/35.5$ $= 1.011$
Simplest whole no. ratio	1	1

[1]

The white precipitate is CuCl.



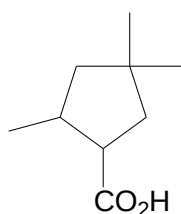
[1]

State symbols not required

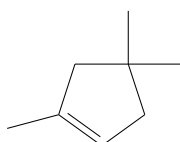
(d)

Information	Type of reaction	Deduction(s)
On treatment with hot acidified concentrated KMnO_4 , H produced a single compound J , $\text{C}_8\text{H}_{14}\text{O}_3$.	Oxidative cleavage	H contains a <u>$\text{C}=\text{C}$ / alkene</u> . Since a single compound is formed (without loss of C), H is a <u>cycloalkene</u> .
J evolved CO_2 with $\text{Na}_2\text{CO}_3(\text{aq})$,	Acid–base	J contains <u>RCO_2H / carboxylic acid</u> .
J gave an orange precipitate with 2,4–DNPH,	Condensation	J contains a <u>ketone</u> . (J cannot contain an aldehyde since J is produced from strong oxidation of H with KMnO_4)
J and gave a yellow precipitate with alkaline aqueous iodine.	Oxidation / tri-iodomethane reaction	J has a <u>$\text{CH}_3\text{CO}-$</u> structure (J cannot have a $\text{CH}_3\text{CH}(\text{OH})-$ structure since J is produced from strong oxidation of H with KMnO_4)

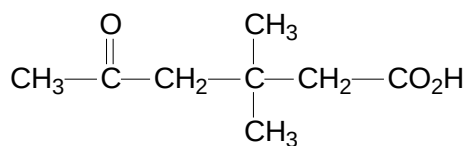
[6]



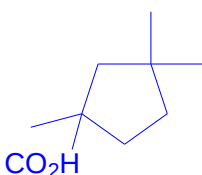
G



H

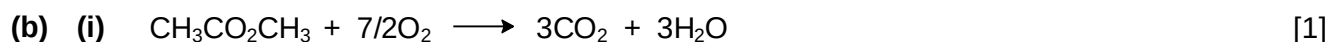
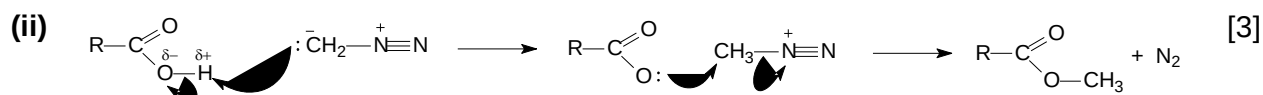


J

Do not accept  *for structure of G as G is a secondary carboxylic acid*

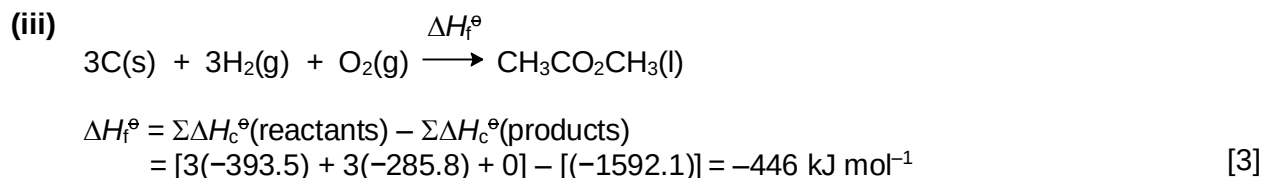
[Total: 20]

2 (a) (i) B [1]



Accept equation multiplied through by 2

(ii) The amount of heat absorbed or evolved when one mole of substance is formed from its constituent elements in their standard states at 298 K and 1 atm. [2]



(c) Heat each compound separately with NaOH(aq), and then add I₂(aq) to the resulting solution. [1]

A yellow precipitate (CHI₃) is observed for HCO₂CH₂CH₃. [1]

No (yellow) precipitate is observed for CH₃CO₂CH₃. [1]

(d) (i) **W** (aluminium) burns in O₂ with an intense white flame to give a white solid of Al₂O₃. [1]

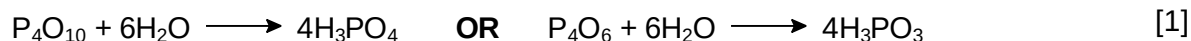
Z (sulfur) burns in O₂ on gentle heating with a pale blue flame to give a colourless gas of SO₂. [1]

(ii) The oxide of **X** (SiO₂) has a giant molecular structure. Large amount of energy is required to break the strong covalent bonds between Si and O atoms. [1]

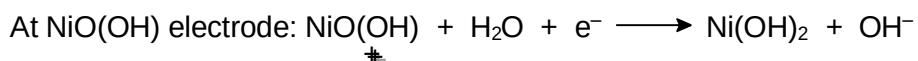
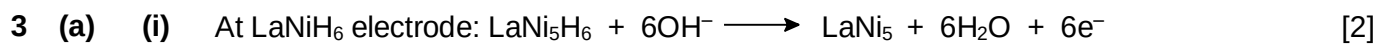
The oxide of **Y** (P₄O₁₀ or P₄O₆) has a simple molecular structure. Less energy is required to break the weak van der Waal's forces of attraction between the molecules. [1]

(iii) The oxide of **X** (SiO₂) is insoluble in water. Hence, the pH of the resulting solution is 7. [1]

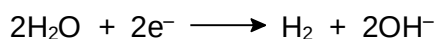
The oxide of **Y** (P₄O₁₀ or P₄O₆) reacts readily in water to produce a strongly acidic solution of pH 2. [1]



[Total: 20]

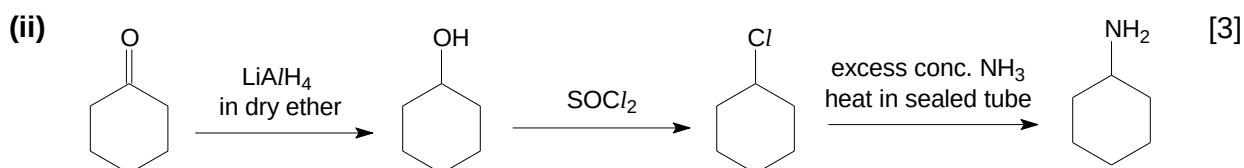
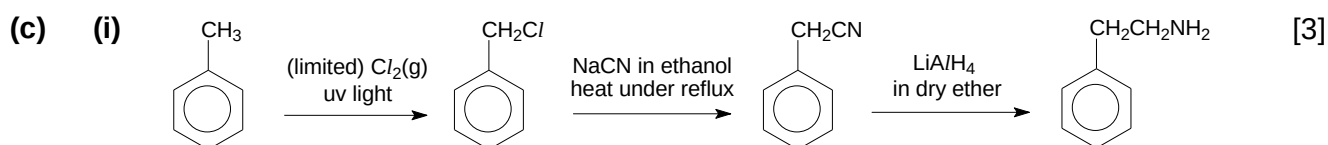


OR



$E^\circ_{\text{cell}} = +1.07 - (-0.76)$
 $= \underline{+1.83 \text{ V} > 0}$ (feasible)

Since it is feasible for the battery to discharge electricity, the $\text{Ce}^{4+}/\text{Ce}^{3+}$ half-cell can be replaced with Br_2/Br^- half-cell. [1]



(d) (i) Since equal volume of $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2$ and $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+$ are mixed, concentration of both species are halved.

$$K_b = \frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+][\text{OH}^-]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}$$

$$10^{-4.3} = \frac{(0.400)[\text{OH}^-]}{0.250} \quad [1]$$

$$[\text{OH}^-] = 3.13 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log(3.13 \times 10^{-5}) = 4.5$$

$$\text{pH} = \underline{9.5} \quad [1]$$

- (ii) Since $pK_b(\text{AMP}) = 4.3$, $pK_a(\text{conjugate acid of AMP}) = 9.7$.

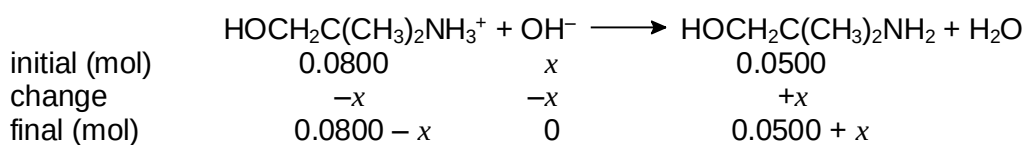
When pH of the buffer = 9.7, the buffer solution is at its maximum buffering capacity.

$$\text{Hence } \frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]} = \underline{1}. \quad [1]$$

$$\text{initial } n(\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+) = 100/1000 \times 0.800 = 0.0800 \text{ mol}$$

$$\text{initial } n(\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2) = 100/1000 \times 0.500 = 0.0500 \text{ mol}$$

Let x be $n(\text{OH}^-)$ added

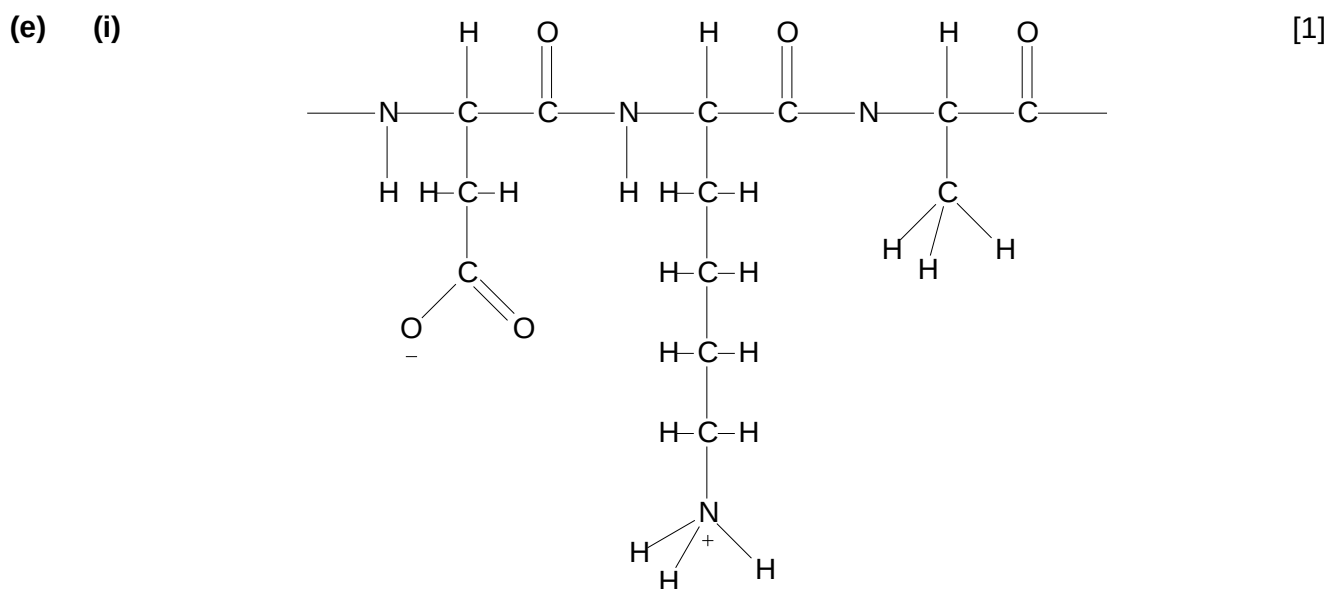


Since $\frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]} = 1,$

$$0.0800 - x = 0.0500 + x$$

$x = 0.015 \text{ mol}$

$$\text{mass of NaOH added} = 0.015 \times (23.0 + 16.0 + 1.0) = \underline{0.600 \text{ g}} \quad [1]$$



- (ii)
 - Ionic bonding between charged R groups containing the CO_2^- groups, NH_3^+ groups.
Example: Between lysine (containing NH_3^+) and aspartic acid (containing CO_2^-) [1]
 - Hydrogen bonding between polar R groups containing the carboxyl groups (CO_2H), amino groups (NH_2) or hydroxyl (OH) groups.
Example: Between aspartic acid and serine or between lysine and serine. [1]

- (iii) Lactic acid dissociates to give H^+ which may protonate the carboxylate group (in glutamic acid) or the amine group (in lysine), disrupting ionic bonds between the charged R groups. [1]

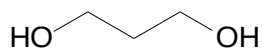
OR

disrupting the hydrogen bonding between the polar R groups (e.g. lysine and serine, leading to denaturation.

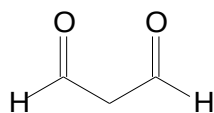
[Total: 20]

4 (a) (i)

[2]

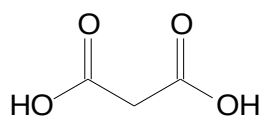


E

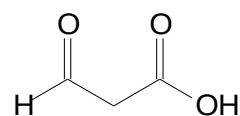


F

(ii)



OR



[1]

Accept "propanedioic acid"

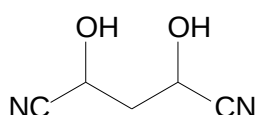
Accept "3-oxopropanoic acid"

(iii) $n(1,3\text{-dibromopropane}) = 9.0 / 201.8 = 0.0446 \text{ mol}$
 mass of F = $0.67 \times 0.0446 \times 72.0 = \underline{2.15 \text{ g}}$

[1]

[1]

(iv)

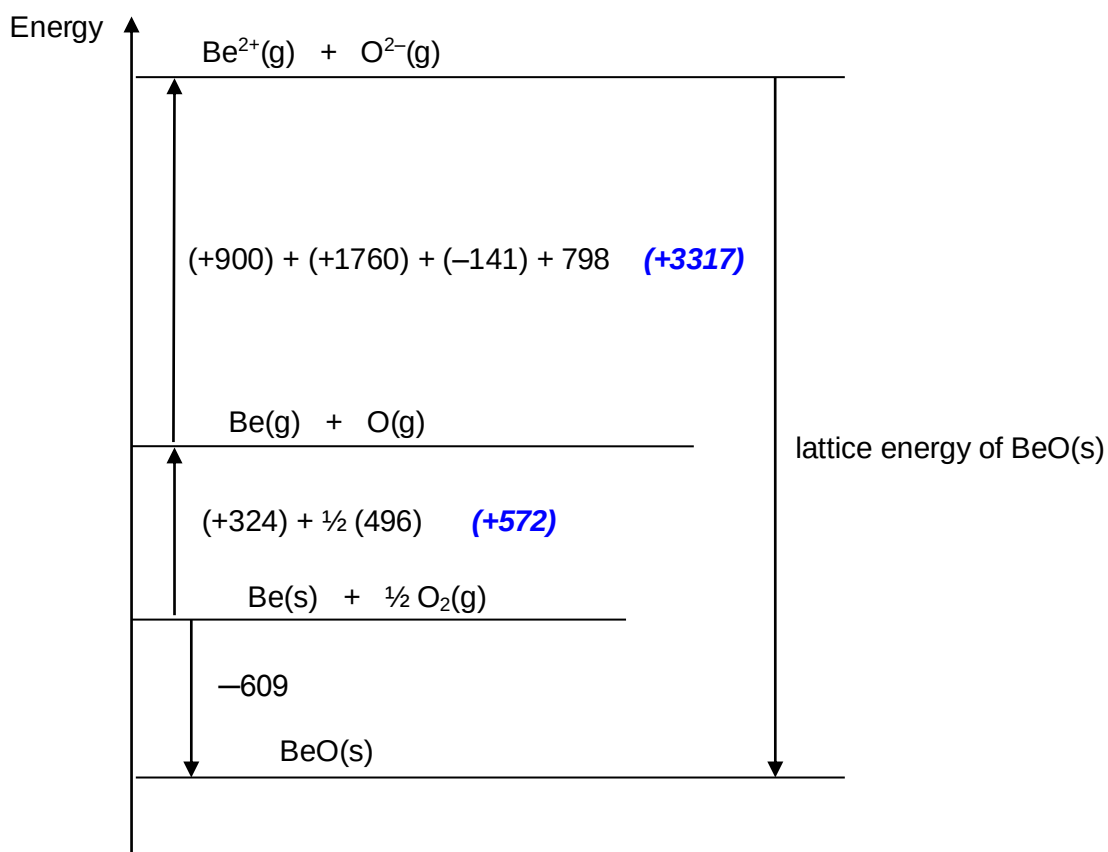


[1]

G

(b) (i)

[2]



$$\begin{aligned} \text{Lattice energy of BeO(s)} &= -(3317 + 572 + 609) \\ &= \underline{-4498 \text{ kJ mol}^{-1}} \end{aligned}$$

[1]

- (ii) Theoretical calculation assumes pure ionic character.
 But Be^{2+} ion is small and highly charged, hence it has high polarising power
 $\Rightarrow \text{BeO}$ exhibits covalent character
 $\Rightarrow$ Attraction is stronger, so observed value is more exothermic. } [1]

- (iii) Given $\text{LE} \propto \frac{q_+q_-}{r_+ + r_-}$
 ionic charge of $\text{Be}^{2+} >$ ionic charge of Na^+
 ionic radius of $\text{Be}^{2+} <$ ionic radius of Na^+ } [1]

Stronger attraction between oppositely charged ions in BeO }
 $\Rightarrow \text{LE}(\text{BeO}) >$ of $\text{LE}(\text{Na}_2\text{O})$ in magnitude } [1]

- (iv) $\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{NaOH}(\text{aq})$
 Sodium oxide dissolves in water to produce sodium hydroxide } [1]

$\text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{NaClO}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 Chlorine undergoes disproportionation reaction when reacted with NaOH . } [1]

State symbols not required

- (c) (i) $\text{CrO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \longrightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$

 $\text{CrO}_4^{2-} + 3\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} + 4\text{H}_2\text{O}$ [1]

- (ii) chromium(III) hydroxide **OR** $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$ **OR** $\text{Cr}(\text{OH})_3$
 $2[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{CO}_3^{2-} \longrightarrow 2[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3] + 3\text{CO}_2 + 3\text{H}_2\text{O}$ [1]
 $\text{Cr}^{3+}(\text{aq})$ undergoes hydrolysis with water liberating $\text{H}^+(\text{aq})$ }
 Undergoes acid-base reaction with $\text{Na}_2\text{CO}_3(\text{aq})$ } [1]

- (d) (i) • a state function that measures the degree of disorder / randomness in a system [1]
OR
 • gives a measure of the extent to which particles and energy are distributed within the system **OR**
 • the greater the disorder / randomness, the larger is the entropy.

- (ii) In reaction I, there is no change in number of particles in aqueous solution, } [1]
 whereas in reaction II, there is an increase of 3 particles. }

$\Rightarrow$ Increase in number of ways of arrangement and energy distribution of the particles
 $\Rightarrow \Delta S_r^\ominus$ is more positive [1]

[Total: 20]

[1]

[1]

(ii)	$2\text{N}_2\text{O}(\text{g}) \longrightarrow$	$2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$
initial / kPa	25	0 0
change / kPa	-x	+x +1/2x
final at any time, t / kPa	25 - x	x 1/2x

$$25 - x + x + 1/2x = P$$

$$25 + 1/2x = P$$

$$x = 2P - 50$$

[1]

Hence, partial pressure of N_2O at any time, t , is

$$25 - x = 25 - (2P - 50)$$

$$= 25 - 2P + 50$$

$$= \underline{75.0 - 2P \text{ (shown)}}$$

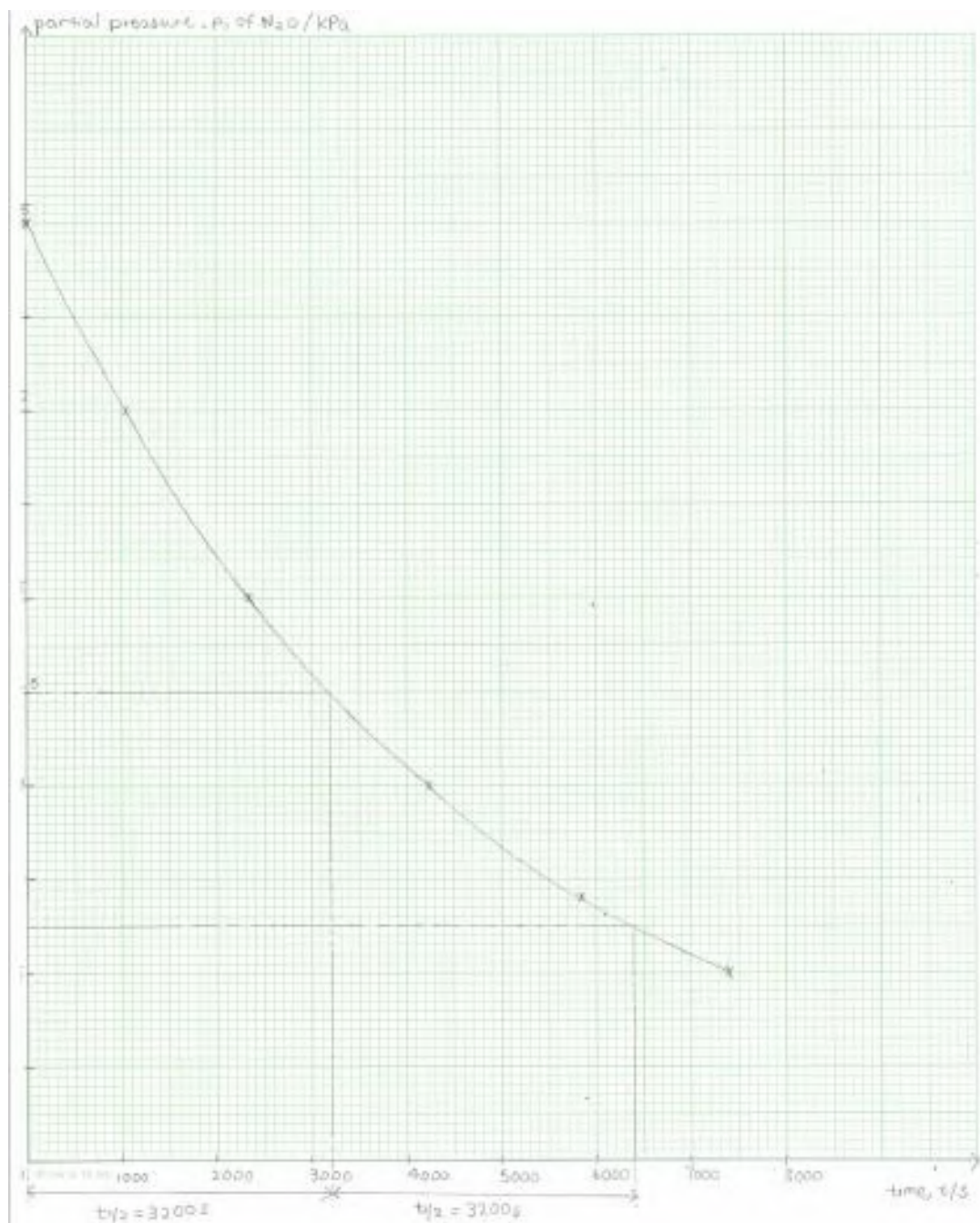
[1]

(iii)

P / kPa	27.5	30.0	32.5	34.0	35.0
t / s	1030	2360	4230	5870	7420
p of N ₂ O / kPa	<u>20</u>	<u>15</u>	<u>10</u>	<u>7</u>	<u>5</u>

[1]

(iv)



[2]

Since $t_{1/2}$ is constant at 3200 s, the order of reaction w.r.t. N_2O is 1.

[1]

(v) rate = $k p_{N_2O}$

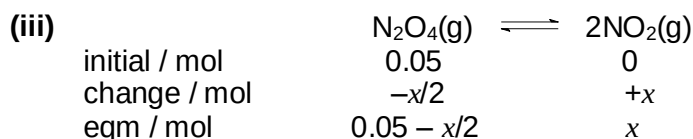
[1]

$$\begin{aligned} t_{1/2} &= \frac{\ln 2}{k} \\ k &= \frac{\ln 2}{t_{1/2}} \\ &= \frac{\ln 2}{3200} = 2.17 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

[1]
[1]

(c) (i) $n(\text{N}_2\text{O}_4) = 4.60 / 92.0 = \underline{0.0500 \text{ mol}}$ [1]

(ii) $pV = nRT$
 $n = pV / RT$
 $= \frac{101 \times 10^3 \times 1.48 \times 10^{-3}}{8.31 \times 300} = \underline{0.0600 \text{ mol}}$ [1]



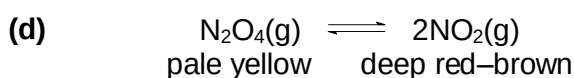
$0.05 - x/2 + x = 0.06$
 $x = 0.02$ [1]

$n(\text{N}_2\text{O}_4) \text{ dissociated} = x/2 = 0.02/2 = 0.01$
 $\% \text{ of } \text{N}_2\text{O}_4 \text{ dissociated} = 0.01 / 0.05 \times 100 = \underline{20.0 \%}$ [1]

(iv) $K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$ [1]

$p(\text{NO}_2) = 0.02/0.06 \times 1.00$
 $= 1/3 \text{ atm}$
 $p(\text{N}_2\text{O}_4) = 0.04/0.06 \times 1.00$
 $= 2/3 \text{ atm}$ [1]

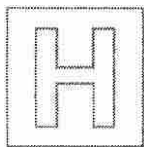
$K_p = \frac{(1/3)^2}{2/3} = 1/6 \approx \underline{0.17 \text{ (shown)}}$ [1]



When the equilibrium mixture is suddenly compressed in a gas syringe, $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$ increase due to the reduced volume. [1]

Compression of the gas also results in an increase in pressure. The position of the above equilibrium shifts left to decrease pressure by producing fewer gas molecules. The [1]
 mixture becomes paler as $[\text{N}_2\text{O}_4]$ increases.

[Total: 20]



CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

Wednesday 31 August 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name and HT group on the Answer Sheet in the spaces provided.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **17** printed pages and 1 blank page.

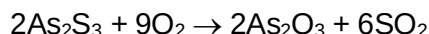
Section A

For each question there are **four** possible answers, **A**, **B**, **C** and **D**. Choose the one you consider to be **correct** and record your choice in soft pencil on the **separate Answer Sheet** provided.

- 1 Use of the Data Booklet is relevant to this question.

Arsenic(III) sulfide, As_2S_3 , is a bright yellow solid which has been used as a pigment in paintings.

When arsenic(III) sulfide is heated in air, it reacts with oxygen to give arsenic(III) oxide and sulfur(IV) oxide.



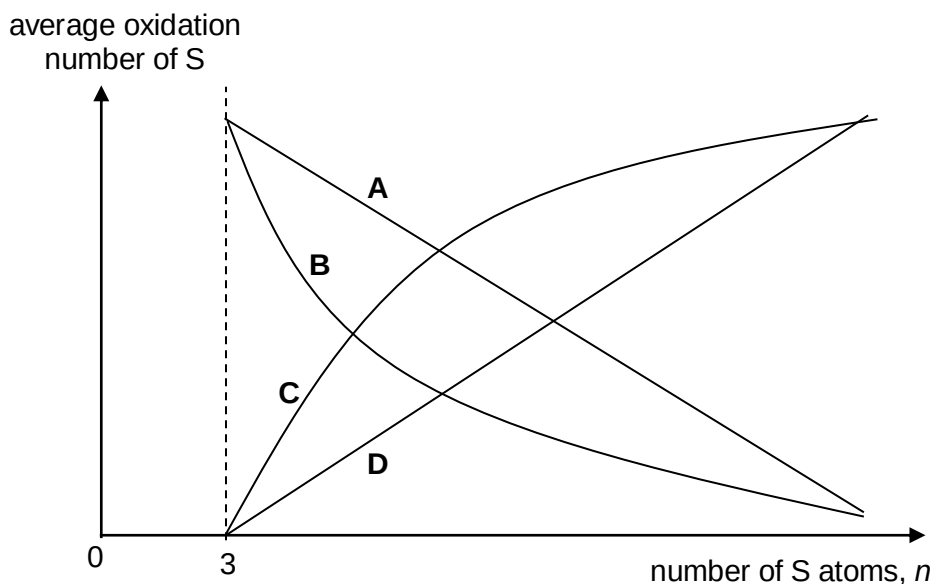
What would be the mass of arsenic(III) oxide produced if 550 dm^3 oxygen, measured at room temperature and pressure, reacted with arsenic(III) sulfide?

- A 1010 g B 1070 g C 2010 g D 2160 g
- 2 Incomplete combustion of 20 cm^3 of a gaseous hydrocarbon gave carbon dioxide and carbon monoxide in a 6:1 ratio, as well as water vapour. It was found that the carbon dioxide took up a volume of 51.4 cm^3 whereas the water vapour took up a volume of 80 cm^3 . All gas volumes are measured at the same temperature and pressure.

What is the molecular formula of the hydrocarbon?

- A C_2H_4 B C_2H_6 C C_3H_6 D C_3H_8
- 3 Polythionates are a series of sulfur-oxo anions with the general formula $\text{S}_n\text{O}_6^{2-}$, where $n > 2$. A simple example is tetrathionate ion, $\text{S}_4\text{O}_6^{2-}$.

Which of the following graphs best illustrates the variation in the average oxidation number of sulfur in $\text{S}_n\text{O}_6^{2-}$ with n ?



4 Which of the following species has the smallest bond angle around the central atom?

- A** NCl_3 **B** PCl_3 **C** SO_3 **D** BF_3

5 Which of the following shows the correct bonds present in solid CHI_3 ?

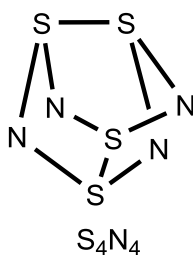
- A** Covalent bonds only
B Ionic bonds only
C Covalent bonds & temporary dipole-induced dipole forces of attraction
D Covalent bonds & permanent dipole-permanent dipole forces of attraction

6 Polymerisation is a process in which large number of small molecules (monomers) are joined together to form long-chain molecules.

Considering that polymerisation is a spontaneous reaction, what are the correct signs of ΔS and ΔH for the process?

	ΔS	ΔH
A	–	–
B	–	+
C	+	–
D	+	+

7 S_4N_4 is a thermochromic solid which changes colour with temperature. S_4N_4 has a cage structure as shown in the diagram.



Given the following data, what is the average bond energy of dissociation of S-N, in kJ mol^{-1} ?

$$\Delta H_f^\circ (\text{S}_4\text{N}_4) = +460 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{at}}^\circ (\text{sulfur}) = +279 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{at}}^\circ (\text{nitrogen}) = +497 \text{ kJ mol}^{-1}$$

$$(\text{S-S}) \text{ bond energy of dissociation in } \text{S}_4\text{N}_4 = +204 \text{ kJ mol}^{-1}$$

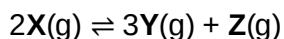
- A** +150 **B** +280 **C** +395 **D** +559

- 8 At 25 °C, a dented ping pong ball has an internal volume of 31.0 cm³ and internal pressure of 110 kPa. It is then placed in a water bath maintained at 60 °C, which returned the ball to its original spherical shape with internal volume of 33.5 cm³.

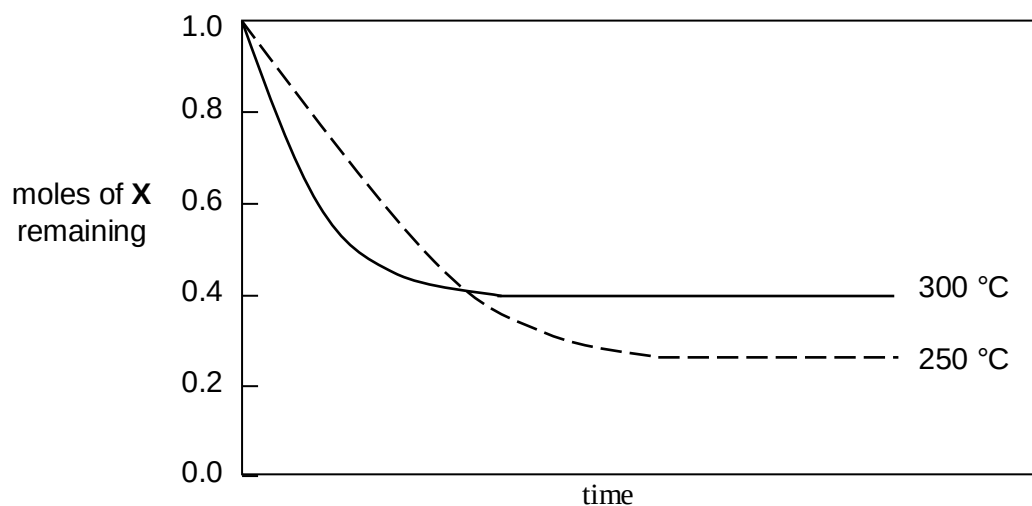
Assuming ideal gas behaviour, what is the pressure of air inside the ball at 60 °C in its original spherical shape?

- A 101 kPa B 114 kPa C 122 kPa D 244 kPa

- 9 Gas **X** decomposes to two other gases, **Y** and **Z**, according to the following equation:



The graph below shows the decomposition of 1.0 mol of pure gas **X** in the presence of a catalyst at various temperatures.



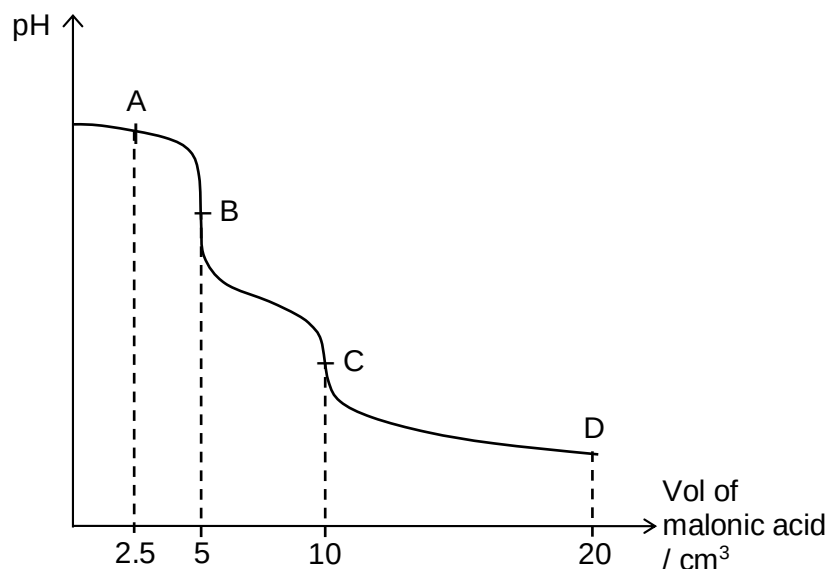
Which one of the following statements about the above system is **correct**?

- A The decomposition of **X** is endothermic.
 B The K_p of the system decreases with increasing temperature.
 C The percentage decomposition of **X** is 40 % at 300 °C.
 D The system becomes less disordered when it reaches equilibrium state.

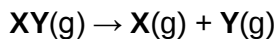
- 10 Malonic acid, $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$, is a weak dibasic acid.

Malonic acid is titrated against 20.0 cm^3 of sodium hydroxide of the same concentration, the following pH-volume curve is obtained.

At which point on the titration curve is the mixture **most** able to resist pH change upon addition of a small amount of aqueous acid or base?



- 11 The following is the reaction for compound **XY**,



If the rate constant for the reaction is $5.78 \times 10^{-3} \text{ s}^{-1}$, what is the time taken for the concentration of a sample of **XY** to decrease from 1.80 mol dm^{-3} to $0.225 \text{ mol dm}^{-3}$?

- A 120 s B 240 s C 360 s D 480 s
- 12 The reaction between **C** and **D** is as follows:



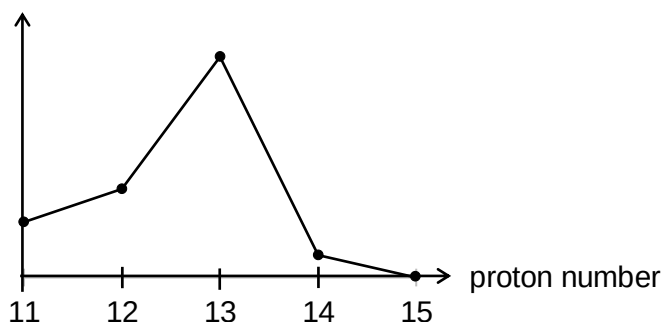
In an experiment to investigate the effect of concentrations on the rate of reaction, the following results were obtained at constant temperature.

Experiment	$[\text{C}] / \text{mol dm}^{-3}$	$[\text{D}] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3}\text{s}^{-1}$
1	1.0	1.0	0.0008
2	1.0	2.0	0.0016
3	1.0	3.0	x
4	2.0	2.0	0.0032

What is the value of **x**?

- A 0.0008 B 0.0016 C 0.0024 D 0.0032

- 13 The following graph shows how a property of the elements in Period 3, from Na to P, or their compounds, varies with proton number.



What property is shown by the graph?

- A Melting point of element
 - B Melting point of oxide
 - C pH of aqueous chloride
 - D Electrical conductivity of element
- 14 Which of the following statements about calcium, strontium and barium is correct?
- A The magnitude of the hydration energy of the M^{2+} ion increases from calcium to barium
 - B The energy required for the process $M(g) \rightarrow M^{2+}(g) + 2e^{-}$ increases from calcium to barium.
 - C The reducing power decreases from calcium to barium.
 - D The reactivity of the elements with water increases from calcium to barium.
- 15 When 1.0 g of each of the following Group II metals is added to cold water and any gas produced is collected at 25 °C and 1 atm, which sample will most likely produce the largest volume of gas?
- A Mg B Ca C Sr D Ba
- 16 Which statement about the trends in the properties of the halogens is correct?
- A The volatility of halogens increases down the group.
 - B The electronegativity of halogens increases down the group.
 - C The reactivity of halogens with hydrogen decreases down the group.
 - D The bond dissociation energy of halogens increases down the group.

- 17 "Bromine tablets" are used as disinfectants. It is a source of $\text{HClO}(\text{aq})$ and $\text{HBrO}(\text{aq})$, both of which are oxidising agents.

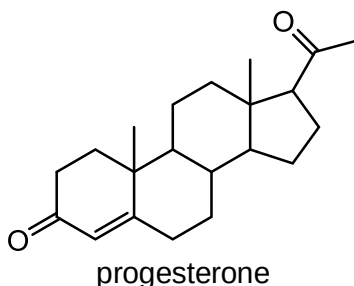
HBrO destroys bacteria, fungi and algae via its oxidising property in the process. HClO is a stronger oxidising agent than HBrO and helps to sustain the effectiveness of the bromine tablets.

What is the likely role of HClO in relation to HBrO ?

- A Oxidises Br^- to BrO^-
 - B Oxidises Br^- to Br_2
 - C Reduces BrO^- to Br^-
 - D Reduces BrO^- to Br_2
- 18 When drops of aqueous ammonia are added to a solution of CuSO_4 , a pale blue precipitate is formed. This precipitate dissolved when excess aqueous ammonia is added, forming a deep blue solution. On addition of dilute hydrochloric acid, the pale blue precipitate is reformed.

Which process does **not** occur in the above?

- A Dative bond formation
 - B Formation of a complex ion
 - C Precipitation of copper(II) hydroxide
 - D Reduction of copper(II) ions
- 19 Progesterone is an endogenous steroid involved in the menstrual cycle and pregnancy, of humans. It has the structure shown below.



How many chiral centers does progesterone contain?

- A 2
- B 4
- C 6
- D 8

- 20 Use of the Data Booklet is relevant to this question.

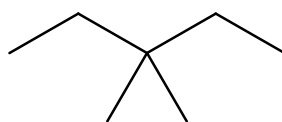
An organic compound **A** is commonly used in skin-care products. It has the following features.

- It is a monobasic acid.
- One mole of compound **A** reacts with Na to give 1 mole of H_2 gas.
- It dimerises in the presence of hot concentrated H_2SO_4 to give an organic compound of relative molecular mass 116.

How many carbon atoms are in one molecule of this organic compound **A**?

- A** 1 **B** 2 **C** 3 **D** 4

- 21 3,3-dimethylpentane, C_7H_{16} , reacts with bromine to form monobromo compounds with molecular formula of $\text{C}_7\text{H}_{15}\text{Br}$.

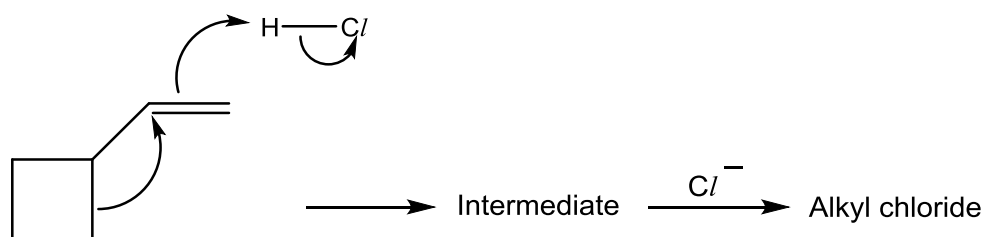


3,3-dimethylpentane

How many possible structural isomers, each with molecular formula $\text{C}_7\text{H}_{15}\text{Br}$, could be produced by 3,3-dimethylpentane?

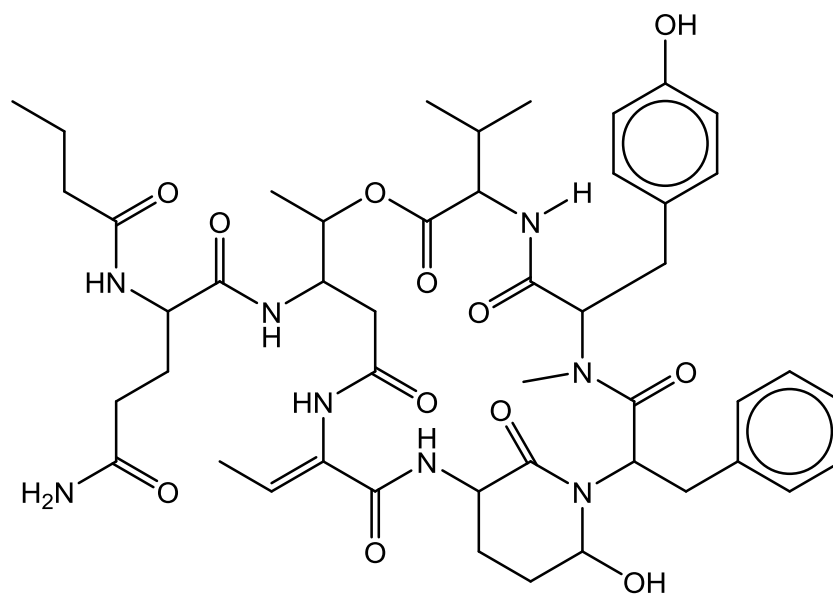
- A** 3 **B** 4 **C** 6 **D** 7

- 22 Vinylcyclobutane can react with HCl to give a rearranged alkyl chloride. With the aid of the flow of electrons represented by the curved arrows, what is the alkyl chloride product obtained?



- A** **B** **C** **D**

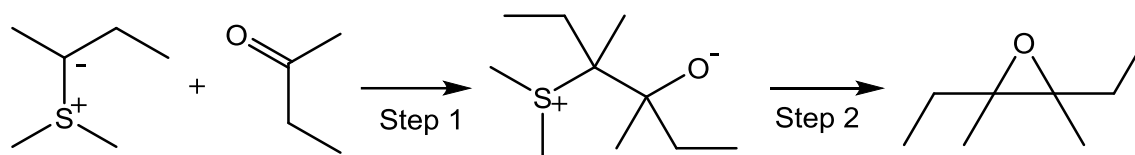
- 23 Yanucamide B can be extracted from a marine sponge and has the structure shown below.



Yanucamide B

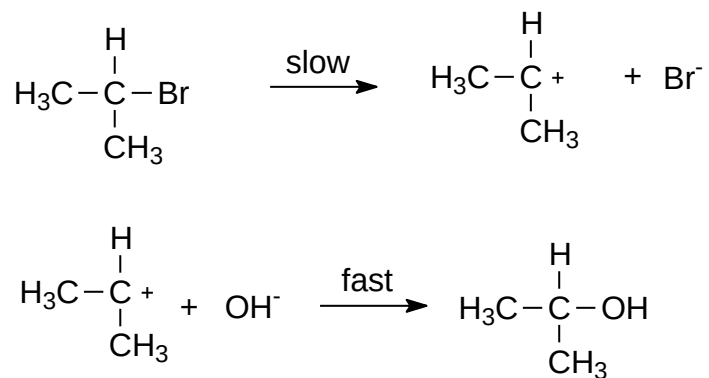
Which of the following set of reagents and conditions will not result in a colour change?

- A Br_2 in CCl_4
 - B neutral $\text{FeCl}_3(\text{aq})$
 - C LiAlH_4 in dry ether
 - D hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$
- 24 In the following sequence of reactions, what is the mechanism of step 1?

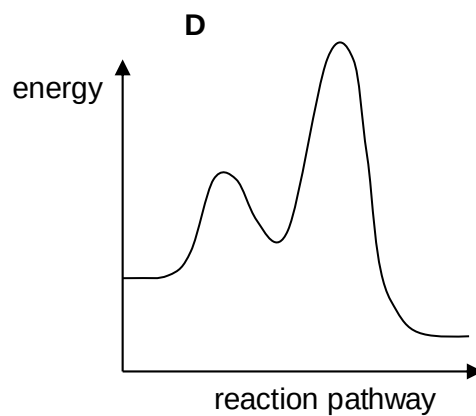
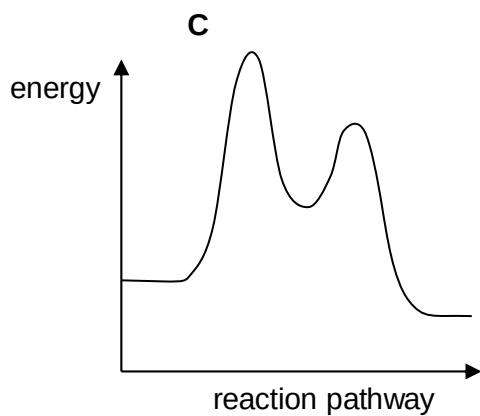
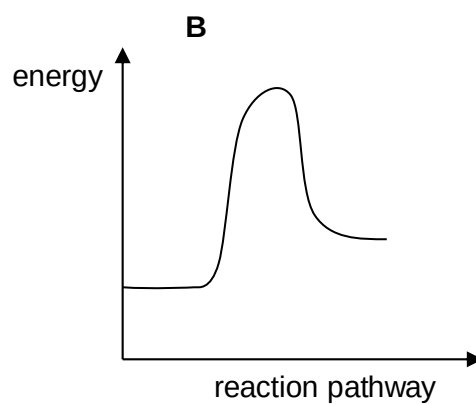
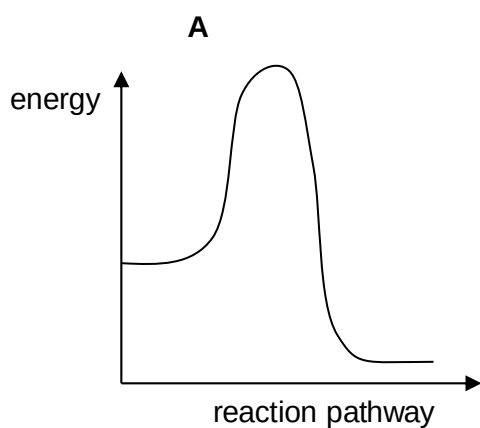


- A Nucleophilic Addition
- B Nucleophilic Substitution
- C Electrophilic Addition
- D Electrophilic Substitution

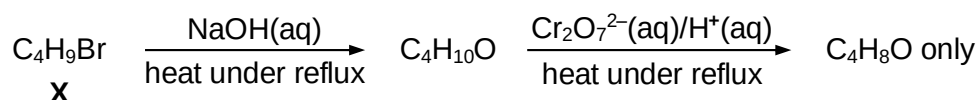
- 25 2-bromopropane undergoes nucleophilic substitution with aqueous NaOH via the following mechanism.



Which of the reaction pathway diagram fits the above mechanism?

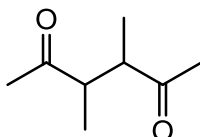


- 26 Compound **X**, C_4H_9Br , undergoes the following reactions:



What is **X** likely to be?

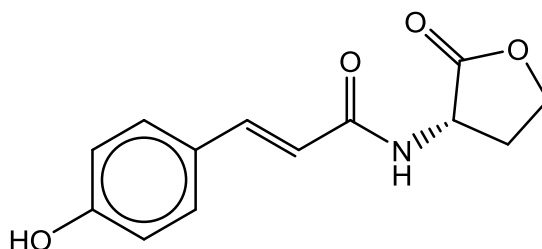
- A** 1-bromobutane
B 2-bromobutane
C 1-bromo-2-methylpropane
D 2-bromo-2-methylpropane
- 27 Compound **X** shown below is an intermediate used to generate pyrroles which are essential to the production of many different chemicals in the pharmaceutical industry.



Compound **X**

Which sentence is correct for compound **X**?

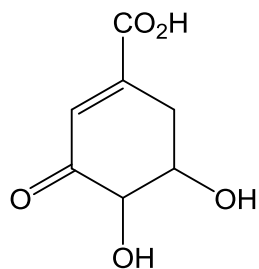
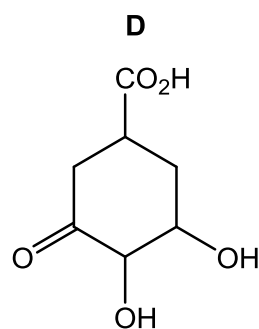
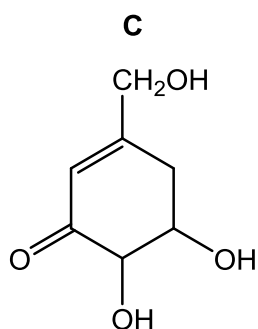
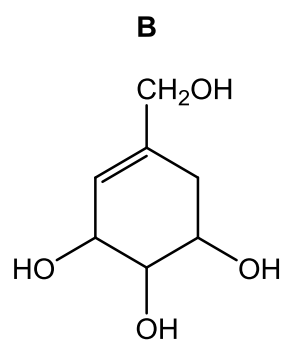
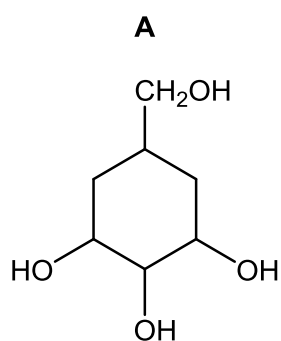
- A** It gives a silver mirror with Tollens' reagent.
B It decolourises acidified potassium manganate(VII).
C It does not give an orange precipitate with 2,4-dinitrophenylhydrazine.
D It gives yellow precipitate with alkaline aqueous iodine.
- 28 4-coumaroyl-HSL is a new type of bacterial, quorum sensing signal compound. When one mole of 4-coumaroyl-HSL is heated under reflux with $NaOH(aq)$ until no further reaction occurs, how many moles of $NaOH$ will react?



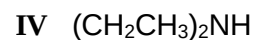
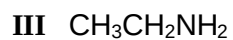
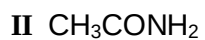
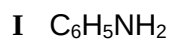
4-coumaroyl-HSL

- A** 1 **B** 2 **C** 3 **D** 4

- 29 Shikimic acid is found in star anise. The following compound **Y**, is the intermediate that can be used to form shikimic acid. When LiAlH_4 is added to compound **Y**, what is the product obtained?

Compound **Y**

- 30 Consider the following compounds below:



Which of the following shows the correct order of decreasing $\text{p}K_b$ values for the above compounds?

- A** II, III, I, IV
B II, I, III, IV
C III, IV, I, II
D IV, III, I, II

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Use of the Data Booklet is relevant to this question.

Which of the following species has the electronic configuration of [Ar] 3d⁵ 4s¹?

- 1** Cr
- 2** Mn⁺
- 3** Fe²⁺

32 The value of the ionic product of water, K_w , varies with temperature.

temperature / °C	K_w / mol ² dm ⁻⁶
25	1.0×10^{-14}
62	1.0×10^{-13}

Which of the following statement is correct?

- 1** The ionic dissociation of water is an endothermic process.
- 2** Water is a neutral liquid at 62 °C.
- 3** pH < 7 at 62 °C.

33 Which of the following has the same value as the standard enthalpy change of formation, $\Delta H_f^\ominus$, of carbon monoxide?

- 1** $\Delta H_{\text{combustion}}^\ominus (\text{C}) - \Delta H_{\text{combustion}}^\ominus (\text{CO})$
- 2** $\Delta H_f^\ominus (\text{CO}_2) - \Delta H_{\text{combustion}}^\ominus (\text{CO})$
- 3** $\frac{1}{2} \Delta H_f^\ominus (\text{CO}_2)$

The responses **A** to **D** should be selected on the basis of

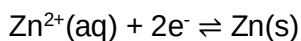
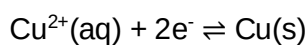
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

34 *Use of the Data booklet is relevant to this question.*

In the Daniell cell, copper and zinc electrodes are immersed in a solution of copper(II) sulfate and zinc sulfate respectively.

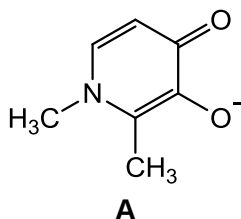
The two half-equations for a Daniell cell are given below



Which statements about this cell are correct when it is used?

- 1** The electron flow from the zinc electrode to the copper electrode in the external circuit.
- 2** The overall cell reaction is $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$.
- 3** The cell potential is +1.10V.

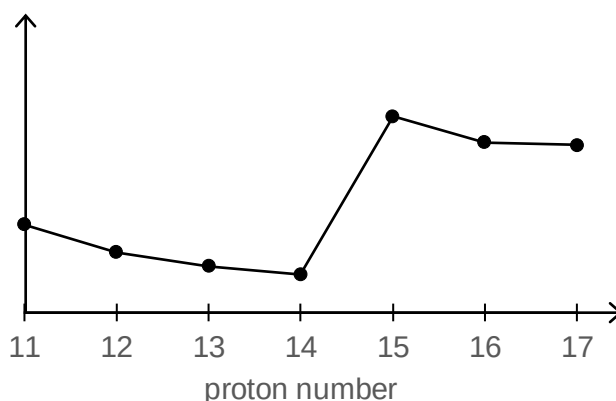
35 A neutral, red complex, FeA_3 , is formed when a bidentate ligand **A** is added to an aqueous solution of Fe^{3+} ions.



Which of the following statements is correct?

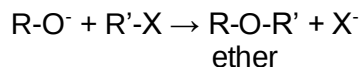
- 1** The complex has a coordination number of 3.
- 2** The complex absorbs radiation in the blue-green region of the visible spectrum.
- 3** The complex has a smaller energy gap between d-orbitals compared to yellow $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

- 36 The graph shows how a property from Na to Cl in Period 3 varies with proton number.



What is this property?

- 1 Ionic radius
 - 2 First ionisation energy
 - 3 Electronegativity
- 37 Williamson synthesis is one of the better methods to prepare ethers, R-O-R'. It involves a S_N2 displacement of halide ion in halogenoalkane (R'X) by an alkoxide ion nucleophile (RO⁻) as shown.



Which of the following statements are true?

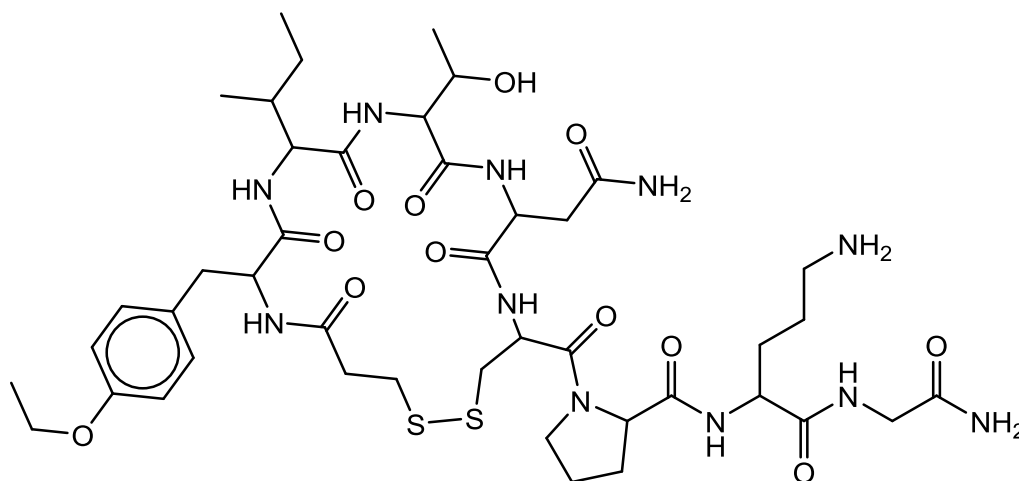
- 1 The rate equation involved is rate=k[RO⁻][R'X]
 - 2 The reaction involving bromomethane will be faster compared to chloromethane.
 - 3 The reaction involving 2-bromopropane will be faster compared to bromomethane.
- 38 Cars are fitted with a catalytic converter. What reactions typically occur in a catalytic converter?
- 1 $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$
 - 2 $\text{C}_x\text{H}_y + \left(\frac{x}{2} + \frac{y}{4}\right) \text{O}_2 \rightarrow x\text{CO} + \left(\frac{y}{2}\right)\text{H}_2\text{O}$
 - 3 $\text{CO}_2 + \text{NO} \rightarrow \text{CO} + \text{NO}_2$

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 39** Atosiban, a protein, is used as an intravenous medication as a birth labour repressant to halt premature labour.

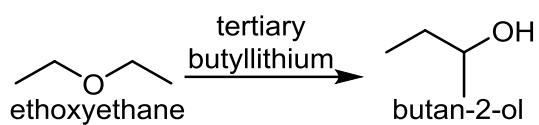


Atosiban

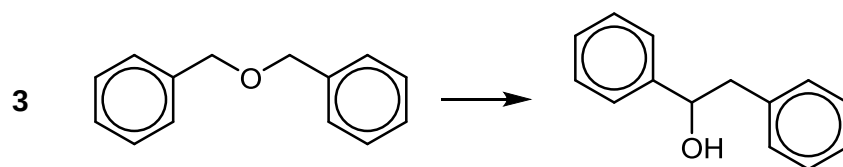
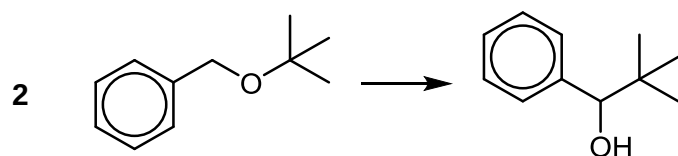
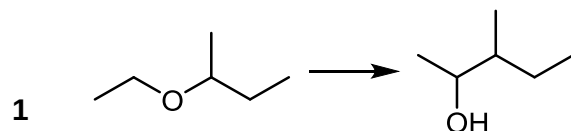
Which of the following R group interactions in the protein are possible?

- 1** Hydrogen bond
- 2** Disulfide bond
- 3** Ionic bond

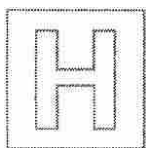
- 40 The isomerisation of ethoxyethane to produce the corresponding alcohol is shown below.



Which of the following shows the correct product formed under the same conditions?



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CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE
NAME

CLASS

2T

CHEMISTRY

Paper 2 Structured Questions

9647/02

Monday 22 August 2016
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do **not** use staples, paper clips, or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

	For Examiner's Use		
Paper 1			40
Paper 2	Q 1	12	72
	Q 2	15	
	Q 3	15	
	Q 4	15	
	Q 5	15	
Paper 3	Q 1	20	80
	Q 2	20	
	Q 3	20	
	Q 4	20	
	Q 5	20	
Total			192

This document consists of **16** printed pages.

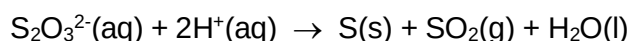
1 Planning (P)

One method of studying the kinetics of a chemical reaction, to find the order of reaction with respect to a particular reactant, is to measure the initial rates, by using the 'clock experiment'.

To determine the initial rate, we can measure the time taken for a prominent visual change to occur in the course of a reaction.

When aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to a solution containing dilute hydrochloric acid, HCl , a fine, pale yellow precipitate of solid sulfur will be formed after a while. This is the prominent visual change that can be clearly identified.

The overall equation for the reaction is represented as follows:



The initial rate of this reaction is determined by measuring the time taken for sufficient precipitate of sulfur to be formed to just obscure a 'cross' marked on a piece of white paper below a reaction container.

A student carried out a series of preliminary experiments, using approximate volumes of the two reactants and each reaction mixture was made up to the same total volume with deionised water. The student found that the time taken for the pale yellow precipitate to appear doubled when the volume of hydrochloric acid added was halved.

- (a) (i)** State the relationship between the initial rate of reaction and the time taken for the pale yellow precipitate to appear.

.....
[1]

- (ii)** Explain why it is necessary to top up the reaction mixture with deionised water to the same total volume.

.....

[1]

- (b) Hence, based on the results of the student's preliminary experiments, predict the order of the reaction with respect to H^+ ions.

.....

.....

.....

.....

.....[1]

- (c) You are to design an experiment to study the kinetics of the reaction between $\text{S}_2\text{O}_3^{2-}$ ions and H^+ ions.

The following data in tabulated form is shown below.

experiment	volume of 1.00 mol dm^{-3} $\text{Na}_2\text{S}_2\text{O}_3 / \text{cm}^3$	volume of 1.00 mol dm^{-3} HCl / cm^3	volume of deionised water $/ \text{cm}^3$	time taken for the 'marked cross' to be obscured / s
1	10	20	20	t_1
2		20		t_2
3	10			t_3

- (i) Fill in the blanks in the table above, appropriate volumes of the reactants and deionised water to be used in experiments 2 and 3 such that the order of reaction with respect to $\text{S}_2\text{O}_3^{2-}$ and H^+ ions can be determined and verified. [1]
- (ii) Outline in a series of numbered steps, how **experiment 1** could be carried out. Your **plan** should include:
- the **apparatus** used to measure the various volumes,
 - the **order** that the various solutions are mixed,
 - how the **time** to determine the rate of reaction is measured, and
 - other **experimental details** to ensure the **consistency** of the experiment.

Based on the table in (c)(i), explain how the results of any two of the three experiments can be used to determine the order of reaction with respect to $\text{S}_2\text{O}_3^{2-}$ ions.

.....

.....

.....

.....

.....

.....[7]

-[1]

9647/02/CJC JC2 Preliminary Examination 2016

- 2** Silver halides (silver chloride, silver bromide and silver iodide) are useful in qualitative analysis as they are insoluble in water. In qualitative analysis, silver nitrate is added to a test solution to identify the presence of halide ions by forming a precipitate.

- (a) (i)** When aqueous silver nitrate was added to a test solution which was known to contain a halide ion, a cream precipitate was formed.

Identify the precipitate and deduce the identity of the halide ion present in the solution.

.....
.....[1]

- (ii)** To confirm the identity of the halide, aqueous ammonia was added dropwise, and the precipitate remained unchanged at first, but as more ammonia was added, the precipitate dissolved.

With the aid of an equation, briefly explain why the precipitate dissolved.

.....
.....
.....[2]

- (iii)** Draw the structure of the silver-containing product in solution after the precipitate dissolved, displaying any lone pair of electrons where appropriate.

[1]

In photography, after an image is developed, sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is used to dissolve any remaining silver halide away, to “fix” the image and ensure that it does not change upon further exposure to light.

- (iv)** An equal volume of sodium thiosulfate was added to the solution from **(ii)**. State the type of reaction that occurred when sodium thiosulfate was added.

.....[1]

- (v)** Suggest the identity of the silver-containing product which has a coordination number of 2.

.....[1]

- (b) The table below shows data about silver and two other metals, iron and copper.

	silver	iron	copper
electronic configuration	[Kr] 4d ¹⁰ 5s ¹	[Ar] 3d ⁶ 4s ²	[Ar] 3d ¹⁰ 4s ¹
conductivity at room temperature/ S m ⁻¹	6.3 × 10 ⁷	1.0 × 10 ⁷	?

- (i) Explain, in terms of structure and bonding, why the three metals have **high** electrical conductivity.

.....

[2]

- (ii) Silver and copper are known to be excellent metallic conductors at room temperature. Noting the electronic configuration, suggest the value of the conductivity of copper at room temperature.

..... S m⁻¹ [1]

- (iii) Iron is used as a catalyst in the synthesis of ammonia in the Haber process. State the type of catalysis and explain clearly how it carries out its function.

.....

[3]

- (c) When a jar is filled with gaseous hydrogen iodide, HI, and a red-hot glass rod inserted into the jar, violet fumes are observed.

- (i) State the identity of the violet fumes.

.....[1]

- (ii) When the same procedure is carried out with HBr instead of HI, no fumes are observed, but on strong heating, reddish-brown vapour is obtained.

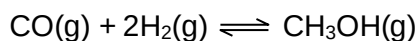
With reference to values in the *Data Booklet*, explain the difference in the behaviour of HBr and HI.

.....
.....
.....
.....
.....
.....
.....[2]

[Total: 15]

- 3** Methanol is one of the alternative fuels proposed to replace fossil fuels. It has the advantage of more efficient production and ease of storage as compared to other alternatives.

Methanol can be formed from carbon monoxide and hydrogen as shown below.



The reaction was investigated by mixing 3.2 mol of CO and 3.2 mol of H₂ in a 10.0 dm³ sealed vessel, and equilibrium was established at 120 °C under a pressure of 1.60 x 10⁶ Pa.

- (a) (i)** Assuming ideal gas behaviour, determine the total amount of gas in moles, at equilibrium.

[2]

- (ii)** Hence, calculate the amounts of CO, H₂ and CH₃OH in moles, present at equilibrium.

[3]

- (iii)** Write an expression for the equilibrium constant, K_c for the above reaction, and use your answers in **(a)(ii)** to calculate its value under the stated conditions.

[2]

- (b) Standard Gibbs free energy change, ΔG° is related to K_c by the following equation.

$$\Delta G^\circ = -RT \ln K_c$$

where ΔG° is in **joules per mole**, T is the temperature at which equilibrium is established and R is the molar gas constant.

- (i) Use this equation and your answer in (a) to calculate ΔG° for the formation of methanol from carbon monoxide and hydrogen at 120 °C.

[1]

- (ii) With reference to the *Data Booklet*, calculate the enthalpy change of formation of methanol from carbon monoxide and hydrogen. Use 1072 kJ mol⁻¹ for the bond energy of C≡O bond.

[2]

- (iii) Hence, state briefly why higher temperature is not used industrially for the formation of methanol from carbon monoxide and hydrogen.

.....

[2]

- (iv) Use your answers in (b)(i) and (ii) to calculate the standard entropy change for the reaction at 298 K.

[1]

- (v) Explain the significance of the sign of the calculated entropy change and comment if this is expected.

For
Examiner's
Use

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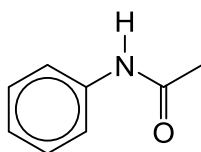
.....

.....[2]

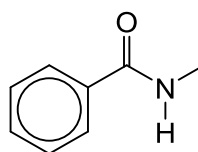
[Total:15]

- 4 (a) Acetanilide was the first aniline derivative found to possess analgesic and antipyretic properties. It was introduced into medical practice under the name of the drug, Antifebrin.

Suggest the reagents and conditions that can be used to distinguish acetanilide from compound X. State clearly the expected observations for each compound.



Acetanilide



Compound X

Reagents and conditions

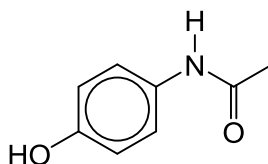
.....

Observations

.....

.....[2]

- (b) It was later discovered that acetanilide was toxic and thus paracetamol, a derivative of acetanilide, was produced.



Paracetamol

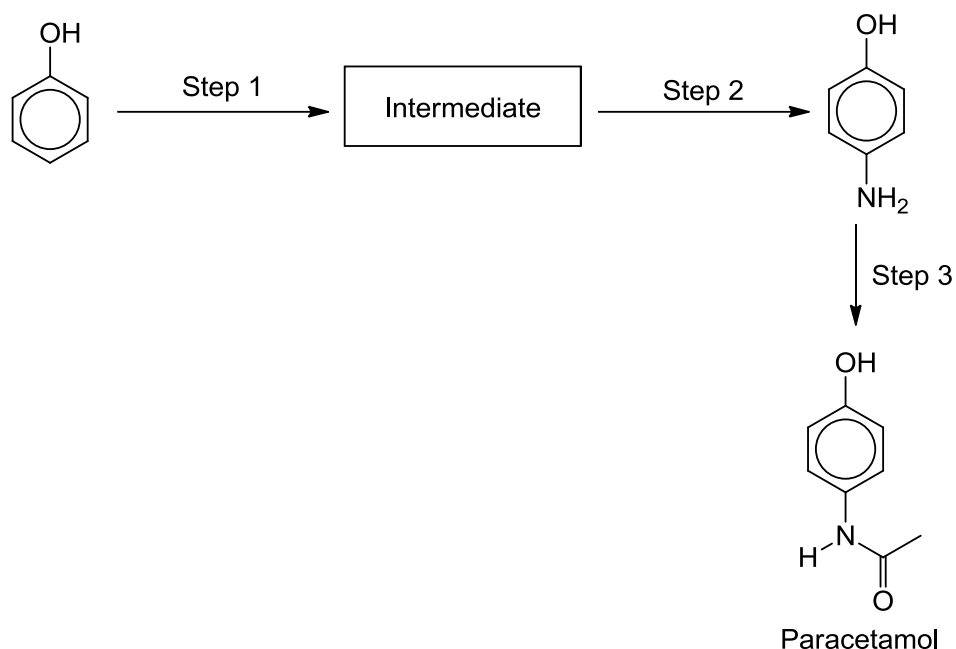
- (i) State the shape about N atom in paracetamol and hence identify the type of hybridisation involved.

Shape about N atom

Hybridisation of N

[2]

- (ii) A reaction scheme was proposed for the synthesis of paracetamol from phenol. Fill in the boxes provided with the reagents, conditions and intermediates for the synthesis.



Reagents and conditions:

Step 1

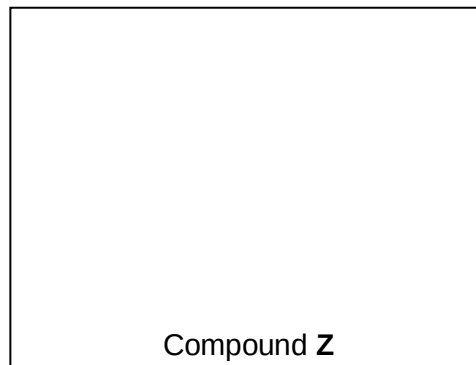
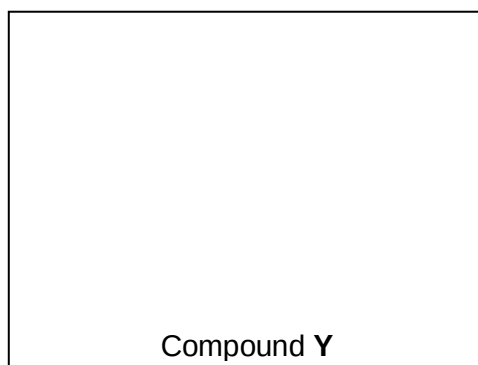
Step 2

Step 3

Structure of intermediate:

[4]

- (iii) In the synthesis of paracetamol from phenol, two possible side-products, compound **Y** and **Z**, are formed. Given that only compound **Y** is a position isomer of paracetamol, suggest the identities of compound **Y** and **Z**.



[2]

- (iv) Predict, with explanation, how the boiling point of paracetamol might compare to that of compound Y.

.....

[2]

- (c) In a typical pain relief tablet, there are 500 mg of paracetamol.

- (i) An adult can consume up to a maximum dosage of 4000 mg of paracetamol within 24 hours. The average adult weight is 62 kg. Calculate the number of tablets a child who weighs 45 kg, can consume within 24 hours. (Maximum dosage is dependent on weight of an individual.)

[2]

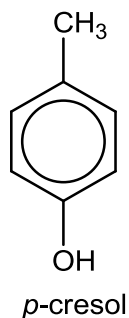
- (ii) It was recommended to consume the tablets at 6 hours intervals. Using your answer in (c)(i), calculate the recommended number of tablets the child should take at each interval without exceeding dosage.

[1]

[Total: 15]

- 5 The compound *p*-cresol is used in the production of antioxidants. It is also used in the fragrance and dye industries.

For
Examiner's
Use

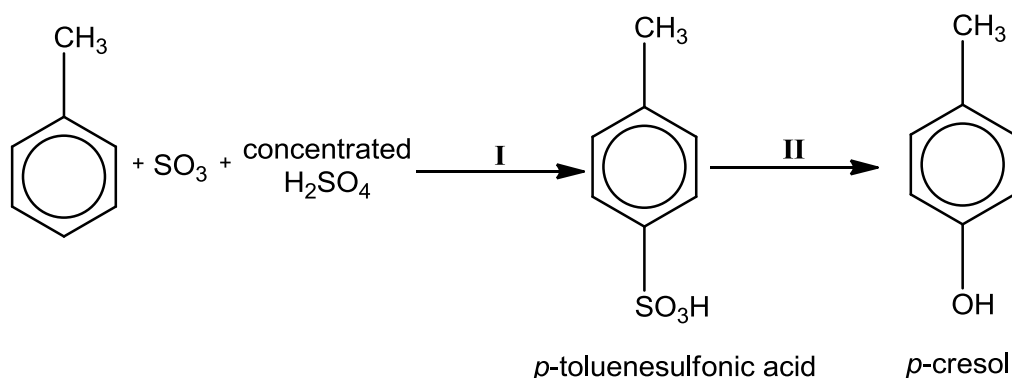


- (a) Draw the displayed formula of a functional group isomer of *p*-cresol, and describe a laboratory test that will distinguish these two compounds. You should state the reagents used and the observations expected.

.....

[3]

- (b) *p*-Cresol can be prepared industrially by a 2-step process as shown below.



Reaction I involves sulfonation of methyl benzene to give *p*-toluenesulfonic acid. The proposed mechanism of reaction I involves electrophilic substitution.

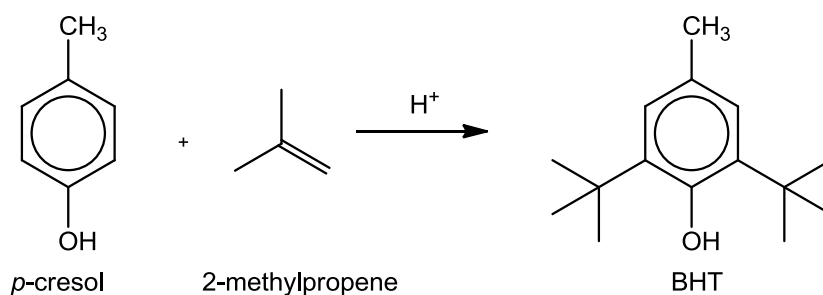
- (i) The first step of the proposed mechanism of reaction I involves acid-base reaction in the generation of an electrophile, HSO_3^+ . Write an equation to show how the electrophile HSO_3^+ is formed.

.....[1]

- (ii) Complete the proposed mechanism to produce *p*-toluenesulfonic acid as shown above. In the mechanism, show clearly the curly arrows to indicate the movement of electrons and all charges.

[3]

- (c) *p*-Cresol is used in the production of antioxidants such as butylated hydroxytoluene, BHT, which is mainly used as an antioxidant in the food industry. The reaction involves a dialkylation of *p*-cresol with 2-methylpropene in the presence of an acid catalyst given below.



- (i) Draw a labelled diagram to show how the orbitals overlap to form the C=C bond in 2-methylpropene and state the type of hybridisation involved.

[1]

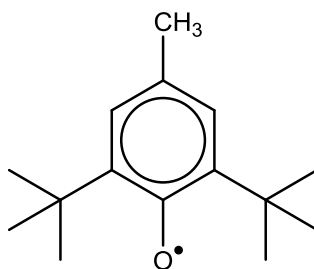
Type of hybridisation:[1]

- (ii) Explain why 2-methylpropene cannot exhibit geometric isomerism.

.....

.....[1]

- (iii) In order for BHT to act as an antioxidant, it forms a very stable radical on the oxygen atom as shown below. Suggest an explanation why this stable BHT radical is unable to react further with other molecules.



BHT radical

.....
[1]

- (iv) Compound **R**, $C_{14}H_{20}O_2$, is a metabolite derived from the biotransformation of BHT. It is structurally related to BHT, $C_{15}H_{24}O$, and is also a cyclic compound.

State the type of reaction and deduction for the following observations.

- I 1 mole of Compound **R** will react with 2 moles of 2, 4-DNPH.

Type of reaction:

Deduction:[1]

- II Compound **R** will not react with Tollens' reagent.

Deduction:[1]

- III 1 mole of compound **R** will decolourise 2 moles of aqueous Br_2 but no HBr is formed.

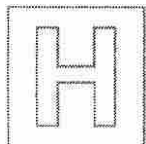
Type of reaction:

Deduction:[1]

- IV Deduce the structure of compound **R**.

[1]

[Total: 15]



CHEMISTRY

Paper 3 Free Response

9647/03

Friday 26 August 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This documents consists of **10** printed pages.

Answer any **four** questions.

1 Use of the Data Booklet is relevant to this question.

- (a) When potassium manganate(VII), KMnO_4 , is heated with concentrated sodium hydroxide, NaOH , bubbles of oxygen are seen and a green solution of MnO_4^{2-} is obtained. The addition of barium chloride, BaCl_2 , to this solution precipitated out a solid **X** with composition by mass of 53.5% barium, 21.5% manganese and 25.0% oxygen.

(i) Calculate the empirical formula of **X**. [1]

(ii) When the green solution above is acidified, a brown precipitate in a purple solution is formed.

Suggest the identities of the species formed upon acidification and hence state the type of reaction that has occurred. [3]

- (b) A solution of acidified potassium manganate(VII), KMnO_4 , can be standardised through titration against sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. The ethanedioate ion is oxidised to carbon dioxide in this reaction.

(i) State the oxidation numbers of C in the ethanedioate ion and in carbon dioxide. [1]

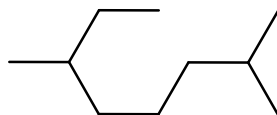
(ii) Write the half-equation for the oxidation of the ethanedioate ion. [1]

(iii) Hence, write the overall balanced equation for the reaction between acidified manganate(VII) and ethanedioate ions. [1]

(iv) In one such standardisation procedure, 25.0 cm^3 of $0.0150 \text{ mol dm}^{-3}$ $\text{Na}_2\text{C}_2\text{O}_4$ solution required 28.85 cm^3 of acidified KMnO_4 to reach the end-point.

Determine the concentration of KMnO_4 in the solution. You may assume that $2\text{MnO}_4^- \equiv 5\text{C}_2\text{O}_4^{2-}$. [3]

- (c) Myrcene, **A** and ocimene, **B**, are isomers with the molecular formula $\text{C}_{10}\text{H}_{16}$. When subjected to hydrogen with platinum catalyst, both isomers give 2,6-dimethyloctane, $\text{C}_{10}\text{H}_{22}$.



2,6-dimethyloctane

When treated with hot concentrated acidified KMnO_4 , **A** gives CO_2 and compound **C**, $\text{C}_7\text{H}_{10}\text{O}_4$; **B** gives CO_2 and compounds **D**, $\text{C}_5\text{H}_8\text{O}_3$, and **E**, $\text{C}_3\text{H}_4\text{O}_3$.

Compounds **C**, **D** and **E** give one mole of CHI_3 with alkaline aqueous iodine. On addition of aqueous NaHCO_3 , compounds **C**, **D** and **E** produce effervescence.

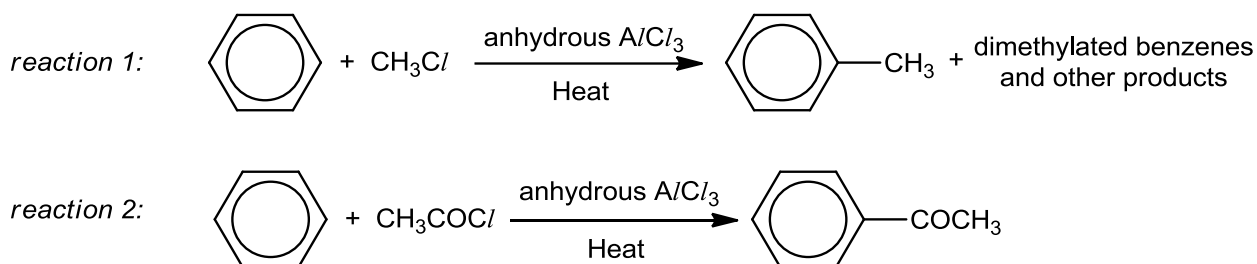
Suggest structures for **A-E**, and explain the observations described above. [10]

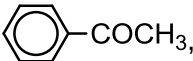
[Total: 20]

- 2 The table below lists the standard enthalpy change of formation of four compounds.

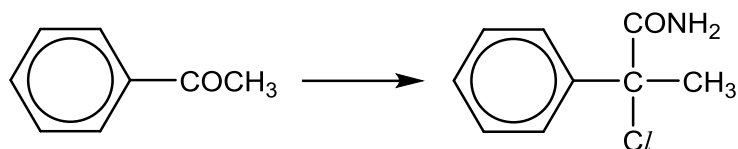
Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{H}_2\text{O}(\text{l})$	– 286
$\text{HCl}(\text{g})$	– 92.0
$\text{SiO}_2(\text{s})$	– 910
$\text{SiCl}_4(\text{l})$	– 640

- (a) What is meant by the term, standard enthalpy change of formation of a compound? [1]
- (b) $\text{SiCl}_4(\text{l})$ undergoes hydrolysis to give $\text{SiO}_2(\text{s})$.
- (i) Write the balanced equation with state symbols for the hydrolysis reaction. [1]
- (ii) Using the above data, calculate the standard enthalpy change for the hydrolysis reaction. State one assumption made in your calculation. [1]
- (iii) Does the hydrolysis have a positive, negative or zero entropy change? Explain your answer. [1]
- (iv) Hence, by the use of the Gibbs free energy, $\Delta G^\ominus$, explain why the hydrolysis of $\text{SiCl}_4(\text{l})$ is always a spontaneous process. [1]
- (c) Consider *reaction 1* and *reaction 2* shown below.



- (i) Both *reaction 1* and *reaction 2* proceed via a similar mechanism. Name the type of reaction undergone. [1]
- (ii) Suggest why *reaction 1* gives a mixture of organic products while *reaction 2* gives only one mono-substituted product. [2]
- (d) The organic product in *reaction 2*, phenylethanone, , reacts with HCN to produce the corresponding cyanohydrin under certain experimental conditions.
- (i) State the experimental conditions. [1]
- (ii) Describe the mechanism of reaction, of phenylethanone with HCN, showing clearly the curly arrows to indicate the movement of electrons and all charges. [3]

- (iii) Hence, suggest the reagents and conditions used in the following conversion, stating clearly the intermediate products in the process of synthesis. [2]



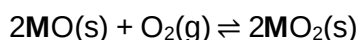
- (e) The rate of reaction between phenylethanone and iodine in acid medium to give 2-iodo-1-phenylethanone, , is found to be independent of $[I_2]$, but directly proportional to $[H^+]$ and directly proportional to [phenylethanone].

- (i) Write the rate equation for this reaction and state the overall order and the units of the rate constant. [2]
- (ii) The reaction between phenylethanone and bromine proceeds by a similar mechanism. How would you expect the rate of this reaction to compare with that of the above reaction? Explain your answer. [1]
- (iii) When a basic medium is used instead for the reaction between phenylethanone and iodine, a different mechanism of reaction is followed and different organic products are produced.
 - (I) State the type of reaction undergone. [1]
 - (II) Give the structures of all the organic products formed in this reaction. [2]

[Total: 20]

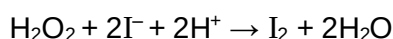
- 3 Fireworks are a traditional part of many celebrations. Their colours can come from heating of Group II metals and their salts. These salts often contain anions such as chlorates, perchlorates, and nitrates which are oxidising agents.

- (a) One of the Group II metals, **M**, when heated with oxygen under pressure, forms a metal peroxide which can be used as an oxidising agent in fireworks to produce a vivid green colour. The equation for the reaction is shown below:

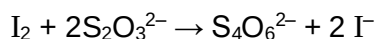


When equilibrium is attained, the mixture of oxides was found to have a mass of 1.60 g, where **MO**₂ has a percentage mass of 18.7%. When the mixture was treated with dilute sulfuric acid, a white solid was precipitated and a solution of hydrogen peroxide was produced.

An excess of acidified potassium iodide was added to the hydrogen peroxide solution. The reaction between hydrogen peroxide and acidified potassium iodide is as follows.



The iodine liberated needed 11.80 cm³ of 0.300 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃, for complete reaction.



- (i) Write a balanced equation to represent the reaction between **MO**₂ and sulfuric acid. [1]
- (ii) By determining the amount of **MO**₂ that has reacted, calculate the relative atomic mass of **M** and suggest its identity. [5]
- (b) Strontium nitrate, Sr(NO₃)₂ is an oxidising agent and is commonly used as a red colouring agent in fireworks.
- (i) Write a balanced equation for the reaction that occurs when Sr(NO₃)₂ undergoes thermal decomposition. [1]
- (ii) Predict whether the decomposition temperature of Sr(NO₃)₂ will be higher or lower than the decomposition temperature of Mg(NO₃)₂. Explain your answer. [3]
- (c) Another oxidising agent used in fireworks is potassium chlorate(V), KClO₃. When KClO₃ undergoes thermal decomposition, two products are obtained, one of which is KCl.
- (i) Write a balanced equation to show how KClO₃ is produced from Cl₂ gas and hot, aqueous potassium hydroxide. [1]
- (ii) Write a balanced equation for the thermal decomposition of KClO₃ and hence suggest why KClO₃ is an important ingredient used in fireworks. [2]

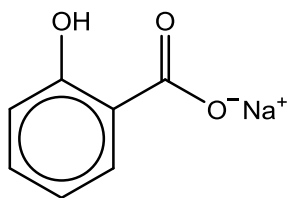
- (d) Fireworks which produce bright sparks, flashes and coloured flames also involve the elements phosphorus, sulfur and chlorine.

The table below gives the melting points of these elements.

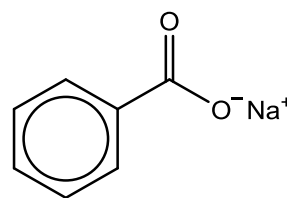
element	phosphorus	sulfur	chlorine
melting point / K	317	392	172

In terms of structure and bonding, explain why sulfur has the highest melting point among the three elements. [2]

- (e) Sodium salicylate and sodium benzoate are used as whistle mixes in fireworks. Both are white crystalline powder.

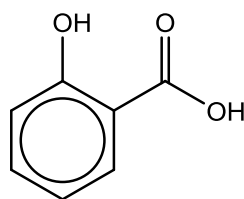


sodium salicylate



sodium benzoate

- (i) Suggest methods by which sodium salicylate and sodium benzoate can be distinguished from each other by a simple chemical test. State the reagents and conditions used and the expected observations for each compound. [2]
- (ii) The pK_a values of the two acidic groups in salicylic acid are $pK_{a1} = 2.98$ and $pK_{a2} = 13.6$.



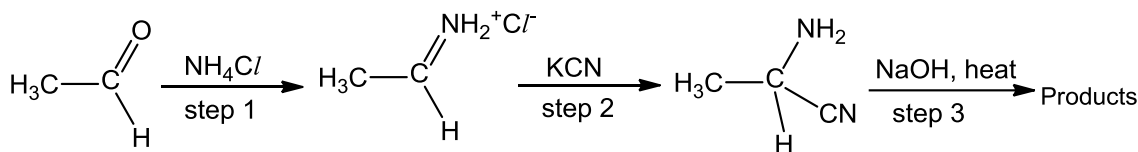
salicylic acid

Draw the displayed formula of the mono-anion produced after the dissociation of the carboxylic acid group and use your formula to explain why the dissociation of the phenol group is unlikely to occur. [3]

[Total: 20]

- 4 Strecker synthesis is a method used for the synthesis of amino acids. It is often studied due to the simplicity of the process.

(a) Alanine, an amino acid, can be formed using this method as shown below.



- (i) Construct a balanced equation for step 1 and suggest the type of reaction that has occurred. [2]
- (ii) Give the structural formulae for all the products formed in step 3. [2]
- (b) Insulin is a hormonal protein which was first discovered in 1921. In 1959, it became the first protein to have its primary structure determined. These led to the award of two Nobel Prizes, in Physiology/Medicine and Chemistry respectively.

The basic unit of insulin consists of two polypeptides, A-chain and B-chain. A-chain has 21 amino acid residues, and some of these are listed in the following table (You may use the abbreviations for your answers).

amino acid	abbreviation	formula of R group side chain at pH 7.4 (physiological pH)	number of amino acid residues in A-chain
cysteine	cys	$-\text{CH}_2\text{SH}$	4
glutamic acid	glu	$-\text{CH}_2\text{CH}_2\text{CO}_2^-$	2
glutamine	gln	$-\text{CH}_2\text{CH}_2\text{CONH}_2$	2
glycine	gly	$-\text{H}$	1
isoleucine	ile	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	2
threonine	thr	$-\text{CH}(\text{OH})\text{CH}_3$	1
valine	val	$-\text{CH}(\text{CH}_3)\text{CH}_3$	1

In order to determine the sequence of the A-chain, partial hydrolysis was carried out with two separate methods to obtain several polypeptide fragments. One method of hydrolysis involves the use of $6 \text{ mol dm}^{-3} \text{ HCl}$ or NaOH , while the other method causes hydrolysis at specific peptide bonds.

- (i) State what may be used in the method for the hydrolysis at specific peptide bonds. [1]
- (ii) One of the polypeptides was isolated and subjected for further hydrolysis giving the following smaller tri-peptide fragments.

cys-cys-thr, ile-val-glu, glu-gln-cys, gly-ile-val

Using the same abbreviations, write out the amino acid sequence of the **smallest** polypeptide that could produce the above fragments. [2]

- (iii) Describe the tertiary structure of insulin A-chain, include the type of bondings or interactions with reference to all the relevant amino acid residues listed in the above table. [4]
- (iv) In further confirmation of structures of insulin, chemicals can be used to affect the structures. Suggest one type of bond or interaction from your answer in (b)(iii) that can be broken by chemicals and state the chemicals that can be used. [2]
- (v) Zinc has an important role in the the production, storage and use of insulin. Zinc cation can bind to insulin through interactions with the amino acids. Suggest the type of interaction and state an amino acid that may be involved. [1]
- (c) Zinc compounds are often used in paints for various purposes. The properties of some of these compounds are given below.

compound	solubility product, K_{sp}	use in paints
$Zn(OH)_2$	3.00×10^{-17}	White pigment
ZnS	3.21×10^{-23}	Luminous pigment
$ZnCO_3$	1.46×10^{-10}	Fire Retardant

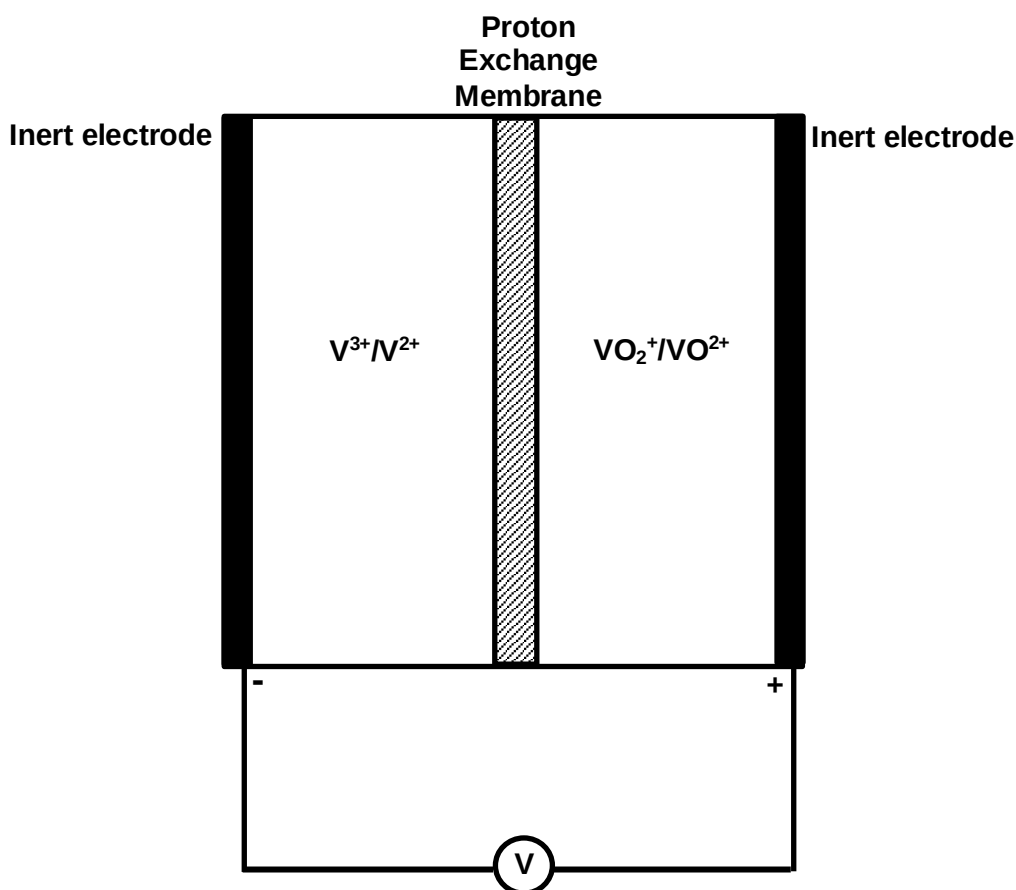
- (i) Write an expression for K_{sp} for $Zn(OH)_2$ and determine its solubility. Hence, calculate the pH of a saturated solution of $Zn(OH)_2$. [4]
- (ii) In preparation of a water-based luminous paint mixture, all 3 of the above compounds have to be precipitated. Given that concentration of Zn^{2+} is $2.00 \times 10^{-7} \text{ mol dm}^{-3}$, calculate the minimum amount of S^{2-} that must be present in 250 cm^3 of this mixture. [2]

[Total: 20]

5 Use of the Data Booklet is relevant to this question.

A redox flow battery is a type of rechargeable battery where rechargeability is provided by two chemical components dissolved in liquids contained within the system. The two half-cells are separated by a ion-exchange membrane instead of a salt bridge. A typical redox flow battery uses vanadium ions and inert electrodes.

- (a) Vanadium flow battery stores energy using vanadium redox couples. During the discharge cycle, V^{2+} loses an electron to the external circuit to form V^{3+} in the negative half-cell and acidified VO_2^+ accepts an electron from the external circuit to form VO^{2+} in the positive half-cell.



- (i) Write out the two half-equations for the electrode processes that occur at the two half-cells. [2]
- (ii) Calculate the e.m.f. of the cell. [1]
- (iii) Suggest why vanadium ions can be used in this redox flow battery. [1]
- (iv) Suggest the role of a proton exchange membrane. [1]

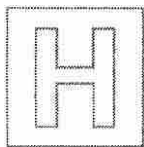
- (b) Calcium hydride is used in the synthesis of proton exchange membrane used in the vanadium flow battery. Data about calcium and vanadium are given below.

	Calcium	Vanadium
Electronic configuration	[Ar]4s ²	[Ar]3d ³ 4s ²
Relative atomic mass	40.1	50.9
Atomic radius/ nm	0.197	0.122
Density/ g cm ⁻³	1.54	6.07

- (i) Using relevant data from the table, suggest why the density of vanadium is significantly greater than that of calcium. [2]
- (ii) Explain why vanadium compounds are usually coloured whereas calcium compounds are usually colourless. [4]
- (c) Compounds of calcium contain the Ca²⁺ ion. The corresponding ion of vanadium is V²⁺.
- (i) Write an equation to show the third ionization energy for calcium. [1]
- (ii) Hence explain why Ca³⁺ compounds do not exist whilst V³⁺ compounds do. [2]
- (d) The following properties and reactions are exhibited by Compound **X**, C₇H₉ON.
- Compound **X** is insoluble in dilute NaOH, but dissolves in dilute HCl(aq).
 - On reaction with acidified potassium dichromate(VI) under certain condition, compound **X** forms compound **Y**, C₇H₇ON.
 - On reaction with ethanoyl chloride, CH₃COCl, **X** forms compound **Z**, C₁₁H₁₃NO₃.

Deduce the structures of compounds **X**, **Y** and **Z**. Explain the chemistry of the reactions described. Write an equation for the formation of compound **Z**. [6]

[Total: 20]



CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

Wednesday 31 August 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name and HT group on the Answer Sheet in the spaces provided.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

WORKED SOLUTIONS

This document consists of **30** printed pages.

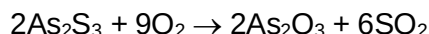
Section A

For each question there are **four** possible answers, **A**, **B**, **C** and **D**. Choose the one you consider to be **correct** and record your choice in soft pencil on the **separate Answer Sheet** provided.

- 1 Use of the Data Booklet is relevant to this question.

Arsenic(III) sulfide, As_2S_3 , is a bright yellow solid which has been used as a pigment in paintings.

When arsenic(III) sulfide is heated in air, it reacts with oxygen to give arsenic(III) oxide and sulfur(IV) oxide.



What would be the **mass** of arsenic(III) **oxide** produced if **550 dm³ oxygen**, measured at **room** temperature and pressure, reacted with arsenic(III) sulfide?

- A 1010 g B 1070 g C 2010 g D 2160 g

Answer: A

$$\text{Number of moles of O}_2 = \frac{550}{24} = 22.9 \text{ mol}$$

$$\text{Since } 9\text{O}_2 \equiv 2\text{As}_2\text{O}_3$$

$$\text{Number of moles of As}_2\text{O}_3 = \frac{22.9}{9} \times 2 = 5.09 \text{ mol}$$

$$M_r \text{ of As}_2\text{O}_3 = 74.9 \times 2 + 16.0 \times 3 = 197.8$$

$$\text{Mass of As}_2\text{O}_3 = 5.09 \times 197.8 = 1007 \text{ g}$$

- 2 Incomplete combustion of 20 cm³ of a gaseous hydrocarbon gave carbon dioxide and carbon monoxide in a 6:1 ratio, as well as water vapour. It was found that the carbon dioxide took up a volume of 51.4 cm³ whereas the water vapour took up a volume of 80 cm³. All gas volumes are measured at the same temperature and pressure.

What is the molecular formula of the hydrocarbon?

- A C₂H₄ B C₂H₆ C C₃H₆ D C₃H₈

Answer: D



Reduction of 80 cm³ after passing through dehydrating agent

$$\Rightarrow \text{volume of water vapour was } 80 \text{ cm}^3$$

Reduction of 51.4 cm³ after passing through KOH (aq)

$$\Rightarrow \text{volume of CO}_2 \text{ was } 51.4 \text{ cm}^3$$

$$\text{Mole ratio of C}_x\text{H}_y : \text{CO}_2 = 7 : 6x = 20 : 51.4$$

$$\frac{6x}{7} = \frac{51.4}{20}$$

$$x = 2.99 \approx 3$$

$$\text{Mole ratio of } C_xH_y : H_2O = 7 : \frac{7y}{2} = 20 : 80$$

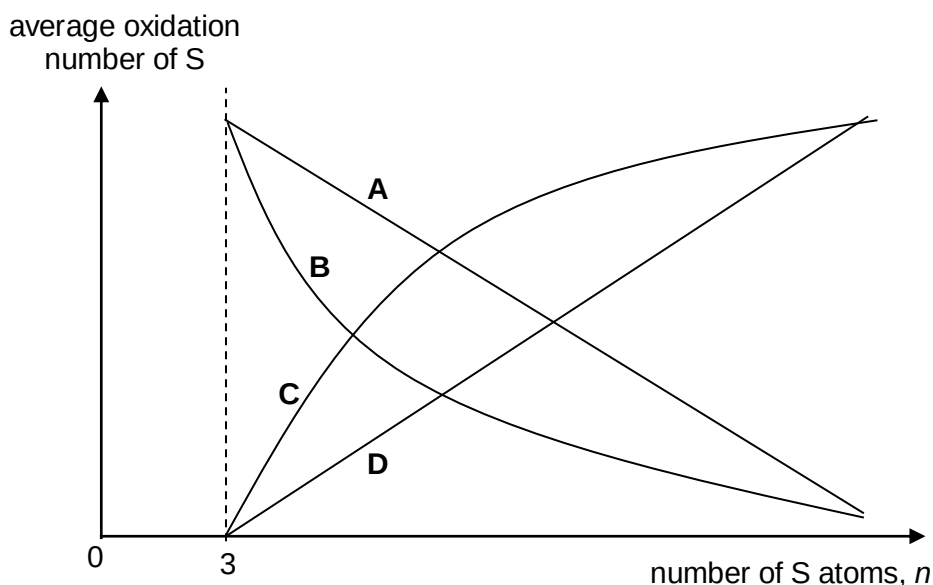
$$\frac{7y}{2} = 4$$

$$y = 8$$

Therefore, the molecular formula of the hydrocarbon is C_3H_8 .

- 3 Polythionates are a series of sulfur-oxo anions with the general formula $S_nO_6^{2-}$, where $n > 2$. A simple example is tetrathionate ion, $S_4O_6^{2-}$.

Which of the following graphs best illustrates the variation in the average oxidation number of sulfur in $S_nO_6^{2-}$ with n ?



Answer: B

Let the average oxidation number of S be y

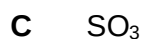
$$\text{For } S_nO_6^{2-}, \quad -2 = 6(-2) + ny$$

$$ny = +10$$

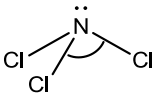
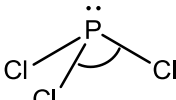
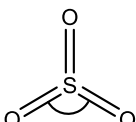
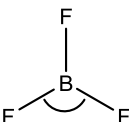
$$y = +\frac{10}{n}$$

Hence the graph is a hyperbolic graph starting from the point $(3, +10/3)$, which corresponds to graph **B**.

- 4 Which of the following species has the **smallest** bond angle around the central atom?



Answer: B

 3 bp, 1 lp 107°	 3 bp, 1 lp And P is less electronegative than N, so electron pairs less attracted to P, hence smallest bond angle, <107°	 3 bp, 0 lp 120°	 3 bp, 0 lp 120°

- 5 Which of the following shows the correct bonds present in solid CHI_3 ?
- A Covalent bonds only
 - B Ionic bonds only
 - C Covalent bonds & temporary dipole-induced dipole forces of attraction
 - D Covalent bonds & permanent dipole-permanent dipole forces of attraction

Answer: D

CHI_3 (triiodomethane) is a simple covalent molecule which is polar, hence it contains covalent bonds between atoms and permanent dipole-permanent dipole forces of attraction between molecules.

- 6 Polymerisation is a process in which large number of small molecules (monomers) are joined together to form long-chain molecules.

Considering that polymerisation is a spontaneous reaction, what are the correct signs of ΔS and ΔH for the process?

	ΔS	ΔH
A	–	–
B	–	+
C	+	–
D	+	+

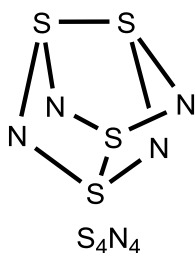
Answer: A

ΔG = negative because it is a spontaneous reaction

ΔS = negative because the degree of disorderness decreases as polymerisation form orderly long-chain molecules.

Since $\Delta G = \Delta H - T\Delta S$, with ΔG = negative and $(-T\Delta S)$ = positive, ΔH has to be negative

- 7 S_4N_4 is a thermochromic solid which changes colour with temperature. S_4N_4 has a cage structure as shown in the diagram.



Given the following data, what is the average bond energy of dissociation of S-N, in kJ mol^{-1} ?

$$\Delta H_f^\circ (S_4N_4) = +460 \text{ kJ mol}^{-1}$$

$$\Delta H_{at}^\circ (\text{sulfur}) = +279 \text{ kJ mol}^{-1}$$

$$\Delta H_{at}^\circ (\text{nitrogen}) = +497 \text{ kJ mol}^{-1}$$

$$(\text{S-S}) \text{ bond energy of dissociation in } S_4N_4 = +204 \text{ kJ mol}^{-1}$$

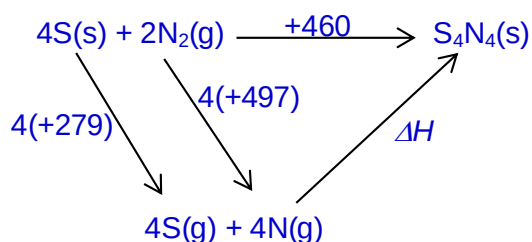
A +150

B +280

C +395

D +559

Answer: B



$$\Delta H = -[4(+279) + 4(+497)] + 460 = -2644 \text{ kJ mol}^{-1}$$

$$\text{Total Bond Energy} = 2644 \text{ kJ mol}^{-1} = 8 \text{ BE (S-N)} + 2 \text{ BE (S-S)}$$

$$8 \text{ BE (S-N)} = 2644 - (2)(+204)$$

$$\text{BE (S-N)} = +279.5 = 280 \text{ kJ mol}^{-1}$$

- 8 At 25°C , a dented ping pong ball has an internal volume of 31.0 cm^3 and internal pressure of 110 kPa . It is then placed in a water bath maintained at 60°C , which returned the ball to its original spherical shape with internal volume of 33.5 cm^3 .

Assuming ideal gas behaviour, what is the pressure of air inside the ball at 60°C in its original spherical shape?

A 101 kPa

B 114 kPa

C 122 kPa

D 244 kPa

Answer: B

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

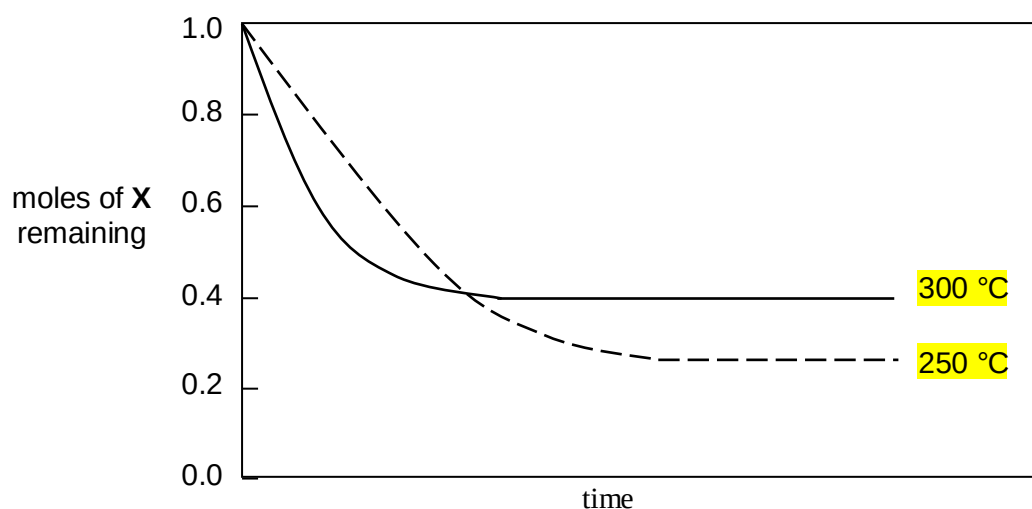
$$\frac{(110)(31.0)}{(298)} = \frac{P_2(33.5)}{(333)}$$

$$p_2 = 113.7 \text{ kPa}$$

- 9 Gas X decomposes to two other gases, Y and Z, according to the following equation:



The graph below shows the decomposition of 1.0 mol of pure gas X in the presence of a catalyst at various temperatures.



Which one of the following statements about the above system is **correct**?

- A The decomposition of X is endothermic.
- B The K_p of the system decreases with increasing temperature.
- C The percentage decomposition of X is 40 % at 300 °C.
- D The system becomes less disordered when it reaches equilibrium state.

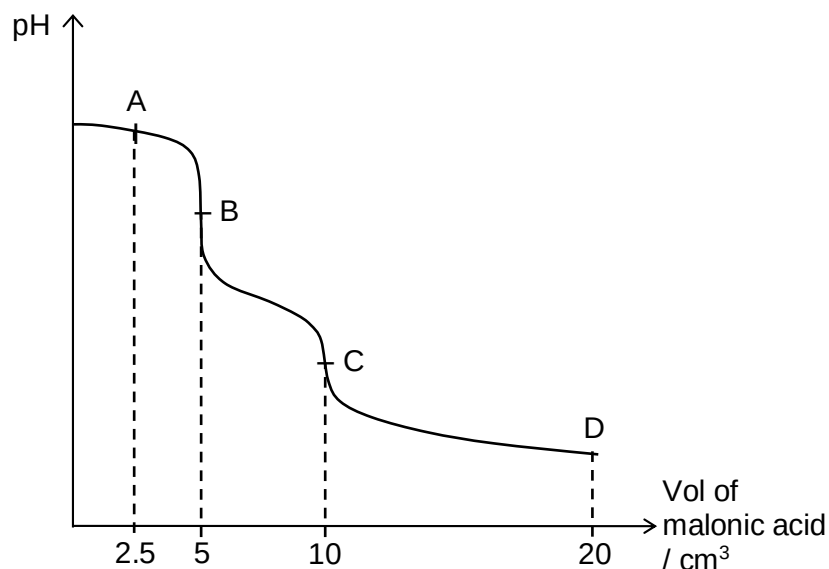
Answer: B

- A – As T increased, amount of X remaining at equilibrium increased. This shows that position of equilibrium shifts left, hence backward reaction is endothermic. Forward reaction is thus exothermic. $\Rightarrow$ incorrect
- B – Position of equilibrium shifts left with increasing T to favour endothermic reaction (since forward reaction is exothermic). Thus K_p will decrease with increasing T. $\Rightarrow$ correct
- C – At 300 °C, amount of X remaining is 0.4 mol. Hence, percentage decomposition of X is 60 % instead of 40%. $\Rightarrow$ incorrect
- D – There is an increase in the number of moles of gaseous particles resulting in an increase in degree of randomness. $\Rightarrow$ incorrect

- 10 Malonic acid, $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$, is a weak dibasic acid.

Malonic acid is titrated against 20.0 cm^3 of sodium hydroxide of the same concentration, the following pH-volume curve is obtained.

At which point on the titration curve is the mixture most able to resist pH change upon addition of a small amount of aqueous acid or base?



Answer: D

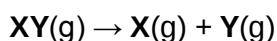
A – NaOH will be present in excess. No buffer present.

B – NaOH still present in excess.

C – First equivalence point. $\text{HO}_2\text{CHCHCO}_2^-$ and water present.

D – Maximum buffering capacity where $\text{HO}_2\text{CHCHCO}_2^-$ (weak acid) and $^- \text{O}_2\text{CHCHCO}_2^-$ (salt) are present

- 11 The following is the reaction for compound **XY**,



If the rate constant for the reaction is $5.78 \times 10^{-3} \text{ s}^{-1}$, what is the time taken for the concentration of a sample of **XY** to decrease from 1.80 mol dm^{-3} to $0.225 \text{ mol dm}^{-3}$?

A 120 s

B 240 s

C 360 s

D 480 s

Answer: C

$$t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{\ln 2}{(5.78 \times 10^{-3})}$$

$$t_{1/2} = 119.9 \text{ s}$$

$$1.80 \rightarrow 0.90 \rightarrow 0.45 \rightarrow 0.225$$

$$3 \times 119.9 = 360 \text{ s}$$

- 12 The reaction between **C** and **D** is as follows:



In an experiment to investigate the effect of concentrations on the rate of reaction, the following results were obtained at constant temperature.

Experiment	[C] / mol dm ⁻³	[D] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	1.0	1.0	0.0008
2	1.0	2.0	0.0016
3	1.0	3.0	x
4	2.0	2.0	0.0032

What is the value of x?

- A** 0.0008 **B** 0.0016 **C** 0.0024 **D** 0.0032

Answer: C

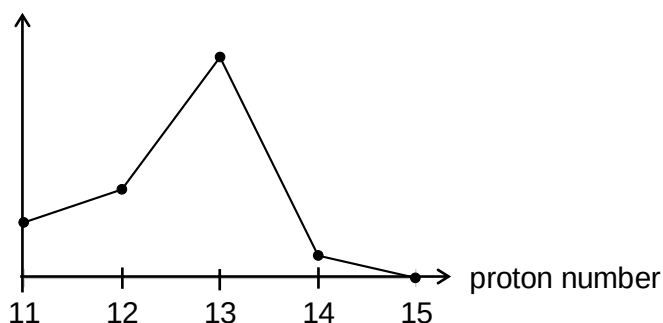
Comparing experiments 1 and 2, when [D] is doubled, rate doubles. Order of reaction wrt **D** is 1

Comparing experiments 2 and 4, when [C] is doubled, rate doubles. Order of reaction wrt **C** is 1.

Rate = $k[\text{C}][\text{D}]$

Comparing experiments 1 and 3, when [D] triples, rate should triple. Hence, value of **x** is $0.008 \times 3 = 0.0024 \text{ mol dm}^{-3} \text{ s}^{-1}$

- 13 The following graph shows how a property of the elements in Period 3, from Na to P, or their compounds, varies with proton number.



What property is shown by the graph?

- A** Melting point of element
B Melting point of oxide
C pH of aqueous chloride
D Conductivity of element

Answer: D

Electrical conductivity increases from Na to Al due to the increase in number of mobile delocalised electrons. Electrical conductivity then decrease to Si as Si is a semi-conductor and has poor conductivity under normal conditions. P does not conduct electricity as it neither have delocalised electrons nor mobile charge carriers.

14 Which of the following statements about calcium, strontium and barium is correct?

- A** The magnitude of the hydration energy of the M^{2+} ion increases from calcium to barium
- B** The energy required for the process $M(g) \rightarrow M^{2+}(g) + 2e^{-}$ increases from calcium to barium.
- C** The reducing power decreases from calcium to barium.
- D** The reactivity of the elements with water increases from calcium to barium.

Answer: D

- A** – hydration energy $\propto \frac{\text{charge}}{\text{size}}$. Since size increases down the group, magnitude of hydration energy decreases.
- B** – IE decreases down the group as valence electrons are less strongly attracted to the metal nucleus.
- C** – Reducing power (or ease of being oxidised, ie. loss of electrons to form M^{2+}) increases down the group.
- D** – Reactivity does increase down the group, due to increased reducing power down the group.

15 When **1.0 g** of each of the following **Group II metals** is added to **cold water** and any gas produced is collected at 25 °C and 1 atm, which sample will most likely produce the **largest volume of gas**?

- A** Mg **B** Ca **C** Sr **D** Ba

Answer: B

Group II metals react with cold water to form their hydroxides and hydrogen gas:



- A** – No. of mol of Mg = $\frac{1.0}{24.3} = 0.0412$ mol, but there will be almost no reaction in cold water due to insoluble $Mg(OH)_2$ layer preventing further reaction.
- B** – No. of mol of Ca = $\frac{1.0}{40.1} = 0.0250$ mol, and although $Ca(OH)_2$ is only partially soluble, the reaction should go to completion. Largest amount (in moles) of gas produced, hence largest volume.
- C** – No. of mol of Sr = $\frac{1.0}{87.6} = 0.0114$ mol (< 0.0250)
- D** – No. of mol of Ba = $\frac{1.0}{137} = 0.00730$ mol (< 0.0250)

16 Which statement about the trends in the properties of the halogens is correct?

- A The volatility of halogens increases down the group.
- B The electronegativity of halogens increases down the group.
- C The reactivity of halogens with hydrogen decreases down the group.
- D The bond dissociation energy of halogens increases down the group.

Answer: C

- A – Boiling point increases down the group (gas to solid), hence volatility decreases down the group.
- B – Electronegativity decreases down the group as atomic radius increases.
- C – Reactivity decreases down the group as strength of H-X bond decreases.
- D – Bond dissociation energy decreases down the group, as size of atoms increase, reducing effectiveness of orbital overlap.

- 17 “Bromine tablets” are used as disinfectants. It is a source of $\text{HClO}(\text{aq})$ and $\text{HBrO}(\text{aq})$, both of which are **oxidising agents**.

HBrO destroys bacteria, fungi and algae via its oxidising property in the process. HClO is a **stronger** oxidising agent than HBrO and helps to **sustain the effectiveness** of the bromine tablets.

What is the likely role of HClO in relation to HBrO ?

- A Oxidises Br^- to BrO^-
- B Oxidises Br^- to Br_2
- C Reduces BrO^- to Br^-
- D Reduces BrO^- to Br_2

Answer: A

Oxidation state of Br in HBrO is +1. When HBrO destroys bacteria through its oxidising property, it gets reduced to Br^- . However, since HClO is a stronger oxidising agent than HBrO , hence it will oxidise Br^- to BrO^- . This helps to sustain the effectiveness of the bromine tablets by regenerating BrO^- .



$$E^\ominus_1 > E^\ominus_2$$

- 18 When drops of aqueous ammonia are added to a solution of CuSO_4 , a pale blue precipitate is formed. This precipitate dissolved when excess aqueous ammonia is added, forming a deep blue solution. On addition of dilute hydrochloric acid, the pale blue precipitate is reformed.

Which process does **not** occur in the above?

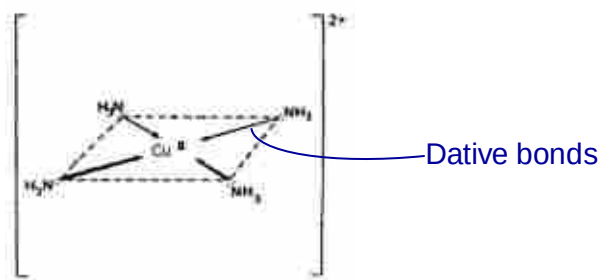
- A Dative bond formation
- B Formation of a complex ion
- C Precipitation of copper(II) hydroxide
- D Reduction of copper(II) ions

Answer: D

When a few drops of aqueous ammonia are added to solution of CuSO_4 , the following reaction occurs and a pale blue ppt, $\text{Cu}(\text{OH})_2$ is formed.



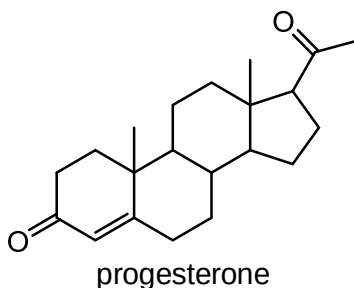
Upon addition of excess ammonia, the pale blue ppt dissolves. A complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is formed.



When **dilute** hydrochloric acid is added, it reacts with the ammonia ligands and causes equilibrium position (1) to shift to the left, forming back $\text{Cu}(\text{OH})_2$, seen as the blue ppt.

Reduction of copper (II) ions does not occur.

- 19 Progesterone is an endogenous steroid involved in the menstrual cycle and pregnancy, of humans. It has the structure shown below.



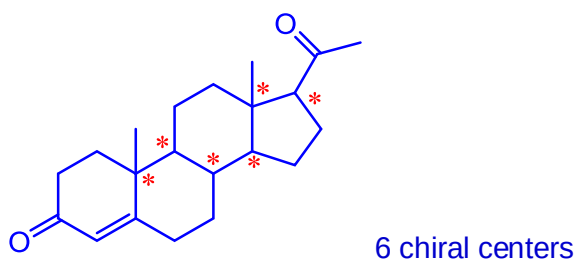
How many **chiral centers** does progesterone contain?

A 2

B 4

C 6

D 8

Answer: C

20 Use of the Data Booklet is relevant to this question.

An organic compound **A** is commonly used in skin-care products. It has the following features.

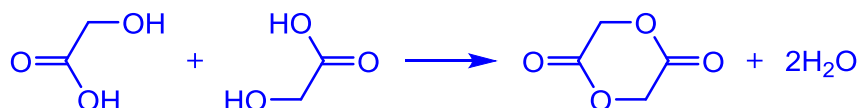
- It is a monobasic acid.
- One mole of compound **A** reacts with Na to give 1 mole of H_2 gas.
- It dimerises in the presence of hot concentrated H_2SO_4 to give an organic compound of relative molecular mass 116.

How many carbon atoms are in one molecule of this organic compound **A**?

- A** 1 **B** 2 **C** 3 **D** 4

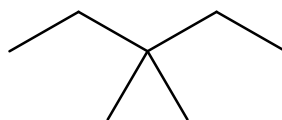
Answer: B

- It is monobasic. $\Rightarrow$ 1 $-\text{CO}_2\text{H}$ functional group present
- Since $\text{ROH} + \text{Na} \rightarrow \frac{1}{2} \text{H}_2 + \text{RO}^-\text{Na}^+$ and 1 mol of **A** gives 1 mole of H_2 gas.
 $\Rightarrow$ 2 $-\text{OH}$ functional groups present
- It dimerises in the presence of hot concentrated H_2SO_4 to give a compound of relative molecular mass 116. $\Rightarrow$ the acid has $-\text{CO}_2\text{H}$ group and $-\text{OH}$ group. In the presence of H_2SO_4 , esterification will occur. A cyclic product is formed.



Given the M_r , there are 4 carbons in the product, since product is formed from the dimerisation of compound **A**, thus compound **A** has 2 carbons.

21 3,3-dimethylpentane, C_7H_{16} , reacts with bromine to form monobromo compounds with molecular formula of $\text{C}_7\text{H}_{15}\text{Br}$.



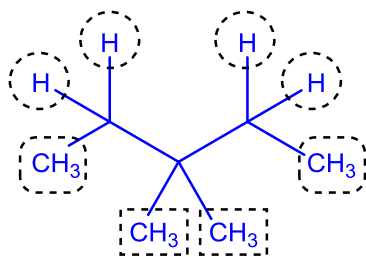
3,3-dimethylpentane

How many possible structural isomers, each with molecular formula $\text{C}_7\text{H}_{15}\text{Br}$, could be produced by 3,3-dimethylpentane?

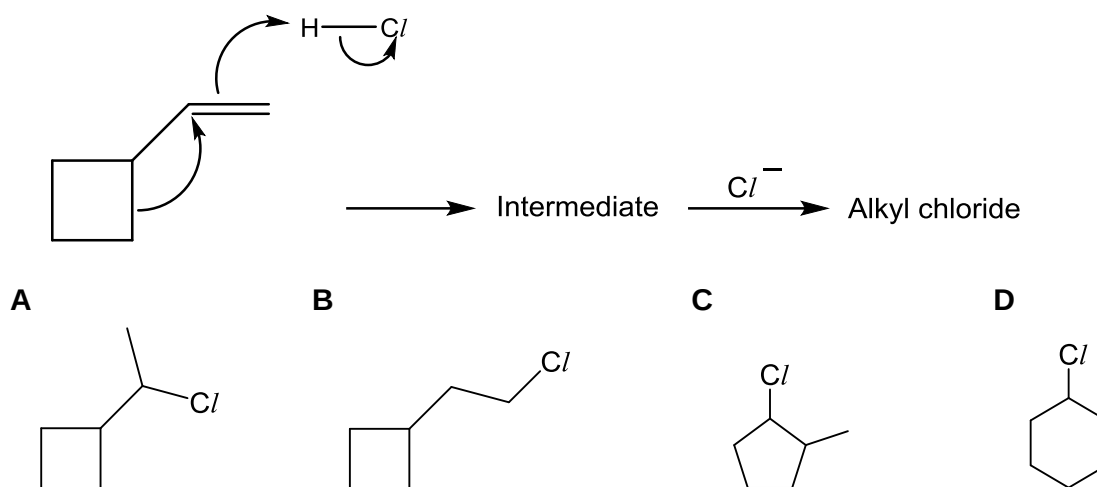
- A** 3 **B** 4 **C** 6 **D** 7

Answer: A

3,3-dimethylpentane undergoes free radical substitution in the presence of sunlight. There are 3 different sets of chemically equivalent hydrogen atoms that can be substituted to give 3 different monobromo products. Note that the molecule is symmetrical.

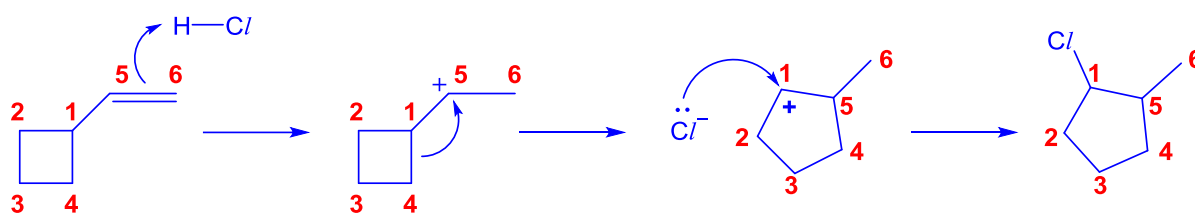


- 22 Vinylcyclobutane can react with HCl to give a rearranged alkyl chloride. With the aid of the flow of electrons represented by the curved arrows, what is the alkyl chloride product obtained?



Answer: C

The diagram below shows the breakdown of the flow of electrons. However, the first 2 steps should be concerted.



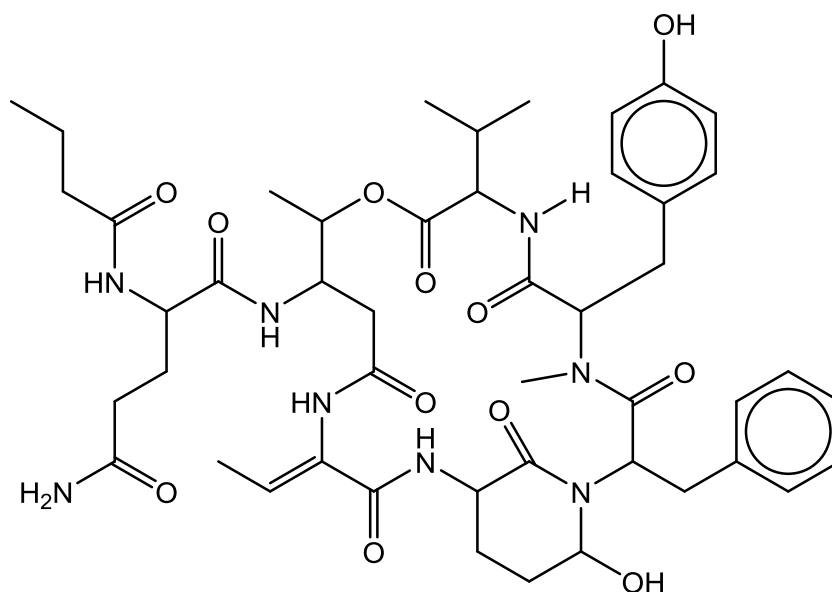
The alkene functional group will undergo electrophilic addition with HCl .

By following the arrow which represents the flow of electrons:

- the bond between C1 and C4 is broken
- a new bond is formed between C4 and C5
- C1 will be positively charged.
- A 5 membered-ring is formed.

Thus, the Cl^- will attack the carbocation on C1.

- 23 Yanucamide B can be extracted from a marine sponge and has the structure shown below.



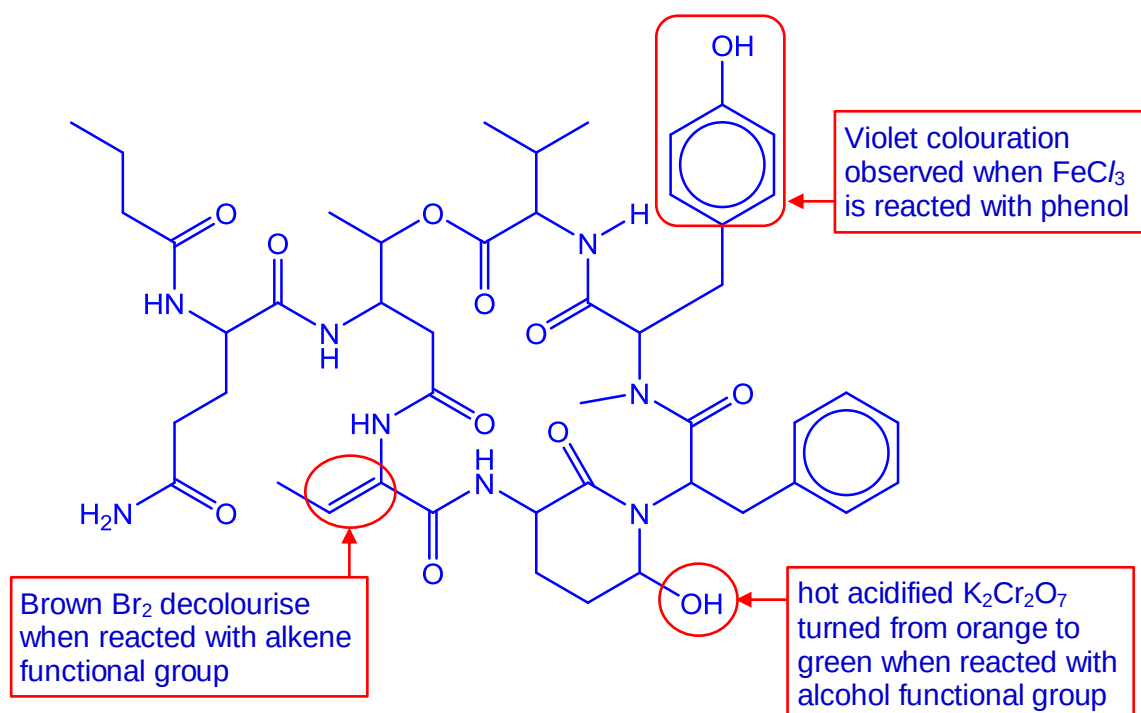
Yanucamide B

Which of the following set of reagents and conditions will not result in a colour change?

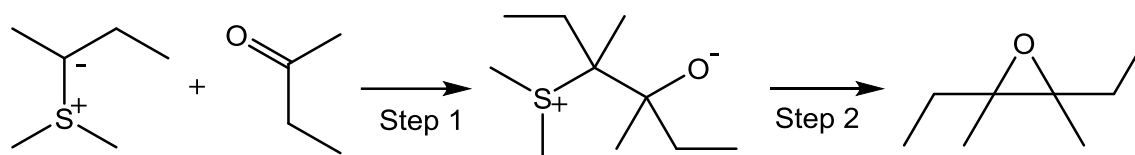
- A Br_2 in CCl_4
- B neutral $\text{FeCl}_3(\text{aq})$
- C LiAlH_4 in dry ether
- D hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$

Answer: C

LiAlH_4 react with Yanucamide B by reducing the amide and ester functional groups, however there is no colour change.

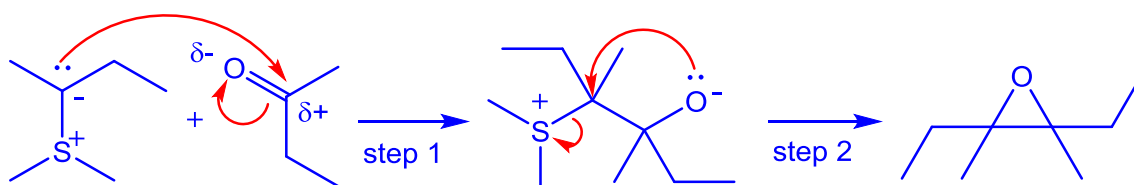


24 In the following sequence of reactions, what is the mechanism of step 1?

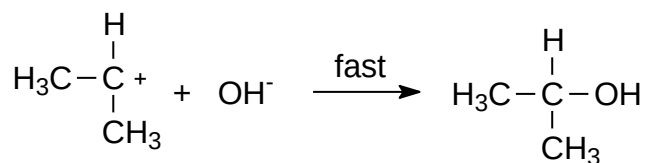
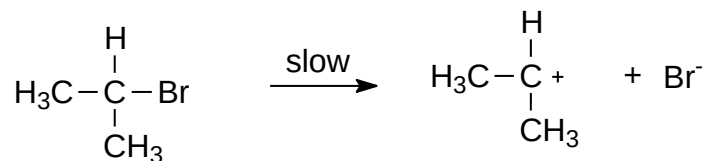


- A Nucleophilic Addition
- B Nucleophilic Substitution
- C Electrophilic Addition
- D Electrophilic Substitution

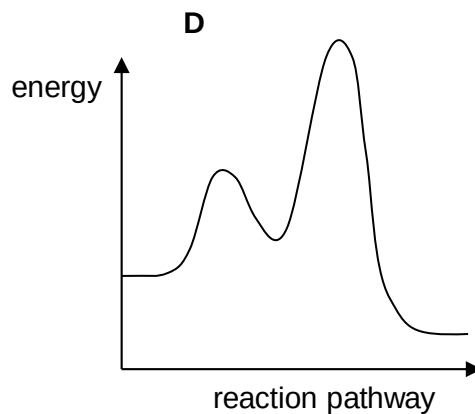
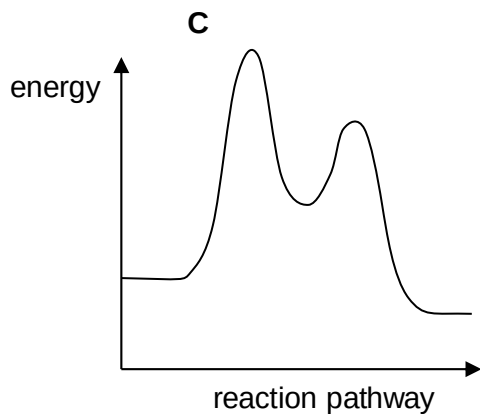
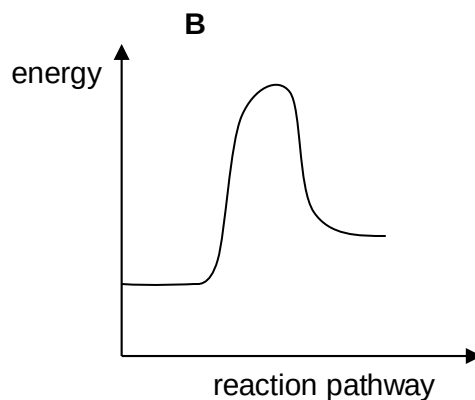
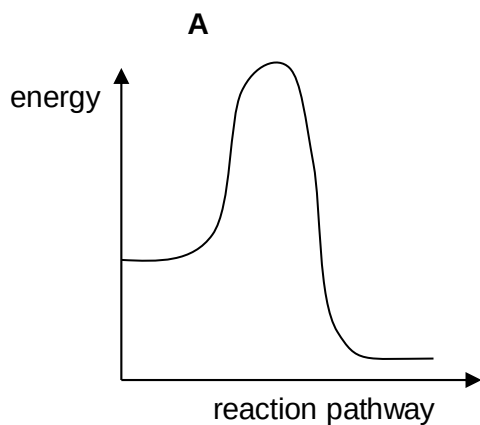
Answer: A



- 25 2-bromopropane undergoes nucleophilic substitution with aqueous NaOH via the following mechanism.

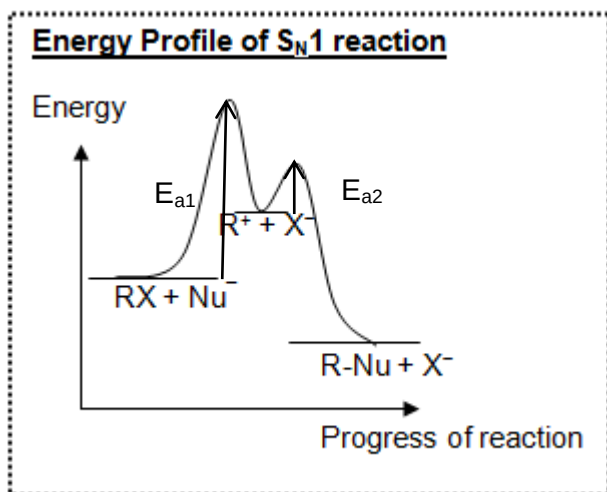


Which of the reaction pathway diagram fits the above mechanism?



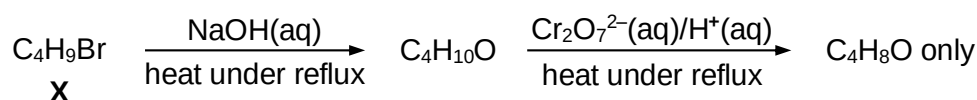
Answer: C

Since this is a 2-step reaction mechanism and a carbocation intermediate is formed, reaction proceeds via an $\text{S}_{\text{N}}1$ mechanism, where the slow step of the mechanism is unimolecular. The energy profile of a $\text{S}_{\text{N}}1$ reaction is as shown below.



Step 1 is the slow, rate-determining step, thus it would have the largest activation energy. $E_{a1} > E_{a2}$. Thus, option C is the answer.

- 26 Compound X, C₄H₉Br, undergoes the following reactions:

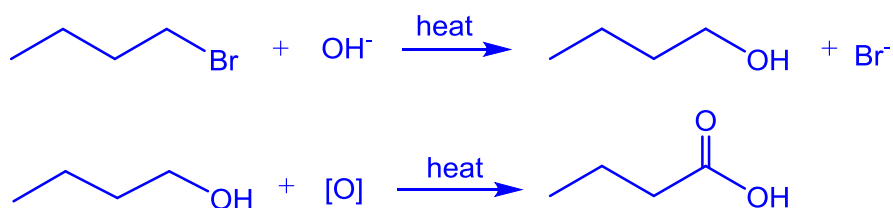


What is X likely to be?

- A 1-bromobutane
- B 2-bromobutane
- C 1-bromo-2-methylpropane
- D 2-bromo-2-methylpropane

Answer: B

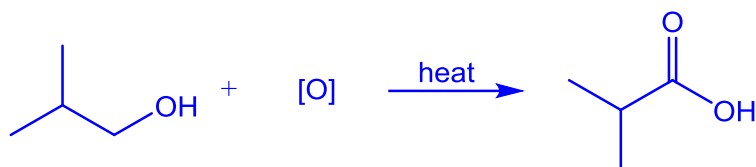
A – incorrect as reaction of 1-bromobutane (primary RX) will produce primary alcohol of substitution and in turn, result in carboxylic acid as the final product, having molecular formula, C₄H₈O₂.



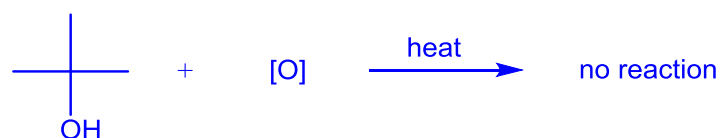
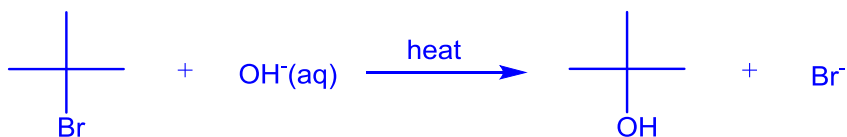
B – correct as substitution of 2-bromobutane (secondary RX) gives butan-2-ol (secondary alcohol) which in turn undergoes oxidation to yield butanone with molecular formula C₄H₈O.



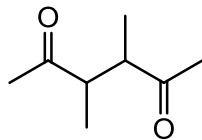
C – incorrect as reaction of 1-bromo-2-methylpropane (primary RX) will produce primary alcohol of substitution and in turn, result in carboxylic acid of molecular formula of $\text{C}_4\text{H}_8\text{O}_2$.



D – incorrect as 2-bromo-2-methylpropane (tertiary RX) undergoes substitution to give a tertiary alcohol. Tertiary alcohols do not undergo oxidation reactions. Molecular formula of tert-butanol is $\text{C}_4\text{H}_{10}\text{O}$.



- 27** Compound **X** shown below is an intermediate used to generate pyrroles which are essential to the production of many different chemicals in the pharmaceutical industry.



Compound **X**

Which sentence is correct for compound **X**?

- A** It gives a silver mirror with Tollens' reagent.
- B** It decolourises acidified potassium manganate(VII).
- C** It does not give an orange precipitate with 2,4-dinitrophenylhydrazine.
- D** It gives yellow precipitate with alkaline aqueous iodine.

Answer: D

Compound **X** is a diketone.

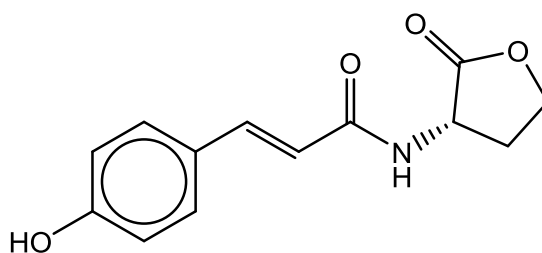
Option A is incorrect since there is no aldehyde functional group in compound X and thus cannot give a silver mirror with Tollens' reagent.

Option B is incorrect since ketone cannot undergo further oxidation.

Option C is incorrect as ketone can undergo condensation with 2,4-DNPH to give an orange precipitate.

Option D is correct since it has $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$ group and thus able to give a yellow precipitate with alkaline aqueous iodine.

- 28** 4-coumaroyl-HSL is a new type of bacterial, quorum sensing signal compound. When one mole of 4-coumaroyl-HSL is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?



4-coumaroyl-HSL

A 1

B 2

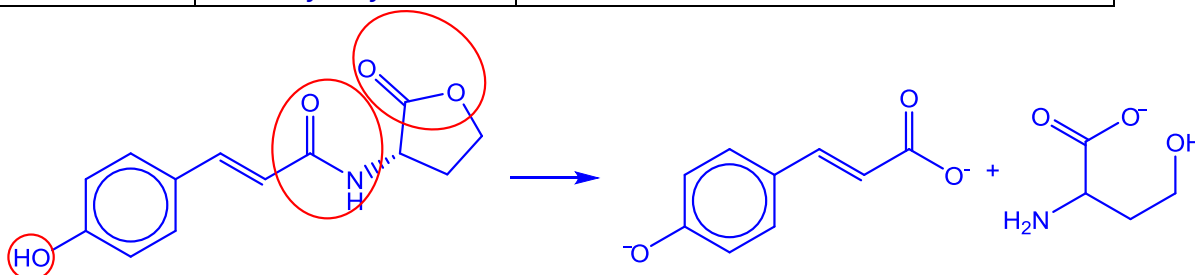
C 3

D 4

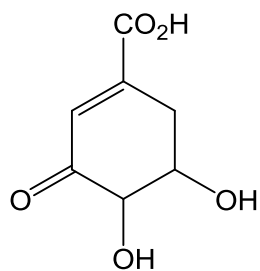
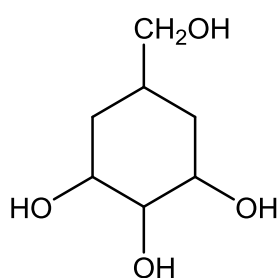
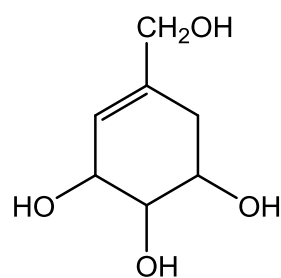
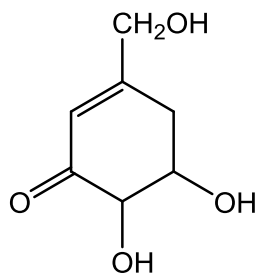
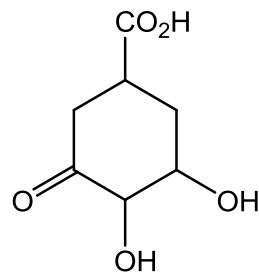
Answer: C

Phenol, amide and ester can undergo reaction with NaOH. Alcohol is neutral and will not undergo reaction with NaOH.

Functional group	Type of reaction	Equation
Phenol	Acid-base reaction	$\text{RC}_6\text{H}_4\text{OH} + \text{NaOH} \rightarrow \text{RC}_6\text{H}_4\text{O}^- + \text{H}_2\text{O}$
Amide	Basic hydrolysis	$\text{RCONHR}' + \text{OH}^- \rightarrow \text{RCOO}^- + \text{R}'\text{NH}_2$
Ester	Basic hydrolysis	$\text{RCOOR}' + \text{OH}^- \rightarrow \text{RCOO}^- + \text{R}'\text{OH}$

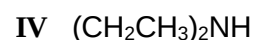
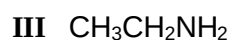
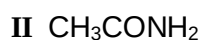
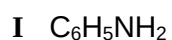


- 29 Shikimic acid is found in star anise. The following compound **Y**, is the intermediate that can be used to form shikimic acid. When LiAlH_4 is added to compound **Y**, what is the product obtained?

Compound **Y****A****B****C****D****Answer: B**

LiAlH_4 is a reducing agent that can reduce carboxylic acid and ketone to primary and secondary alcohols respectively. However, it cannot reduce alkene.

30 Consider the following compounds below:



Which of the following shows the correct order of decreasing $\text{p}K_{\text{b}}$ values for the above compounds?

A II, III, I, IV

B II, I, III, IV

C III, IV, I, II

D IV, III, I, II

Answer: B

The stronger the base, the lower the $\text{p}K_{\text{b}}$ value. Basicity depends on the availability of lone pair of electrons on N atom to attract a proton.

II is an amide which is neutral so it would have the highest $\text{p}K_{\text{b}}$ value.

I is the weakest base as the lone pair of electrons on N is delocalised into the benzene ring thus making the lone pair of electrons on N atom less available to attract a proton.

III is a stronger base than **I** due to the presence of an electron-donating ethyl group that increases the availability of lone pair of electrons on N atom to attract a proton.

IV is the most basic as it has 2 electron-donating ethyl groups which increase the availability of lone pair of electrons on N atom to attract a proton to a larger extent.

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1 , 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Use of the Data Booklet is relevant to this question.

Which of the following species has the electronic configuration of $[\text{Ar}] 3d^5 4s^1$?

- 1** Cr
- 2** Mn^+
- 3** Fe^{2+}

Answer: B (1 and 2 only)

1 – Cr: $[\text{Ar}] 3d^5 4s^1 \Rightarrow$ correct

2 – Mn: $[\text{Ar}] 3d^5 4s^2$

Thus Mn^+ : $[\text{Ar}] 3d^5 4s^1 \Rightarrow$ correct

3 – Fe: $[\text{Ar}] 3d^6 4s^2$

Thus Fe^{2+} : $[\text{Ar}] 3d^6 \Rightarrow$ incorrect

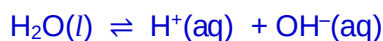
32 The value of the ionic product of water, K_w , varies with temperature.

temperature / °C	$K_w / \text{mol}^2 \text{dm}^{-6}$
25	1.0×10^{-14}
62	1.0×10^{-13}

Which of the following statement is correct?

- 1** The ionic dissociation of water is an endothermic process.
- 2** Water is a neutral liquid at 62 °C.
- 3** $\text{pH} < 7$ at 62 °C.

Answer: A (1, 2 and 3)



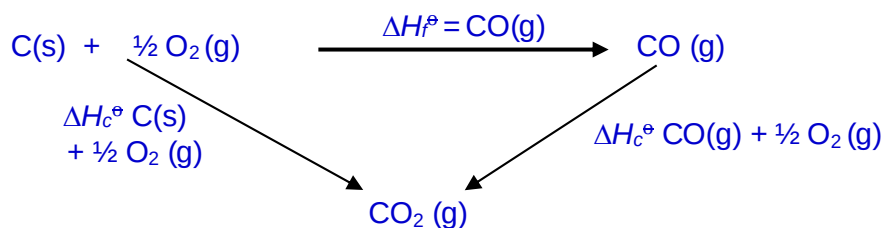
$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

- 1 – When temperature increases, K_w increases. Position of equilibrium shifts to the right. Therefore the forward reaction is endothermic.
- 2 – $[\text{H}^+] = [\text{OH}^-]$ as water dissociates to the same extent.
- 3 – Since water is neutral, $[\text{H}^+] = [\text{OH}^-] = (1.0 \times 10^{-14})^{1/2} = 3.16 \times 10^{-7} \text{ mol dm}^{-3}$
 $\text{pH} = -\log (3.16 \times 10^{-7}) = 6.5 < 7$

33 Which of the following has the same value as the standard enthalpy change of formation, $\Delta H_f^\ominus$, of carbon monoxide?

- 1 $\Delta H_{\text{combustion}}^\ominus (\text{C}) - \Delta H_{\text{combustion}}^\ominus (\text{CO})$
- 2 $\Delta H_f^\ominus (\text{CO}_2) - \Delta H_{\text{combustion}}^\ominus (\text{CO})$
- 3 $\frac{1}{2} \Delta H_f^\ominus (\text{CO}_2)$

Answer: B (1 & 2 only)



$$\Delta H_f^\ominus \text{CO(g)} = \Delta H_{\text{combustion}}^\ominus (\text{C}) - \Delta H_{\text{combustion}}^\ominus (\text{CO})$$

$$\Delta H_f^\ominus \text{CO(g)} = \Delta H_{\text{formation}}^\ominus (\text{CO}_2) - \Delta H_{\text{combustion}}^\ominus (\text{CO})$$

Note:

The standard enthalpy change of combustion of a compound is defined as the enthalpy change when 1 mol of the substance is burnt completely in oxygen under standard conditions of 298 K and 1 atm.



The standard enthalpy change of formation of a compound is defined as the enthalpy change when 1 mol of the substance is formed from its elements under standard conditions of 298 K and 1 atm. (Elements must be in most stable physical form).

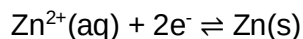
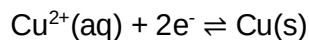


Thus, $\Delta H_{\text{combustion}}^\ominus (\text{C})$ and $\Delta H_{\text{formation}}^\ominus (\text{CO}_2(\text{g}))$ are the same.

- 34 **Use of the Data booklet** is relevant to this question.

In the Daniell cell, copper and zinc electrodes are immersed in a solution of **copper(II) sulfate and zinc sulfate** respectively.

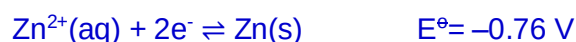
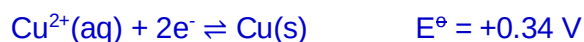
The two half-equations for a Daniell cell are given below



Which statements about this cell are correct when it is used?

- 1 The electron flow from the zinc electrode to the copper electrode in the external circuit.
- 2 The overall cell reaction is $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$.
- 3 The cell potential is +1.10V.

Answer: A (1, 2 and 3)



Since $E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})}$ is more positive than $E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})}$, thus reduction occurs at copper electrode (cathode) whereas oxidation occurs at zinc electrode (anode).

Overall equation: $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} - E_{\text{oxd}}^{\circ} = 0.34 - (-0.76) = +1.10 \text{ V}$$

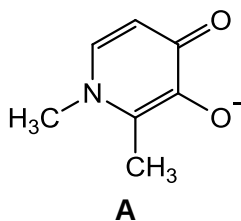
Hence, all the options are correct.

Option 1 is correct as electron always flow from the anode to cathode.

Option 2 is correct since E_{cell}° is positive, thus reaction is feasible.

Option 3 is correct as shown in the calculation above.

- 35 A **neutral, red** complex, FeA_3 , is formed when a **bidentate** ligand **A** is added to an aqueous solution of Fe^{3+} ions.

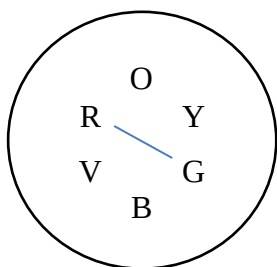


Which of the following statement is correct?

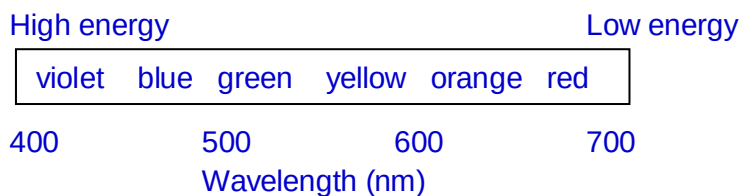
- 1 The complex has a coordination number of 3.
- 2 The complex absorbs radiation in the blue-green region of the visible spectrum.
- 3 The complex has a smaller energy gap between d-orbitals compared to yellow $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Answer: C (2 & 3 only)

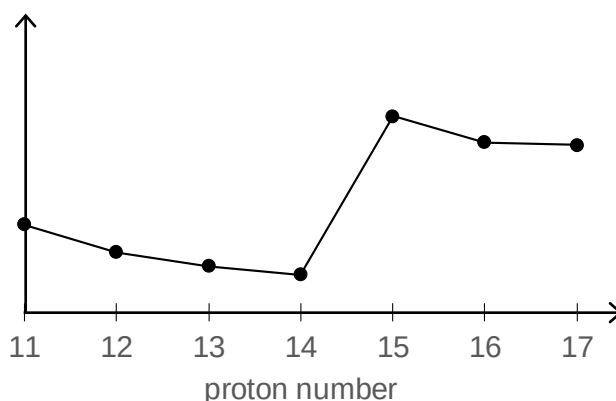
- 1 – **A** is bidentate, as the complex formed is neutral, hence there must be 3 ligands forming 2 coordinate bonds each to balance out the Fe^{3+} , forming an octahedral complex (coordination number 6).
- 2 – The colour of the complex is the complementary colour to the wavelengths absorbed.



- 3 – As seen from the colours, the red complex is due to blue-green light being absorbed, with a lower wavelength or higher energy than the violet light that is absorbed to give yellow $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, hence the energy of the light absorbed is lower in the red complex, which corresponds to a smaller energy gap.



- 36 The graph shows how a property from Na to Cl in Period 3 varies with proton number.



What is this property?

- 1 Ionic radius
- 2 First ionisation energy
- 3 Electronegativity

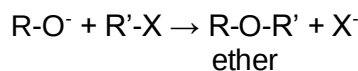
Answer: D (1 only)

- 1 – For each isoelectronic series, as we go across a period, nuclear charge increases. The electrons are pulled closer to the nucleus so the ionic radius decreases. Thus, the cationic radius decreases from $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Si}^{4+}$ and anionic radius decreases from $\text{P}^{3-} > \text{S}^{2-} > \text{Cl}^-$

The anions are much larger than the cations because anions have one more filled electron shell, hence there is a larger shielding effect resulting weaker attraction of the outermost electrons from the nucleus.

- 2 – Ionisation energy generally increases across a period due to the increase in nuclear charge and a decrease in atomic radii.
- 3 – Recall the definition of electronegativity. Electronegativity is a measure of the ability of an atom in a covalent bond to attract the bonding electrons. Electronegativity increases across the period. From Na to Cl, atomic radius decreases and the nucleus has more attraction to bonding electrons.

- 37 Williamson synthesis is one of the better methods to prepare ethers, $\text{R-O-R}'$. It involves a $\text{S}_{\text{N}}2$ displacement of halide ion in halogenoalkane ($\text{R}'\text{X}$) by an alkoxide ion nucleophile (RO^-) as shown.

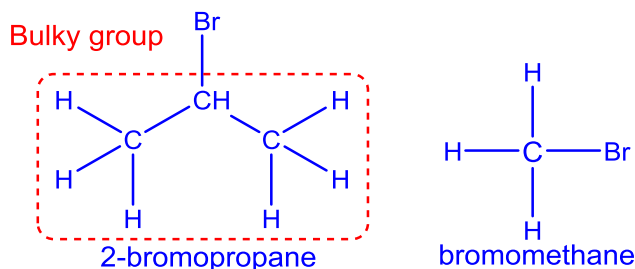


Which of the following statements are true?

- 1 The rate equation involved is $\text{rate} = k[\text{RO}^-][\text{R}'\text{X}]$
- 2 The reaction involving bromomethane will be faster compared to chloromethane.
- 3 The reaction involving 2-bromopropane will be faster compared to bromomethane.

Answer: B (1 & 2 only)

- 1 – Correct as a S_N2 mechanism consist both halogenoalkan and alkoxide ions present in the rate-determining step of the mechanism.
- 2 – Correct since C-Br bond is longer than C-Cl bond, thus C-Br bond (240 kJ mol^{-1}) is weaker than C-Cl (340 kJ mol^{-1}) and more easily broken, thus the reaction involving bromoethane will be faster.
- 3 – Incorrect since presence of 2 bulky methyl groups in 2-bromopropane hinders approach (steric hindrance) of the nucleophile to the halogenoalkane, making bond formation difficult. Hence, the reaction involving 2-bromopropane should be slower than bromomethane.



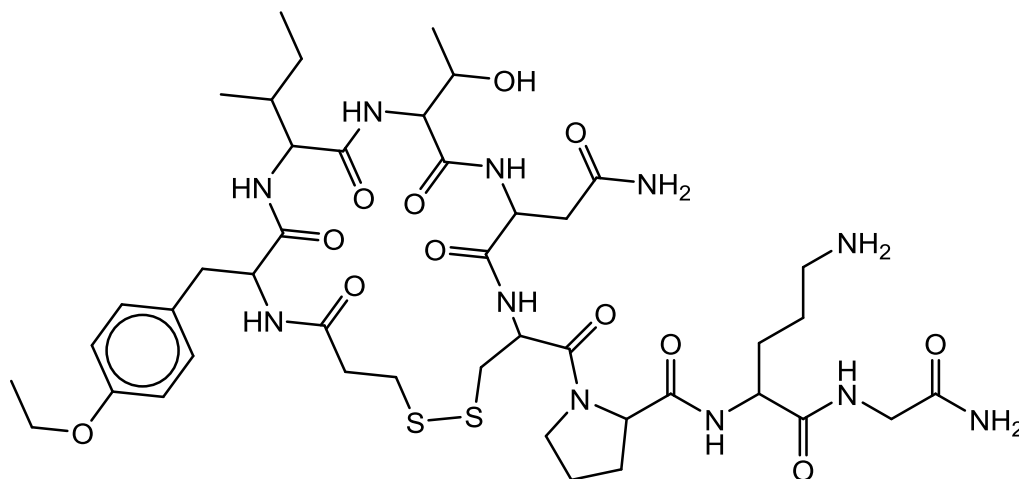
38 Cars are fitted with a catalytic converter. What reactions typically occur in a catalytic converter?

- 1 $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$
- 2 $\text{C}_x\text{H}_y + \left(\frac{x}{2} + \frac{y}{4}\right) \text{O}_2 \rightarrow x\text{CO} + \left(\frac{y}{2}\right) \text{H}_2\text{O}$
- 3 $\text{CO}_2 + \text{NO} \rightarrow \text{CO} + \text{NO}_2$

Answer: D (1 only)

Catalytic converters are used to remove pollutants such as CO, NO_x and unburnt hydrocarbons to form less harmful CO_2 , N_2 and H_2O . Thus, options 2 and 3 are incorrect as CO and NO_2 should not be formed.

39 Atosiban, a protein, is used as an intravenous medication as a birth labour repressant to halt premature labour.

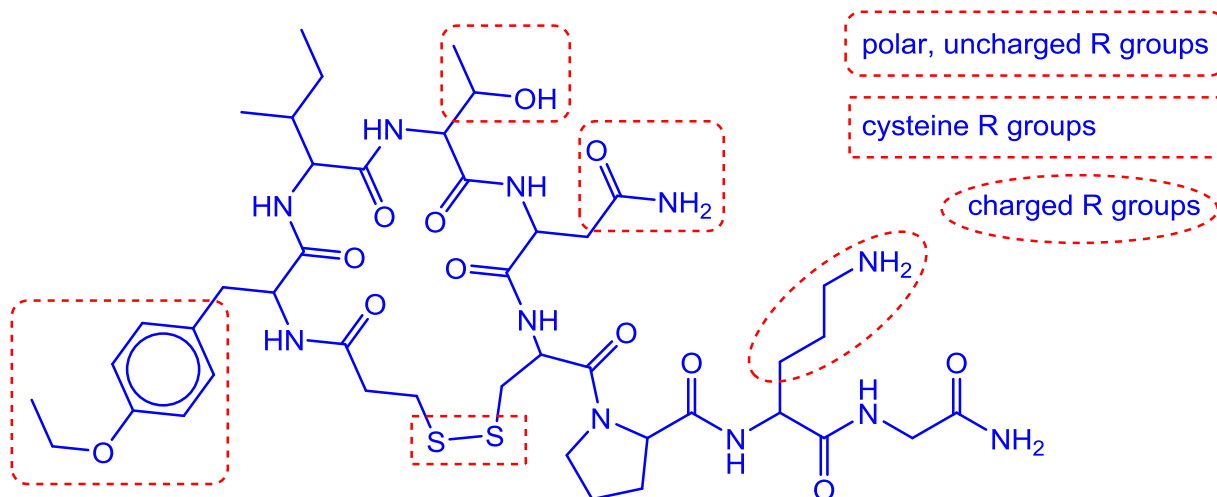


Atosiban

Which of the following R group interactions in the protein are possible?

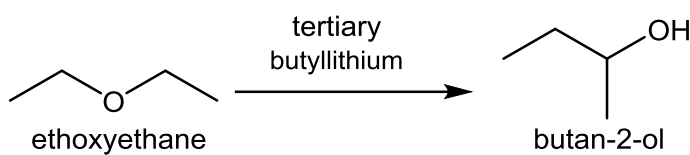
- 1 Hydrogen bond
- 2 Disulfide bond
- 3 Ionic bond

Answer: B (1 and 2)

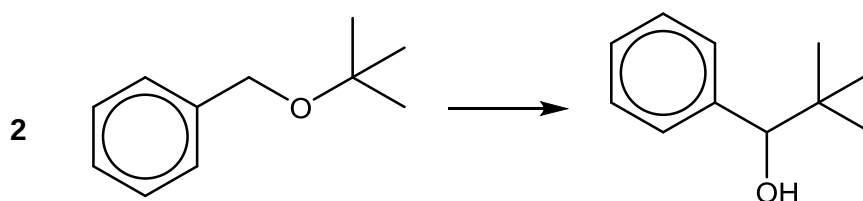
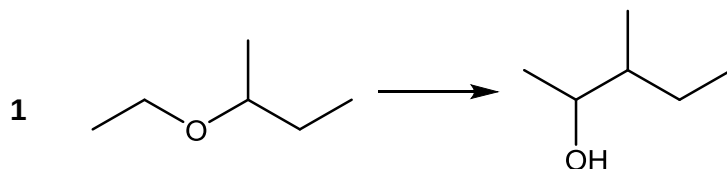


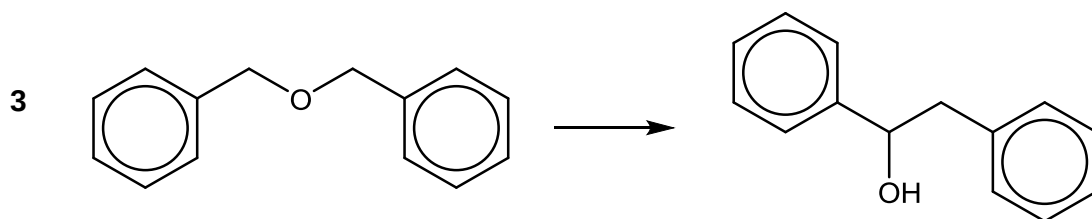
- 1 – Correct as there are polar uncharged R groups which can form hydrogen bonding.
- 2 – Correct since there is a S-S bond in the protein.
- 3 – Incorrect since there is only 1 charged R group present in the protein (a positively charged $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$ group). For ionic bonding to form, there must be at least 2 charged R groups and each of **opposite** charge.

- 40 The isomerisation of ethoxyethane to produce the corresponding alcohol is shown below.



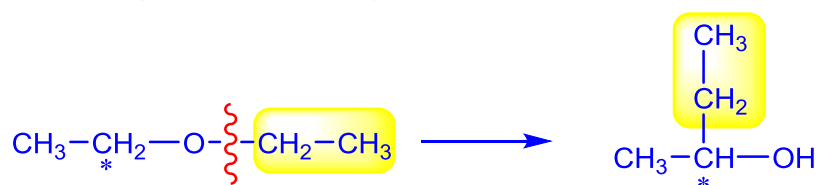
Which of the following shows the correct product formed under the same conditions?





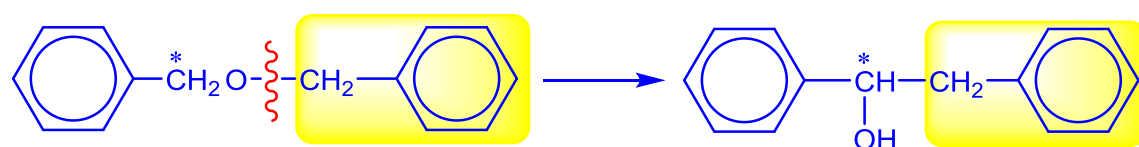
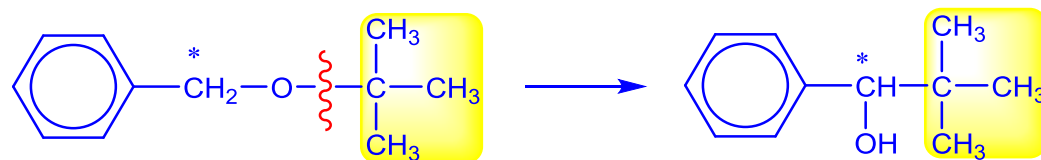
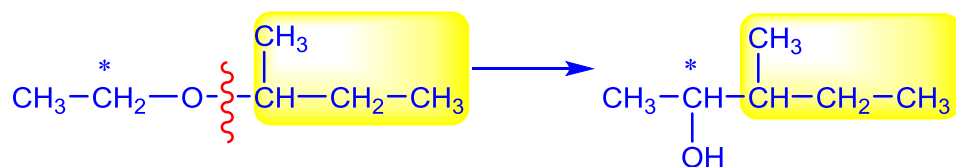
Answer: A (1, 2 and 3)

According to the scheme given,

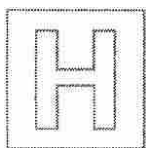


The ethyl group next to the O is shifted to the C*.

Thus, following this pattern,



1	A	11	C	21	A	31	B
2	D	12	C	22	C	32	A
3	B	13	D	23	C	33	B
4	B	14	D	24	A	34	A
5	D	15	B	25	C	35	C
6	A	16	C	26	B	36	D
7	B	17	A	27	D	37	B
8	B	18	D	28	C	38	D
9	B	19	C	29	B	39	B
10	D	20	B	30	B	40	A



CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE
NAME

CLASS

2T

CHEMISTRY

Paper 2 Structured Questions

9647/02

Monday 22 August 2016
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do **not** use staples, paper clips, or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

ANSWER SCHEME

	For Examiner's Use		
Paper 1			40
Paper 2	Q 1	12	72
	Q 2	15	
	Q 3	15	
	Q 4	15	
	Q 5	15	
Paper 3	Q 1	20	80
	Q 2	20	
	Q 3	20	
	Q 4	20	
	Q 5	20	
Total			192

This document consists of 18 printed pages.

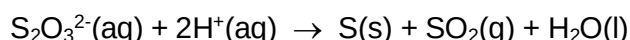
1 Planning (P)

One method of studying the kinetics of a chemical reaction, to find the order of reaction with respect to a particular reactant, is to measure the initial rates, by using the 'clock experiment'.

To determine the initial rate, we can measure the time taken for a prominent visual change to occur in the course of a reaction.

When aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to a solution containing dilute hydrochloric acid, HCl , a fine, pale yellow precipitate of solid sulfur will be formed after a while. This is the prominent visual change that can be clearly identified.

The overall equation for the reaction is represented as follows:



The initial rate of this reaction is determined by measuring the time taken for sufficient precipitate of sulfur to be formed to just obscure a 'cross' marked on a piece of white paper below a reaction container.

A student carried out a series of preliminary experiments, using approximate volumes of the two reactants and each reaction mixture was made up to the same total volume with deionised water. The student found that the time taken for the pale yellow precipitate to appear doubled when the volume of hydrochloric acid added was halved.

- (a) (i) State the relationship between the initial rate of reaction and the time taken for the pale yellow precipitate to appear.

$$\text{rate} \propto \frac{1}{\text{time}} \quad \text{OR}$$

Rate of reaction is inversely proportional to time, the time taken for the pale yellow precipitate to appear is low/short if the rate is high.[1]

- (ii) Explain why it is necessary to top up the reaction mixture with deionised water to the same total volume.

$$\text{volume} \propto \text{concentration} \quad \text{or}$$

To ensure that the total volume of the resultant reaction mixture remains the same in all experiments so that the volume of each reactant is proportional to its concentration in the resultant solution. When the volume of that reactant added doubles, its concentration in the resultant solution doubles.[1]

- (b) Hence, based on the results of the student's preliminary experiments, predict the order of the reaction with respect to H^+ ions.

The time taken for the pale yellow precipitate to appear doubled when the volume of hydrochloric acid added was halved.

Since $\text{volume} \propto \text{concentration}$ and $\text{rate} \propto \frac{1}{\text{time}}$, when the concentration of hydrochloric acid added was halved, the rate was halved.

$\therefore$ rate of reaction $\propto [\text{H}^+]$ or the reaction is first order with respect to H^+ .

[1]

- (c) You are to design an experiment to study the kinetics of the reaction between $\text{S}_2\text{O}_3^{2-}$ ions and H^+ ions.

The following data in tabulated form is shown below.

experiment	volume of $1.00 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3 / \text{cm}^3$	volume of $1.00 \text{ mol dm}^{-3} \text{ HCl} / \text{cm}^3$	volume of deionised water / cm^3	time taken for the 'marked cross' to be obscured / s
1	10	20	20	t_1
2	20	20	10	t_2
3	10	10	30	t_3

- (i) Fill in the blanks in the table above, appropriate volumes of the reactants and deionised water to be used in experiments 2 and 3 such that the order of reaction with respect to $\text{S}_2\text{O}_3^{2-}$ and H^+ ions can be determined and verified. [1]

Appropriate volumes of reactants and deionised water stated correctly in experiments 2 and 3.

- (ii) Outline in a series of numbered steps, how **experiment 1** could be carried out. Your **plan** should include:
- the **apparatus** used to measure the various volumes,
 - the **order** that the various solutions are mixed,
 - how the **time** to determine the rate of reaction is measured, and
 - other **experimental details** to ensure the **consistency** of the experiment.

Based on the table in (c)(i), explain how the results of any two of the three experiments can be used to determine the order of reaction with respect to $\text{S}_2\text{O}_3^{2-}$ ions.

.....

.....

.....

[7]

Inspection Method

The concentration of $\text{HC}/(\text{aq})$ is kept constant, while the concentration of $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ is varied.

Order	Explanation
0	If $t_2 = t_1$, then the rates for both reactions remain unchanged, though the concentration of $S_2O_3^{2-}$ is doubled. So the reaction rate is independent of the change in concentration of $S_2O_3^{2-}$. Zero order.
1	If t_2 is halved that of t_1 , the rate for experiment 2 is twice that of experiment 1. Since the rate is doubled when the concentration of $S_2O_3^{2-}$ is doubled, the reaction is first order with respect to $S_2O_3^{2-}$.
2	If t_2 is four times less than that of t_1 , the rate for experiment 2 is four times that of experiment 1. Since the rate is quadrupled when the concentration of $S_2O_3^{2-}$ is doubled, the reaction is second order with respect to $S_2O_3^{2-}$.

	times greater than that of experiment 1. Since the rate is four times greater when the concentration of $\text{S}_2\text{O}_3^{2-}$ is doubled, the reaction is second order with respect to $\text{S}_2\text{O}_3^{2-}$.

OR

V x t method

Order	Explanation
0	t is constant, $t_1 = t_2$
1	$(V_{\text{S}_2\text{O}_3^{2-}}) \times t = \text{constant}$ or $10 \times t_1 = 20 \times t_2$
2	$(V_{\text{S}_2\text{O}_3^{2-}})^2 \times t = \text{constant}$ or $10^2 \times t_1 = 20^2 \times t_2$

[3]

- (d) Identify one potential safety hazard in this experiment and state how you would minimise this risk.

HCl(aq) is corrosive, wear hand gloves to prevent direct contact with it.

SO_2 gas liberated is toxic, wear protective mask or perform the experiment in a well ventilated place or using a fume cupboard. [1]

Either one

[Total: 12]

- 2 Silver halides (silver chloride, silver bromide and silver iodide) are useful in qualitative analysis as they are insoluble in water. In qualitative analysis, silver nitrate is added to a test solution to identify the presence of halide ions by forming a precipitate.

- (a) (i) When aqueous silver nitrate was added to a test solution which was known to contain a halide ion, a cream precipitate was formed.

Identify the precipitate and deduce the identity of the halide ion present in the solution.

The cream precipitate formed is AgBr, hence the solution contains Br⁻ ions. [1]

.....[1]

- (ii) To confirm the identity of the halide, aqueous ammonia was added dropwise, and the precipitate remained unchanged at first, but as more ammonia was added, the precipitate dissolved.

With the aid of an equation, briefly explain why the precipitate dissolved.

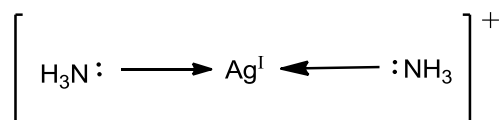


.....

When excess/concentrated ammonia is added, a soluble complex ion is formed.

.....[2]

- (iii) Draw the structure of the silver-containing product in solution after the precipitate dissolved, displaying any lone pair of electrons where appropriate.



[1]

In photography, after an image is developed, sodium thiosulfate, Na₂S₂O₃, is used to dissolve any remaining silver halide away, to “fix” the image and ensure that it does not change upon further exposure to light.

- (iv) An equal volume of sodium thiosulfate was added to the solution from (ii). State the type of reaction that occurred when sodium thiosulfate was added.

Ligand exchange/displacement reaction.

.....[1]

- (v) Suggest the identity of the silver-containing product which has a coordination number of 2.



.....[1]

- (b) The table below shows data about silver and two other metals, iron and copper.

	silver	iron	copper
electronic configuration	[Kr] 4d ¹⁰ 5s ¹	[Ar] 3d ⁶ 4s ²	[Ar] 3d ¹⁰ 4s ¹
conductivity at room temperature/ S m ⁻¹	6.3 × 10 ⁷	1.0 × 10 ⁷	?

- (i) Explain, in terms of structure and bonding, why the three metals have **high** electrical conductivity.

The three transition metals have giant metallic structures with strong metallic bonds between metal cations and a sea of delocalized electrons.

They have many d and s valence electrons which can be delocalized and hence can conduct electricity through the movement of the electrons. [2]

- (ii) Silver and copper are known to be excellent metallic conductors at room temperature. Noting the electronic configuration, suggest the value of the conductivity of copper at room temperature.

Any value between 1.1 × 10⁷ – 6.2 × 10⁷

..... S m⁻¹ [1]

Actual value: 5.9 × 10⁷ S m⁻¹ (units are Siemens per metre, reciprocal of resistivity)

- (iii) Iron is used as a catalyst in the synthesis of ammonia in the Haber process. State the type of catalysis and explain clearly how it carries out its function.

Iron can act as a heterogeneous catalyst in the Haber process.

It has partially-filled 3d orbitals which allows the ready exchange of electrons to and from reactant molecules (N₂ and H₂). Reactants are adsorbed onto the surface, weakening the bonds and thereby lowering the activation energy, as well as increasing the surface concentration of reactants, thus increasing the rate of reaction.

..... [3]

- (c) When a jar is filled with gaseous hydrogen iodide, HI, and a red-hot glass rod inserted into the jar, violet fumes are observed.

- (i) State the identity of the violet fumes.

I_2 [1]

- (ii) When the same procedure is carried out with HBr instead of HI, no fumes are observed, but on strong heating, reddish-brown vapour is obtained.

With reference to values in the *Data Booklet*, explain the difference in the behaviour of HBr and HI.

From Data Booklet, ...

BE of H–I = 299 kJ mol⁻¹

BE of H–Br = 366 kJ mol⁻¹

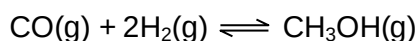
As the bond energy of is H–Br greater/stronger than H–I, (due to smaller atomic size/radius, and shorter bond length), H-Br does not decompose when heated by contact with a red-hot glass rod, but requires stronger heating/more energy to decompose.

.....[2]

[Total: 15]

- 3 Methanol is one of the alternative fuels proposed to replace fossil fuels. It has the advantage of more efficient production and ease of storage as compared to other alternatives.

Methanol can be formed from carbon monoxide and hydrogen as shown below.



The reaction was investigated by mixing 3.2 mol of CO and 3.2 mol of H₂ in a 10.0 dm³ sealed vessel, and equilibrium was established at 120 °C under a pressure of 1.60 x 10⁶ Pa.

- (a) (i) Assuming ideal gas behaviour, determine the total amount of gas in moles, at equilibrium.

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{(1.60 \times 10^6)(10.0 \times 10^{-3})}{(8.31)(273+120)}$$

$$n = 4.899 \text{ or } 4.90 \text{ mol}$$

[2]

- (ii) Hence, calculate the amounts of CO, H₂ and CH₃OH in moles, present at equilibrium.

	CO	+	2H ₂	$\rightleftharpoons$	CH ₃ OH
Initial /mol	3.2		3.2		0
Change / mol	- x		- 2x		+x
Equilibrium/ mol	3.2 - x		3.2 - 2x		x

$$n = 4.90 = 3.2 - x + 3.2 - 2x + x$$

$$4.9 = 6.4 - 2x$$

$$n(\text{CH}_3\text{OH}) = x = 0.750 \text{ mol}$$

$$n(\text{CO}) = 3.2 - 0.75 = 2.45 \text{ mol}$$

$$n(\text{H}_2) = 3.2 - 2(0.75) = 1.70 \text{ mol}$$

[3]

- (iii) Write an expression for the equilibrium constant, K_c for the above reaction, and use your answers in (a)(ii) to calculate its value under the stated conditions.

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

$$K_c = \frac{\frac{0.75}{V}}{\frac{2.45}{V} \left(\frac{1.7}{V} \right)^2} = \frac{0.75}{2.45 \left(\frac{1.7}{10} \right)^2}$$

$$K_c = 10.6 \text{ mol}^{-2} \text{ dm}^6$$

[2]

- (b) Standard Gibbs free energy change, ΔG° is related to K_c by the following equation.

$$\Delta G^\circ = -RT \ln K_c$$

where ΔG° is in **joules per mole**, T is the temperature at which equilibrium is established and R is the molar gas constant.

- (i) Use this equation and your answer in (a) to calculate ΔG° for the formation of methanol from carbon monoxide and hydrogen at 120 °C.

$$\Delta G^\circ = - (8.31)(273+120) \ln 10.6$$

$$\Delta G^\circ = -7710 \text{ J mol}^{-1}$$

[1]

- (ii) With reference to the *Data Booklet*, calculate the enthalpy change of formation of methanol from carbon monoxide and hydrogen. Use 1072 kJ mol⁻¹ for the bond energy of C≡O bond.

<u>Δ Bonds broken (ΔH)</u>		<u>Bonds formed (ΔH)</u>	
2 H-H	2(+436)	3 C-H	3(410)
C≡O	1072	C-O	360
		O-H	460
$\Delta H^\circ = 2(+436) + 1072 - 3(410) - 360 - 460$			
$= -106 \text{ kJ mol}^{-1}$			

[2]

- (iii) Hence, state briefly why higher temperature is not used industrially for the formation of methanol from carbon monoxide and hydrogen.

The forward reaction is exothermic. Higher temperature will result in position of equilibrium to shift to the left, resulting in lower yield of product, hence it is not preferred.

[2]

- (iv) Use your answers in (b)(i) and (ii) to calculate the standard entropy change for the reaction at 298 K.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta G^\circ - \Delta H^\circ}{-T}$$

$$= \frac{-7710 - (-106 \times 10^3)}{-298} = -330 \text{ J K}^{-1} \text{ mol}^{-1}$$

[1]

- (v) Explain the significance of the sign of the calculated entropy change and comment if this is expected.

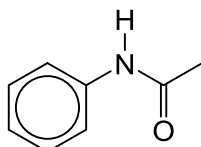
Calculated entropy change is negative as expected which means the entropy has decreased, therefore the system becomes less disordered as there is a decrease in number of moles of gas after the reaction.

.....[2]

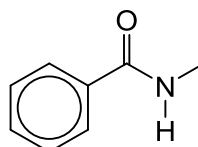
[Total:15]

- 4 (a) Acetanilide was the first aniline derivative found to possess analgesic and antipyretic properties. It was introduced into medical practice under the name of the drug, Antifebrin.

Suggest the reagents and conditions that can be used to distinguish acetanilide from compound X. State clearly the expected observations for each compound.



Acetanilide



Compound X

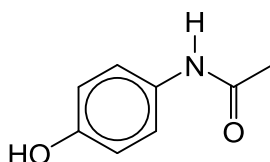
Reagents and conditions Step 1: NaOH(aq), heat

Step 2: Br₂(aq), rtp

Observations . Orange aqueous bromine discharged and white ppt was formed for acetanilide. However, no such decolourisation and precipitation observed for compound X.

OR Ethylamine gas released by compound X after base hydrolysis which turns moist red litmus paper blue. However, gas released will not turn moist red litmus paper blue for acetanilide. [2]

- (b) It was later discovered that acetanilide was toxic and thus paracetamol, a derivative of acetanilide, was produced.



Paracetamol

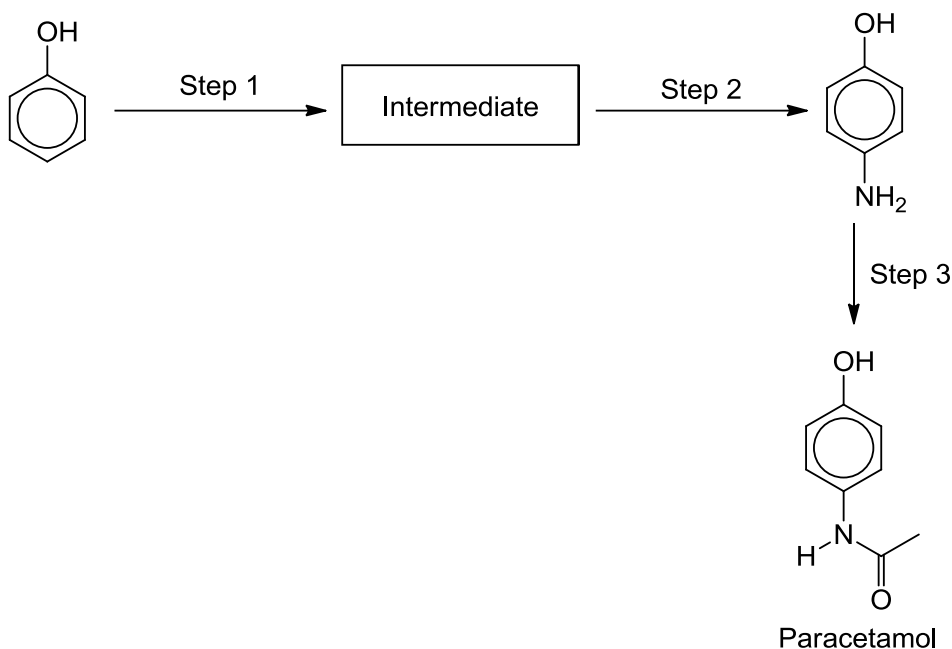
- (i) State the shape about N atom in paracetamol and hence identify the type of hybridisation involved.

Shape about N atom Trigonal planar

Hybridisation of N sp²

[2]

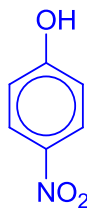
- (ii) A reaction scheme was proposed for the synthesis of paracetamol from phenol. Fill in the boxes provided with the reagents, conditions and intermediates for the synthesis.



Reagents and conditions:

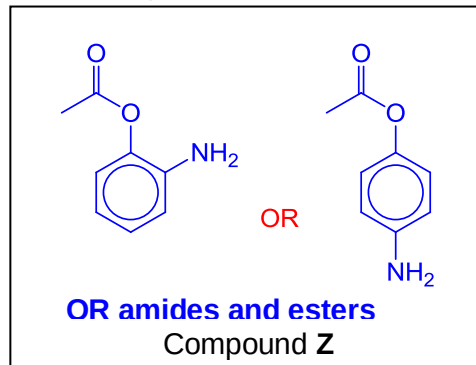
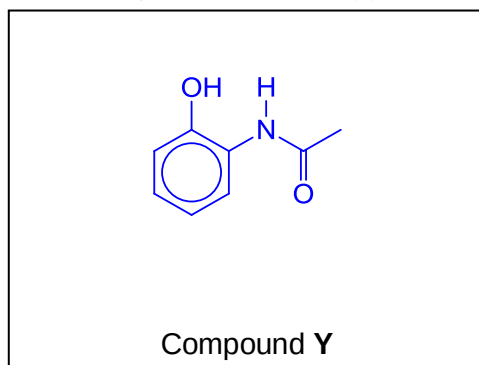
- Step 1 Dilute HNO_3 , rt
- Step 2 1) Sn , conc HCl , heat 2) NaOH(aq) , rt
- Step 3 $\text{CH}_3\text{COC/}$

Structure of intermediate:



[4]

- (iii) In the synthesis of paracetamol from phenol, two possible side-products, compound **Y** and **Z**, are formed. Given that only compound **Y** is a position isomer of paracetamol, suggest the identities of compound **Y** and **Z**.



[2]

- (iv) Predict, with explanation, how the boiling point of paracetamol might compare to that of compound Y.

Paracetamol has a higher boiling point than compound Y.

Paracetamol can form more extensive intermolecular hydrogen bonding as unlike compound Y, paracetamol does not have intramolecular hydrogen bonding.

[2]

- (c) In a typical pain relief tablet, there are 500 mg of paracetamol.

- (i) An adult can consume up to a maximum dosage of 4000 mg of paracetamol within 24 hours. The average adult weight is 62 kg. Calculate the number of tablets a child who weighs 45 kg, can consume within 24 hours. (Maximum dosage is dependent on weight of an individual.)

Max paracetamol a child can consume

$$= \frac{4000}{62} \times 45 = 2903 \text{ mg}$$

Max no. of tablets that can be consumed

$$= \frac{2903}{500} = 5.81 \text{ tablets}$$

≈ 5 tablets

[2]

- (ii) It was recommended to consume the tablets at 6 hours intervals. Using your answer in (c)(i), calculate the recommended number of tablets the child should take at each interval without exceeding dosage.

No. of times to consume tablets in 24 h

$$= \frac{24}{6} = 4 \text{ times}$$

Max no. of tablets that can be consumed each time

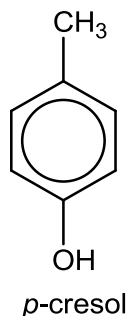
$$= \frac{5}{4} = 1.25 \text{ tablets}$$

≈ 1 tablet

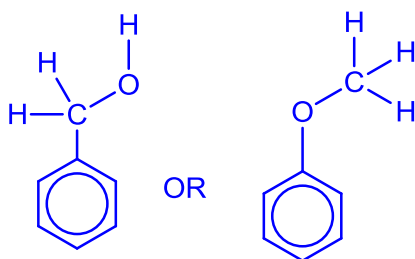
[1]

[Total: 15]

- 5 The compound *p*-cresol is used in the production of antioxidants. It is also used in the fragrance and dye industries.



- (a) Draw the displayed formula of a functional group isomer of *p*-cresol, and describe a laboratory test that will distinguish these two compounds. You should state the reagents used and the observations expected.

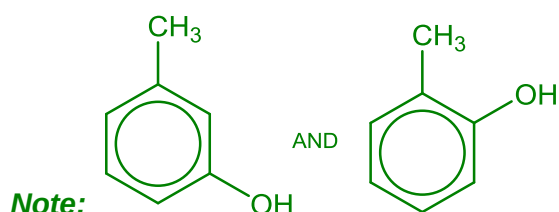


To separate test tube containing each sample, add neutral FeCl₃. Violet colouration will be formed with *p*-cresol whereas no violet colouration for its isomer. OR

To separate test tube containing each sample, add aqueous Br₂. Orange bromine solution decolourise and a white precipitate is formed with *p*-cresol. whereas no decolourisation of orange bromine solution with its isomer. [3]

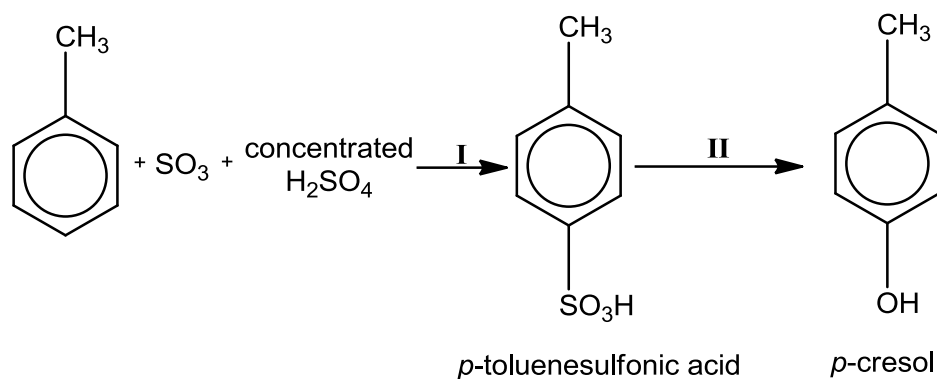
NOT ACCEPTED: PCl_5

Note: Oxidation using $KMnO_4/H_2SO_4$ is not accepted for *p*-cresol and phenylmethanol since both can undergo side-chain oxidation.



are not accepted because these are positional isomers of *p*-cresol. Positional isomers have the same carbon chain, but different positions of functional groups. Functional group isomers have different functional groups.

- (b) *p*-Cresol can be prepared industrially by a 2-step process as shown below.

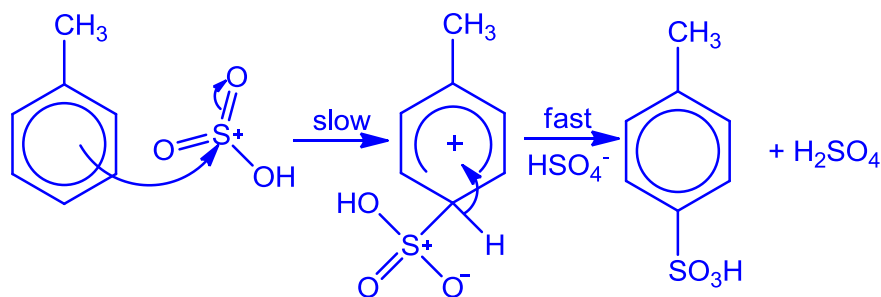


Reaction I involves sulfonation of methyl benzene to give *p*-toluenesulfonic acid. The proposed mechanism of reaction I involves electrophilic substitution.

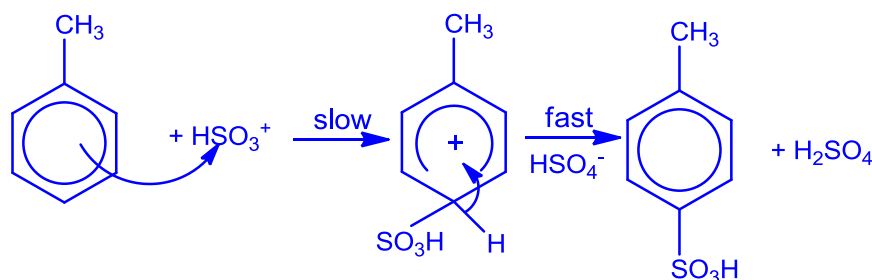
- (i) The first step of the proposed mechanism of reaction I involves acid-base reaction in the generation of an electrophile, HSO_3^+ . Write an equation to show how the electrophile HSO_3^+ is formed.



- (ii) Complete the proposed mechanism to produce *p*-toluenesulfonic acid as shown above. In the mechanism, show clearly the curly arrows to indicate the movement of electrons and all charges.

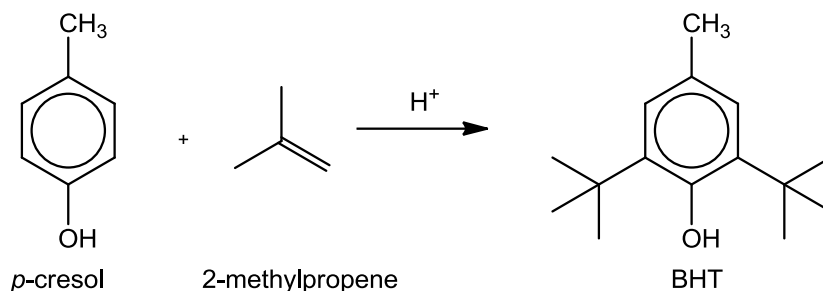


OR



[3]

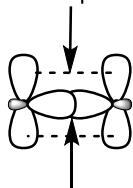
- (c) *p*-Cresol is used in the production of antioxidants such as butylated hydroxytoluene, BHT, which is mainly used as an antioxidant in the food industry. The reaction involves a dialkylation of *p*-cresol with 2-methylpropene in the presence of an acid catalyst given below.



- (i) Draw a labelled diagram to show how the orbitals overlap to form the C=C bond in 2-methylpropene and state the type of hybridisation involved.

sp² hybridisation

side-on overlap between unhybridised p orbital (to form pi bond)



head-on overlap between sp² hybrid orbitals (to form sigma bond)

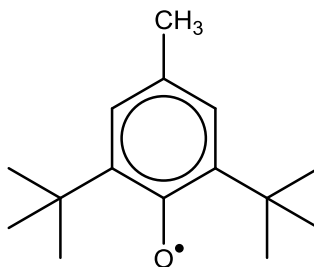
[2]

- (ii) Explain why 2-methylpropene cannot exhibit geometric isomerism.

One carbon atom of the C=C double bond has the same methyl group ...
attached to it.

[1]

- (iii) In order for BHT to act as an antioxidant, it forms a very stable radical on the oxygen atom as shown below. Suggest an explanation why this stable BHT radical is unable to react further with other molecules.



BHT radical

The 2 large/bulky alkyl groups pose steric hindrance (repel incoming molecules) that prevent the radical to react with other molecules.
 OR The radical is stable due to the delocalisation of unpaired electron from oxygen atom into the benzene ring. OR Presence of electron-donating alkyl groups will stabilize the radical. [1]

- (iv) Compound **R**, $C_{14}H_{20}O_2$, is a metabolite derived from the biotransformation of BHT. It is structurally related to BHT, $C_{15}H_{24}O$, and is also a cyclic compound.

State the type of reaction and deduction for the following observations.

- I 1 mole of compound **R** will react with 2 moles of 2, 4-DNPH.

Type of reaction: Condensation

Deduction: Compound R is a (aldehyde/ketone) carbonyl compound [1]

- II Compound **R** will not react with Tollens' reagent.

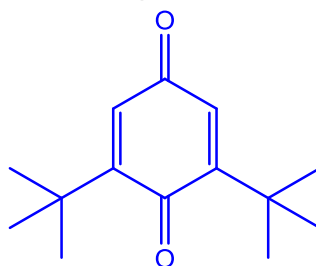
Deduction: Compound R has no aldehyde present. (Compound R is a ketone and not an aldehyde) [1]

- III 1 mole of compound **R** will decolourise 2 moles of aqueous Br_2 but no HBr is formed.

Type of reaction: Electrophilic addition

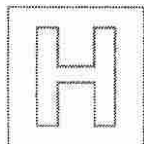
Deduction: Compound R has 2 alkene functional groups. [1]

- IV Deduce the structure of compound **R**.



[1]

[Total: 15]



CHEMISTRY

Paper 3 Free Response

9647/03

Friday 26 August 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

**ANSWER SCHEME
&
EXAMINERS'
COMMENTS**

This document consists of **17** printed pages and **1** blank page.

Answer any **four** questions.

1 Use of the Data Booklet is relevant to this question.

- (a) When potassium manganate(VII), KMnO_4 , is heated with concentrated sodium hydroxide, NaOH , bubbles of oxygen are seen and a green solution of MnO_4^{2-} is obtained. The addition of barium chloride, BaCl_2 , to this solution precipitated out a solid **X** with composition by mass of 53.5% barium, 21.5% manganese and 25.0% oxygen.

- (i) Calculate the empirical formula of **X**. [1]

Element	Ba	Mn	O
% mass	53.5	21.5	25.0
A_r	137	54.9	16.0
No. of moles	0.391	0.392	1.56
Mole ratio	1	1	4

Empirical formula of **X** is BaMnO_4

- (ii) When the green solution above is acidified, a brown precipitate in a purple solution is formed.

Suggest the identities of the species formed upon acidification and hence state the type of reaction that has occurred. [3]

Brown precipitate is MnO_2

Purple solution is MnO_4^-

Disproportionation

- (b) A solution of acidified potassium manganate(VII), KMnO_4 , can be standardised through titration against sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. The ethanedioate ion is oxidised to carbon dioxide in this reaction.

- (i) State the oxidation numbers of C in the ethanedioate ion and in carbon dioxide. [1]

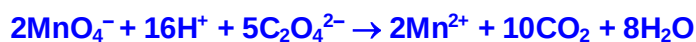
O.N. of C in $\text{C}_2\text{O}_4^{2-} = +3$

O.N. of C in $\text{CO}_2 = +4$

- (ii) Write the half-equation for the oxidation of the ethanedioate ion. [1]



- (iii) Hence, write the overall balanced equation for the reaction between acidified manganate(VII) and ethanedioate ions. [1]



- (iv) In one such standardisation procedure, 25.0 cm³ of 0.0150 mol dm⁻³ Na₂C₂O₄ solution required 28.85 cm³ of acidified KMnO₄ to reach the end-point.

Determine the concentration of KMnO₄ in the solution. You may assume that $2\text{MnO}_4^- \equiv 5\text{C}_2\text{O}_4^{2-}$. [3]

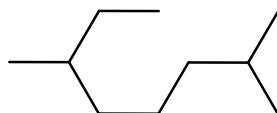
$$\begin{aligned}\text{No. of moles of C}_2\text{O}_4^{2-} &= \frac{25.0}{1000} \times 0.0150 \\ &= 0.000375 \text{ mol}\end{aligned}$$

Since $2\text{MnO}_4^- \equiv 5\text{C}_2\text{O}_4^{2-}$,

$$\begin{aligned}\text{No. of moles of MnO}_4^- &= \frac{2}{5} \times 0.000375 \\ &= 0.000150 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Concentration of KMnO}_4 &= \frac{0.000150}{28.85} \times 1000 \\ &= 0.00520 \text{ mol dm}^{-3}\end{aligned}$$

- (c) Myrcene, **A** and ocimene, **B**, are isomers with the molecular formula C₁₀H₁₆. When subjected to hydrogen with platinum catalyst, both isomers give 2,6-dimethyloctane, C₁₀H₂₂.

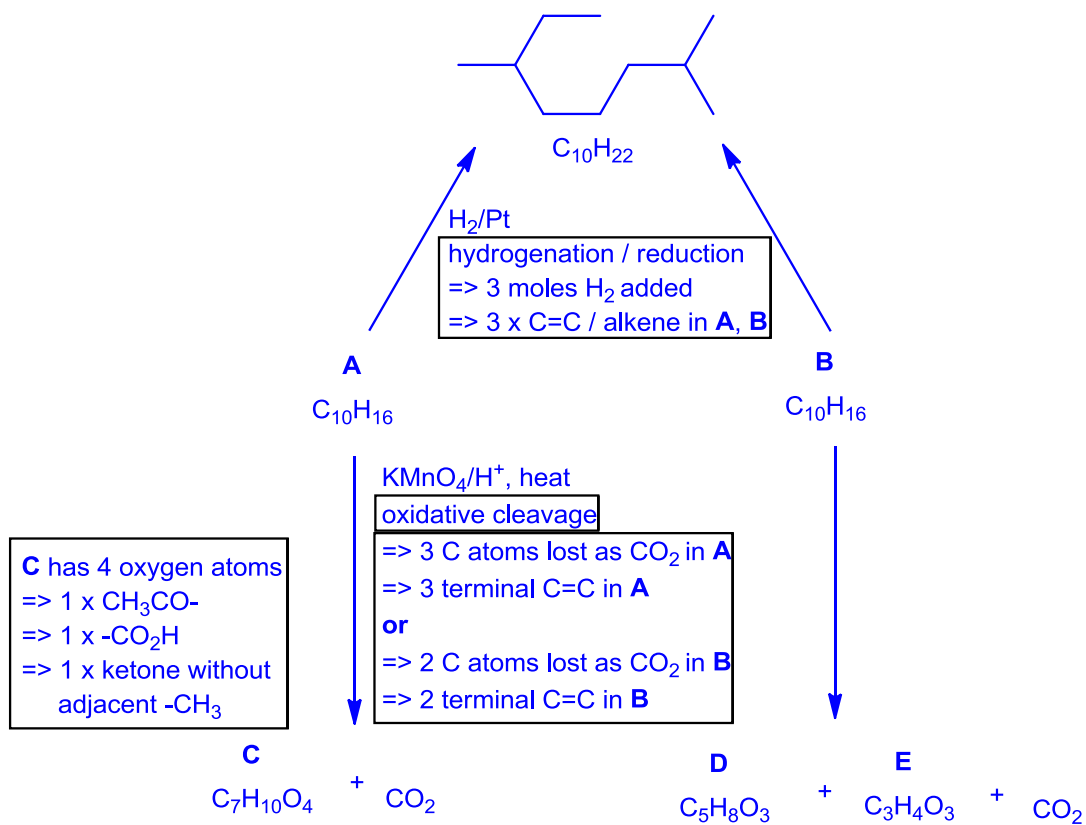


2,6-dimethyloctane

When treated with hot concentrated acidified KMnO₄, **A** gives CO₂ and compound **C**, C₇H₁₀O₄; **B** gives CO₂ and compounds **D**, C₅H₈O₃, and **E**, C₃H₄O₃.

Compounds **C**, **D** and **E** give one mole of CHI₃ with alkaline aqueous iodine. On addition of aqueous NaHCO₃, compounds **C**, **D** and **E** produce effervescence.

Suggest structures for **A-E**, and explain the observations described above. [10]



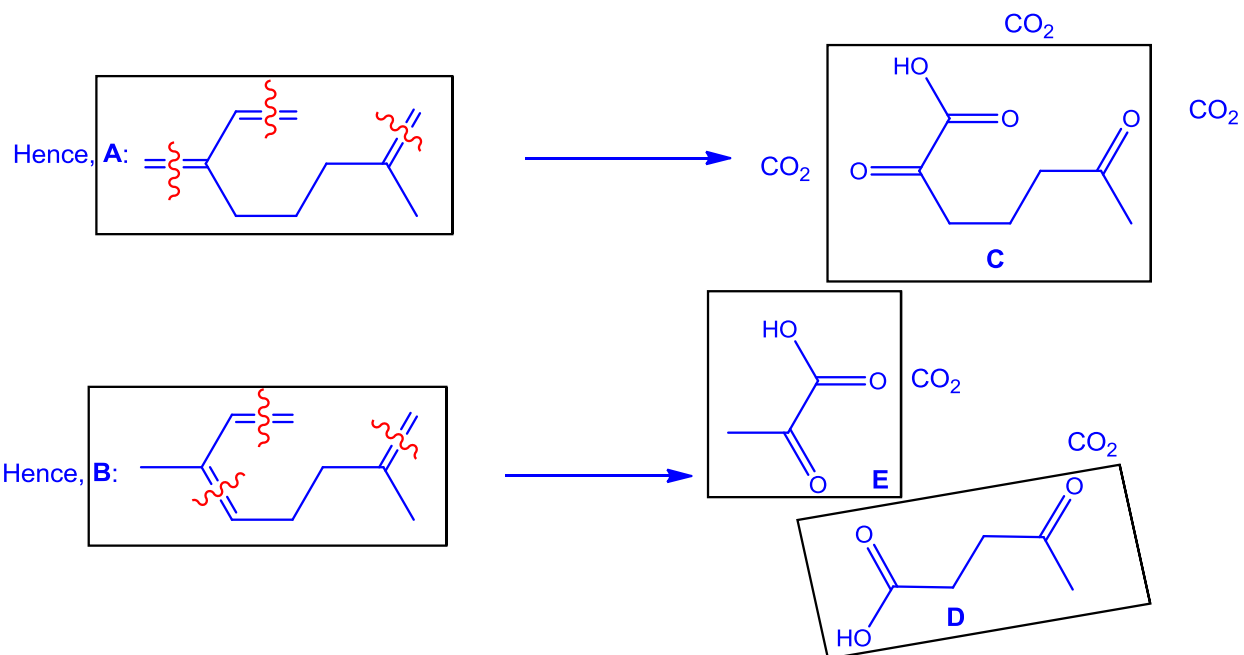
$KMnO_4/H^+$, heat
 oxidative cleavage

$\Rightarrow$ **C**, **D** and **E** have ketone and/or carboxylic acid groups

Iodoform/Triiodomethane test
 $\Rightarrow$ **C**, **D** and **E** have CH_3CO- groups

$NaHCO_3(aq)$

Acid-carbonate/acid-base/neutralisation reaction
 $\Rightarrow$ **C**, **D** and **E** produce CO_2
 $\Rightarrow$ they have carboxylic acid groups



[Total: 20]

- 2 The table below lists the standard enthalpy change of formation of four compounds.

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{H}_2\text{O}(\text{l})$	– 286
$\text{HCl}(\text{g})$	– 92.0
$\text{SiO}_2(\text{s})$	– 910
$\text{SiCl}_4(\text{l})$	– 640

- (a) What is meant by the term, standard enthalpy change of formation of a compound? [1]
The enthalpy change when 1 mol of a compound is formed from its elements (in its most stable form), under standard conditions (25°C, 1 atm pressure).

- (b) $\text{SiCl}_4(\text{l})$ undergoes hydrolysis to give $\text{SiO}_2(\text{s})$.

- (i) Write the balanced equation with state symbols for the hydrolysis reaction. [1]
 $\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{g})$

- (ii) Using the above data, calculate the standard enthalpy change for the hydrolysis reaction. State one assumption made in your calculation. [1]

$$\begin{aligned}\Delta H_r^\ominus &= \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants}) \\ &= [-910 + 4(-92.0)] - [-640 + 2(-286)] \\ &= -66.0 \text{ kJ mol}^{-1}\end{aligned}$$

Assumption:

- **$\text{SiCl}_4(\text{l})$ is in excess. The hydrolysis gives $\text{HCl}(\text{g})$ instead of $\text{HCl}(\text{aq})$.**
- **Hess' Law is followed/obeyed.**

- (iii) Does the hydrolysis have a positive, negative or zero entropy change? Explain your answer. [1]

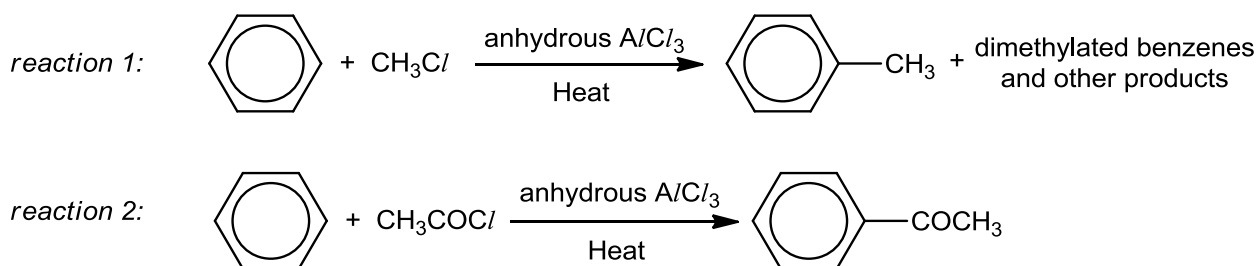
Positive entropy change. 4 moles of gas (HCl) are produced. There is an increase in disorder of the system as there are more ways of arranging the particles in the system.

- (iv) Hence, by the use of the Gibbs free energy, $\Delta G^\ominus$, explain why the hydrolysis of $\text{SiCl}_4(\text{l})$ is always a spontaneous process. [1]

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

Since $\Delta H^\ominus$ is negative and $\Delta S^\ominus$ is positive, $\Delta G^\ominus$ is always negative. So the process is spontaneous.

- (c) Consider reaction 1 and reaction 2 shown below.



- (i) Both *reaction 1* and *reaction 2* proceed via a similar mechanism. Name the type of reaction undergone. [1]
Electrophilic substitution.
- (ii) Suggest why *reaction 1* gives a mixture of organic products while *reaction 2* gives only one mono-substituted product. [2]

Reaction 1

The CH_3 is an electron donating or activating group. It activates the benzene ring and so makes the delocalised π electrons more susceptible/available to electrophilic attack/electrophiles. This favours further substitution to give multi-substituted products.

Reaction 2

The C=O is an electron withdrawing or deactivating group. It deactivates the benzene ring and so makes the delocalised π electrons less susceptible/available to electrophilic attack/electrophiles. Further substitution is less favourable.

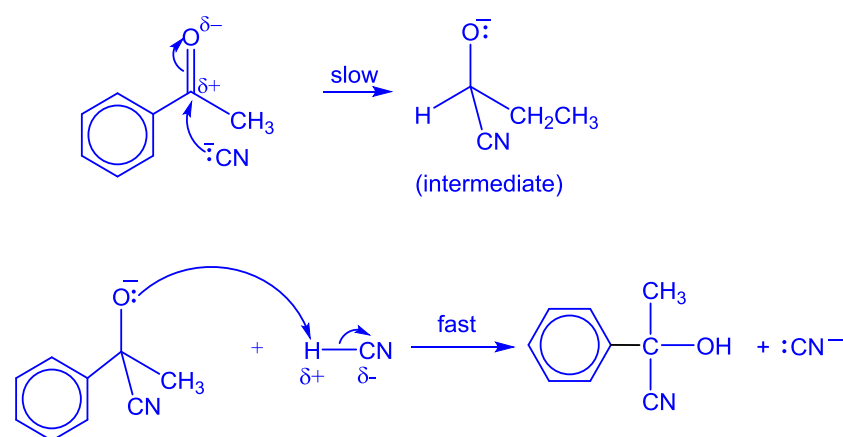
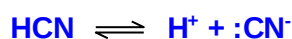
- (d) The organic product in *reaction 2*, phenylethanone, $\text{C}_6\text{H}_5\text{COCH}_3$, reacts with HCN to produce the corresponding cyanohydrin under certain experimental conditions.

- (i) State the experimental conditions. [1]

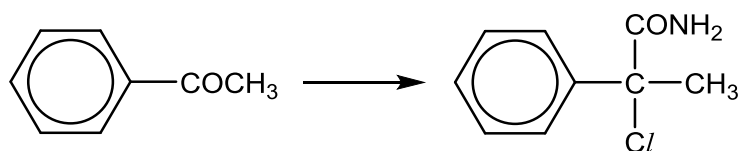
Trace amount of NaOH/NaCN and $10 - 20^\circ\text{C}$

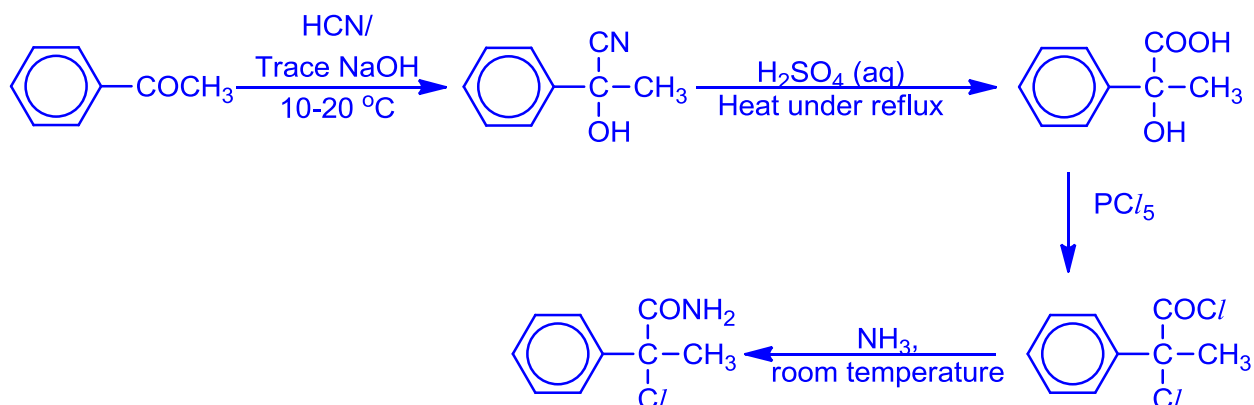
- (ii) Describe the mechanism of reaction, of phenylethanone with HCN , showing clearly the curly arrows to indicate the movement of electrons and all charges. [3]

Nucleophilic Addition Mechanism.



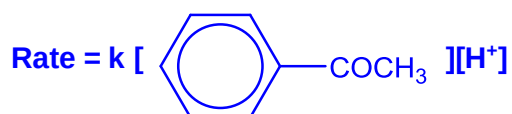
- (iii) Hence, suggest the reagents and conditions used in the following conversion, stating clearly the intermediate products in the process of synthesis. [2]





- (e) The rate of reaction between phenylethanone and iodine in acid medium to give 2-iodo-1-phenylethanone, , is found to be independent of $[I_2]$, but directly proportional to $[H^+]$ and directly proportional to [phenylethanone].

- (i) Write the rate equation for this reaction and state the overall order and the units of the rate constant. [2]



Overall order = 2, units: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

- (ii) The reaction between phenylethanone and bromine proceeds by a similar mechanism. How would you expect the rate of this reaction to compare with that of the above reaction? Explain your answer. [1]

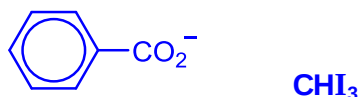
The reaction rate is unchanged as it is also independent of $[Br_2]$ like I_2 .

- (iii) When a basic medium is used instead for the reaction between phenylethanone and iodine, a different mechanism of reaction is followed and different organic products are produced.

- (I) State the type of reaction undergone. [1]

Triiodomethane/iodoform reaction.

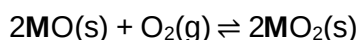
- (II) Give the structures of all the organic products formed in this reaction. [2]



[Total: 20]

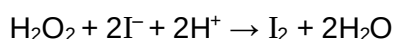
- 3 Fireworks are a traditional part of many celebrations. Their colours can come from heating of Group II metals and their salts. These salts often contain anions such as chlorates, perchlorates, and nitrates which are oxidising agents.

- (a) One of the Group II metals, **M**, when heated with oxygen under pressure, forms a metal peroxide which can be used as an oxidising agent in fireworks to produce a vivid green colour. The equation for the reaction is shown below:

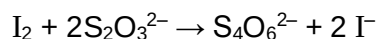


When equilibrium is attained, the mixture of oxides was found to have a mass of 1.60 g, where **MO**₂ has a percentage mass of 18.7%. When the mixture was treated with dilute sulfuric acid, a white solid was precipitated and a solution of hydrogen peroxide was produced.

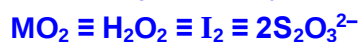
An excess of acidified potassium iodide was added to the hydrogen peroxide solution. The reaction between hydrogen peroxide and acidified potassium iodide is as follows.



The iodine liberated needed 11.80 cm³ of 0.300 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃, for complete reaction.



- (i) Write a balanced equation to represent the reaction between **MO**₂ and sulfuric acid.[1]
MO₂ + H₂SO₄ → MSO₄ + H₂O₂
- (ii) By determining the amount of **MO**₂ that has reacted, calculate the relative atomic mass of **M** and suggest its identity. [5]



$$\text{Amount of S}_2\text{O}_3^{2-} = 11.8 \times 10^{-3} \times 0.3$$

$$= 3.54 \times 10^{-3} \text{ mol}$$

$$\text{Amount of MO}_2 = 0.5 \times 3.54 \times 10^{-3}$$

$$= 1.77 \times 10^{-3} \text{ mol}$$

Let the relative atomic mass of **M** be x g

$$\text{Mass of MO}_2 = (x + 2 \times 16.0) \times 1.77 \times 10^{-3}$$

$$\frac{18.7}{100} \times 1.60 = (x + 2 \times 16.0) \times 1.77 \times 10^{-3}$$

$$x = 137$$

Identity of **M**: Barium

- (b) Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$ is an oxidising agent and is commonly used as a red colouring agent in fireworks.

- (i) Write a balanced equation for the reaction that occurs when $\text{Sr}(\text{NO}_3)_2$ undergoes thermal decomposition. [1]



- (ii) Predict whether the decomposition temperature of $\text{Sr}(\text{NO}_3)_2$ will be higher or lower than the decomposition temperature of $\text{Mg}(\text{NO}_3)_2$. Explain your answer. [3]

Higher.

cationic radius Sr^{2+} is larger than that of Mg^{2+} and charge density or polarising power of Sr^{2+} is smaller.

electron cloud of NO_3^- anion is less distorted, N-O bond weakened to a smaller extent, does not break as easily.

Thus $\text{Sr}(\text{NO}_3)_2$ is thermally more stable than MgNO_3 , and decomposition temperature is higher.

- (c) Another oxidising agent used in fireworks is potassium chlorate(V), KClO_3 . When KClO_3 undergoes thermal decomposition, two products are obtained, one of which is KCl .

- (i) Write a balanced equation to show how KClO_3 is produced from Cl_2 gas and hot, aqueous potassium hydroxide. [1]



- (ii) Write a balanced equation for the thermal decomposition of KClO_3 and hence suggest why KClO_3 is an important ingredient used in fireworks. [2]



O_2 gas is produced when heat is applied to potassium chlorate. O_2 gas supports subsequent combustion of fireworks/explosives, therefore it is an important ingredient.

- (d) Fireworks which produce bright sparks, flashes and coloured flames also involve the elements phosphorus, sulfur and chlorine.

The table below gives the melting points of these elements.

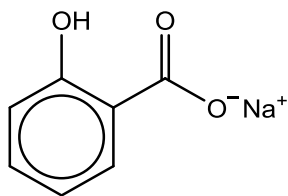
element	phosphorus	sulfur	chlorine
melting point / K	317	392	172

In terms of structure and bonding, explain why sulfur has the highest melting point among the three elements. [2]

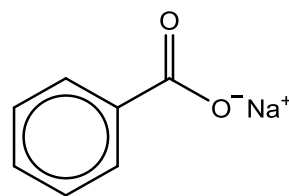
All 3 elements exist as simple covalent molecules with van der Waals' forces between the molecules.

S_8 has the largest number of electrons, compared to P_4 and Cl_2 ; it has the strongest van der Waals' forces, hence it needs the largest amount of energy to overcome these attractions during melting.

- (e) Sodium salicylate and sodium benzoate are used as whistle mixes in fireworks. Both are white crystalline powder.



sodium salicylate



sodium benzoate

- (i) Suggest methods by which sodium salicylate and sodium benzoate can be distinguished from each other by a simple chemical test. State the reagents and conditions used and the expected observations for each compound. [2]

Method 1

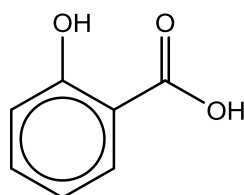
To 2 separate test tubes containing sodium salicylate and sodium benzoate, add neutral $\text{FeCl}_3(\text{aq})$. A violet colouration will be observed in the test tube containing sodium salicylate. No violet colouration is seen in the test tube containing sodium benzoate.

OR

Method 2

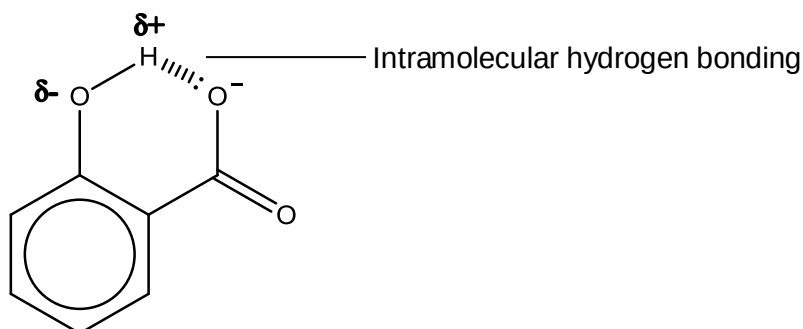
To 2 separate test tubes containing sodium salicylate and sodium benzoate, add aqueous Br_2 and shake. White precipitate formed in test tube containing sodium salicylate and orange bromine water decolourises. Orange aqueous bromine water remains orange in test tube containing sodium benzoate.

- (ii) The pK_a values of the two acidic groups in salicylic acid are $\text{pK}_{a1} = 2.98$ and $\text{pK}_{a2} = 13.6$.



salicylic acid

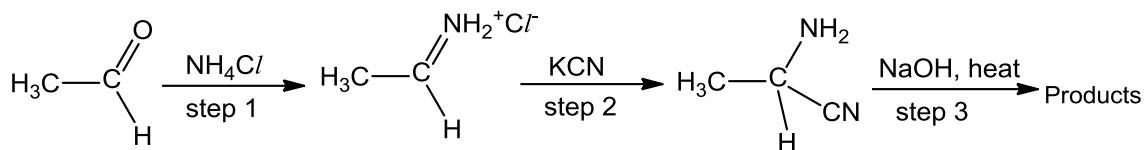
Draw the displayed formula of the mono-anion produced after the dissociation of the carboxylic acid group and use your formula to explain why the dissociation of the phenol group is unlikely to occur. [3]



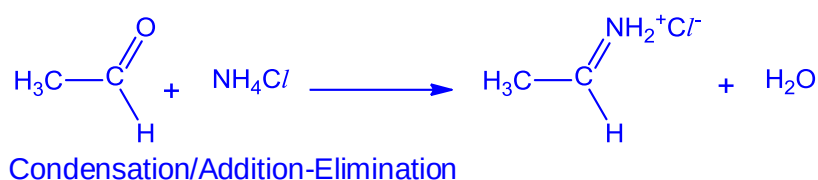
[Total: 20]

- 4 Strecker synthesis is a method used for the synthesis of amino acids. It is often studied due to the simplicity of the process.

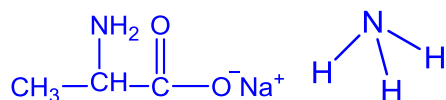
(a) Alanine, an amino acid, can be formed using this method as shown below.



- (i) Construct a balanced equation for step 1 and suggest the type of reaction that has occurred. [2]



- (ii) Give the structural formulae for all the products formed in step 3. [2]



- (b) Insulin is a hormonal protein which was first discovered in 1921. In 1959, it became the first protein to have its primary structure determined. These led to the award of two Nobel Prizes, in Physiology/Medicine and Chemistry respectively.

The basic unit of insulin consists of two polypeptides, A-chain and B-chain. A-chain has 21 amino acid residues, and some of these are listed in the following table (You may use the abbreviations for your answers).

amino acid	abbreviation	formula of R group side chain at pH 7.4 (physiological pH)	number of amino acid residues in A-chain
cysteine	cys	$-\text{CH}_2\text{SH}$	4
glutamic acid	glu	$-\text{CH}_2\text{CH}_2\text{CO}_2^-$	2
glutamine	gln	$-\text{CH}_2\text{CH}_2\text{CONH}_2$	2
glycine	gly	$-\text{H}$	1
isoleucine	ile	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	2
threonine	thr	$-\text{CH}(\text{OH})\text{CH}_3$	1
valine	val	$-\text{CH}(\text{CH}_3)_2$	1

In order to determine the sequence of the A-chain, partial hydrolysis was carried out with two separate methods to obtain several polypeptide fragments. One method of hydrolysis involves the use of $6 \text{ mol dm}^{-3} \text{ HCl}$ or NaOH , while the other method causes hydrolysis at specific peptide bonds.

- (i) State what may be used in the method for the hydrolysis at specific peptide bonds.[1]
Enzyme

- (ii) One of the polypeptides was isolated and subjected for further hydrolysis giving the following smaller tri-peptide fragments.

cys-cys-thr, ile-val-glu, glu-gln-cys, gly-ile-val

Using the same abbreviations, write out the amino acid sequence of the **smallest** polypeptide that could produce the above fragments. [2]

gly-ile-val-glu-gln-cys-cys-thr

- (iii) Describe the tertiary structure of insulin A-chain, include the type of bondings or interactions with reference to all the relevant amino acid residues listed in the above table. [4]

The tertiary structure of insulin A-chain is the overall 3-dimensional shape of the protein resulting from folding or coiling of the chains due to various R-group interactions within a polypeptide chain. These may be hydrogen bonding between R-groups of gln and thr residues, covalent disulfide linkages between sulfur of cys residues and van der Waals' between R-groups of gly,ile and val residues.

- (iv) In further confirmation of structures of insulin, chemicals can be used to affect the structures. Suggest one type of bond or interaction from your answer in **(b)(iii)** that can be broken by chemicals and state the chemicals that can be used. [2]

Disulfide linkage can be broken by heavy metal ions, such as Ag^+ or Hg^{2+} , hence either AgNO_3 or $\text{Hg}(\text{NO}_3)_2$ can be used.

- (v) Zinc has an important role in the the production, storage and use of insulin. Zinc cation can bind to insulin through interactions with the amino acids. Suggest the type of interaction and state an amino acid that may be involved. [1]

Ionic interactions with glutamic acid (glu); OR ion-dipole attractions with threonine (thr) or glutamine (gln); OR Covalent dative bonds with glutamic acid (glu), threonine (thr) or glutamin (gln).

- (c) Zinc compounds are often used in paints for various purposes. The properties of some of these compounds are given below.

compound	solubility product, K_{sp}	use in paints
Zn(OH)_2	3.00×10^{-17}	White pigment
ZnS	3.21×10^{-23}	Luminous pigment
ZnCO_3	1.46×10^{-10}	Fire Retardant

- (i) Write an expression for K_{sp} for Zn(OH)_2 and determine its solubility. Hence, calculate the pH of a saturated solution of Zn(OH)_2 . [4]



$$K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

Let solubility of Zn(OH)_2 be $x \text{ mol dm}^{-3}$

$$K_{sp} = (x)(2x)^2$$

$$3.00 \times 10^{-17} = 4x^3$$

$$x = \sqrt[3]{\frac{3.00 \times 10^{-17}}{4}} = 1.96 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[\text{OH}^-] = 2x = 2(1.96 \times 10^{-6}) = 3.92 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg (3.92 \times 10^{-6}) = 5.41$$

$$\text{pH} = 14 - 5.41 = 8.59$$

- (ii) In preparation of a water-based luminous paint mixture, all 3 of the above compounds have to be precipitated. Given that concentration of Zn^{2+} is $2.00 \times 10^{-7} \text{ mol dm}^{-3}$, calculate the minimum amount of S^{2-} that must be present in 250 cm^3 of this mixture. [2]

For precipitation, $[\text{Zn}^{2+}][\text{S}^{2-}] > K_{sp}$

$$[\text{S}^{2-}] > 3.21 \times 10^{-23} / 2.00 \times 10^{-7}$$

$$[\text{S}^{2-}] > 1.605 \times 10^{-16}$$

$$\text{Minimum amount of } \text{S}^{2-} = 1.605 \times 10^{-16} \times 250/1000$$

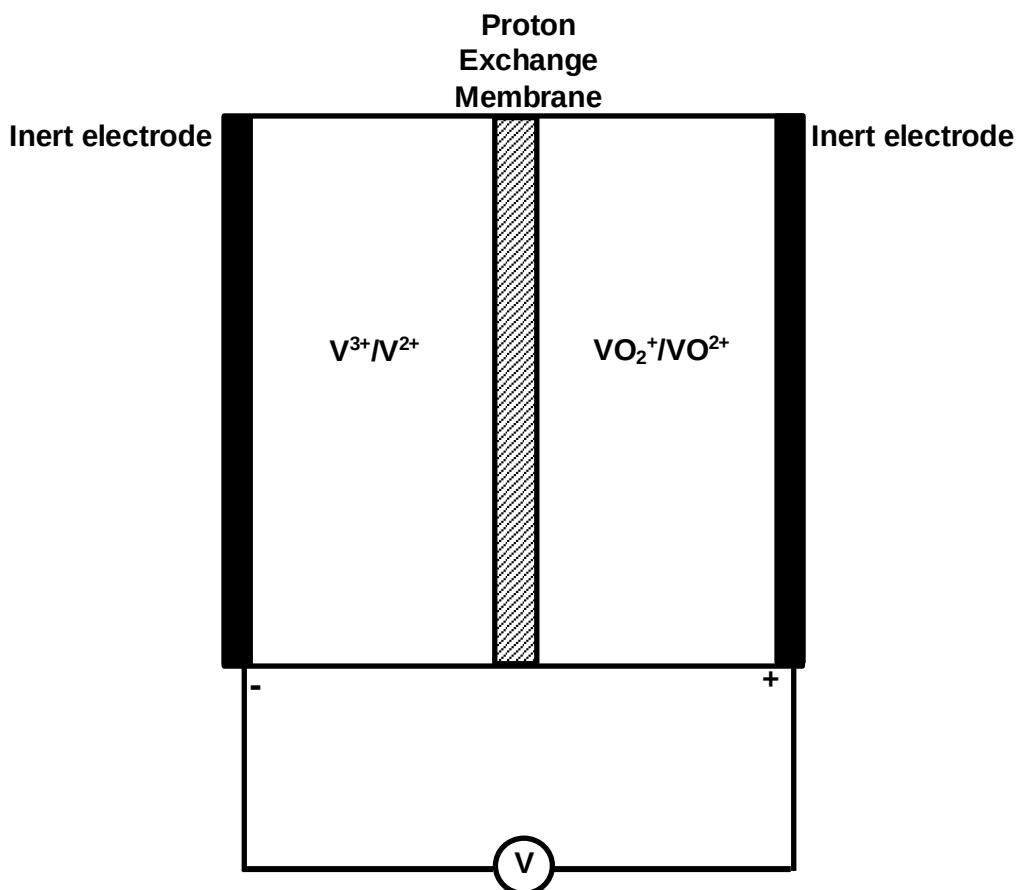
$$= 4.0125 \times 10^{-17} \text{ mol} = 4.02 \times 10^{-17} \text{ mol}$$

[Total: 20]

5 Use of the Data Booklet is relevant to this question.

A redox flow battery is a type of rechargeable battery where rechargeability is provided by two chemical components dissolved in liquids contained within the system. The two half-cells are separated by a ion-exchange membrane instead of a salt bridge. A typical redox flow battery uses vanadium ions and inert electrodes.

- (a) Vanadium flow battery stores energy using vanadium redox couples. During the discharge cycle, V^{2+} loses an electron to the external circuit to form V^{3+} in the negative half-cell and acidified VO_2^+ accepts an electron from the external circuit to form VO^{2+} in the positive half-cell.



- (i) Write out the two half-equations for the electrode processes that occur at the two half-cells. [2]
Negative half-cell: $V^{2+} \rightarrow V^{3+} + e^-$
Positive half-cell: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$
- (ii) Calculate the e.m.f. of the cell. [1]
 $E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{oxi}} = (+1.00) - (-0.26) = +1.26V$
- (iii) Suggest why vanadium ions can be used in this redox flow battery. [1]
Ability to exist in different oxidation states
- (iv) Suggest the role of a proton exchange membrane. [1]
To maintain electrical neutrality

- (b) Calcium hydride is used in the synthesis of proton exchange membrane used in the vanadium flow battery. Data about calcium and vanadium are given below.

	Calcium	Vanadium
Electronic configuration	[Ar]4s ²	[Ar]3d ³ 4s ²
Relative atomic mass	40.1	50.9
Atomic radius/ nm	0.197	0.122
Density/ g cm ⁻³	1.54	6.07

- (i) Using relevant data from the table, suggest why the density of vanadium is significantly greater than that of calcium. [2]

Both vanadium and calcium have a metallic structure. The relative atomic mass of vanadium is higher than that of calcium. The atomic volume ($V = \frac{4}{3}\pi r^3$) of vanadium is lower than that of calcium due to its smaller atomic radius.

With the greater A_r of vanadium and its smaller atomic volume, the density of vanadium is significantly higher since density = mass/volume.

- (ii) Explain why vanadium compounds are usually coloured whereas calcium compounds are usually colourless. [4]

Vanadium compounds are usually coloured because they have incompletely filled d- orbitals. In the presence of ligands, the 3d orbitals become non-degenerate and split into two groups with slightly different energy (d-d* splitting). When a d-electron from the lower energy group is promoted to the higher energy group (d-d* electronic transition), radiation in the visible region of the electromagnetic spectrum is absorbed. The complementary colour not absorbed will be seen.

Calcium compounds are usually colourless because they have no d-electrons and so, d-d* electronic transition cannot take place.

- (c) Compounds of calcium contain the Ca²⁺ ion. The corresponding ion of vanadium is V²⁺.

- (i) Write an equation to show the third ionization energy for calcium. [1]
 $\text{Ca}^{2+}(\text{g}) \rightarrow \text{Ca}^{3+}(\text{g}) + \text{e}^-$

- (ii) Hence explain why Ca³⁺ compounds do not exist whilst V³⁺ compounds do. [2]

Formation of Ca³⁺ involves removing an electron from the inner principal quantum shell (3p subshell) which is more strongly attracted by the nucleus and this requires a large amount of energy to remove the electron. Hence Ca³⁺ compounds do not exist.

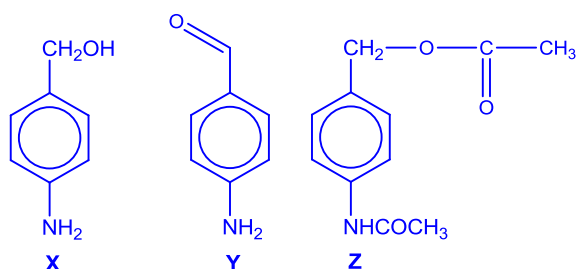
Formation of V³⁺ involves removal of electrons from the 3d orbital which has a comparable energy with that of 4s orbital. Therefore, it is less strongly attracted by the nucleus and this requires much less energy to remove the electron. Hence V³⁺ compounds can be formed.

(d) The following properties and reactions are exhibited by Compound **X**, C_7H_9ON .

- Compound **X** is insoluble in dilute NaOH, but dissolves in dilute HCl(aq).
- On reaction with acidified potassium dichromate(VI) under certain condition, compound **X** forms compound **Y**, C_7H_7ON .
- On reaction with ethanoyl chloride, CH_3COCl , **X** forms compound **Z**, $C_{11}H_{13}NO_3$.

Deduce the structures of compounds **X**, **Y** and **Z**. Explain the chemistry of the reactions described. Write an equation for the formation of compound **Z**. [6]

Structures of **X**, **Y** and **Z** are:

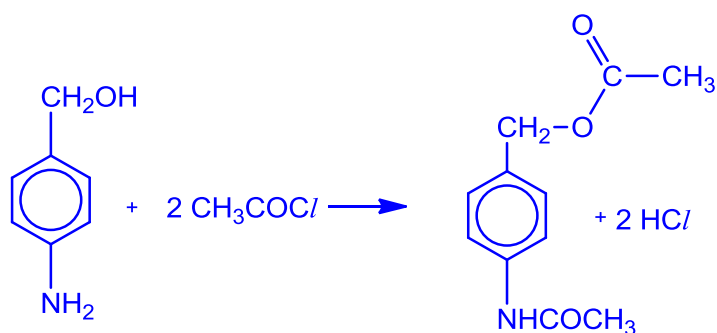


Compound **X** dissolves in HCl(aq) shows that it contains a basic group.

Compound **X** does not dissolve in NaOH(aq), Hence, it does not contain a phenol group.

Compound **X** undergo oxidation with acidified potassium dichromate (VI) and therefore, it is a (primary/secondary) alcohol.

Compound **X** undergo condensation/ acylation/ addition-elimination with ethanoyl chloride to give compound **Z**.



[Total: 20]

Name:		Index Number:		Class:	



DUNMAN HIGH SCHOOL
Preliminary Examinations 2016
Year 6

H2 CHEMISTRY

9647/01

Paper 1 Multiple Choice

27 September 2016

1 hour

Additional Materials: Optical Mark Sheet
 Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name** and **class** on this question paper.
- 2 There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical Mark Sheet.
- 3 Each correct answer will score one mark. A mark will not be deducted for wrong answer.
- 4 Any rough working should be done in this booklet.
- 5 You may use a calculator.

Section A

For each question, there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 Ferrous sulfate (FeSO_4) tablets are commonly prescribed by doctors as 350 mg tablets and serve as a dietary supplement for pregnant women. However, it was found that these tablets may cause poisoning in young children if accidentally consumed. The lethal dosage for a 12.0 kg child is 590 mg of Fe^{2+} .

What is the minimum number of tablets that would constitute a lethal dose to a 12.0 kg child?

- A 1
- B 2
- C 4
- D 5

- 2 25.0 cm^3 of a solution of $0.0518 \text{ mol dm}^{-3}$ hydroxylammonium chloride, $\text{NH}_3\text{OH}^+\text{Cl}^-$ was added to a solution containing an excess of acidified Fe^{3+} ions and the mixture boiled. The Fe^{2+} ions in the resultant solution was titrated with 25.90 cm^3 of 0.02 mol dm^{-3} potassium manganate (VII) solution.

Given the mole ratio $\text{MnO}_4^- \equiv 5\text{Fe}^{2+}$, which of the following nitrogen-containing species is formed in the reaction?

- A NH_4^+
- B N_2O
- C NO_2
- D NO_3^-

- 3 Two elements, **Y** and **Z**, have the following properties.

Property 1: **Y** and **Z** form ionic compounds Na_3Y and Na_3Z respectively.

Property 2: Element **Z** forms ZCl_5 molecule whereas **Y** is unable to form YCl_5 .

Which pair of electronic configurations of **Y** and **Z** is correct?

	Y	Z
A	$[\text{He}] 2s^2 2p^2$	$[\text{Ne}] 3s^2 3p^3$
B	$[\text{He}] 2s^2 2p^3$	$[\text{Ne}] 3s^2 3p^3$
C	$[\text{He}] 2s^2 2p^2$	$[\text{He}] 2s^2 2p^3$
D	$[\text{Ne}] 3s^2 3p^2$	$[\text{Ne}] 3s^2 3p^3$

- 4 For one mole of an ideal gas, which plot produces a straight line graph passing through the origin?

	Y-axis	X-axis	
A	PV	P	at constant T (K)
B	P	V	at constant T (K)
C	P/p	T (°C)	at constant V
D	P	1/V	at constant T (K)

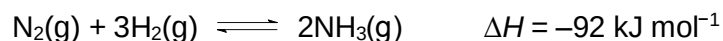
- 5 Use of *Data Booklet* is relevant to this question.
Which substance is considered to have the largest covalent character?

A AlF_3 B Al_2O_3 C Be_3N_2 D BeO

- 6 Which substance does **not** contain an atom that has an unpaired electron?

A ClO_2 B NO C NO_2 D N_2O

- 7 Ammonia is made via the Haber Process. The reactants are nitrogen and hydrogen.



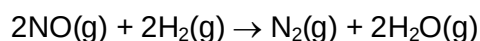
What will increase the rate of the forward reaction?

- A Adding argon to the mixture but keeping the total volume constant.
 B Decreasing the temperature.
 C Increasing the total pressure by reducing the total volume at constant temperature.
 D Removing nitrogen from the mixture but keeping the total volume of the mixture the same.
- 8 How much water must be added to a 10 cm^3 solution of 0.05 mol dm^{-3} sulfuric acid in order to increase its pH to 2.0?
- A 10 cm^3
 B 50 cm^3
 C 90 cm^3
 D 100 cm^3

- 9 Given that the K_{sp} for magnesium hydroxide, $Mg(OH)_2$, is $1.80 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ at 298 K, calculate the pH of a saturated solution of $Mg(OH)_2$.

- A 3.48
B 3.78
C 10.2
D 10.5

- 10 The reaction of nitrogen monoxide and hydrogen gas



is hypothesised to involve the following steps:

- I $NO + NO \rightleftharpoons N_2O_2$ (fast)
II $N_2O_2 + H_2 \rightarrow H_2O + N_2O$ (slow)
III $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

Which of the following is true about the reaction?

- A H_2 acts as a catalyst in this reaction.
B The overall order of the reaction is 2.
C There are 2 intermediates present in the reaction mechanism.
D Increasing the concentration of NO will increase the rate constant.
- 11 The radius and charge of each of the six ions are shown in the table.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

Which of the following pair shows the first compound having a smaller magnitude of lattice energy than the second?

- A JX, MZ
B JX, LX
C JY, LX
D MZ, LY

- 12** The common rubber band has very interesting thermodynamic properties due to its randomly coiled long polymeric molecular structure. When the rubber band is stretched, a slight warming effect is felt.

What are the correct signs of ΔS , ΔH and ΔG if the stretched rubber band is released quickly?

	ΔS	ΔH	ΔG
A	+	+	–
B	+	–	+
C	–	–	+
D	–	+	–

- 13** The nickel–cadmium cell is a rechargeable battery which contains an alkaline electrolyte such as aqueous KOH.

During the discharging process, Cd is oxidised to solid $\text{Cd}(\text{OH})_2$ while $\text{NiO}(\text{OH})$ is reduced to solid $\text{Ni}(\text{OH})_2$.

Which statement is true about this rechargeable battery?

- A** Water is produced in the discharging process.
- B** The mass of cadmium remains unchanged.
- C** The alkaline electrolyte can be replaced by an acid.
- D** The concentration of the alkaline electrolyte remains unchanged in the discharging process.
- 14** Which statement regarding the oxides across Period 3 is true?
- A** The covalent character decreases from Na to S.
- B** The oxides of the elements changes from basic to neutral then to acidic from Na to S.
- C** The oxides formed are increasing soluble in water from Na to S.
- D** The standard entropy change of formation of the oxides becomes more negative from Na to Al.

- 15** The following information is about a Period 3 element **L**.

The oxide of **L** is a solid at room temperature.

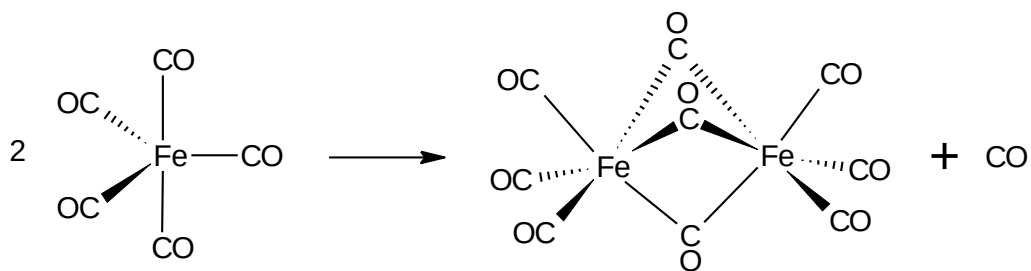
The oxide of **L**, when added to water, gives a non-acidic solution.

The aqueous chloride of **L** gives a white precipitate with aqueous sodium hydroxide.

In which Group of the Periodic Table could **L** be found?

- A** V only
 - B** I and III only
 - C** II and III only
 - D** II, III and IV only
- 16** Which property shows an increasing trend down Group II from Mg to Ba?
- A** Polarising power of metal cation
 - B** Second ionisation energy
 - C** Reducing strength
 - D** Melting point
- 17** Which statement regarding the halogens or their hydrides is correct?
- A** HCl has a higher melting point than HF due to its larger electron cloud.
 - B** Iodine, when dissolved in hexane, gives a colour that is similar to its vapour.
 - C** The halogens become less volatile from fluorine to iodine due to the weaker covalent bonds.
 - D** HF is less thermally stable than HI because of the larger electronegativity difference between the H and F atoms.

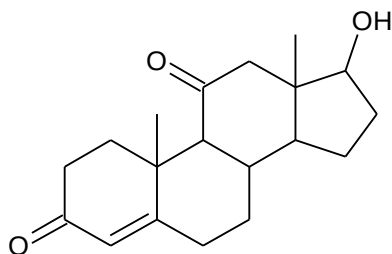
- 18 Photolysis of a solution of $\text{Fe}(\text{CO})_5$ in ethanoic acid produces $\text{Fe}_2(\text{CO})_9$ according to the following equation.



What is the oxidation state of Fe in $\text{Fe}(\text{CO})_5$ and the coordination number of Fe in $\text{Fe}_2(\text{CO})_9$?

	oxidation state of Fe in $\text{Fe}(\text{CO})_5$	coordination number of Fe in $\text{Fe}_2(\text{CO})_9$
A	+5	9
B	+5	6
C	0	9
D	0	6

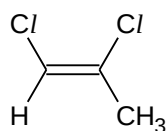
- 19 The structure of 11-ketotestosterone, a sex hormone in fish, is shown below.



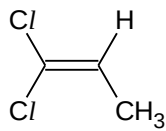
Which statement about 11-ketotestosterone is correct?

- A Its molecular formula is $\text{C}_{19}\text{H}_{26}\text{O}_3$.
- B It has a total of 2^7 stereoisomers.
- C It has six sp^2 -hybridised carbon atoms.
- D It has a tertiary alcohol functional group.

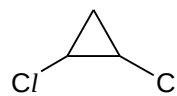
- 20 The following compounds have the same molecular formula.



X



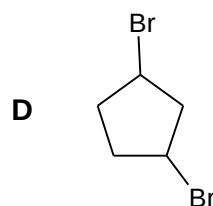
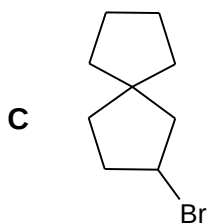
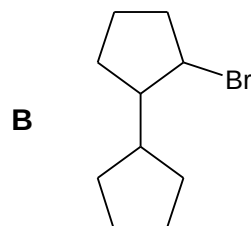
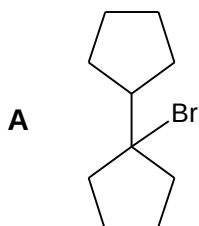
Y



Z

Which of the following best describes the isomeric relationships between the compounds?

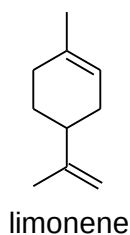
	X and Y	Y and Z
A	chain	optical
B	positional	functional group
C	cis-trans	positional
D	positional	chain
- 21 Which of the following is a **non**-greenhouse gas that could be released from the catalytic converter of a car exhaust?
- A CO_2
 B H_2O
 C CH_4
 D N_2
- 22 Which compound is **not** possibly formed when cyclopentane is reacted with excess bromine gas in the presence of ultraviolet light?



- 23** Carbonyl groups in aldehydes and ketones, $C=O$, undergo nucleophilic addition while alkene groups, $C=C$, undergo electrophilic addition.

Which statement explains the above reactions?

- A** Oxygen is more reactive than carbon.
B The different lengths of the double bonds.
C The different strengths of the double bonds.
D The electronegativity difference between the carbon and oxygen atoms in the carbonyl group.
- 24** The citrus flavour of lemons is due to the compound limonene, present in both the peel and the juice.



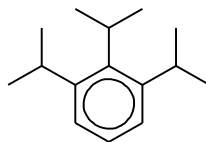
Limonene is separately treated with

- cold, dilute acidified $KMnO_4$,
- hot, concentrated acidified $KMnO_4$.

What is the change in the **number** of chiral carbon atoms in the molecule during each reaction?

	cold, dilute acidified $KMnO_4$	hot, concentrated acidified $KMnO_4$
A	+3	0
B	+3	-1
C	+4	0
D	+4	-1

- 25 The diagram shows the structure of a derivative of propofol.

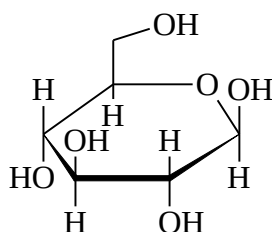


When reacted with a dilute solution of Cl_2 , a chlorine atom may substitute a hydrogen atom on the benzene ring but **not** for a hydrogen atom on the alkyl branches.

Given that any number of the benzene hydrogen atoms may be substituted, how many possible products of the reaction are there?

- A 3
 B 4
 C 5
 D 6
- 26 In the body, cellular respiration produces energy from the oxidation of glucose.

The diagram shows the structure of glucose.

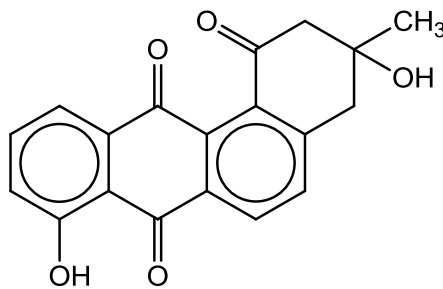


A new artificial sweetener has been produced by replacing all of the hydroxyl groups attached directly to the ring carbon atoms in glucose with chlorine atoms.

What is the empirical formula of this chlorinated glucose?

- A CH_2Cl
 B $\text{C}_3\text{H}_4\text{Cl}_2\text{O}$
 C $\text{C}_6\text{H}_7\text{Cl}_5\text{O}$
 D $\text{C}_6\text{H}_8\text{Cl}_4\text{O}_2$

- 27 *Tetrangomycin* is one of the first member of the class of antibiotics under the angucycline group. What is the maximum number of optical isomers that can be obtained when 1 mole of *tetrangomycin* fully reacts with NaBH_4 ?



Tetrangomycin

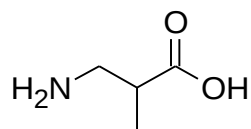
- A 2
B 8
C 16
D 32
- 28 The small hive beetle, which invades colonies of the honeybee, identifies these colonies by detecting the bees' own alarm signal, the pheromone 3-methylbutyl ethanoate.

How may this ester be made in the laboratory?

- A $\text{CH}_3\text{COCl} + (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH} \rightarrow \text{ester} + \text{HCl}$
 B $\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH} \rightarrow \text{ester} + \text{HCl}$
 C $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{heat}]{\text{conc. H}_2\text{SO}_4} \text{ester} + \text{H}_2\text{O}$
 D $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{heat}]{\text{conc. H}_2\text{SO}_4} \text{ester} + \text{H}_2\text{O}$

- 29 Why are amides, RCONH_2 , less basic than amines, RNH_2 ?
- A Amides form a zwitterion in which the nitrogen atom carries a positive charge.
 B Amides have a resonance structure involving the movement of a pair of electrons from the nitrogen atom to the oxygen atom.
 C Electrons on the nitrogen atom of amides move on the C-N bond giving it some double bond character so that it is more difficult to break.
 D The amide carbonyl group withdraws electrons from the $-\text{NH}_2$ group to make the hydrogen atoms acidic.

- 30 3-aminoisobutyric acid was shown to prevent diet induced diabetes in mouse. It has the structure shown below.



Which statement about 3-aminoisobutyric acid is **not** true?

- A It migrates to the cathode at pH 10.
- B It exists predominately as a zwitterion at pH 7.
- C It reacts with ethanoyl chloride to form an amide.
- D It exists as a crystalline solid at room temperature.

Section B

For each question, one or more of the three numbered statements **1** to **3** may be correct.

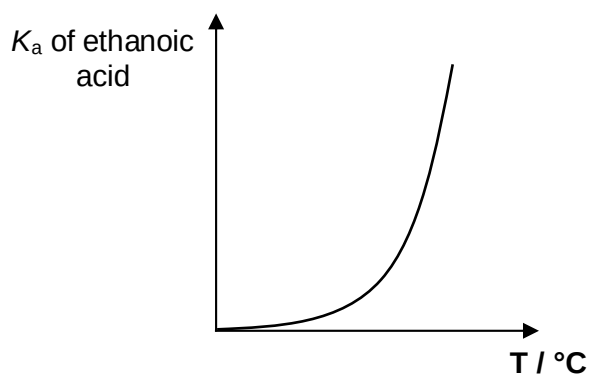
Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Which statement about ethanoic acid can be deduced from the sketch below?



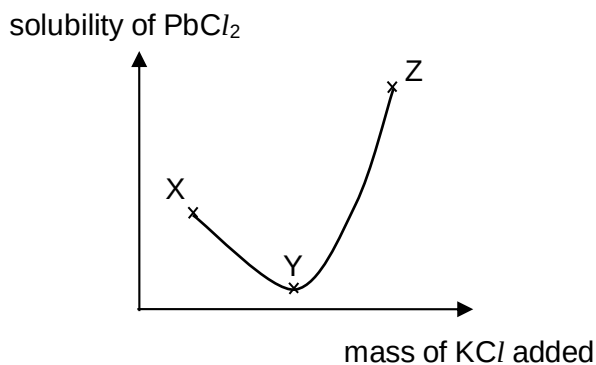
- 1** The ionic dissociation of ethanoic acid is an endothermic process.
- 2** The pH of the ethanoic acid decreases with increasing temperature.
- 3** At $T = 40\text{ }^{\circ}\text{C}$, $\text{pH of ethanoic acid} = 14 - \text{pOH}$

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

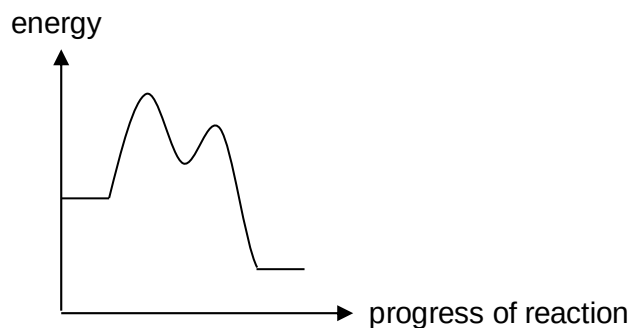
- 32** The following graph represents how the solubility of a sparingly soluble salt lead(II) chloride, PbCl_2 , changes upon addition of solid potassium chloride.



Which statement is correct?

- 1** The K_{sp} value decreases along XY and then increases along YZ.
 - 2** The change in solubility along XY is caused by common ion effect.
 - 3** The change in solubility along YZ is caused by the formation of a complex between Pb^{2+} and Cl^- ions.
- 33** In a chemical reaction, **P** reacts with **Q** to form **R**. The rate equation is found to be $\text{rate} = k [\text{P}] [\text{Q}]$.

The energy profile diagram for the reaction is as shown.



Which is the likely overall equation of the above reaction?

- 1** $2\text{P} + \text{Q} \rightarrow \text{R}$
- 2** $\text{P} + 2\text{Q} \rightarrow \text{R}$
- 3** $\text{P} + \text{Q} \rightarrow \text{R}$

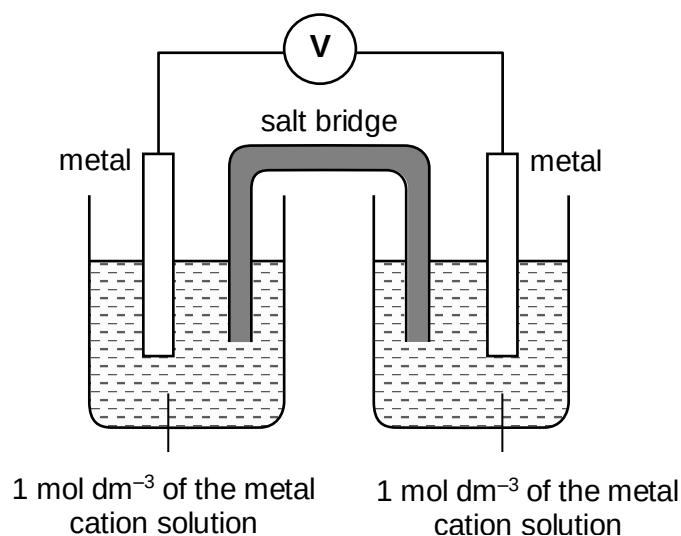
The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

34 *Use of the Data Booklet is relevant to this question.*

The half-cells for four metals: Mg, **X**, **Y** and **Z** were in turn connected in pairs and the potential difference was recorded at room temperature.



The results obtained are as shown in the table below.

positive electrode	negative electrode	$E^{\ominus} / \text{V}$
X	Mg	+2.10
Y	Mg	+2.72
Mg	Z	+0.33

Which of the following statements is true?

- 1** **Y** is likely to be copper metal.
- 2** **X** is stronger than **Y** in terms of reducing power.
- 3** Ease of oxidation of metals: **Z** < **X** < **Y**.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

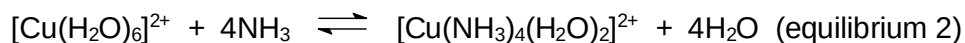
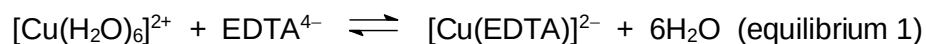
No other combination of statements is used as a correct response.

- 35** Solid **P** dissolves in aqueous chlorine to give a solution **Q** which gives precipitate **R** on adding excess aqueous sodium thiosulfate followed by aqueous lead(II) nitrate.

Which combination could agree with the procedure above?

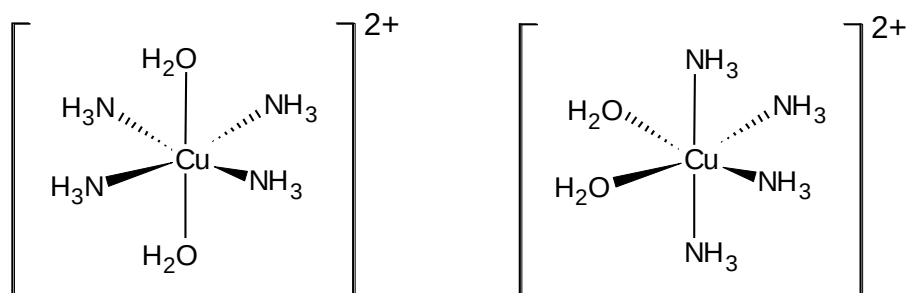
	Identity of P	Colour of Q	Colour of R
1	NaI	brown	mixture of white and bright yellow
2	NaBr	orange	white only
3	NaCl	colourless	white only

- 36** Consider the two reactions of $\text{Cu}^{2+}(\text{aq})$ below.



What can you deduce from the equilibria above?

- The entropy change of equilibrium 1 is more positive than that of equilibrium 2.
- $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ in equilibrium 2 has two possible isomers:



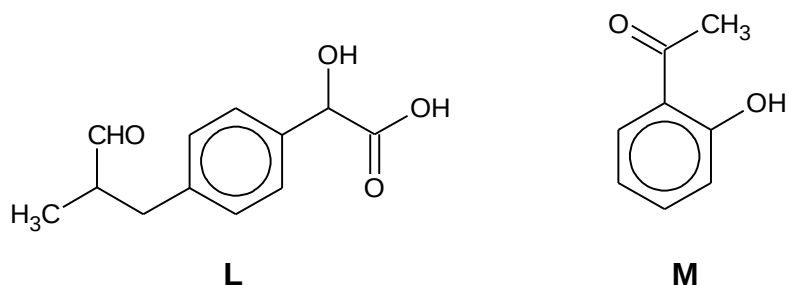
- EDTA⁴⁻ is a stronger ligand than NH₃.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

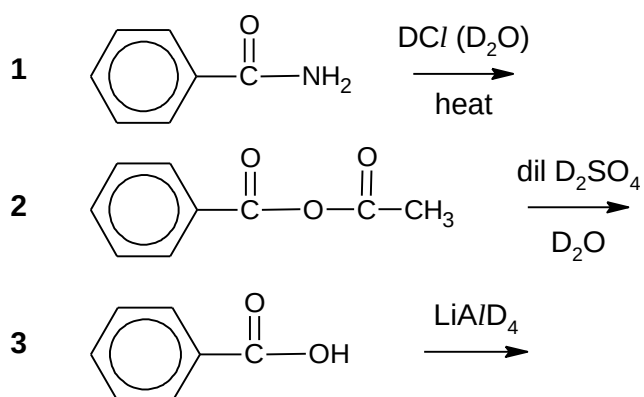
37 Compounds **L** and **M** are precursors to the synthesis of some analgesic drugs.



Which statement is true?

- 1** Only **L** reacts with KBr in concentrated H_2SO_4 to give a bromine-based compound under heat.
- 2** Both **L** and **M** react with HCN to form a product with at least one chiral carbon atom.
- 3** **L** is expected to be more acidic than **M**.

38 Which of the following will yield an organic compound containing deuterium? ($\text{D} = {}^2\text{H}$)

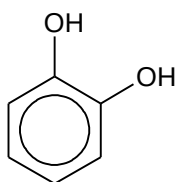


The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

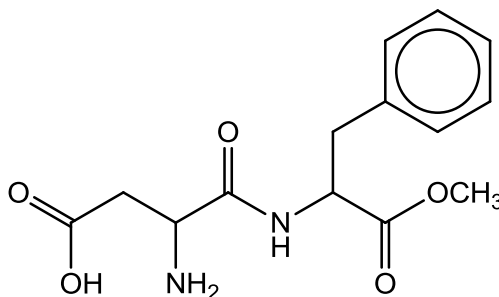
- 39** Which reagent can be used to distinguish catechol from benzene –1,2 – dicarboxylic acid?



catechol

- 1** Sodium bicarbonate solution
- 2** Neutral iron(III) chloride solution
- 3** Aqueous bromine solution

- 40** Aspartame is an artificial sweetener used as a sugar substitute in some foods and beverages. The structure is shown below:



Which deduction about the reactions of aspartame can be made from this structure?

- 1** It undergoes hydrolysis to form two α -amino acids.
- 2** It reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate.
- 3** The solution remains orange when heated with acidified potassium dichromate(VI).

Name:		Index Number:		Class:	



DUNMAN HIGH SCHOOL
Preliminary Examination 2016
Year 6

H2 CHEMISTRY

Paper 2 Structured

9647/02

16 September 2016

2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page.
- 2 Answer ***all*** questions.
- 3 Write your answers in the spaces provided on the question paper.
- 4 A *Data Booklet* is provided.
- 5 The number of marks is given in brackets [] at the end of each question or part question.
- 6 You may use a calculator.

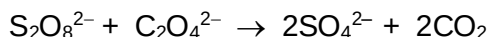
Question No.	1	2	3	4	5	Total	%
Marks	12	15	15	15	15	[72]	

This question paper consists of **16** printed pages and **2** blank pages.

Answer **all** questions in the spaces provided.

1 Planning (P)

The reaction between peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$, and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, is slow and can be catalysed by Cu^{2+} ions.



To determine the rate law of this reaction, it is necessary to selectively vary the concentrations of $\text{S}_2\text{O}_8^{2-}$ and $\text{C}_2\text{O}_4^{2-}$ ions and determine how the rate of reaction responds to these changes. The concentrations of the reactants are varied in such a way that one is in excess compared to the other in each experiment.

A suitable end point (the point at which the final time reading is made) for the experiments will be when the reaction produced the same volume of CO_2 gas. With the measured reaction time, relative rate of the reaction can be determined.

You are required to write a plan to determine the rate law of the reaction between $\text{S}_2\text{O}_8^{2-}$ and $\text{C}_2\text{O}_4^{2-}$ ions.

- (a) Suggest an explanation why this reaction is slow when performed in the absence of a catalyst.

[1]

- (b) You may assume that you are provided with

- 1.00 mol dm⁻³ peroxodisulfate ions
- 1.00 mol dm⁻³ ethanedioate ions
- 10 cm³ aqueous copper (II) ions
- the equipment and materials normally found in a school laboratory.

It can be assumed that a reactant is in excess if its volume is at least **five** times the volume of the other reactant used.

Your plan should include the following:

- quantities of reactants and condition you would use in **four** different reaction mixtures
- the measurements you would take
- an outline of how **one** of the reaction mixtures is prepared
- brief, but specific details of how the results would then be used to determine the rate law of reaction

[8]

- (c) Temperature can also affect the rate of reaction and the activation energy, E_a , of this reaction can be found by repeating the experiments at several different temperatures.

Using equation (1) and by means of a suitable graph, the activation energy of the reaction can be determined.

$$\ln (\text{relative rate}) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln (\text{constant}) \quad \text{--- (1)}$$

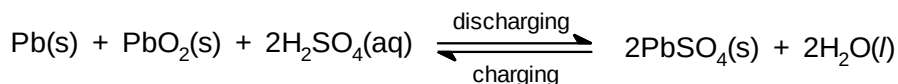
Briefly describe, with specific experimental details, of how the activation energy, E_a , of the reaction could be determined.

[3]

[Total: 12]

- 2 (a) A lead–acid car battery is a reversible cell that consists of a lead anode and a grid of lead coated with lead (IV) oxide as the cathode. The electrolyte is a 30% solution of sulfuric acid. When the cell supplies electric current to power the car, the process is known as discharging. The reversible process is thus known as charging.

The overall reaction that takes place in the lead–acid car battery is as follows:



- (i) Write the half–equations, with state symbols, for the reactions that take place at the anode and the cathode during the discharging process. Hence, state the polarity at the two electrodes.

	Half–equations	Polarity
Anode		
Cathode		

[3]

- (ii) When the lead and lead (IV) oxide have been converted to lead (II) sulfate, the cell can no longer give a current and the battery becomes flat. As the car moves, the generator then charges the battery. When the lead–acid battery is fully charged, the sulfuric acid has a relative density of about 1.275.

Predict and explain what happens to the relative density of the sulfuric acid during the discharging process.

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[2]

- (iii) Overcharging the lead–acid battery with high voltages causes hydrogen and one other gas to form. In addition, the electrolyte level is observed to have dropped.

Explain briefly what happens during overcharging and hence, suggest the identity of the other gas that is formed.

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[2]

- (iv) A simple rechargeable cell similar to that of lead–acid car battery may be constructed by dipping two lead electrodes into aqueous lead (II) nitrate and passing a current for a few minutes. During the charging process, lead (IV) oxide is deposited on one of the electrodes. By reference to the *Data Booklet*, calculate the value of $E^\ominus$ when the cell discharges.

[2]

- (v) The voltage of a typical lead–acid battery is 2.0 V. Explain the difference in the voltage and the $E^\ominus$ calculated in (a)(iv), based on the concentration of ions.

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[2]

- (b) (i) Pb^{2+} ions are often used in qualitative analysis to identify halide ions as they form insoluble precipitates. However, it is not an ideal test to distinguish between Cl^- and Br^- ions as both ions form white precipitate with Pb^{2+} ions.

Suggest another simple chemical test involving precipitation that could be used to distinguish between Cl^- and Br^- ions, stating clearly the steps and reagents involved and the expected observations.

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[2]

- (ii) With reference to your answer in (b)(i), explain the chemistry involved and writing equations where appropriate.

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[2]

[Total: 15]

- 3 Cobalt and vanadium are transition elements with more than one oxidation state and many of its compounds are coloured.

- (a) When a few drops of aqueous ammonia is added to a test-tube containing $\text{Co}^{3+}(\text{aq})$, a brown precipitate, **X** is observed. The chemical formula of **X** does not contain water molecules. The precipitate then dissolves in excess aqueous ammonia to give a cation **Y** which has a co-ordination number of 6.

- (i) Complete the electronic configuration of cobalt (III) ions.

Co^{3+} : $1s^2 2s^2 2p^6$ [1]

- (ii) Suggest the identities of **X** and **Y**.

X:

Y:

[2]

- (iii) With the use of appropriate ionic equations, explain the formation of **X** and **Y**.

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[3]

- (b) When concentrated hydrochloric acid is added to $\text{Co}^{2+}(\text{aq})$, the colour changes from pink to blue. When water is added to the blue solution, it returns to the pink colour.

The chemistry of $\text{Co}^{2+}(\text{aq})$ with concentrated hydrochloric acid closely resembles that of $\text{Cu}^{2+}(\text{aq})$.

Write a balanced ionic equation to account for the observations. In your answer, state the change in co-ordination number of cobalt ion in this reaction (if any).

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[2]

- (c) Vanadium is also another commercially important transition element.

- (i) Explain why V^{2+} is coloured.

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[2]

- (ii) V_2O_5 is used as a catalyst to speed up the conversion of SO_2 into SO_3 in the contact process for making sulfuric acid.



For the reaction above, explain clearly how the catalyst works.

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[2]

- (iii) When a 2:1 ratio of sulfur dioxide and oxygen is passed over V_2O_5 , the catalyst in a fixed volume steel vessel at 430°C , the percentage conversion of SO_2 to SO_3 is 95%.

Given that K_p is 7200 atm^{-1} at 430°C , calculate the initial total pressure, in atm, in the steel vessel.

[2]

- (iv) Comment on the effect on the rate of conversion if another unreactive but toxic gas was accidentally added to V_2O_5 .

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[1]

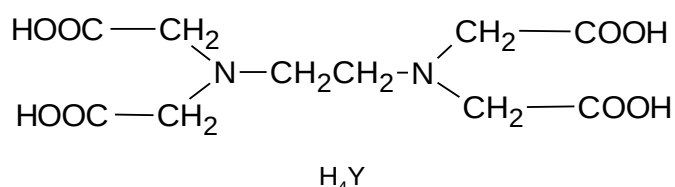
[Total: 15]

- 4 One of the factors that establishes the quality of a water supply is its degree of hardness. Water hardness is usually reported as parts per million (ppm) of calcium carbonate in the water sample.

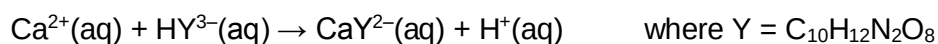
$$\text{ppm CaCO}_3 = \frac{\text{mass of CaCO}_3}{\text{mass of water}} \times 10^6$$

Water Supply Classification	
calcium carbonate (ppm)	Hardness Level
0–43	soft
43–150	slightly hard
150–300	moderately hard
300–450	hard
>450	very hard

Water hardness can be determined by titrating Ca^{2+} ions with ethylenediaminetetraacetic acid (represented by H_4Y).



The titration is often carried out in a buffered basic medium, where H_4Y exists mainly as HY^{3-} (buffered solution).



- (a) A 50 g sample of hard water was titrated against the buffered solution of concentration $0.0149 \text{ mol dm}^{-3}$. The volume of the buffered solution required was 25.55 cm^3 .
- (i) Calculate the mass of CaCO_3 present in the water sample.

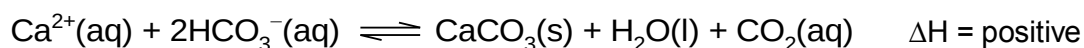
[1]

- (ii) Hence calculate the ppm of CaCO_3 in the water sample and determine its hardness level.

[2]

There are two types of water hardness, temporary and permanent. The difference is due to the presence of different dissolved calcium compounds in the water.

Temporary hardness is caused by the presence of dissolved calcium hydrogencarbonate, $\text{Ca}(\text{HCO}_3)_2$. This type of hardness is called temporary hardness because the calcium ions can be removed from the water causing it to precipitate as CaCO_3 .



- (b) Using the given equilibrium, suggest and explain one way how the removal of Ca^{2+} from the water sample can be enhanced.

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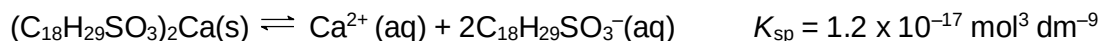
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[2]

A common detergent contains sodium dodecylbenzenesulfonate, $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$. In hard water, it is ineffective as a detergent because it reacts with calcium ions to give a precipitate.



A typical sample of hard water has a concentration of calcium ions of $2.5 \times 10^{-4} \text{ mol dm}^{-3}$.

- (c) (i) Calculate the maximum concentration of $\text{C}_{18}\text{H}_{29}\text{SO}_3^{-}$ in a solution of hard water.

[1]

The manufacturers claim that the detergent contains 17.4% by mass of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ [$M_r = 348$]. In hard water, 1.0 g of the detergent should be used per dm^3 of hard water.

- (ii) Calculate the number of moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ added to 1 dm^3 of hard water.

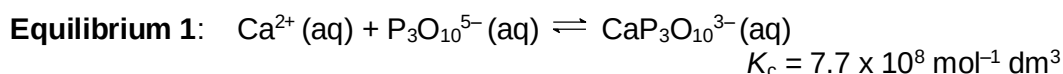
[1]

- (iii) Using your answer in (c)(i) and (c)(ii), show that 99% of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ in the detergent added will precipitate out of the hard water.

[2]

- (d) In order for the detergent to be used in hard water, sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, is added as a water softening agent.

The sodium tripolyphosphate 'softens' water by complexing with calcium ions.



- (i) Explain qualitatively why the addition of $\text{Na}_5\text{P}_3\text{O}_{10}$ will allow the detergent to be used in the hard water.

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[2]

- (ii) What is the oxidation state of phosphorus in sodium tripolyphosphate?

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[1]

- (iii) Suggest a likely structure for the tripolyphosphate anion.

[1]

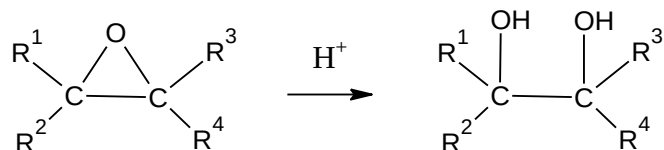
- (iv) Magnesium ions can also cause water hardness. It forms a complex with tripolyphosphate ions as well.

State the effect, if any, of adding magnesium ions on the equilibrium position and value of K_c of **Equilibrium 1** at constant temperature. Explain your answer.

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[2]

[Total: 15]

- 5 The male silk moth secretes 'juvenile hormone', $C_{16}H_{26}O_4$, which contains an unknown number of epoxide rings. Epoxide rings are readily hydrolysed by cold aqueous acid.



The reactions that 'juvenile hormone' and the resulting derivatives undergo are shown in the table below.

Reactant	Reagent	Result
'Juvenile hormone'	hydrogen in the presence of a palladium catalyst	S , $C_{16}H_{28}O_4$, formed.
	cold dilute hydrochloric acid	T , $C_{16}H_{30}O_6$, containing four alcoholic groups and three chiral centres is formed.
T	warmed with aqueous sodium hydroxide and then acidified	Methanol and U , $C_{15}H_{28}O_6$ are formed.
U	Mild oxidation	V , $C_{15}H_{24}O_6$, which has two alcoholic groups, is formed.
V	hot concentrated acidified $KMnO_4$	Two moles of carbon dioxide and one mole of W , $C_{13}H_{22}O_5$ are formed.
W	2,4 – dinitrophenylhydrazine reagent	orange precipitate formed.
	alkaline aqueous iodine	yellow precipitate formed.

In addition, it is known that 'juvenile hormone' has a continuous 12-carbon long backbone. There are **three methyl substituents** on the skeletal backbone of 'juvenile hormone' and that **each** methyl substituent is five carbon atoms apart from the next methyl substituent.

- (a) Give the products that will be formed when methylethyl ether, $CH_3OCH_2CH_3$ undergoes hydrolysis with aqueous acid.

[1]

- (b) State and explain the number of epoxide ring(s) in 'juvenile hormone'.

[2]

- (c) State the type of reaction that **T** has undergone and the functional group that it contains other than the four alcoholic groups.

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[1]

- (d) Classify the two alcoholic groups in **V** into either primary, secondary and tertiary alcohols. State the number of each alcohol and explain how you arrive at your conclusion.

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[2]

- (e) **V** produced an intermediate upon reacting with hot concentrated acidified KMnO_4 which eventually produced carbon dioxide. Draw the displayed formula of this intermediate.

[1]

- (f) State the type of reaction between **W** and 2,4 – dinitrophenylhydrazine reagent. State the deduction about **W** from the result of **W** reacting with aqueous alkaline iodine.

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[2]

(g) Suggest the structures for compounds **S** to **W** and for 'juvenile hormone'.

Compound	Structure
'Juvenile hormone'	
S	
T	
U	
V	
W	

[6]

[Total: 15]

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Name:		Index Number:		Class:	



DUNMAN HIGH SCHOOL
Preliminary Examination 2016
Year 6

H2 CHEMISTRY

9647/03

Paper 3 Free Response

20 September 2016

2 hours

Additional Materials: Data Booklet
Writing Papers
Graph Paper

INSTRUCTIONS TO CANDIDATES

Write your **name**, **index number** and **class** on this question paper and on the Cover Sheet provided.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Start each question on a fresh sheet of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

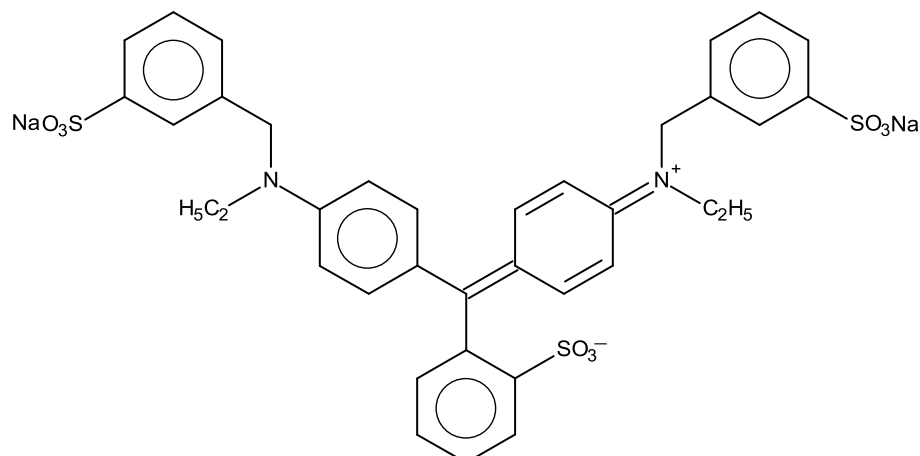
At the end of the examination:

- Fasten all work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

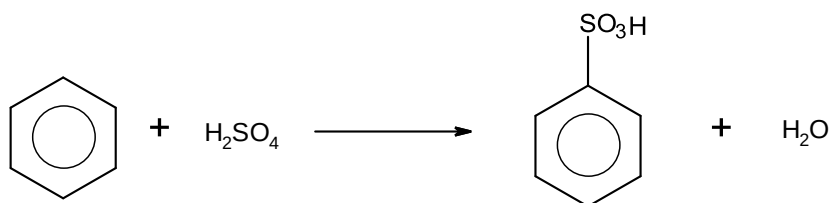
The total marks for this paper is 80 marks.

Answer *any four* questions.

- 1 Blue #1 ($\text{Na}_2\text{C}_{37}\text{H}_{34}\text{N}_2\text{S}_3\text{O}_9$) is a synthetic food colouring often found in ice cream.



- (a) One of the main compounds used to produce Blue #1 is benzenesulfonic acid, which is produced by heating benzene under reflux with concentrated sulfuric acid for several hours.

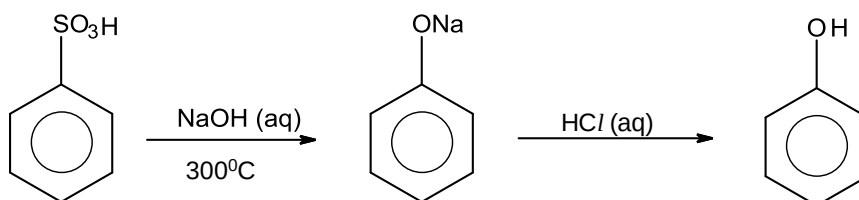


- (i) The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

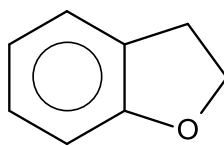
Name the type of reaction and describe the mechanism. In your answer, show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons.

[4]

- (ii) Benzenesulfonic acid is a useful starting material as it can be easily converted to phenol by heating with NaOH(aq) at 300°C followed by acidification. It also has similar chemical reactivity as nitrobenzene.



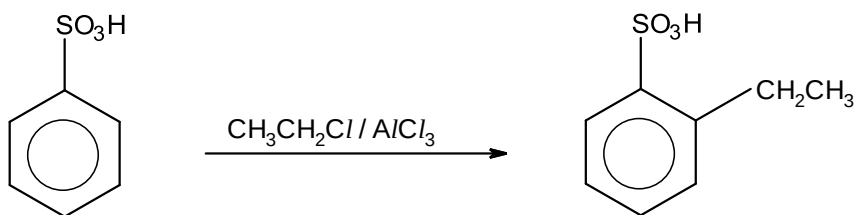
Compound **A** can be synthesised from either benzenesulfonic acid or ethylbenzene in not more than 4 steps.



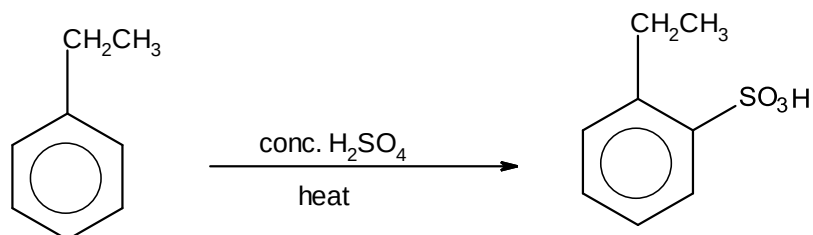
A

The first step of the synthesis using either benzenesulfonic acid or ethyl benzene is as shown below in Scheme 1 and 2 respectively:

Scheme 1:



Scheme 2:



Identify the correct scheme that will give compound **A** and copy the synthetic scheme in your answer.

Using information in **(a)(ii)**, suggest the next three steps to synthesise compound **A**. Show all intermediates, reagents and conditions clearly in your synthetic route.

[4]

- (b) Blue #1 can be oxidised by household bleach to form colourless products, as represented by the equation below.



To study the kinetics of the reaction, a student used an UV spectrophotometer to study the absorbance of Blue #1 over time during the bleaching process.

In experiment 1, the student mixes 3.0 cm³ of 0.1 mol dm⁻³ Blue #1, 1.0 cm³ of water and 0.5 cm³ of 3.5 mol dm⁻³ bleach together. The results of experiment 1 are as shown below.

Time (s)	15	30	45	60	75	90	105	120	135
Absorbance	0.495	0.424	0.371	0.328	0.285	0.251	0.218	0.191	0.170

- (i) Explain why bleach is used in large excess as compared to that of Blue #1. [1]
- (ii) Given that absorbance measured varies linearly with the concentration of Blue #1, use a suitable graphical method to determine the order of reaction with respect to the blue food colouring, Blue #1. [3]
- (iii) The student subsequently conducted a few more experiments using other volumes of Blue #1 and bleach. The table below shows the results obtained.

Experiment	Volume of Blue #1 / cm ³	Volume of distilled water / cm ³	Volume of bleach / cm ³	Rate constant
1	3.0	1.0	0.5	
2	4.0	0.0	0.5	0.00882
3	3.0	0.5	1.0	0.01698

Using results from (b)(ii), determine the rate constant for experiment 1. Hence, deduce the overall order of reaction, showing your reasoning clearly.

[3]

- (c) (i) Household bleach is also often known as “chlorine water”. The active chemical responsible for the bleaching action in household bleach is the anion, OCl⁻, which is easily formed by the disproportionation of chlorine in water.

Write a balanced equation between chlorine and water, and hence, suggest the identity of the other compound formed.

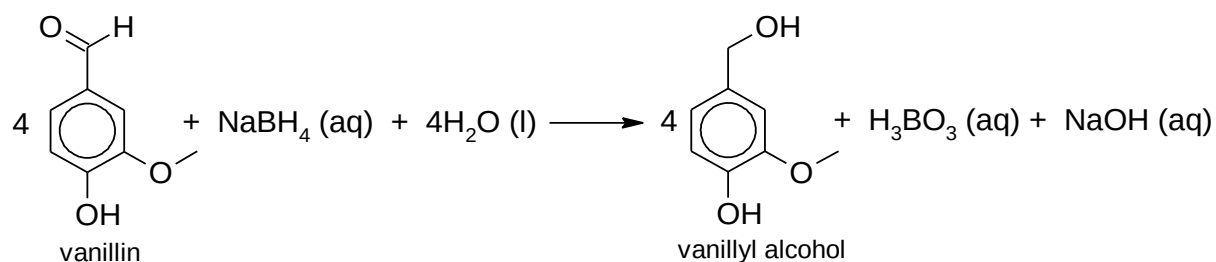
[1]

- (ii) Chlorine reacts with Period 3 elements, Mg and Si, to give chlorides. The two chlorides differ in their reaction with water. Describe their differences, and explain them in terms of the different structures and types of chemical bonding. Write an equation for the reaction, if any.

[4]

[Total: 20]

- 2 Vanillin and vanillyl alcohol (derived from vanillin) are both used as flavouring, usually in sweet foods such as chocolate. Vanillyl alcohol is commonly synthesised via the reduction of vanillin using sodium borohydride, as shown below.



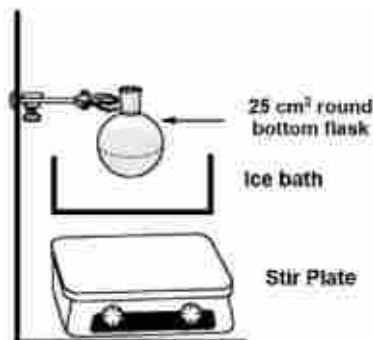
- (a) (i) Draw a 'dot-and-cross' diagram to show the bonding in sodium borohydride. [1]
- (ii) Suggest why sodium borohydride is used in this reduction instead of lithium aluminium hydride. [1]
- (iii) Given that the melting points of vanillin and vanillyl alcohol are 355 K and 388 K respectively, predict and explain the sign of the entropy change of reaction at 360 K. [1]
- (iv) A higher temperature leads to a faster rate of reaction. However, thermodynamic factors must also be taken into consideration when considering appropriate conditions for a reaction.

Explain how higher temperatures will affect the thermodynamic outcome.

[2]

(b) The procedure for the reduction of vanillin to vanillyl alcohol is as follows:

1. Place 2 g of vanillin in a 25 cm³ round bottom flask followed by 4 cm³ ethanol. Add a magnetic stirrer, clamp the flask above a stir plate and commence stirring at room temperature to dissolve vanillin.
2. After the vanillin dissolves, add an ice bath under the flask to cool the solution.

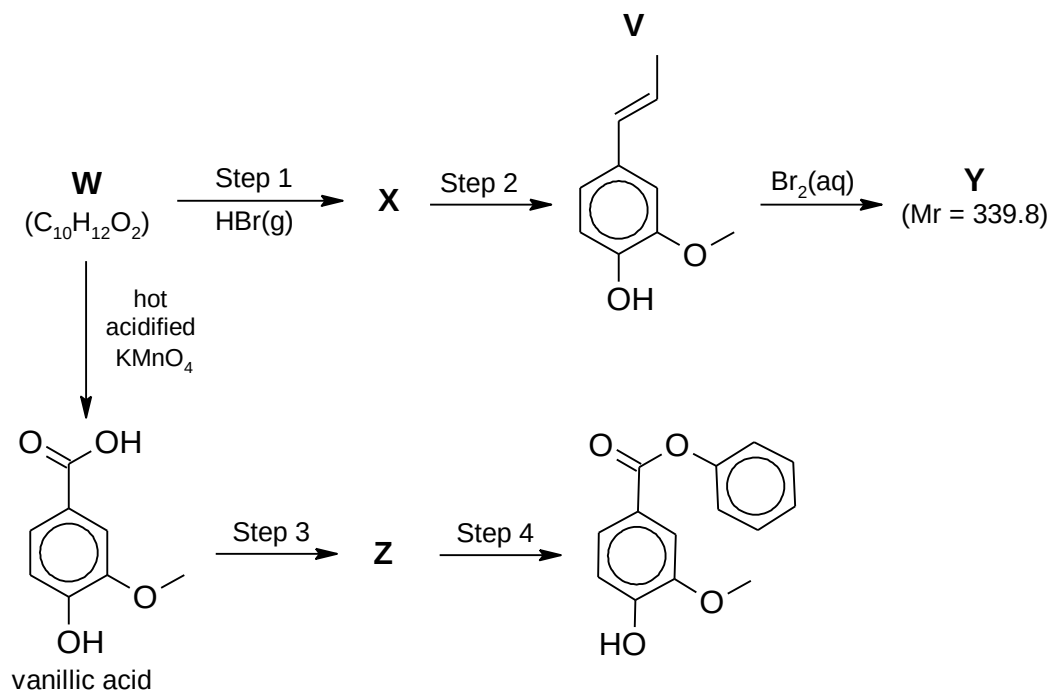


3. In a separate reaction vial, dissolve 0.5 g of NaBH₄ in 3.8 cm³ of 1 mol dm⁻³ NaOH solution.
 4. Using a glass pipette, slowly add the NaBH₄ solution dropwise to the vanillin solution over a period of 10 minutes.
 5. Only after the addition is complete, remove the ice bath. This is because NaBH₄ decomposes at high temperatures.
 6. Stir the resulting mixture for 10 minutes at room temperature.
 7. Add 6 mol dm⁻³ HCl dropwise until the evolution of hydrogen gas stops.
 8. Stir to allow the product to precipitate from solution.
- (i)** State a reason why sodium borohydride must be added dropwise to the reaction mixture (in Step 4). [1]
- (ii)** In Step 7, hydrochloric acid was added to react with excess sodium borohydride present in the reaction mixture. Write an equation for this reaction, given that boric acid (H₃BO₃) is one of the products formed. [1]
- (iii)** State one way you could modify the procedure to increase the isolated yield. [1]
- (iv)** A preliminary way to determine whether the reaction has gone to completion is to draw out aliquots of the reaction mixture and test for the presence of vanillin in it.

Describe a simple chemical test to test for the presence of vanillin. Give the expected observations and write a balanced equation for the reaction with vanillin.

[2]

- (c) Compound **W**, an isomer of **V**, can also be used as a starting reagent to synthesise vanillic acid and other organic compounds shown in the reaction scheme below.



- (i) Draw the structures of compounds **W**, **X** and **Y**, and state the reagents and conditions for Steps 2 and 4.

[4]

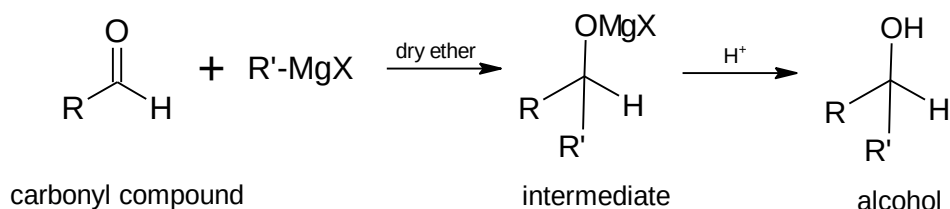
- (ii) Vanillic acid (4-hydroxy-3-methoxybenzoic acid) has an isomer, 2-hydroxy-3-methoxybenzoic acid.

State which of the two isomers has a higher boiling point. Explain your answer.

[2]

- (d) Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols.

A common type of organometallic compound are Grignard reagents. They have the formula $RMgX$, where X is a halogen and R is an alkyl or aryl group.



Draw the structure of the intermediate formed when vanillin reacts with ethylmagnesium bromide.

[1]

- (e) The chemistry of lithium and its compounds differs significantly from the rest of the Group I metals. In fact, lithium shows many similarities to magnesium exemplifying the so-called “diagonal relationship” because of their positions in the periodic table.

In an experiment, a sample of solid magnesium amide, $\text{Mg}(\text{NH}_2)_2$ and lithium amide, LiNH_2 are heated separately.

Magnesium amide decomposes when heated to give magnesium nitride, Mg_3N_2 and ammonia gas.

- (i) Write a balanced chemical equation for the decomposition of lithium amide.

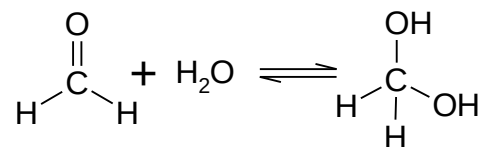
[1]

- (ii) With reference to *Data Booklet*, predict the decomposition temperature of LiNH_2 when compared to $\text{Mg}(\text{NH}_2)_2$, given that the ionic radius of Li^+ is 0.060 nm. Explain your answer.

[2]

[Total: 20]

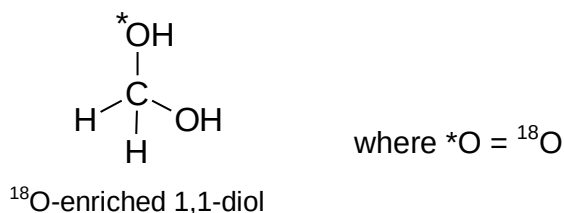
- 3 (a) Methanal undergoes reaction with water to yield 1,1-diol. The reaction is reversible and the 1,1-diol can eliminate water to regenerate methanal.



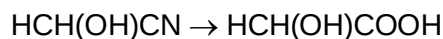
- (i) State the type of reaction for the above reaction. [1]
- (ii) The reaction is slow but the rate is increased by the addition of a small amount of NaOH as catalyst. Suggest why NaOH is needed to initiate the reaction in the mechanism. [1]

The oxygen in water is primarily 99.8% ^{16}O but water enriched with the heavy isotope, ^{18}O , is also available. When methanal is dissolved in ^{18}O -enriched water, the isotopic label becomes incorporated into the 1,1-diol which regenerates methanal.

- (iii) Using your answer to (a)(ii), suggest how ^{18}O is incorporated into the 1,1-diol.



- [1]
- (iv) The addition of water to aldehydes proceeds more rapidly than it does to ketones. Suggest a reason why. [1]
- (b) Methanal also reacts with HCN to form 2-hydroxyacetonitrile, $\text{HCH}(\text{OH})\text{CN}$. The 2-hydroxyacetonitrile formed can be further converted to 2-hydroxyethanoic acid, as shown below.



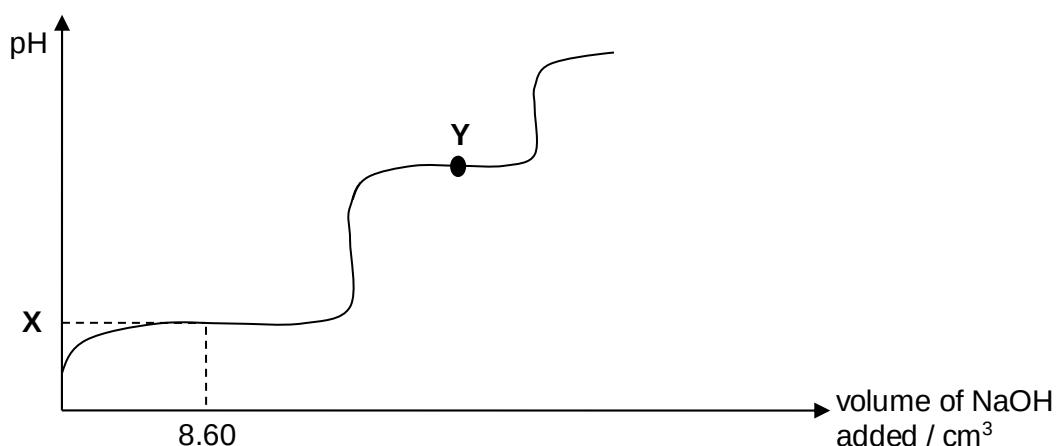
- (i) Explain whether 2-hydroxyethanoic acid has a larger or smaller K_a than ethanoic acid. [2]

Phenol and 2-hydroxyethanoic acid are weak Brønsted acids with $\text{p}K_a$ values of 9.80 and 3.86 respectively.

A mixture of 20.0 cm^3 of phenol and 2-hydroxyethanoic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein and bromothymol blue indicators are used in this titration.

It was found that the first colour change occurs at 17.20 cm³ and the second colour change occurs at 26.80 cm³ of sodium hydroxide used.

A sketch (not drawn to scale) of the pH titration curve is shown below.



- (ii) Both phenolphthalein and bromothymol blue are weak acids. State the effect on the volume of sodium hydroxide used for titration, if both indicators are added in larger amount.

[1]

- (iii) State the value of point X.

[1]

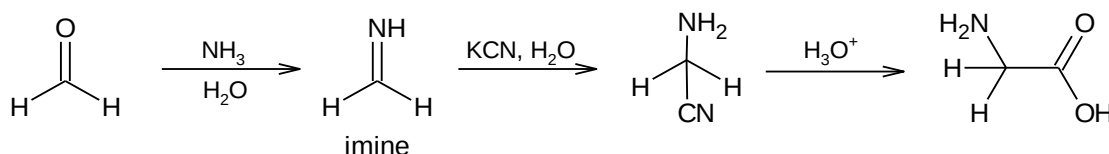
- (iv) Write an equation to illustrate how the species found in point Y can maintain the pH of a solution when a small amount of H⁺(aq) is added.

[1]

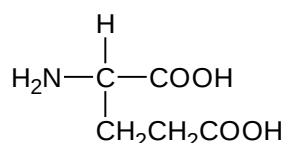
- (v) Calculate the concentration of phenol and 2-hydroxyethanoic acid in the original mixture.

[2]

- (c) The Strecker synthesis is a route to preparing amino acids. Methanal can be used to synthesise glycine, 2-aminoethanoic acid, in this way.



The amino acid shown below is glutamic acid.

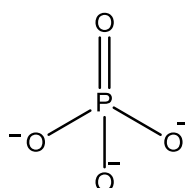


- (i) Identify the aldehyde-containing compound and the imine intermediate which are needed to synthesise glutamic acid via the Strecker synthesis. [2]

- (ii) Suggest, with a reason, if there is any difference in the optical activity of a sample of glutamic acid synthesised by Strecker's method and that of natural occurring glutamic acid. [1]

- (d) Glycine and glutamic acid are among the many amino acids which constitute the long amino acid sequence of *protein kinase*. *Protein kinase* is an enzyme which plays a major role in protein regulation. It modifies other proteins by chemically adding phosphate groups to them. This process is called phosphorylation.
- (i) In phosphorylation, a phosphate group (PO_4^{3-}) from adenosine triphosphate (ATP) is transferred to and replaces a free hydroxyl group of amino acid. Shown below are the structures of three amino acids and phosphate group.

serine (ser)	glycine (gly)	glutamic acid (glu)
$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\ \\ \text{CH}_2\text{CH}_2\text{COOH} \end{array}$



phosphate group (PO_4^{3-}):

Draw the structure of the tripeptide, ser-gly-glu, after phosphorylation.

- (ii) The secondary structure of *protein kinase* consists of segments of α -helix. Describe the bonding which holds the α -helix in place. [2]
- (iii) The *protein kinase* is destroyed during the process of denaturation. Explain how this can occur by heating. [2]

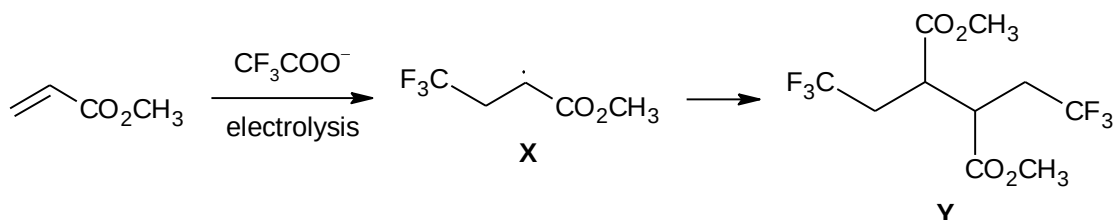
[Total: 20]

- 4 In 1849, the German chemist Adolf Kolbe reported his investigations into the electrolysis of aqueous solutions of some carboxylate anions, using inert platinum electrodes. The Kolbe electrolysis of trifluoroacetate (CF_3CO_2^-), for example, is known to produce trifluoromethyl radical ($\cdot\text{CF}_3$, $M_r = 69$) and a gas at the anode.

(a) Suggest the identity of the gas and hence construct a half-equation for the reaction at the anode.

[2]

When the Kolbe electrolysis of trifluoroacetate was carried out in the presence of alkenes such as $\text{CH}_2=\text{CHCO}_2\text{CH}_3$, the radical intermediate **X** was formed which further dimerised to yield product **Y** shown below.



(b) State the oxidation number of the carbonyl carbon atom in $\text{CH}_2=\text{CHCO}_2\text{CH}_3$.

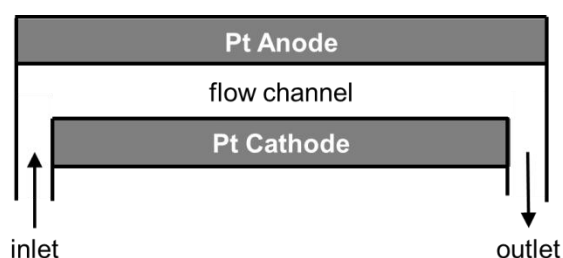
[1]

(c) Suggest a two-step mechanism for the reaction above to form **Y**, starting from the reaction between trifluoromethyl radical ($\cdot\text{CF}_3$) and the alkene. Use curly arrows to indicate the movement of single electrons and indicate any unpaired electrons by a dot ($\bullet$).

[3]

The Kolbe electrolysis in (c) was performed by continuous introduction of a water/ CH_3CN solution containing trifluoroacetate and the alkene into an electrochemical microreactor at constant current and room temperature.

The electrochemical microreactor has a flow channel sandwiched between two platinum electrodes as shown in the figure below.



(d) (i) Given that the flow channel has a volume of $23\ \mu\text{L}$ and reaction mixture was injected at a rate of $20\ \mu\text{L}\ \text{min}^{-1}$, calculate the time (in seconds) in which the current was passed through the solution.

($1\ \mu\text{L} = 10^{-3}\ \text{cm}^3$)

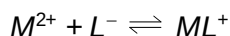
[1]

(ii) The purified product **Y** ($M_r = 310$) was obtained as a colourless solid weighing $0.401\ \text{g}$. Using your answers from (a) and (d)(i), calculate the current (in ampere) that would have been applied to the microreactor.

[2]

- (e) (i) How many stereoisomers does **Y** have? [1]
- (ii) Draw the isomer of **Y** that is **not** optically active, showing clearly the stereochemistry of the molecule using wedged $\blacktriangleleft$ and dashed bonds $\cdots$. [1]
- (f) When the Kolbe electrolysis of trifluoroacetate was carried out in the presence of another alkene, $\text{CH}_2=\text{CHCONH}_2$ ($M_r = 71$), a non-dimer product ($M_r = 209$) was formed instead. Suggest the structure of the product obtained. [1]
- (g) The trifluoromethyl ($-\text{CF}_3$) group is regarded as an important structural feature in many pharmaceutically relevant molecules because it is known to enhance chemical inertness. Suggest an explanation for its property. [1]
- (h) (i) Deduce the structure of the radical intermediate formed when Kolbe electrolysis of difluoroacetate, $\text{CHF}_2\text{CO}_2^-$, was carried out in the presence of the alkene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$. [1]
- (ii) The yield of the dimer product for this electrolysis was much poorer than that for trifluoroacetate and $\text{CH}_2=\text{CHCO}_2\text{CH}_3$. Use your answer in (h)(i) to suggest a reason for the difference in yield. [2]

Some carboxylate anions, L^- , are also known to form 1:1 complexes with divalent metal ions, M^{2+} , according to the following equilibrium.



- (i) The table below gives the values of $\log K$ for some 1:1 metal-carboxylate complexes.

metal ion	acetate (CH_3COO^-)	chloroacetate ($\text{CH}_2\text{ClCOO}^-$)
Cd^{2+}	1.30	0.99
Cu^{2+}	1.76	1.07
Ni^{2+}	0.72	0.23

Using relevant data from the table, deduce

- I the relative stabilities of the metal complexes formed with the acetate ligand. [1]
- II the relative magnitude of the $\log K$ values of 1:1 Cu^{2+} - CH_3COO^- and Cu^{2+} - HCOO^- complexes and suggest a reason for your answer. [3]

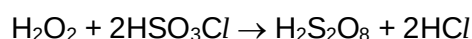
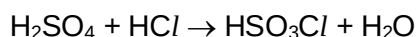
[Total: 20]

5 This question is about Period 3 elements and the uses of its compounds.

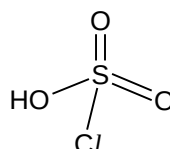
- (a) A sample of magnesium oxide is suspected to be contaminated with a substantial amount of aluminium oxide. Describe a simple gravimetric method to prove that the contamination has taken place. Include equation(s) for the chemical reaction(s) involved, if any.

[3]

- (b) Another Period 3 oxide, sulfur trioxide dissolves in water to form sulfuric acid, H_2SO_4 which can be converted into peroxodisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$ via the two-step process below, with chlorosulfonic acid, HSO_3Cl , as an intermediate:



- (i) The structure of HSO_3Cl is given below.



The boiling point of H_2SO_4 is 290°C whereas that of HSO_3Cl is 152°C . By making reference to the structures of the two compounds, explain the difference in the boiling points.

[2]

- (ii) Draw the structure of a $\text{H}_2\text{S}_2\text{O}_8$ molecule, showing the spatial arrangement and estimated bond angle around any one sulfur atom. The $\text{H}_2\text{S}_2\text{O}_8$ molecule contains a $\text{O}-\text{O}$ bond.

[2]

- (c) Chlorine forms an oxide, Cl_2O_7 , with the structure $\text{O}_3\text{ClOClO}_3$ and a boiling point of 82°C . Its standard enthalpy change of formation is -546 kJ mol^{-1} .

- (i) Write the equation which corresponds to the standard enthalpy change of formation of Cl_2O_7 .

[1]

- (ii) Given that the bond energy of $\text{Cl}-\text{O}$ bond is 269 kJ mol^{-1} and using relevant data from the *Data Booklet*, estimate the average bond energy of the $\text{Cl}=\text{O}$ bond.

[2]

- (iii) The bond energy calculated in (c)(ii) could have been more accurate if the value of an additional enthalpy change is known. State what process this enthalpy change corresponds to.

[1]

- (iv) Given that the value of the enthalpy change in (c)(iii) is $+45\text{ kJ mol}^{-1}$, construct an energy level diagram to calculate the enthalpy change of formation of gaseous Cl_2O_7 .

[3]

- (d) Aluminium oxide is used extensively in organic synthesis as a dehydrating agent.

An organic compound **A**, $C_{12}H_{18}O$, contains a benzene ring with 2 substituents on the 1- and 4- positions on the ring. **A** is optically active. When it is treated with Al_2O_3 , compound **B** is formed. **B** can be converted into another optically active compound **C** by reacting with dry gaseous HCl . When **C** is heated under reflux with acidified $KMnO_4$, compound **D**, $C_{11}H_{14}O_2$, is produced. Treatment of **D** with PCl_5 produces compound **E**. When **E** is heated with gaseous NH_3 , a neutral compound **F** is formed.

Identify the six compounds **A – F**.

[6]

[Total: 20]

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2016 DHS H2 CHEMISTRY YEAR 6 PRELIMS
Paper 1 MCQ – Answers

1	2	3	4	5	6	7	8	9	10
D	B	B	D	C	D	C	C	D	C

11	12	13	14	15	16	17	18	19	20
A	A	D	D	C	C	B	D	A	B

21	22	23	24	25	26	27	28	29	30
D	C	D	A	C	B	C	A	B	A

31	32	33	34	35	36	37	38	39	40
B	C	B	B	A	B	A	A	A	D

Answer **all** questions in the spaces provided.

1 (a)

Repulsion between two negatively charged ions causes the activation energy to be high.

[1]

(b)

Preparation of reaction mixture

1. Using a 50.0 cm³ measuring cylinder, add 25.0 cm³ of peroxodisulfate ions into a 250 cm³ conical flask.
2. Using a 10.0 cm³ measuring cylinder, add 2.0 cm³ of aqueous copper (II) ions into the same conical flask.
3. Using a 50.0 cm³ measuring cylinder, add 45.5 cm³ of deionised water into the conical flask.
4. Using a 10.0 cm³ measuring cylinder, measure out 2.5 cm³ of ethanedioate ions.
5. Transfer the ethanedioate ions into the conical flask and insert a rubber bung into the conical flask. The rubber bung has a delivery tube connected to rubber tubing with the other end of the tubing inserted into an inverted burette filled with water.
6. Start the stopwatch immediately and gently swirl the conical flask continuously.
7. Monitor the water level in the burette and stop the stopwatch when 40.00 cm³ of CO₂ is produced. Record the time taken.
8. Repeat step 1 to 7 using the following volumes of reactants, copper (II) ions and deionised water shown in experiment 2 to 4, at the same temperature.

Experiment	Volume of S ₂ O ₈ ²⁻ / cm ³	Volume of C ₂ O ₄ ²⁻ / cm ³	Volume of Cu ²⁺ / cm ³	Volume of water / cm ³
1	25.0	2.5	2.0	45.5
2	25.0	5.0	2.0	43.0
3	2.5	25.0	2.0	45.5
4	5.0	25.0	2.0	43.0

Treatment of results

1. Relative rates (= 1/t) of expt 1 to 4 are calculated. Since total volume of mixture is constant in expt 1 to 4, concentration of reactant is proportional to its volume used.
2. Compare the relative rates of expt 1 to 2 and 3 to 4, to find the order of reaction with respect to (w.r.t) C₂O₄²⁻ and S₂O₈²⁻ respectively. If volume of C₂O₄²⁻ doubles and rate remains the same, it is zero order w.r.t C₂O₄²⁻. If volume of C₂O₄²⁻ doubles, and rate remains doubles, it is first order w.r.t C₂O₄²⁻. If volume of C₂O₄²⁻ doubles and rate quadruples, it is second order w.r.t C₂O₄²⁻. The same applies for S₂O₈²⁻.
3. The rate law of reaction can then be found, rate = k[S₂O₈²⁻]ⁿ[C₂O₄²⁻]^m, where n and m are the orders of reaction w.r.t to S₂O₈²⁻ and C₂O₄²⁻ respectively.

[8]

(c)

1. Repeat one of the experiments (e.g. expt 2) at two (at least) different temperatures, other than that for experiment 1 to 4 above. This can be done by immersing conical flasks in water bath maintained at different constant temperatures e.g. 40 °C and 60 °C.
2. Using the results in experiment 2 and that of the two further experiments, relative rate, followed by $\ln$ (relative rate) for each expt is calculated.
3. A graph of $\ln$ (relative rate) against $\frac{1}{T}$ is plotted. The gradient of the best fit line is then determined, where gradient = $-\frac{E_a}{R}$. E_a is given by |gradient x R|.

[3]

[Total: 12]

2 (a) (i)

	Half-equations	Polarity
Anode	$\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$	–
Cathode	$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$	+

[3]

(ii)

The relative density of the sulfuric acid will decrease.

During discharging, as sulfuric acid is used up to produce PbSO_4 , the concentration of sulfuric acid will decrease, resulting in a decrease in density.

[2]

(iii)

Overcharging will result in electrolysis of water.
Identity of other gas: Oxygen

[2]

(iv)

$$E^\ominus = 1.47 - (-0.13) = +1.60 \text{ V}$$

[2]

(v)

Lead–acid battery has a higher voltage as PbSO_4 formed is insoluble, which resulted in a lower concentration of Pb^{2+} in the electrolyte, thus driving the forward reaction.

[2]

(b) (i)

To 1 cm³ of halide ions, add AgNO₃(aq) dropwise. Then add aqueous NH₃ in excess.

Cl⁻ ions form white ppt with AgNO₃ which is soluble in excess NH₃(aq).

Br⁻ ions form cream ppt with AgNO₃ which is insoluble in excess NH₃(aq) [2]

(ii)

$\text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \rightleftharpoons \text{AgX}(\text{s})$, where X⁻ is Cl⁻ and Br⁻

Both halide ions form insoluble ppt with Ag⁺.

$\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$

Ag⁺ ions form soluble diammine complex which decreases the [Ag⁺], resulting in a corresponding decrease in ionic product (i.e. I.P = [Ag⁺][X⁻]) for both halide ions.

As K_{sp} value of AgCl is much larger than that of AgBr, the ionic product of AgCl will fall below its K_{sp} but not for AgBr.

[2]

[Total: 15]

3 (a) (i)

Co³⁺: 1s²2s²2p⁶3s²3p⁶3d⁶

[1]

(ii) Suggest the identities of X and Y.

X: Co(OH)₃

Y: [Co(NH₃)₆]³⁺

[2]

(iii)

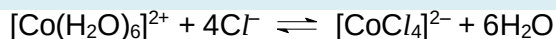
$[\text{Co}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightleftharpoons \text{Co}(\text{OH})_3 + 6\text{H}_2\text{O} \text{ ———(1)}$

When aqueous ammonia is added in excess, a ligand exchange reaction occurs. The stronger NH₃ ligands replace weaker H₂O ligands in the [Co(H₂O)₆]³⁺ ions to form [Co(NH₃)₆]³⁺ complex.

$[\text{Co}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \text{ ———(2)}$

This decreases the concentration of [Co(H₂O)₆]³⁺ in solution. By Le Chatelier's Principle, equilibrium (1) shifts left to increase the concentration of [Co(H₂O)₆]³⁺(aq). Hence the brown precipitate of Co(OH)₃ dissolves [1].

[3]

(b)

There is a change of co-ordination number from 6 to 4.

[2]

(c) (i)

The partially-filled d orbitals of V^{2+} are split into two groups of different energy levels by H_2O ligands. When white light shines on the complex, a d electron undergoes d-d transition and is promoted to a higher energy d orbital. During the transition, the d electron absorbs light from the yellow region of the visible spectrum. The colour observed is the colour of transmitted light, which is a mixture of remaining wavelengths that have not been absorbed.

[2]

(ii)

The reactant molecules are physically adsorbed onto the catalyst surface. This allows for formation of weak bonds between reactants and the surface catalyst, thus weakening the intramolecular bonds in the reactants and helps to catalyse the reaction. After reaction, the reactant molecules desorb from the catalyst surface.

[2]

(iii)

	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g}) \rightleftharpoons$	$2\text{SO}_3(\text{g})$
Initial pressure /atm	0.6667x		0.3333x	0
Change in pressure /atm	-0.6333x		-0.3167x	+0.6333x
Equilibrium pressure /atm	0.0334x		0.0166x	0.6333x

Let the initial total pressure be x atm.

$$K_p = (0.6333x)^2 / (0.0166x)(0.0334x)^2 = 7200$$

$$\therefore x = (0.6333)^2 / 7200(0.0166)(0.0334)^2$$

$$= 3.01 \text{ atm}$$

[2]

(iv)

Rate of conversion will slow down/decrease due to poisoning of the catalyst.

[1]

[Total: 15]

4 (a) (i)

$$\text{No. of moles of } \text{HY}^{3-} \text{ required} = 0.0149 \times \frac{25.55}{1000}$$

$$= 0.00038070 \text{ mol}$$

No. of moles of Ca^{2+} present = 0.00038070 mol

No. of moles of CaCO_3 = 0.00038070 mol

Mass of CaCO_3 = 0.00038070 x [40.1 + 12 + 3(16)]
= 0.0381g (3 sf)

[1]

(ii)

$\text{ppm CaCO}_3 = \frac{0.038107}{50} \times 10^6 = 762$ (3 sf)
The water is very hard.

[2]

(b)

Ca^{2+} can be removed by heating the water sample.

By Le Chatelier's Principle, the position of equilibrium will shift right to remove the heat supplied causing a decrease in the concentration of Ca^{2+} ions.

OR

Ca^{2+} can be removed by heating the water sample.

Heating the water sample removes CO_2 (g) hence decreasing the concentration of CO_2 (aq).

By Le Chatelier's Principle, the position of equilibrium will shift right to increase the concentration of CO_2 (aq) causing a decrease in the concentration of Ca^{2+} ions.

[2]

(c) (i)

$[\text{C}_{18}\text{H}_{29}\text{SO}_3^-] = \sqrt{(1.2 \times 10^{-17} / 2.5 \times 10^{-4})}$
= $2.1908 \times 10^{-7} \text{ mol dm}^{-3}$
= $2.19 \times 10^{-7} \text{ mol dm}^{-3}$

[1]

(ii)

Mass of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ added to 1.0 dm^3 = 0.174 g

No of moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ added to $1.0 \text{ dm}^3 = \frac{0.174}{348} = 5.00 \times 10^{-4} \text{ mol}$

[1]

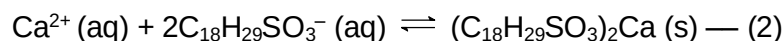
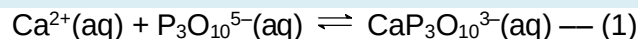
(iii)

Maximum moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3^-$ dissolved in $1.0 \text{ dm}^3 = 2.1908 \times 10^{-7} \text{ mol}$

No of moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3^-$ precipitated out = $5.00 \times 10^{-4} - 2.1908 \times 10^{-7}$
= $4.9978 \times 10^{-4} \text{ mol}$

$$\begin{aligned}\text{Percentage of } \text{C}_{18}\text{H}_{29}\text{SO}_3^- \text{ precipitated} &= \frac{4.9978 \times 10^{-4}}{5.00 \times 10^{-4}} \times 100\% \\ &= 99\% \text{ (shown)}\end{aligned}$$

[2]

(d) (i)

$\text{P}_3\text{O}_{10}^{5-}$ form complexes with Ca^{2+} causing a decrease in the concentration of Ca^{2+} .

By Le Chatelier's Principle, the equilibrium position of (2) shifts left to increase the concentration of Ca^{2+} . Hence reducing the amount of $(\text{C}_{18}\text{H}_{29}\text{SO}_3)_2\text{Ca}$ formed.

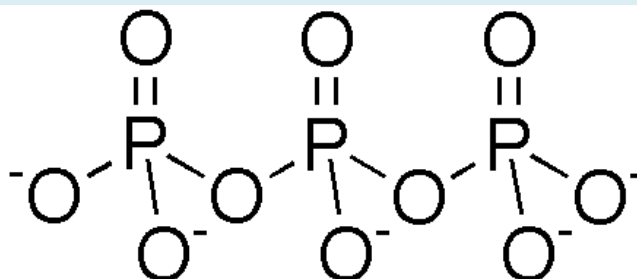
Hence, preventing the formation of precipitate when detergent is added into hard water.

[2]

(ii)

+5

[1]

(iii)

[1]

(iv)

Concentration of $\text{P}_3\text{O}_{10}^{5-}$ decreases as it complexes with the added Mg^{2+} to form $\text{MgP}_3\text{O}_{10}^{3-}$.

By Le Chatelier's Principle, the equilibrium position of (1) will shift left to increase the concentration of $\text{P}_3\text{O}_{10}^{5-}$.

There is no change to the value of K_c as temperature is kept constant.

[2]

[Total: 15]

5 (a)

CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$.

[1]

(b)

Two epoxide rings.

Two alcoholic groups are produced for every epoxide ring that will be hydrolysed. Since there are four alcoholic groups formed after 'juvenile hormone' undergoes hydrolysis, this implies that there are two epoxide rings in 'juvenile hormone'.

[2]

(c) State the type of reaction that T has undergone and the functional group that it contains other than the four alcoholic groups.

T undergoes basic hydrolysis to give methanol and U. T is likely to contain an ester.

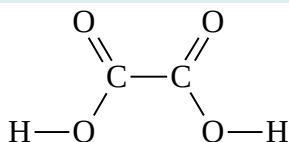
[1]

(d)

Two tertiary alcohol groups.

T has four alcohol groups which were retained in U even after basic hydrolysis. Since V has only two alcohol groups left after mild oxidation, this implies that the two alcohol group must be tertiary in order to resist oxidation.

[2]

(e)

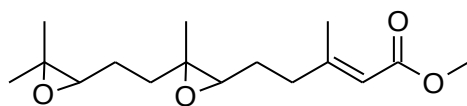
[1]

(f)

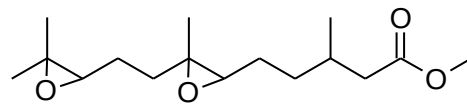
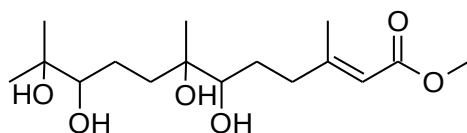
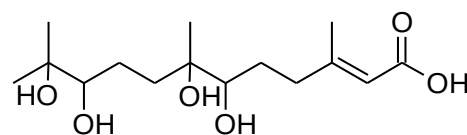
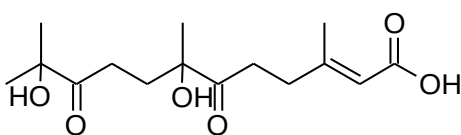
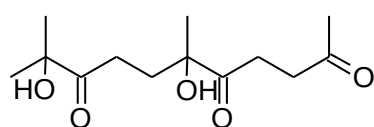
Condensation. W contains either $\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---CH}_3 \end{array}$ or $\begin{array}{c} \text{OH} \\ | \\ \text{---C---CH}_3 \\ | \\ \text{H} \end{array}$

[2]

(g)



Juvenile hormone

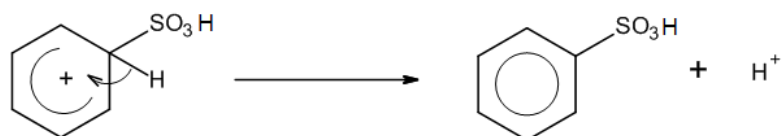
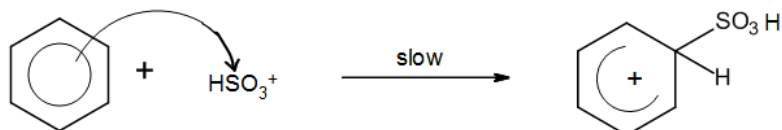
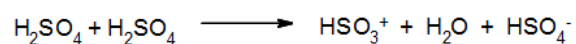
**S****T****U****V****W**

[6]

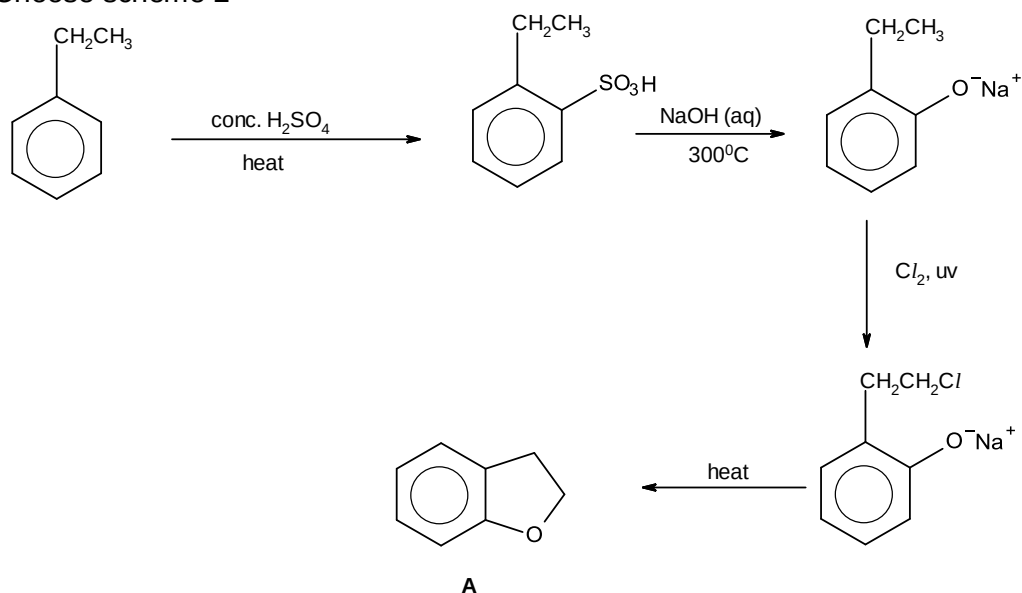
[Total: 15]

**2016 Y6 H2 Chemistry Preliminary Examination Paper 3
(Answer Scheme)**

1 (a) (i) Electrophilic substitution

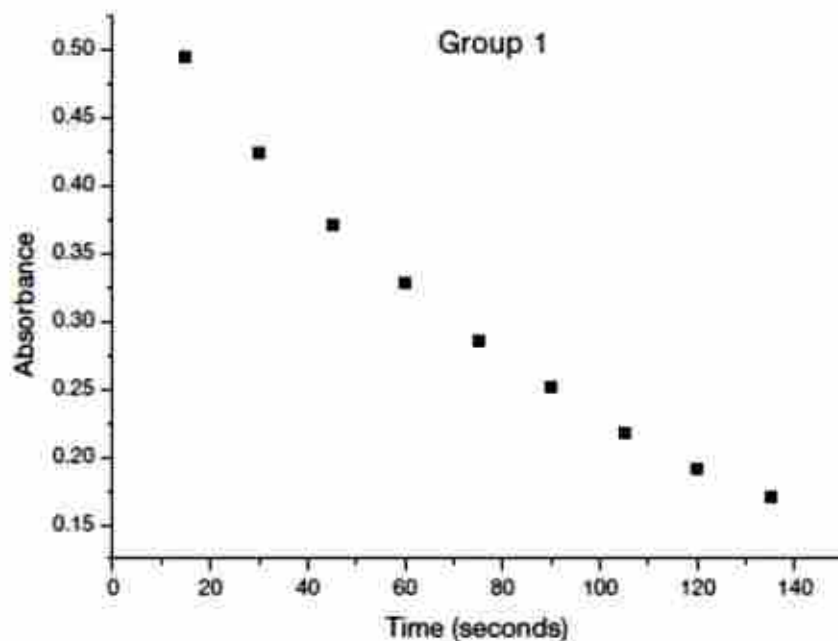


(ii) Choose scheme 2



(b) (i) To ensure that [bleach] remains almost constant throughout the reaction so that the rate can be measured with respect to Blue #1 in a pseudo-order reaction.

(ii)



From graph hand-plotted,

when absorbance decreases from 0.40 to 0.20, $t_{1/2} \approx 78s$

when absorbance decreases from 0.50 to 0.25, $t_{1/2} \approx 76s$

Since almost constant $t_{1/2} \approx 77s$ is observed, the order of reaction wrt to [Blue#1] is 1.

OR

Reaction is first order with respect to [Blue#1].

(iii)

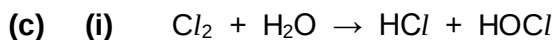
Using $t_{1/2} = \ln 2 / k$, find value of k for experiment 1.

$$k = \ln 2 / 77 = 0.00900 \text{ s}^{-1}$$

Compare experiment 1 and 3, when the volume of bleach doubles, rate constant almost doubles (i.e. $0.01498 / 0.00900 = 1.67 \approx 2$).

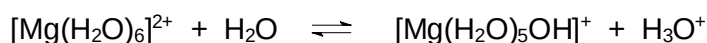
The reaction is first order with respect to [bleach].

Hence, overall order of reaction is 2.



(ii) MgCl_2 is an ionic compound which ionises in water to form hydrated Mg^{2+} and Cl^- ions.

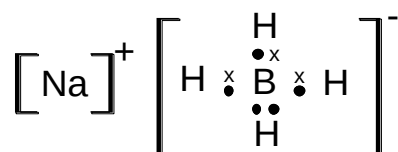
As Mg^{2+} has a high charge and small ionic radius / has a high charge density, it hydrolyses slightly in water to form a weakly acidic solution of pH 6.5



SiCl_4 is a covalent compound which hydrolyses in water to form an acidic solution of pH 2.



2(a) (i)



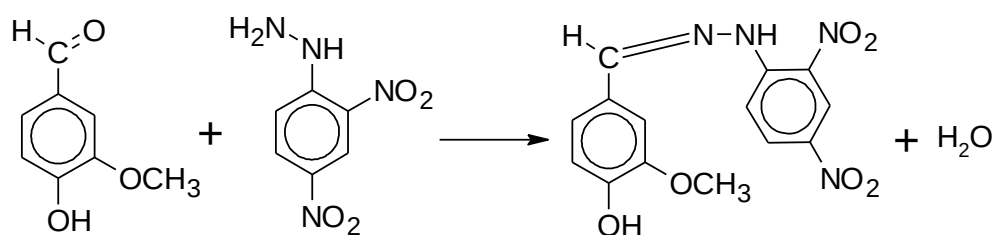
- (ii) Sodium borohydride is a milder reducing agent and hence is less reactive and will not react as violently with water present.

OR

Lithium aluminium hydride is a very strong reducing agent and hence is highly reactive and will react violently with water present.

- (iii)
- At 360 K, vanillin is a liquid while vanillyl alcohol is a solid. There is a decrease in the degree of disorderliness, hence the entropy change of reaction at 360 K is negative.
- (iv)
- ΔH° and ΔS° will change as temperature increases.
 - ΔG° may become more/less negative as temperature increases.
- (b) (i) The reaction is exothermic / large amounts of heat will be produced. If it was added all at once and this may cause NaBH_4 to decompose.
- (ii) $\text{NaBH}_4 + 3\text{H}_2\text{O} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_3\text{BO}_3 + 4\text{H}_2$
- (iii) Use excess NaBH_4 as it may decompose at high temperatures. Allow reactants to stir for a longer period.
- (iv) To the aliquot drawn out, add a small amount of 2,4-DNPH.

An orange precipitate will be seen if vanillin is present.



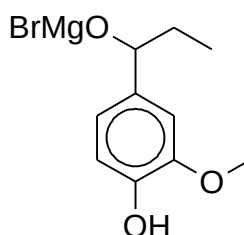
(c)	(i)	<table border="1"> <thead> <tr> <th>W</th><th>X</th><th>Y</th></tr> </thead> <tbody> <tr> <td></td><td></td><td> </td></tr> </tbody> </table>	W	X	Y			
W	X	Y						

Step 2: alcoholic KOH, heat under reflux

Step 4: phenol, room temperature

- (ii)
- Vanillic acid has a higher boiling point.
 - Due to proximity of $-\text{OH}$ and $-\text{COOH}$ groups, 2-hydroxy-3-methoxybenzoic acid is capable of forming intramolecular hydrogen bonding, thus reduces the extent of intermolecular hydrogen bonding formed.
 - More energy is needed to overcome the more extensive intermolecular hydrogen bonds in vanillic acid.

(d)



(e) (i) $3\text{LiNH}_2 \rightarrow \text{Li}_3\text{N} + 2\text{NH}_3$

(ii)

- Charge density: $\text{Li}^+ \left(\frac{1}{0.06} \right) \ll \text{Mg}^{2+} \left(\frac{2}{0.065} \right)$
- Polarising power: $\text{Li}^+ \ll \text{Mg}^{2+}$ OR
Distortion of electron cloud of NH_2^- by both cations: $\text{Li}^+ \ll \text{Mg}^{2+}$
- Therefore LiNH_2 will have a higher decomposition temperature than $\text{Mg}(\text{NH}_2)_2$.

3 (a) (i) Nucleophilic addition

(ii) NaOH provides the OH^- ions which is a stronger nucleophile for the nucleophilic attack on the carbonyl carbon.



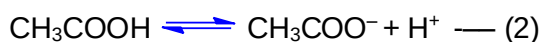
The OH^- will deprotonate the ^{18}O -enriched water to form the ${}^*\text{OH}^-$. ${}^*\text{OH}^-$ then attacks the methanal via nucleophilic addition reaction.

(iv) The carbonyl carbon in aldehyde is less sterically hindered than that in ketones, hence more easily attacked by the nucleophile.

OR

The carbonyl carbon in aldehyde is more electron deficient (δ^+) than that of ketones as ketones have an additional electron donating alkyl group.

(b) (i) 2-hydroxyethanoic acid has a larger K_a as it is a stronger acid.



The electron-withdrawing $-\text{OH}$ group disperses the negative charge on the conjugate base of 2-hydroxyethanoic acid / 2-hydroxyethanoate ion hence stabilising the conjugate base/ 2-hydroxyethanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^+ ions, resulting in 2-hydroxyethanoic acid being a stronger acid.

OR

Intramolecular hydrogen bond can be formed in the 2-hydroxyethanoate ion between the carboxylate ion and the H of the alcohol group hence stabilising the conjugate base/ 2-hydroxyethanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^+ ions resulting in 2-hydroxyethanoic acid being a stronger acid.

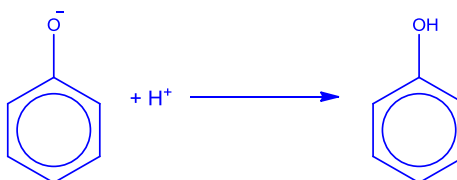
(ii) If both indicators are used in larger amount, a larger volume of sodium hydroxide will be used to reach the end-point to deprotonate the indicators which are also weak acids.

(iii) $X = 3.86$

X corresponds to the pH of the buffer at maximum buffering capacity.

At maximum buffer capacity, $\text{pH} = \text{p}K_a$

(iv)



- (v) First end-point corresponds to the neutralisation of 2-hydroxyethanoic acid.

$$\text{Concentration of 2-hydroxyethanoic acid} = \left(\frac{17.20}{1000} \times 1 \right) \div \frac{20}{1000}$$

$$= 0.860 \text{ mol dm}^3$$

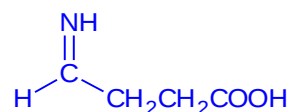
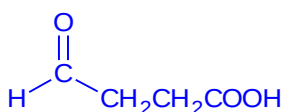
Second end-point corresponds to the neutralisation of phenol.

$$\text{Volume of NaOH used for reaction with phenol} = 26.80 - 17.20 = 9.60 \text{ cm}^3$$

$$\text{Concentration of phenol} = \left(\frac{9.60}{1000} \times 1 \right) \div \frac{20}{1000}$$

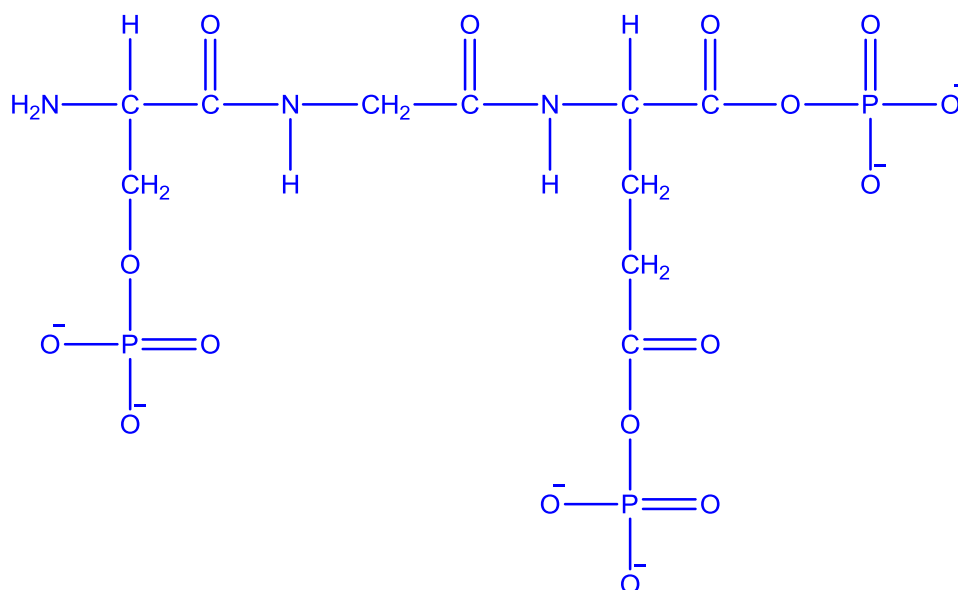
$$= 0.480 \text{ mol dm}^3$$

- (c) (i)



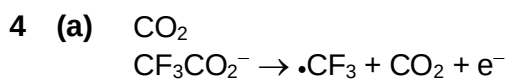
- (ii) Strecker's synthesis produces a racemic mixture and hence, do not display any optical activity while naturally occurring glutamic acid is present as one of the enantiomers and will rotate plane polarised light.

- (d) (i)

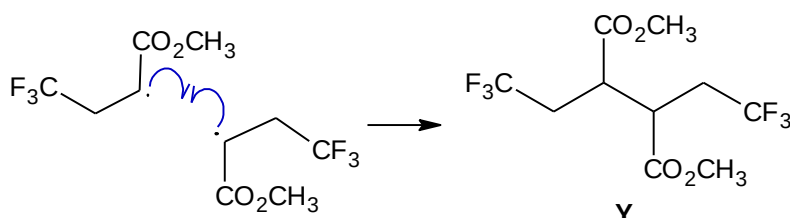
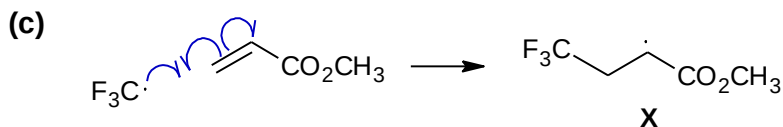


- (ii) The alpha helix is held in place due to hydrogen bonding. Hydrogen bonding occurs between the peptide $-\text{C}=\text{O}$ group of the n th amino acid and the peptide $-\text{NH}$ group of the $(n+4)$ th amino acid which is in the adjacent turn.
- (iii) Heat increases thermal vibrations of the protein molecule, disrupting van der Waals' interactions formed between uncharged R-groups in the tertiary/quaternary structure.

The hydrogen bonds between polar R groups in tertiary structure are also broken.



(b) +3



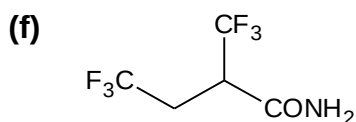
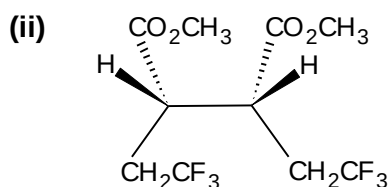
(d) (i) time = $23/20 \times 60 = 69$ s

(ii) $n(\text{Y}) = 0.401/310 = 0.0012935$ mol
 Since $2\text{e}^- \equiv 2\cdot\text{CF}_3 \equiv 2\text{X} \equiv \text{Y}$,
 $n(\text{e}^-) = 0.0025870$ mol

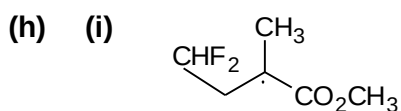
$$Q = (0.0025870)(96500) = 249.65 \text{ C}$$

$$I = 249.65/69 = 3.62 \text{ A}$$

(e) (i) 3



(g) The C-F bonds in the $-\text{CF}_3$ group are relatively strong and hence inert to chemical reactions.



(ii) The presence of the methyl group at the C atom with the unpaired electron makes it more sterically hindered. It is more difficult for two bulkier radicals to collide effectively to form the dimer.

(i) I $\text{CuL}^+ > \text{CdL}^+ > \text{NiL}^+$

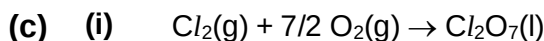
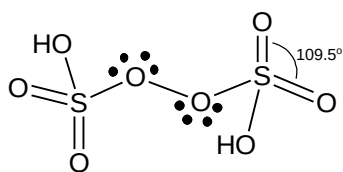
II $\log K (\text{Cu}^{2+}-\text{CH}_3\text{COO}^-) > \log K (\text{Cu}^{2+}-\text{HCOO}^-)$

From the table, the stability of the complexes is in the same order as the availability of the lone pair of electrons on the negatively charged oxygen of the carboxylate anions for dative bonding with the metal ion. Since the lone pair of electrons on the negatively charged oxygen of CH_3COO^- is more available than that of HCOO^- for dative bonding with Cu^{2+} , the $\text{Cu}^{2+}\text{-CH}_3\text{COO}^-$ complex is expected to be more stable than the $\text{Cu}^{2+}\text{-HCOO}^-$ complex.

- 5 (a) 1. Weigh the original sample first.
 2. Add aqueous sodium hydroxide in excess.
 3. Only aluminum oxide will dissolve to form a soluble complex:
 $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl}(\text{OH})_4$
 4. The mixture is then filtered.
 5. Dry the residue and re-weigh the sample again.
 6. If there is contamination, then there should be a difference in mass.

- (b) (i) The molecular formulae suggest that the structure of chlorosulfonic acid is derived from that of sulfuric acid, with $-\text{O}$ atom being replaced by $-\text{Cl}$ atom. Hence the extent of hydrogen bonding is lesser between chlorosulfonic acid molecules and hence requires less energy to overcome, giving it a lower boiling point.

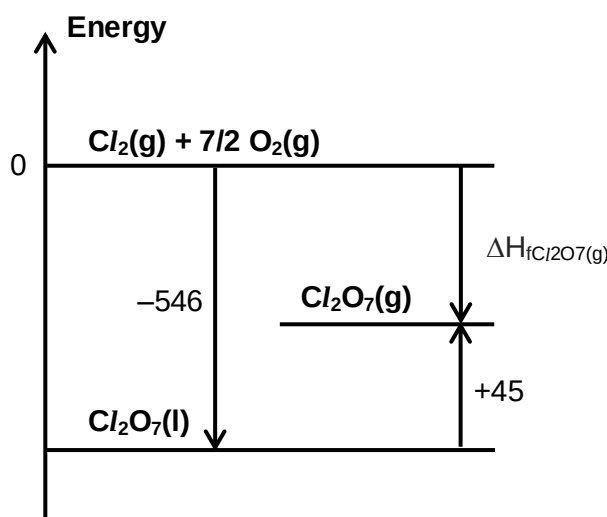
(ii)



- (ii) Bond energy of $\text{Cl}-\text{Cl} = 244 \text{ kJ mol}^{-1}$
 Bond energy of $\text{O}=\text{O} = 496 \text{ kJ mol}^{-1}$
 $-546 = 244 + 7/2(496) - [2 \times 269 + 6(\text{Cl}=\text{O})]$
 Bond energy of $\text{Cl}=\text{O} = +331 \text{ kJ mol}^{-1}$

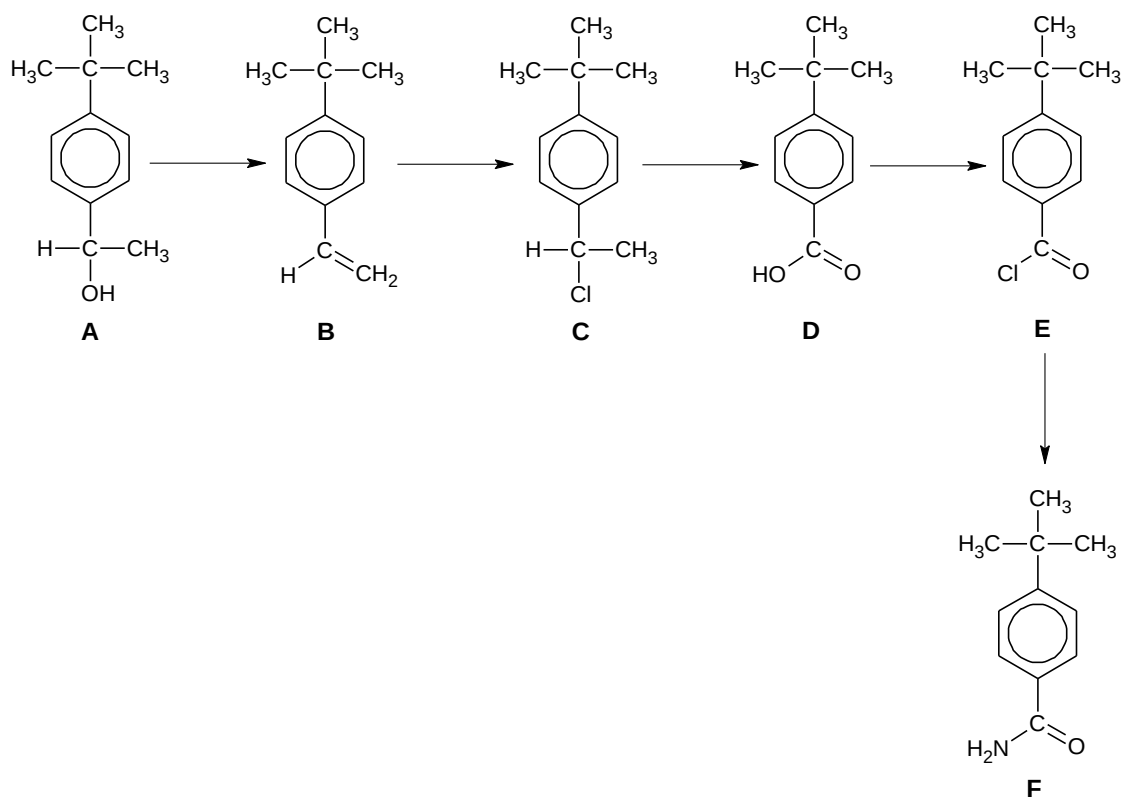
- (iii) Vaporisation of $\text{Cl}_2\text{O}_7(\text{l})$

(iv)



By Hess' Law,
 $\Delta H_{fCl_2O_7(g)} = +45 + (-546)$
 $= -501 \text{ kJ mol}^{-1}$

(d)





HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME

CT GROUP

15S

CENTRE NUMBER

INDEX NUMBER

CHEMISTRY

9647/01

Paper 1 Multiple Choice

21 September 2016

1 hour

Additional Materials: Optical Mark Sheet (OMS)

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Complete the information on the optical mark sheet (OMS) as shown below.

1. Enter your **NAME** (as in NRIC).

2. Enter the **PAPER NUMBER**.

3. Enter your **CT GROUP**.

4. Enter your **NRIC NUMBER** or **FIN Number**

5. Now **SHADE** the corresponding circles in the grid for **EACH DIGIT** or **LETTER**

USE PENCIL ONLY							
FOR ALL ENTRIES ON THIS SHEET							
0	1	2	3	4	5	6	7
☐	☐	☐	☐	☐	☐	☐	☐

NRIC / FIN											
(S)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(A)	(K)	(U)	
(F)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(B)	(L)	(V)	
(G)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(C)	(M)	(W)	
(T)	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(D)	(N)	(X)	

There are **forty** questions on this paper. Answer **all** questions. For each question, there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the OMS.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

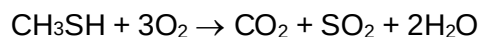
Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

SECTION A

For each question, there are four possible answers **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 Methyl mercaptan, CH_3SH , is one of the substances responsible for bad breath and is often used to impart a smell to natural gas in a pipeline. When a sample of 10 cm^3 of CH_3SH is exploded with 60 cm^3 of oxygen, the final volume of gas after burning is passed into an excess of aqueous alkali. The chemical equation for the combustion process is shown below.



What percentage of the final volume of gas after burning dissolves in the alkali? All gaseous volumes are measured at room temperature and pressure.

- A** 40.0% **B** 28.5% **C** 20.0% **D** 14.3%

- 2 **Figure 1** shows the first six ionisation energies of an element **Q** while **Figure 2** shows the second ionisation energies of eight consecutive elements, including **Q**, in the Periodic Table.

Figure 1

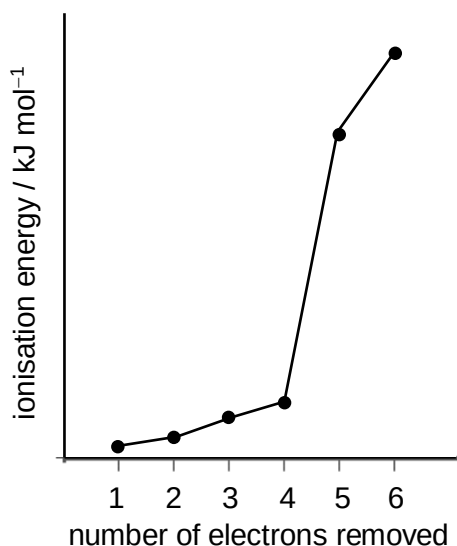
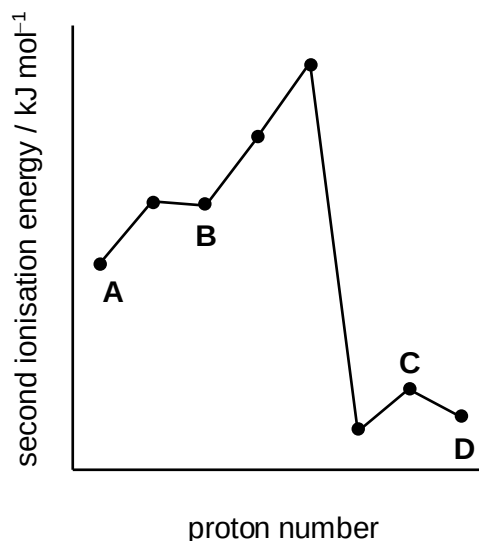


Figure 2

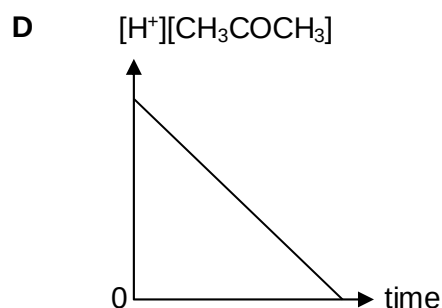
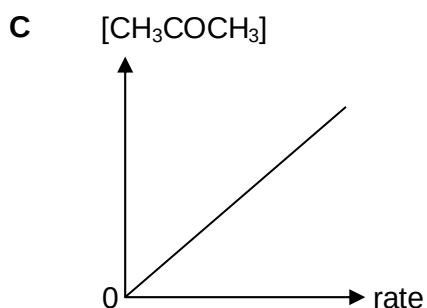
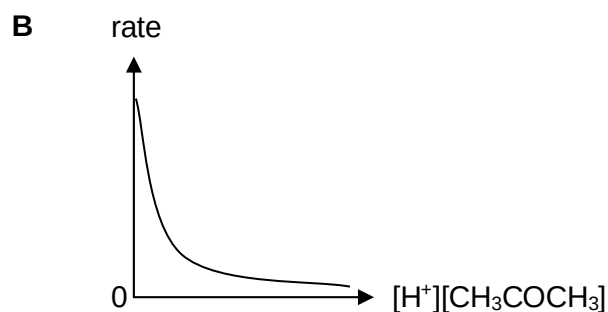
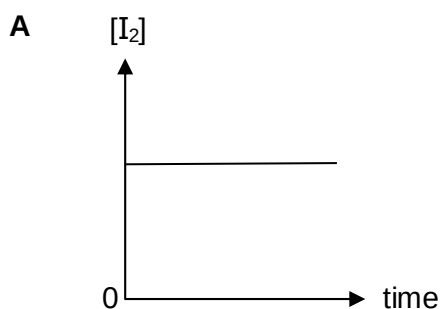


Which of the elements **A**, **B**, **C** or **D** could be the element **Q**?

- 3 Which statement is **not** always true when an ionic solid dissolves in water?
- A** Energy is absorbed to separate the ions in the solid.
- B** Energy is absorbed to break the hydrogen bonding between water molecules.
- C** Energy is released when the ions are hydrated.
- D** Energy is released when the ionic solid dissolves completely.

- 4 Which of the following explains the non-ideal behavior of the gases present in the reaction chamber in the Haber process?
- A the presence of a catalyst
 - B the high temperature of 450 °C
 - C the high pressure of 150 atm
 - D the strong bonds between the atoms in the nitrogen molecules
- 5 Which enthalpy change would best indicate the relative strengths of the intermolecular forces in liquid hydrogen halides?
- A bond dissociation energy
 - B enthalpy change of formation
 - C enthalpy change of solution
 - D enthalpy change of vaporisation
- 6 CH_3COCH_3 and I_2 react in the presence of an acid catalyst. The rate of reaction is independent of $[\text{I}_2]$ but directly proportional to $[\text{H}^+]$ and to $[\text{CH}_3\text{COCH}_3]$.

Which graph is correct?



- 7 When the system $X_2(g) + 3Y_2(g) = 2XY_3(g)$ is at equilibrium at 500 K and 1 atm, the value of the equilibrium constant, K_p , is 100. What is the value of K_p at a pressure of 2 atm at the same temperature?

A 25 **B** 100 **C** 200 **D** 400

- 8 The numerical values of the solubility product of $BaSO_4$, $BaCO_3$ and $Ba(IO_3)_2$ at 25 °C are given in the table below.

Compound	Solubility product
$BaSO_4$	1.1×10^{-10}
$BaCO_3$	2.6×10^{-9}
$Ba(IO_3)_2$	4.0×10^{-9}

An aqueous solution of $BaCl_2$ was added slowly, until in excess, to a solution containing $0.5 \text{ mol dm}^{-3} Na_2SO_4$, $1.0 \text{ mol dm}^{-3} Na_2CO_3$ and $1.5 \text{ mol dm}^{-3} NaIO_3$ at 25 °C.

What is the correct order of precipitation of the three barium salts?

	First to precipitate	→	Last to precipitate
A	$BaSO_4$	$BaCO_3$	$Ba(IO_3)_2$
B	$Ba(IO_3)_2$	$BaCO_3$	$BaSO_4$
C	$BaSO_4$	$Ba(IO_3)_2$	$BaCO_3$
D	$BaCO_3$	$Ba(IO_3)_2$	$BaSO_4$

- 9 What is the pH of the final solution formed when $V \text{ dm}^3$ of dilute hydrochloric acid of pH 1.0 is mixed with $V \text{ dm}^3$ of dilute sulfuric acid of pH 1.0, followed by the addition of $2V \text{ dm}^3$ of water?

A 1.1 **B** 1.3 **C** 2.0 **D** 4.0

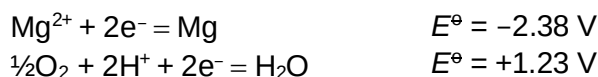
- 10 Stomach juices have a pH of 1.0.

Aspirin is a monobasic acid represented by HA ($K_a = 10^{-4} \text{ mol dm}^{-3}$) which dissociates into H^+ and A^- ions.

What are the relative concentrations of H^+ , A^- and HA when aspirin from a tablet enters the stomach?

- A** $[H^+] > [HA] > [A^-]$ **B** $[H^+] > [A^-] > [HA]$
C $[HA] > [H^+] = [A^-]$ **D** $[H^+] = [A^-] > [HA]$

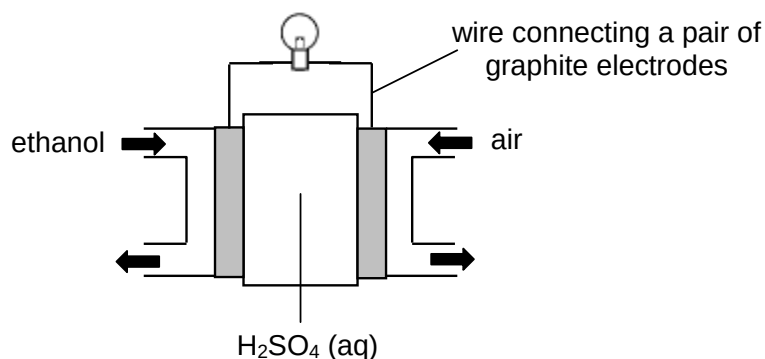
- 11** In the construction of heart 'pacemakers', a tiny magnesium electrode is used which creates an electrochemical cell with the inhaled oxygen. The relevant half-equations are as follows.



Under standard conditions, the cell e.m.f. would be 3.61 V. However, in the body, a potential of 3.25 V is more usual.

Which of the following is an explanation for this lower e.m.f. in the body?

- A** the pH of about 7.4 of the body fluid surrounding the electrodes
 - B** the low concentration of Mg^{2+} ions surrounding the electrodes
 - C** the small size of the magnesium electrode
 - D** the large amount of oxygen inhaled
- 12** Ethanol fuel cells are more practical than hydrogen fuel cells since ethanol is easier to store and transport than hydrogen. Ethanol is converted to carbon dioxide when the fuel cell is operated.



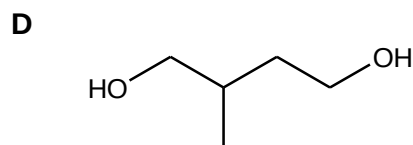
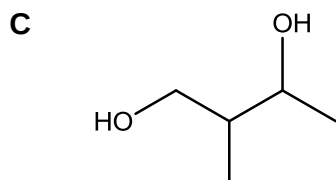
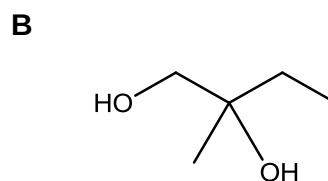
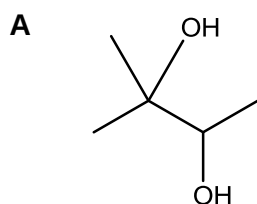
Which statement is correct about ethanol fuel cells?

- A** Ethanol fuel cells can work indefinitely as long as there is a supply of ethanol and air.
- B** For every 1 mol of ethanol oxidised, 6 mol of electrons are produced.
- C** H^{+} ions react with air to produce water at the anode.
- D** The acid needs to be replenished as hydrogen ions are being used up.

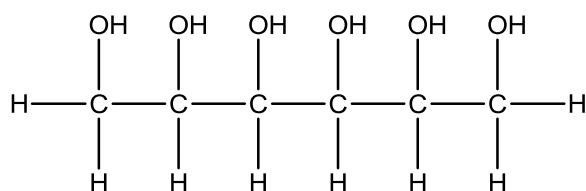
- 13 How many structural isomers of $C_3H_4Br_2$ contain $C=C$ and how many do not contain $C=C$?

	structural isomers with $C=C$	structural isomers without $C=C$
A	4	0
B	4	2
C	5	0
D	5	2

- 14 2-methylbuta-1,3-diene, $CH_2=C(CH_3)-CH=CH_2$, is used as a monomer in the manufacture of synthetic rubbers. Which compound would **not** produce this monomer on treatment with excess concentrated sulfuric acid at $170\text{ }^\circ\text{C}$?



- 15 Sorbitol is a naturally-occurring compound with a sweet taste. It is often used as a substitute for sucrose by the food industry.



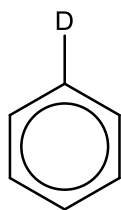
sorbitol

How many chiral centres are present in sorbitol?

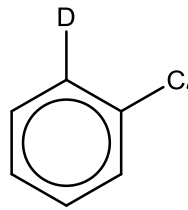
- A** 3 **B** 4 **C** 5 **D** 6

- 16** Deuterium, D, is a heavy isotope of hydrogen. Deuteriobenzene is reacted with chlorine and AlCl_3 under controlled condition so that only monochlorination takes place.

Assuming that the carbon-deuterium bond is broken as easily as a carbon-hydrogen bond, which proportion of the chlorinated products will be 2-chlorodeuteriobenzene?



deuteriobenzene



2-chlorodeuteriobenzene

- A** 16% **B** 20% **C** 33% **D** 40%
- 17** What is the correct set of reagents and conditions for the conversion of methylbenzene to 2-nitromethylbenzene?

- A** dilute nitric acid, 100 °C
B concentrated HNO_3 , 30 °C
C concentrated HNO_3 and concentrated H_2SO_4 , 30 °C
D concentrated HNO_3 and concentrated H_2SO_4 , 100 °C

- 18** Which reaction gives the best yield of products? [(alc) indicates an alcoholic solution.]

- A** $\text{Cyclohexane (alc)} + \text{Cl}_2 (\text{aq}) \xrightarrow{\text{uv light}} \text{Chlorocyclohexane} + \text{HCl}$
- B** $\text{Bromocyclohexene (alc)} + \text{NH}_3 (\text{alc}) \xrightarrow[\text{sealed tube}]{\text{heat}} \text{Cyclohexene-1-amine} + \text{HBr}$
- C** $\text{Bromocyclohexane (alc)} + \text{CH}_3\text{CH}_2\text{ONa (alc)} \xrightarrow{\text{heat}} \text{Cyclohexene} + \text{NaBr} + \text{CH}_3\text{CH}_2\text{OH}$
- D** $\text{Cyclohexanecarboxylic acid (l)} + \text{PCl}_5 (\text{aq}) \xrightarrow{\text{r.t.p.}} \text{Cyclohexanecarbonyl chloride} + \text{POCl}_3 + \text{HCl}$

- 19 Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerators and in making foamed plastics, but are now known to destroy ozone in the upper atmosphere.

Which compound will **not** destroy ozone, and therefore can be used as a replacement for CFCs?

- A CHBr_3
- B CCl_3CBr_3
- C CHClFCClF_2
- D $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

- 20 Compound X has the following properties.

- It changes the colour of acidified sodium dichromate(VI) from orange to green.
- It gives yellow precipitate with alkaline aqueous iodine.

Which compound could be X?

- A**

$$\begin{array}{c} \text{O} \quad \text{OH} \\ \parallel \quad | \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2\text{I} \\ | \\ \text{CH}_3 \end{array}$$

B

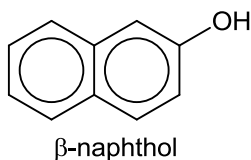
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{OCH}_2\text{CH}_2\text{OH} \end{array}$$
- C**

$$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{H} - \text{C} - \text{C} - \text{CH}_2\text{I} \end{array}$$

D

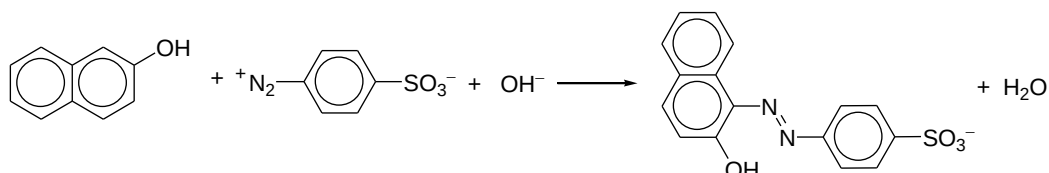
$$\begin{array}{c} \text{I} \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{OH} \\ | \\ \text{OH} \end{array}$$

- 21 β -naphthol is a crystalline solid that is widely used in the production of dyes.

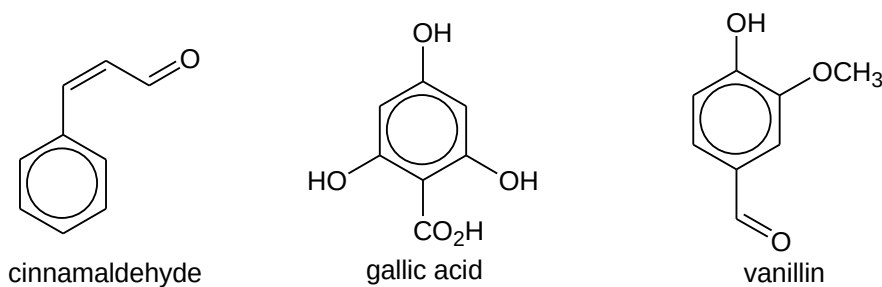


Which of the following is likely to be a property of β -naphthol?

- A Its pK_a is lower than that of phenol.
- B It gives white fumes with SOCl_2 .
- C It reacts with carboxylic acid to form ester.
- D It undergoes nucleophilic substitution in the reaction below.



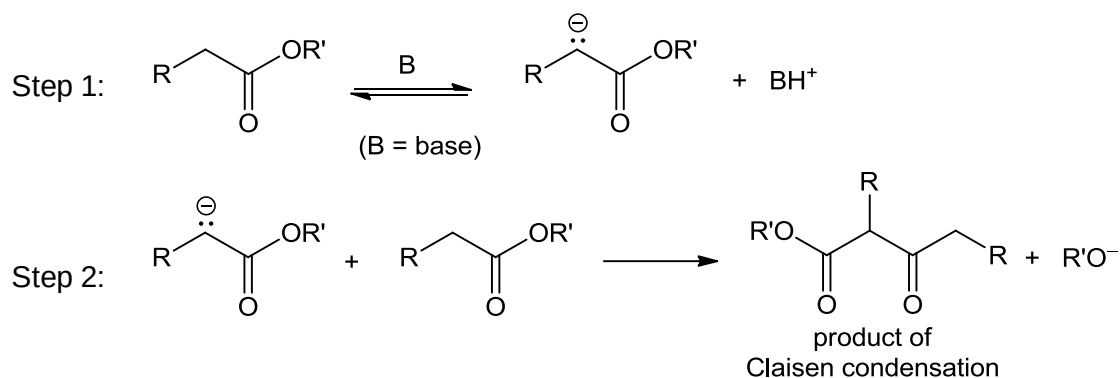
- 22 Cinnamaldehyde, gallic acid and vanillin are naturally occurring organic compounds found in plants.



The CH_3O group is inert and can be disregarded in this question.

Which set of reagents can be used to distinguish these three compounds?

- A Aqueous bromine and aqueous sodium hydrogencarbonate
 - B Aqueous bromine and Tollens' reagent
 - C Fehling's solution and neutral iron(III) chloride
 - D Fehling's solution and hot acidified potassium manganate(VII)
- 23 Two esters can react via Claisen condensation in the presence of a strong base. The two steps of this reaction are shown below.



Which compound will be formed when $\text{CH}_3\text{CH}_2\text{OCOCH}_3$ undergoes Claisen condensation?

- A**

$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$$

B

$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$$

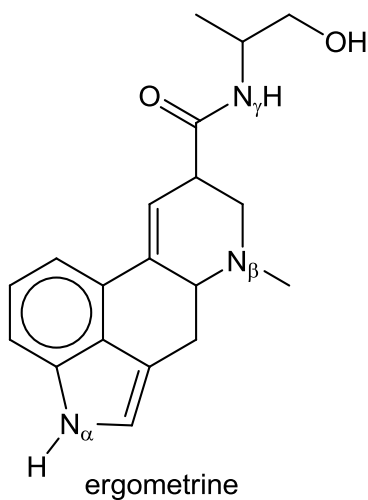
C

$$\text{CH}_3\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$$

D

$$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$$

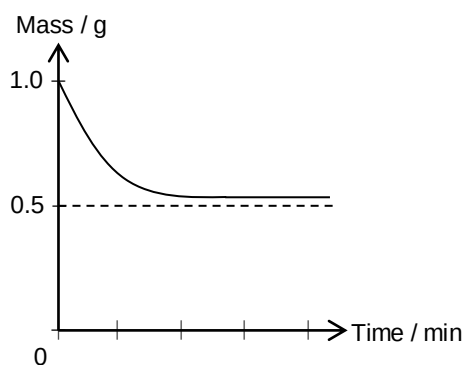
24 Ergometrine is a drug used in obstetrics to treat heavy bleeding after childbirth.



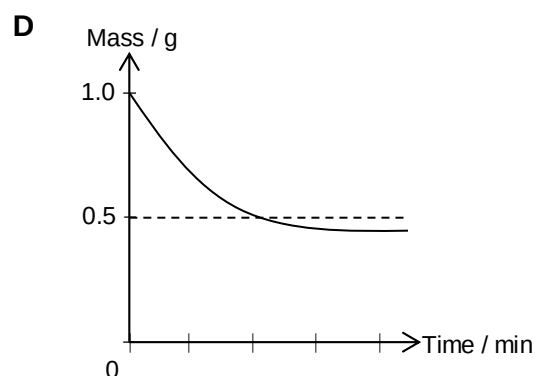
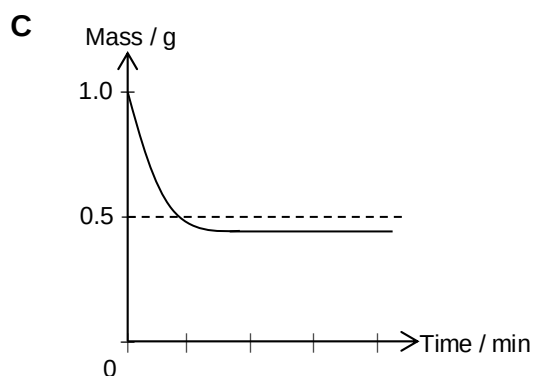
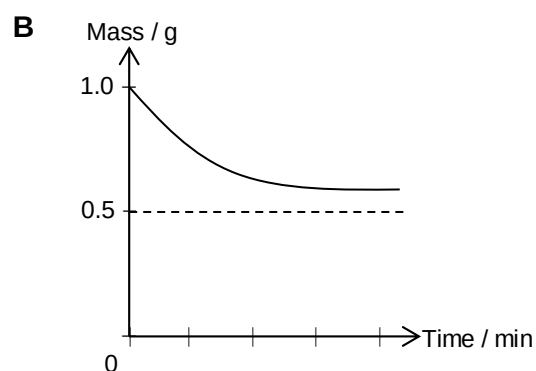
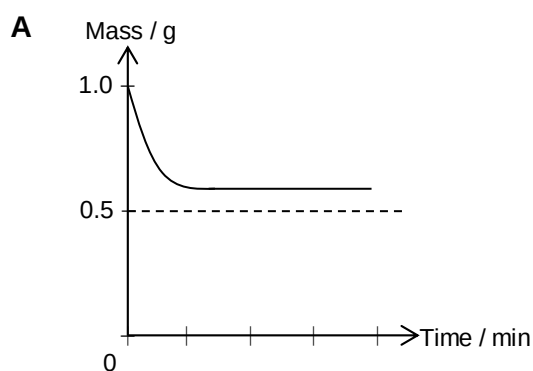
Which statement about ergometrine is correct?

- A pK_b of the labelled three nitrogen atoms in increasing order is $N_\beta < N_\alpha < N_\gamma$.
- B It reacts with both dilute NaOH and dilute HCl at room temperature.
- C It forms orange precipitate with 2,4-dinitrophenylhydrazine.
- D One mole of ergometrine reacts with 3 moles of CH_3COCl .

- 25 The graph represents the change in mass that occurs when 1.0 g of powdered calcium carbonate, CaCO_3 , is heated at a temperature, T .



Which graph would be obtained by heating 1.0 g of powdered magnesium carbonate, MgCO_3 , at the same temperature, T ?



- 26 What chlorine-containing products are formed when chlorine is bubbled into hot aqueous sodium hydroxide?
- A** NaClO only
- B** NaClO_3 only
- C** NaCl and NaClO
- D** NaCl and NaClO_3

27 Which statement concerning the Period 3 elements, sodium to chlorine, is correct?

- A Chlorine has the largest anion.
- B Aluminium has the highest melting point.
- C Chlorine exhibits the most number of different oxidation states.
- D Phosphorus reacts most vigorously with water.

28 Element **X** is one of the first five elements in Period 3 of the Periodic Table. The following four statements were made about the properties of element **X** or its compounds.

Three statements are correct descriptions and one is false.

Which statement does **not** fit with the other three?

- A The oxide of **X** dissolves in excess dilute NaOH(aq).
- B **X** exhibits only one possible oxidation number in its chloride, which is not a solid at room temperature.
- C The oxide of **X** has a very high melting point.
- D The chloride of **X** reacts with water to give an acidic solution with pH 1.

29 Which property of the first row transition elements does **not** remain relatively constant?

A atomic radius	B melting point
C first ionisation energy	D ionic radius of the +2 ions

30 Aqueous platinum(IV) chloride reacts with ammonia to form compounds in which the coordination number of platinum is 6. When dissolved in water, 1 mol of such compound gave 3 mol of ions.

What is the formula of this compound?

A $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$	B $\text{Pt}(\text{NH}_3)_3\text{Cl}_4$
C $\text{Pt}(\text{NH}_3)_4\text{Cl}_4$	D $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$

SECTION B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

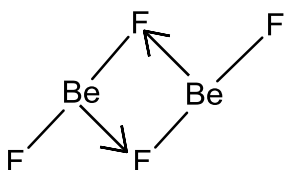
31 Which statements about one mole of a metal are always correct?

- 1** It contains the same number of atoms as one mole of hydrogen atoms.
- 2** It contains the same number of atoms as that in 12 grams of ^{12}C .
- 3** It is liberated by one mole of electrons.

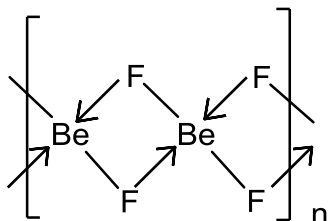
32 Beryllium is the first member of Group II and forms covalent compounds which are said to be electron deficient. In many ways, beryllium resembles aluminium.

Which of the following are possible?

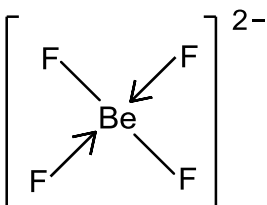
1



2



3



The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 33** When 25.0 cm^3 of a $0.100 \text{ mol dm}^{-3}$ strong monobasic acid was titrated against $0.200 \text{ mol dm}^{-3}$ of a weak base **X**, 12.50 cm^3 of the base was required to completely neutralise the acid.

Which statement is correct for this experiment?

- 1** Bromocresol green ($pK_{\text{in}} = 4.7$) is a suitable indicator for this titration.
- 2** 1 mole of **X** reacts with 1 mole of the monobasic acid.
- 3** A solution of maximum buffering capacity was formed when 6.25 cm^3 of the base was added.

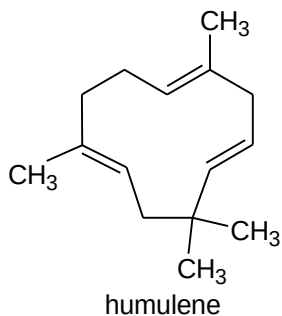
- 34** *The use of the Data Booklet is relevant to this question.*

Electrolysis of a solution of $\text{M}^{n+}(\text{aq})$ led to the deposition of **M** atoms at the cathode. $5.00 \times 10^{-3} \text{ mol}$ of **M** is deposited when 965 C of electricity are passed through the solution.

What could M^{n+} be?

- 1** Sn^{2+}
- 2** Cr^{2+}
- 3** Ag^+

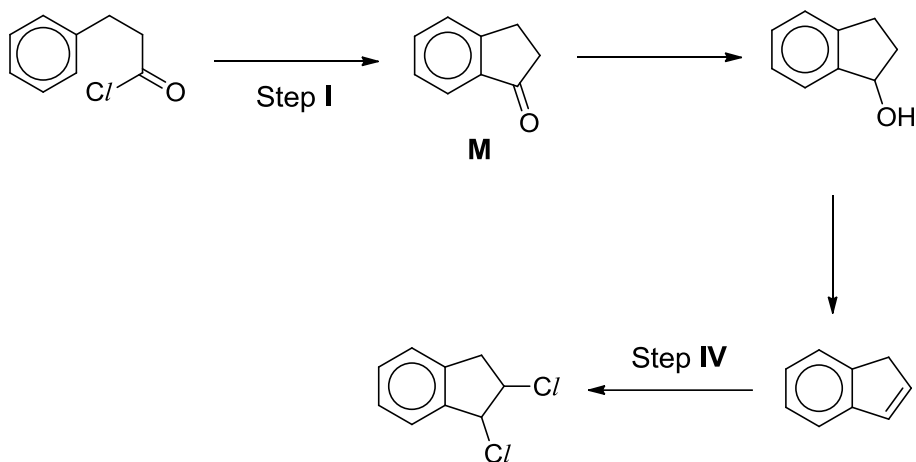
35 Humulene can be extracted from carnation flowers.



Which products are obtained from the reaction of humulene with hot acidified concentrated KMnO_4 ?

- 1 $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$
- 2 $\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$
- 3 $\text{HO}_2\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$

36 Consider the following reaction scheme.



Which of the following statements about this reaction scheme are correct?

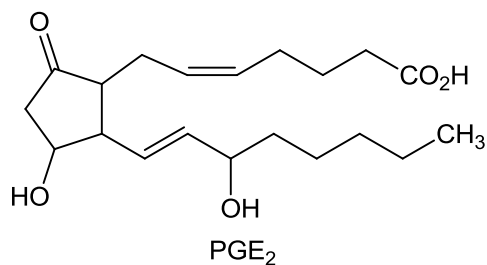
- 1 Step I requires a catalyst.
- 2 Compound **M** is a planar molecule.
- 3 Step IV is a substitution reaction.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

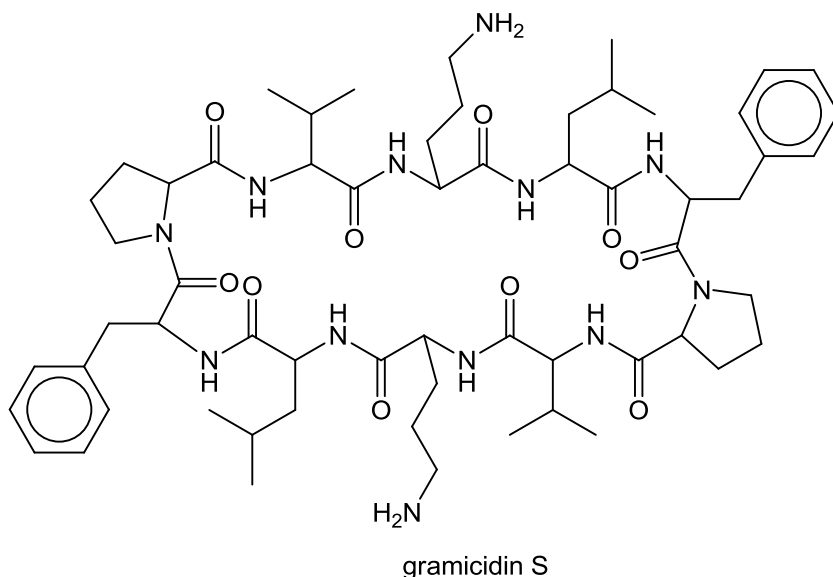
37 PGE₂ is a prostaglandin that has pharmacological activity.



What is the correct number of hydrogen atoms incorporated per molecule of PGE₂ when PGE₂ is reacted with each of the following reducing agents?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of PGE ₂
1	H ₂ / Ni	6
2	LiAlH ₄ in dry ether	4
3	NaBH ₄ in ethanol	4

- 38 The cyclic peptide gramicidin S can act as an antibiotic.



Which statements about gramicidin S are correct?

- 1 It is made up of 5 different amino acids.
 - 2 1 mole of gramicidin S reacts with 10 moles of hot dilute HCl.
 - 3 Its three-dimensional structure can be stabilised by ionic interaction.
- 39 Which of the following are trends across Period 3 of the Periodic Table?
- 1 The electronegativity of the elements increases.
 - 2 The oxides of the elements change from ionic to covalent.
 - 3 The electrical conductivity of the elements decreases.
- 40 Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, is a dark blue pigment often used in painting and dyeing.

It can be synthesised in the laboratory by mixing iron(III) chloride, FeCl_3 , with potassium ferrocyanide, $\text{K}_4[\text{Fe}(\text{CN})_6]$.

Based on the information given above, which conclusions can be made about Prussian blue?

- 1 The percentage by mass of iron in Prussian blue is 45.5%.
- 2 A redox reaction has taken place in the formation of Prussian blue.
- 3 Prussian blue absorbs blue light strongly.

The End



HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

**CANDIDATE
NAME**

CT GROUP

15S

**CENTRE
NUMBER**

**INDEX
NUMBER**

CHEMISTRY

9647/02

Paper 2 Structured Questions

30 August 2016

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1) Write your **name**, **CT group**, **centre number** and **index number** clearly in the spaces at the top of this page.
- 2) Answer **all** questions in the spaces provided in this Question Paper.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [] at the end of each question or part question.

A Data Booklet is provided.

Do not use staples, paper clips, highlighters, glue or correction fluid.

You may use a calculator.

You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
1	/ 12
2	/ 17
3	/ 14
4	/ 13
5	/ 16
Deductions	
Total	/ 72

Calculator Model:

1 Planning (P)

An electrochemical cell is a device that produces an electric current as a result of redox reactions. Any spontaneous redox reaction can be harnessed to produce electrical energy under the right conditions. Electrons are generated at one electrode and driven towards the other by electromotive force, also known as the cell potential, measured in volts.

The Gibbs' Free Energy equation is given as $\Delta G = \Delta H - T\Delta S$. ΔG may be obtained from the cell potential of an electrochemical cell by the relationship:

$$\Delta G = -nFE$$

where n = number of moles of electrons transferred in the reaction

F = Faraday's constant

E = cell potential

By constructing an electrochemical cell, the cell potential can be measured over a range of temperatures. The entropy change of a reaction can then be determined by plotting a suitable linear graph using the data obtained.

- (a) (i) Write an ionic equation for the reaction between Cu and Fe^{3+} . You should include state symbols in your equation.

.....[1]

- (ii) Predict the sign of ΔS for the above reaction. Explain your answer.

.....
.....[1]

- (b) Using the information given above, you are required to write a plan for determining the entropy change for the redox reaction between Cu and Fe^{3+} . You will measure the cell potential over a 30 °C range of temperature.

You are also required to explain how the data you obtain from this experiment may be used to determine the entropy change of the reaction.

You may assume that the values of ΔH and ΔS are constant over this measured temperature change.

You may also assume that you are provided with:

0.20 mol dm⁻³ aqueous FeCl_3

0.10 mol dm⁻³ aqueous CuSO_4

0.50 mol dm⁻³ aqueous H_2SO_4

solid hydrated iron(II) sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

common electrodes

the apparatus normally found in a school or college laboratory.

- a fully-labelled diagram of the set-up of the electrochemical cell you would use to monitor how cell potential varies with temperature;
- details for the preparation of 100 cm³ of 0.20 mol dm⁻³ aqueous acidified FeSO₄;
- details of the appropriate quantities and concentrations of solutions used;
- the temperatures at which the experiments would be carried out;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain;
- how the data obtained from the graph would be used to determine the entropy change for the reaction.

This image shows a full page of white paper with horizontal dashed lines, typical of primary school writing paper. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10

[illegible]

[10]

[Total: 12]

- 2 (a) The transition metals form many complexes. Two examples of complexes formed by Fe^{3+} are $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.

These complexes contain the ligands, H_2O , SCN^- , and CN^- , in which the "donor atom" for dative bonding are O, S and C respectively.

- (i) Explain why the atomic radius of oxygen (0.066 nm) is smaller than that of carbon (0.077 nm).

.....

.....

.....

.....

.....[2]

- (ii) Explain why the atomic radius of sulfur (0.104 nm) is larger than those of oxygen and carbon.

.....

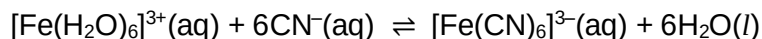
.....

.....[1]

- (b) When water ligands in an aqua complex are replaced by other ligands, the equilibrium constant for the reaction is called the stability constant, K_{stab} , of the new complex.

For
Examiner's
use

For example,



$$K_{\text{stab}} = \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}] [\text{CN}^{-}]^6}$$

The K_{stab} value is an indication of the stability of a complex ion with reference to the aqua complex. The table below lists the K_{stab} values of some iron complexes.

complex	K_{stab}
$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	1×10^2
$[\text{Fe}(\text{CN})_6]^{3-}$	1×10^{31}
$[\text{Fe}(\text{CN})_6]^{4-}$	1×10^{24}
$[\text{Fe}(\text{edta})]^{-}$	1×10^{25}
$[\text{Fe}(\text{edta})]^{2-}$	2×10^{14}



- (i) State the colour of the solution obtained when aqueous potassium thiocyanate, KSCN, is added to aqueous Fe^{3+} .

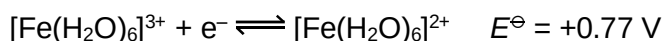
.....[1]

- (ii) Suggest why the colour you stated in (b)(i) is not obtained when aqueous KSCN is added to aqueous $[\text{Fe}(\text{CN})_6]^{3-}$.

.....

[1]

- (iii) Predict whether edta would make the reduction potential for the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ system higher or lower than +0.77 V. Explain your answer.



.....

[1]

(c) A series of tests was conducted as follow:

- I When concentrated hydrochloric acid was added to dissolve black copper(II) oxide, a yellow solution was obtained.
- II Dilution of this yellow solution with water changed its colour to green and then blue.
- III When aqueous ammonia was then added, a pale blue precipitate formed which dissolved in excess aqueous ammonia to give a dark blue solution.

(i) Identify the copper-containing species formed in each test.

Test	Identity of copper-containing species
I	Yellow solution:
II	Blue solution:
III	Pale blue precipitate: Dark blue solution:

[2]

(ii) Write equations to illustrate the ligand exchange reactions in forming the blue solution in Test II:

.....

the dark blue solution in Test III:

..... [2]

(d) Aluminium is extracted from molten aluminium oxide, Al_2O_3 , by electrolysis.

(i) With reference to $E^\ominus$ data from the *Data Booklet*, explain why an aqueous solution of Al^{3+} (from a soluble aluminium salt) would be unsuitable as the electrolyte.

.....

.....

.....[1]

In the industry, Al_2O_3 is dissolved in molten cryolite, Na_3AlF_6 to lower the melting point of Al_2O_3 . The molten mixture is then electrolysed using graphite electrodes.

For
Examiner's
use

- (ii) The electrode reactions are very complicated. In one simplified study, some scientists say that, in molten cryolite, Al_2O_3 ionises into Al^{3+} ions and AlO_2^- ions.

At the cathode, Al^{3+} is converted to Al metal: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

At the anode, AlO_2^- is converted to Al_2O_3 and oxygen gas.

Write an equation for the anode reaction.

..... [1]

- (iii) A typical cell operates at 10^4 A. Calculate the time, in hours, needed to produce 1 tonne of aluminium. (1 tonne = 1000 kg)

[2]

- (e) A saturated solution of XeF_2 ($M_r = 169$) in water at 0°C contains 25.0 g dm^{-3} of XeF_2 . The solution is a strong oxidising agent, quantitatively oxidising another solution containing $0.150 \text{ mol dm}^{-3}$ of a Cr(III) salt. XeF_2 is reduced to Xe in the reaction.

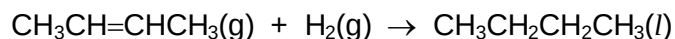
In an experiment, 15.20 cm^3 of the XeF_2 solution is required to completely react with 10.0 cm^3 of the Cr(III) solution.

Determine the oxidation state of Cr after the reaction.

[3]

[Total: 17]

- 3 The hydrogenation of but-2-ene is shown in the equation below



- (a) Describe the changes in bond angle and the type of hybridisation involved at the site of the hydrogenation reaction.

.....

[2]

- (b) Under certain conditions, but-2-ene gives alcohol **A**, $\text{C}_4\text{H}_{10}\text{O}$, which exists as a liquid at room temperature.

- (i) State the reagents and conditions required in this reaction. Draw the displayed formula of alcohol **A** formed in this reaction.

Reagents and conditions:

A:

[2]

- (ii) Explain, in terms of structure and bonding, the difference in the physical state of but-2-ene and alcohol **A** at room temperature. Draw a diagram to illustrate your answer for alcohol **A**.

.....

Diagram:

[3]

- (iii) Ester **C** is used in synthetic fruit flavours. Alcohol **A** reacts with compound **B** at room temperature to give a good yield of ester **C** with relative molecular mass of 116.

Draw the structures of compounds **B** and **C**.

B:

C:

[2]

- (c) (i) In a separate reaction, butane is treated with a small quantity of bromine in the presence of ultraviolet light to give 1-bromobutane and 2-bromobutane. It is found experimentally that the hydrogen atom is substituted by bromine at different rates, as shown in the table below.

Type of H atom	Relative rate of substitution
Primary hydrogen	1
Secondary hydrogen	4.5

Using this information, and considering the number and types of hydrogen within butane, determine the mole ratio of the two monobrominated products.

.....

[2]

- (ii) Name and outline the mechanism for the formation of 2-bromobutane in this reaction.

*For
Examiner's
use*

[3]

[Total: 14]

- 4 (a) Using relevant data from the *Data Booklet*, describe and explain how the thermal stability of the hydrogen halides varies down Group VII.

.....

.....

.....

.....

.....[2]

- (b) In the laboratory, three bottles each containing one of the following reagents were mixed up:

NaI(aq), KBr(aq) and KCl(aq).

Describe chemical test(s), which does **not** involve silver nitrate, that could distinguish and identify the contents of each bottle.

.....

.....

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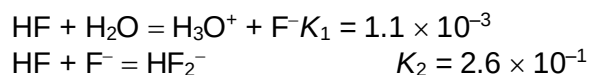
.....

.....

.....

.....[3]

- (c) HF behaves as a medium-strength acid and dissociates only partially in aqueous solutions as shown below. K_1 and K_2 represent the numerical values of the respective equilibrium constants.



- (i) Write the overall equation for the reaction of liquid HF with H_2O to form HF_2^- and calculate the numerical value of the equilibrium constant for this reaction.

[2]

- (ii) The dissociation equilibrium of a solute in a solvent can be significantly shifted by the addition of a suitable substance into the solution. Suggest an inorganic reagent which can be added to increase the dissociation of HF in water. Explain your choice.

.....

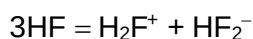
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.....

.....[2]

- (d) Similar to water, pure liquid hydrogen fluoride also undergoes auto-ionisation according to the following equilibrium:



The ionic product of HF is $8.0 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$.

- (i) Draw the structures of both the cationic and anionic species in liquid HF. Label the types of bonding within the anionic species.

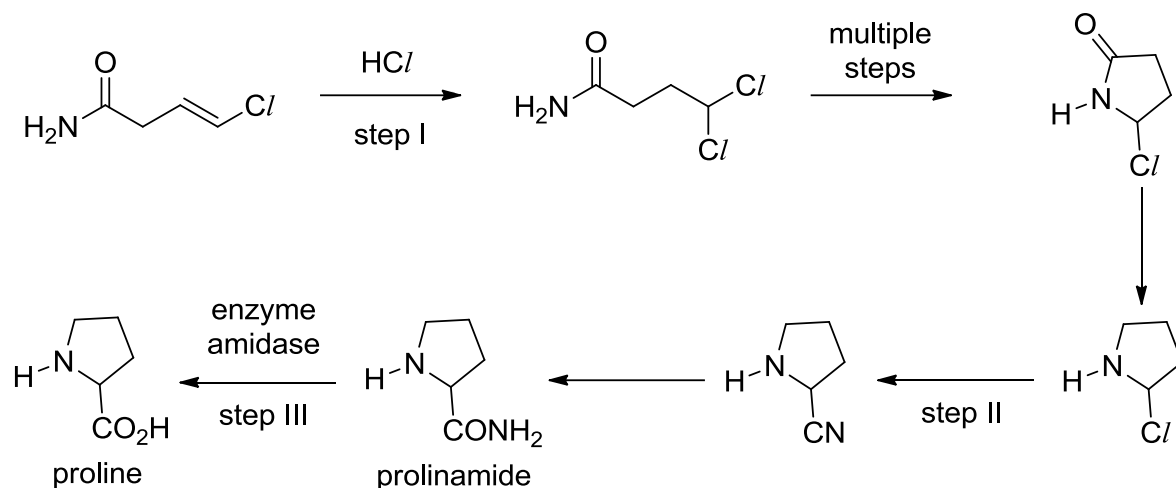
[2]

- (ii) Calculate the fraction of H_2F^+ in liquid HF (density = 1.002 g cm^{-3}), supposing that only these three species are present in the system.

[2]

[Total: 13]

- 5 The following reaction scheme is proposed for the synthesis of the amino acid proline.



- (a) (i) Draw structures of two possible intermediates formed in step I. Hence, explain why the yield of the product in step I is low.

.....

[2]

- (ii) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of reaction in step II.



.....

[3]

- (iii) It was found that only 50% of prolinamide synthesised by the method above could be converted to proline by enzyme amidase in step III. Suggest an explanation for this observation.

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.....

[1]

- (b) The enzyme amidase used in step III contains amino acids listed in the following table.

name	abbreviation	structural formula
aspartic acid	asp	$\text{HO}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
asparagine	asn	$\text{H}_2\text{NCOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
cysteine	cys	$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
glycine	gly	$\text{CH}_2(\text{NH}_2)\text{CO}_2\text{H}$
isoleucine	ile	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
lysine	lys	$\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
phenylalanine	phe	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
serine	ser	$\text{HOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$

- (i) There are three pK_a values associated with aspartic acid: 2.1, 3.7 and 9.8. In the boxes below, draw the structures of the major species present in solutions of aspartic acid at pH 3 and pH 8.

pH 3	pH 8

[2]

- (ii) Complete the following table by indicating the type of interaction between each pair of amino acid residues that stabilises the tertiary structure of enzyme amidase at pH 7.

amino acid residue 1	amino acid residue 2	type of interaction
aspartic acid	lysine	
isoleucine	phenylalanine	
serine	asparagine	

[2]

- (iii) Explain how mercury ion, $\text{Hg}^{2+}(\text{aq})$, affects the activity of the enzyme amidase through denaturation.

.....

.....

.....[2]

- (c) A section of the polypeptide chain in enzyme amidase was partially hydrolysed and the following peptide fragments are produced.

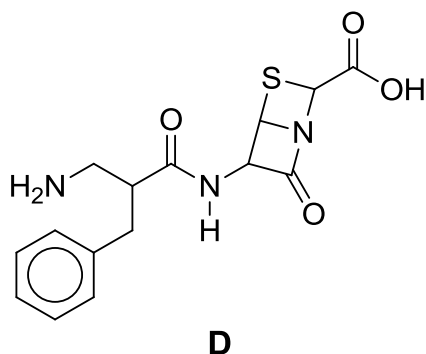
lys-gly, asp-lys-ser, cys-asn-phe, gly-cys-asn, ser-phe-lys

State the **smallest** possible sequence of amino acids in this section of the polypeptide chain using the 3-letter abbreviations.

.....[1]

- (d) A scientist extracted a new compound **D** from microorganisms. He proposed the following structure for **D**.

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- (i) **D** was postulated to be synthesised from amino acids.

Identify from the list in (b), **two** α -amino acids that could be used in the synthesis.

.....[1]

- (ii) Assuming that the S–C bond is inert, draw the organic products if **D** was heated in aqueous H_2SO_4 .

[2]

[Total: 16]



HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE
NAME

CT GROUP

15S

CENTRE
NUMBER

INDEX
NUMBER

CHEMISTRY

9647/03

Paper 3 Free Response

19 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper

Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin each question on a **new** piece of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

<u>Write down the question numbers</u> for the questions attempted on the <u>cover page</u> provided.

Answer any **four** questions.

- 1 (a) Suggest and explain how the boiling points of 1-chlorobutane and 1-bromobutane differ from each other. [2]

- (b) (i) Define the term *standard enthalpy change of combustion*. [1]

- (ii) Use of the *Data Booklet* is relevant to this question.

In an experiment to determine the enthalpy change of combustion of bromobutane, a quantity of the fuel was burnt underneath a copper can containing 200 g of water. It was found that the temperature rose by 45.0 °C after 2.35 g of bromobutane had been burnt. The heat transfer was known to be only 80% efficient.

Calculate the enthalpy change of combustion of the bromobutane. Ignore the heat capacity of the copper can. [2]

- (c) An experiment was set up to study the reaction between 2-bromo-3-methylbutane and sodium hydroxide. The reagents used were **FA1**, containing 0.0100 mol dm⁻³ of 2-bromo-3-methylbutane and **FA2**, containing 0.0100 mol dm⁻³ NaOH. In each experiment, the reagents were dissolved in a suitable solvent to ensure good mixing. The results are recorded in the table below.

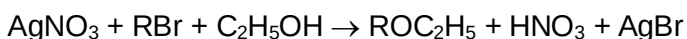
Expt	Volume of FA1 / cm ³	Volume of FA2 / cm ³	Volume of solvent / cm ³	Rate / mol dm ⁻³ s ⁻¹
1	10.0	30.0	60.0	7.40 × 10 ⁻⁷
2	5.0	20.0	25.0	9.86 × 10 ⁻⁷
3	10.0	5.0	35.0	4.93 × 10 ⁻⁷

- (i) Use the data in the table to deduce the order of reaction with respect to 2-bromo-3-methylbutane and sodium hydroxide. Hence, write a rate equation for this reaction. [3]
- (ii) With reference to your answer to (c)(i), describe the mechanism for the reaction between 2-bromo-3-methylbutane and sodium hydroxide. [3]
- (iii) Calculate the rate constant for the reaction, stating the units. [2]

- (d) In a separate experiment, a student performed the following qualitative analysis tests on three different bromoalkanes: 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane. Different solvents were used for **Test 1** and **Test 2** and it was observed that the choice of solvents did have an effect on the type of reaction mechanisms undergone by the bromoalkanes.

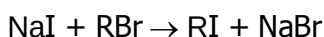
Test 1:

When silver nitrate was added to the bromoalkanes using ethanol as the solvent, silver bromide was precipitated for all three bromoalkanes at different rates.



Test 2:

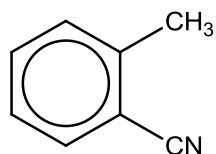
When sodium iodide in propanone solvent was added to the bromoalkanes, sodium bromide was precipitated for 1-bromobutane and 2-bromobutane at different rates, but not 2-bromo-2-methylpropane.



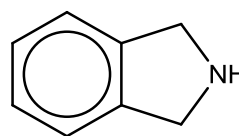
The observations for each test were recorded in the following table.

	Time taken for precipitate to appear	
	Test 1	Test 2
1-bromobutane	5 min	Almost immediately
2-bromobutane	3 min	5 min
2-bromo-2-methylpropane	Almost immediately	No precipitate

- (i) Different nucleophilic substitution mechanisms have been proposed for the reactions in the two tests.
- Considering the information provided, suggest the predominant mechanism undergone in each test. [1]
- (ii) Considering the structure of the bromoalkane, explain why the test results support your answer in (d)(i). [2]
- (iii) Considering the interactions involved with the solvent, explain why the suggested mechanism for **Test 1** occurs predominantly. [1]
- (e) 2-methylbenzonitrile can be used as a starting reagent to form compound **A**. Propose a synthesis route for the formation of compound **A** in no more than 3 steps, showing clearly the reagents, conditions and structures of the intermediates formed.



2-methylbenzonitrile



Compound **A**

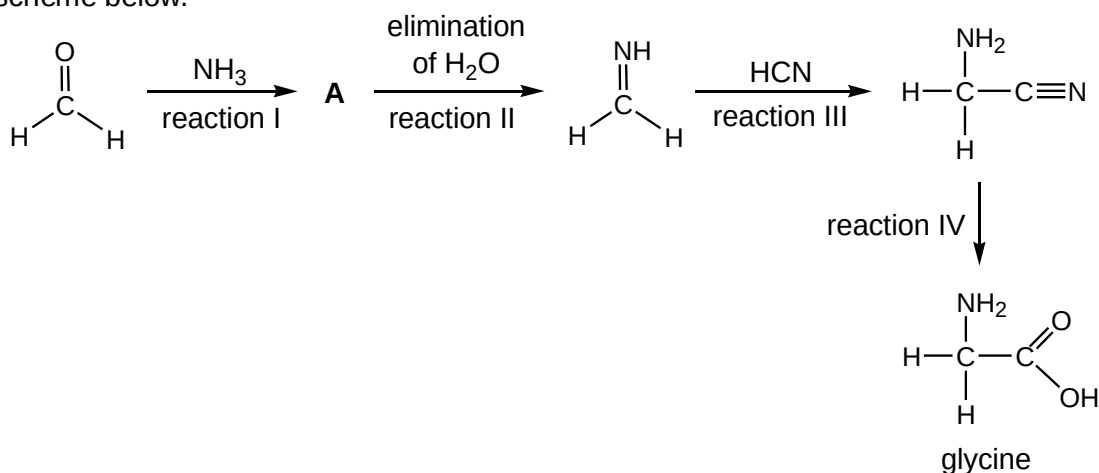
[3]

[Total: 20]

- 2 Ethanoic acid behaves as a weak acid in water, with $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$.
In contrast, ethanoate ion behaves as a weak base in water, with $K_b = 5.6 \times 10^{-10} \text{ mol dm}^{-3}$.

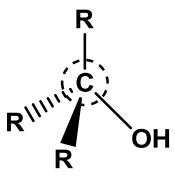
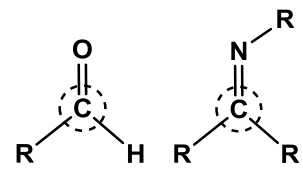
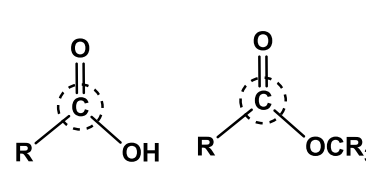
- (a) (i) Write the expressions for K_a and K_b of ethanoic acid and ethanoate ion respectively, and use these expressions to show that the product $K_a \times K_b$ has a constant value at a fixed temperature. [2]
- (ii) Compare the relative strength of ethanoate ion and water as bases, and explain with the aid of an equation, whether a solution of sodium ethanoate is acidic, alkaline, or neutral. [2]
- (iii) Calculate the pH of a solution which contains 0.50 mol dm^{-3} ethanoic acid and 0.50 mol dm^{-3} sodium ethanoate. [1]

- (b) The Strecker synthesis is a route to prepare amino acids. Glycine (2-aminoethanoic acid) can be prepared from methanal as shown in the reaction scheme below.



- (i) Suggest a structure for compound **A**. [1]
- (ii) The product of **reaction II** is an imine, which has a C=N bond. Methanal undergoes reaction with another compound **B** to form an orange solid **C** which also has a C=N bond. Name compound **B** and draw the structure of the orange solid **C**. [2]
- (iii) What *type of reaction* is occurring during **reaction III**? [1]
- (iv) State the reagents and conditions for **reaction IV**. [1]
- (v) Compound **D** is an isomer of glycine. Upon warming **D** with dilute sodium hydroxide, a gas which turns litmus blue is evolved. Draw the structure of **D**. [1]
- (vi) A carbonyl compound **E** can be used as the starting material to prepare another amino acid, alanine (2-aminopropanoic acid) using the Strecker synthesis. Draw the structure of **E**. [1]
- (vii) The synthesis of alanine in (b)(vi) produces a mixture of two optical isomers. State which one of the reactions, **I** to **IV**, gives rise to this mixture, and explain your choice briefly. [2]

- (c) In organic chemistry, the number of bonds that a given carbon atom has with electronegative atoms like O or N is called the functional group level of that carbon atom. Some examples are shown below, but there are many other possibilities.

Functional group level		
1	2	3
		

(R = alkyl or aryl group or H atom)

- (i) State the functional group level of the carbon atom in methane and in carbon dioxide. [1]

Keeping track of the functional group level can be used to understand a large number of organic reactions.

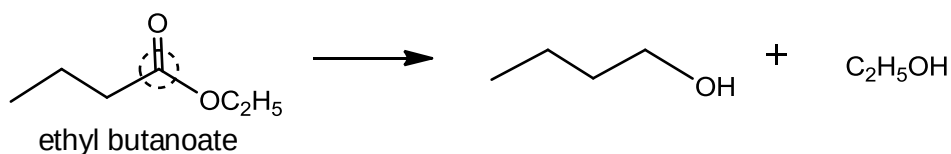
During **oxidation reactions**, the functional group level increases as C–H bonds are converted into new C–O bonds.

During **reduction reactions**, the functional group level decreases as C–O bonds are converted into new C–H bonds.

During **hydrolysis reactions**, the functional group level of every carbon remains the same.

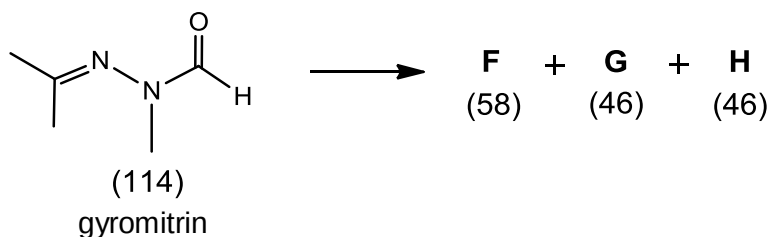
In each of the reactions in (c)(ii) and (c)(iii), no carbon-carbon bonds are broken or formed.

- (ii) Ethyl butanoate undergoes the following reaction to form two products. State the functional group level of the *circled* carbon atom at the start and end of the reaction, and hence deduce whether the reaction is an oxidation, a reduction, or a hydrolysis reaction.



[2]

- (iii) Gyromitrin, a toxin found in fungi, undergoes hydrolysis to give three different products, **F**, **G**, and **H**. Suggest structures for these products using their relative molecular masses (shown in brackets) and the functional group levels of the carbon atoms.



[3]

[Total: 20]

3 Use of the Data Booklet is relevant to this question.

In 2016, 4 new elements were added to the Periodic Table. Part of the Periodic Table showing information about the 4 new elements is shown below.

Key						
—		—		—	—	relative atomic mass
Nh		Mc		Ts	Og	atomic symbol
nihonium		moscovium		tennessine	oganesson	name
113		115		117	118	proton number

Mc, Ts, and Og were synthesised by accelerating calcium ions into atoms of heavier elements. Once in every few billion collisions, the nuclei of the 2 particles would fuse and give rise to the new element. For example, Ts was synthesised using berkelium ($_{97}\text{Bk}$).

(a) (i) State the heavy element used in the synthesis of Mc. [1]

(ii) Based on the relative position of Ts in the Periodic Table, predict the physical state of Ts at room temperature. Give a brief explanation for your answer. [2]

(iii) Scientists have predicted the existence of superheavy elements above proton number 120 that are stable under standard conditions. One such element, if successfully synthesised in large quantities, would give rapid effervescence of a colourless gas in water, and its oxide would be basic in nature. The sulfate compound of the element would be insoluble in water.

State, with reasons, the group of the Periodic Table that this element is likely to belong. [2]

(b) Scientists are already working on the next element of proton number 119 using berkelium and titanium.

(i) Explain, using relevant electronic configurations, why titanium is considered a transition element but not zinc. [2]

(ii) Tetrahydrofuran (THF), $M_r = 72.1$, is a simple covalent molecule that behaves as a monodentate ligand. Titanium forms a complex with zero net charge with THF and chloride ligands. A 1.00 g sample of the complex was completely hydrolysed in water and filtered. The residue contained 2.99×10^{-3} mol of TiO_2 . The filtrate yields 1.72 g of silver chloride after treating with aqueous silver nitrate. Determine the coordination number of the central titanium of the complex. [3]

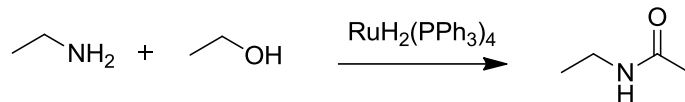
Calcium and titanium are both metals but differ in their chemical and physical properties.

- (c) (i) Compounds of calcium contain the Ca^{2+} ion. The corresponding ion of titanium is Ti^{3+} . Use relevant data from the *Data Booklet* to explain why Ca^{3+} compounds do not exist and Ti^{3+} compounds do. [3]
- (ii) Draw labelled diagrams to show the shapes of the orbitals in the **outermost** occupied quantum shell of a Ca^{2+} ion. [2]
- (iii) Explain why the melting point of titanium is higher than that of calcium. [2]
- (iv) Describe the observations when calcium is burned in air, and excess water is added to the resulting oxide. Write equations where appropriate and suggest the pH value of the aqueous solution formed. [3]

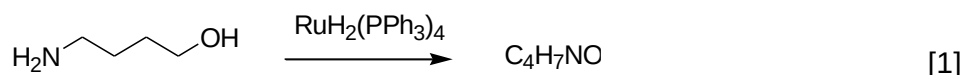
[Total: 20]

- 4 Transition metal catalysed reactions have emerged in recent years as powerful tools for preparing organic compounds from previously unavailable routes. Ruthenium-based catalysts have been at the heart of these advances.

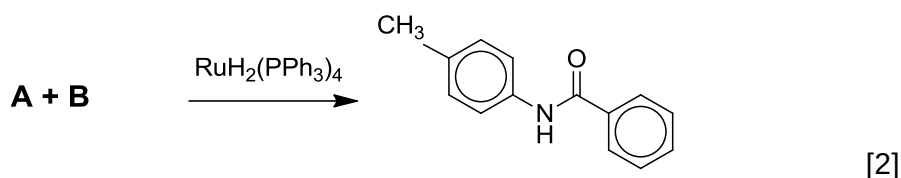
(a) The ruthenium(II) based catalyst $\text{RuH}_2(\text{PPh}_3)_4$, where $\text{PPh}_3 = \text{P}(\text{C}_6\text{H}_5)_3$, is able to catalyse the formation of an amide under suitable conditions, as shown in the scheme below.



(i) Draw the structure of the product for the reaction below.



(ii) $\text{RuH}_2(\text{PPh}_3)_4$ also catalyses the formation of the amide shown in the reaction scheme below. Draw the structures of compounds **A** and **B**.

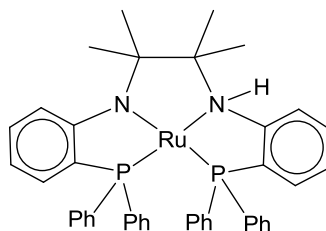


(iii) Propose a synthetic route for the formation of compounds **A** and **B**, using only methylbenzene as the starting compound in each case. [3]

(b) The catalyst $\text{RuH}_2(\text{PPh}_3)_4$ exhibits geometric isomerism. In the cis configuration, the H-Ru-H angle is 90° , while in the trans configuration, the H-Ru-H angle is 180° .

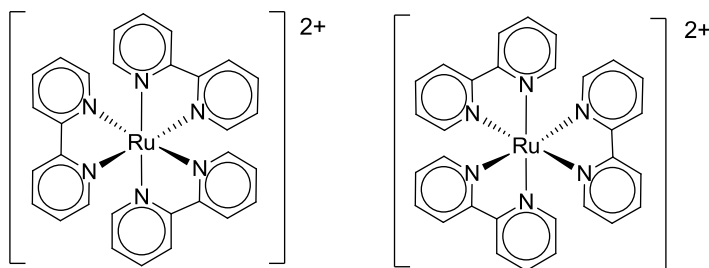
Draw labelled diagrams showing the structures of the two isomers. [2]

(c) In addition to $\text{RuH}_2(\text{PPh}_3)_4$, other ruthenium complexes like the one shown below, also proved to be effective in organic synthesis.

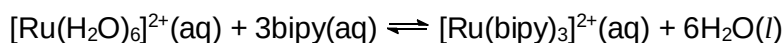


State the oxidation number of ruthenium in the complex above. [1]

- (d) The complex ion tris(bipyridine)ruthenium(II) is a catalyst which has received much attention because of its ability to exhibit optical isomerism. Two of its isomers are shown below.



- (i) Explain why the complex above exhibits optical isomerism. [1]
- (ii) Tris(bipyridine)ruthenium(II) cation contains three bipyridine rings, which can be represented by the symbol, bipy. The formation of tris(bipyridine)ruthenium(II) from aqueous ruthenium(II) ions is shown in the equation below. The enthalpy change for this reaction is approximately zero.



Deduce the sign of the entropy change, ΔS , and hence the sign of the free energy change, ΔG , in this reaction. [3]

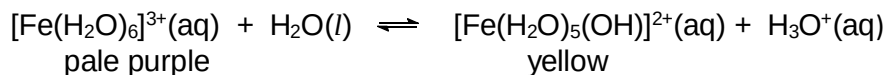
Iron is directly above ruthenium in the transition metal block of the Periodic Table.

- (e) Ligands are able to modify the difference in energy between the non-degenerate d-orbitals in an octahedral crystal field.

The following table lists the different colours of visible light and their corresponding wavelengths. The energy of light is inversely proportional to its wavelength.

Colour	violet	blue	green	yellow	red
Wavelength / nm	400	450	500	600	650

The equation below represents the hydrolysis of Fe(III) ions in water. The pale yellow colour of Fe(III) solutions observed commonly is actually due to the presence of the complex ion $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, while unhydrolysed $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is pale purple in color.

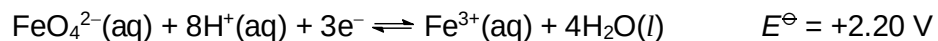


- (i) With reference to the colours of the two complexes above, explain which complex ion has a larger energy gap between their d-orbitals. [2]
- (ii) Electrons in both $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ exhibit a 'high spin' state, where electrons occupy the d-orbitals singly before starting to pair up in the lower energy d-orbitals.

Draw a suitable diagram to show the electron distribution in the 3d subshell of a Fe^{3+} ion in a 'high spin' **excited** state, where an electron from a lower energy d-orbital has been promoted to a higher energy d-orbital by absorbing light of a certain wavelength.

[1]

- (f) K_2FeO_4 is a strong oxidising reagent which is dark red in colour.



Using relevant data from the *Data Booklet*, describe and explain the observations when the following solutions are mixed together in **I** and in **II** respectively. Calculate the $E^\ominus_{\text{cell}}$ and write a balanced equation for any reaction occurred.

I K_2FeO_4 and H_2O_2

II KMnO_4 and $\text{Fe}(\text{NO}_3)_3$

[4]

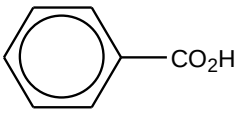
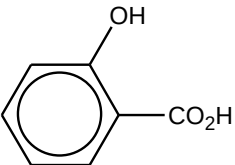
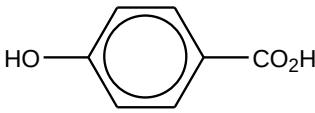
[Total: 20]

- 5 (a) Ag_2CO_3 is a sparingly soluble salt. A 100 cm^3 saturated solution of Ag_2CO_3 in water was found to contain $2.57 \times 10^{-4}\text{ mol dm}^{-3}$ of Ag^+ ions.

(i) Calculate the K_{sp} of Ag_2CO_3 and state its units. [2]

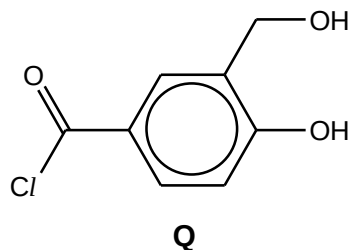
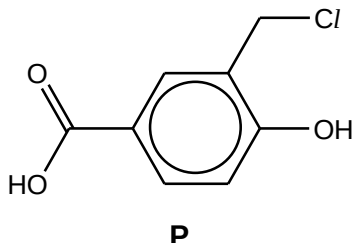
(ii) Hence, calculate the solubility of Ag_2CO_3 when 2.50 g of Na_2CO_3 solid was added to the solution above. [2]

- (b) The table below shows the $\text{p}K_{\text{a}}$ values of benzoic acid and its derivatives.

Acid	benzoic acid	2-hydroxybenzoic acid	4-hydroxybenzoic acid
Structure			
$\text{p}K_{\text{a}}$	4.20	2.98	4.58

Rank the three compounds in order of **increasing** acid strength and account for the trend. [3]

- (c) Compounds **P** and **Q** can be synthesised from 4-hydroxybenzoic acid.



Suggest the reagents and conditions for a reaction that could be used to distinguish between **P** and **Q**. You need to state how **each** of **P** and **Q** react. [2]

- (d) Heating compound **A**, $\text{C}_{13}\text{H}_{14}\text{O}_3$, under reflux with dilute H_2SO_4 produces compound **B**, $\text{C}_8\text{H}_8\text{O}$, and compound **C**, $\text{C}_5\text{H}_8\text{O}_3$.

B reacts with aqueous bromine to give compound **D**, $\text{C}_8\text{H}_7\text{O}_2\text{Br}_3$. On heating **B** with acidified KMnO_4 , 4-hydroxybenzoic acid and carbon dioxide gas are formed.

When **C** is heated with acidified KMnO_4 , compound **E** is the only organic product formed. Both **C** and **E** gave yellow precipitate when warmed with alkaline aqueous iodine. Treatment of **E** with aqueous Na_2CO_3 liberates carbon dioxide gas.

- (i) When vaporised in a suitable apparatus, 0.219 g of **E** occupied a volume of 70 cm^3 at $150\text{ }^\circ\text{C}$ and a pressure of 125 kPa .

Calculate the relative molecular mass of **E** and hence suggest a molecular formula for **E**, given that it contains 3 carbon atoms. [2]

- (ii) Suggest structures for **A** to **E**, explain your reasoning. [9]

[Total: 20]

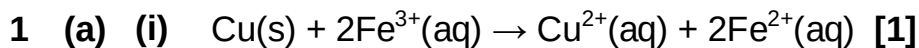


HWA CHONG INSTITUTION
2016 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 1

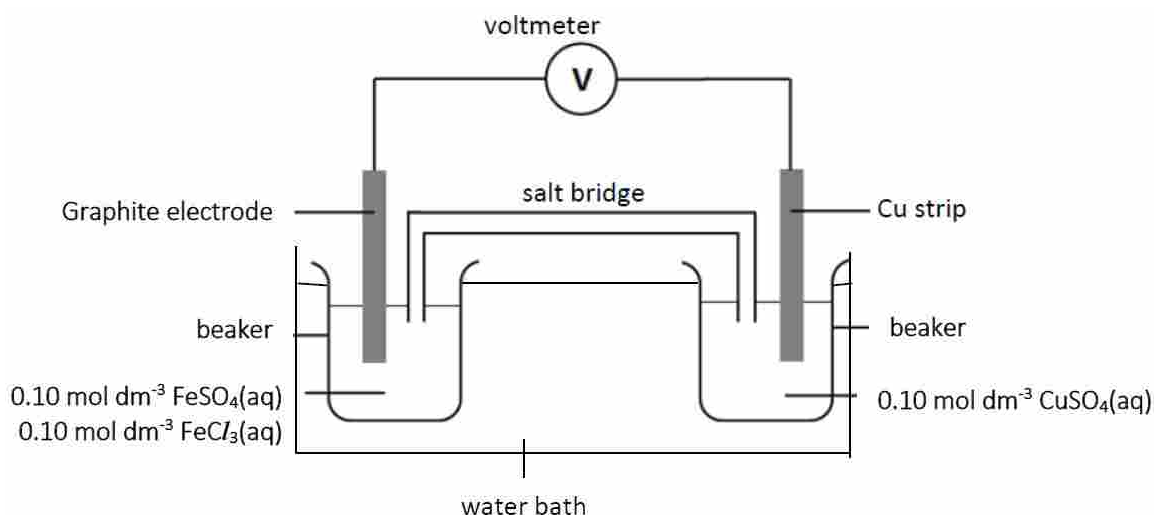
1	2	3	4	5	6	7	8	9	10
A	D	D	C	D	C	B	C	B	A
11	12	13	14	15	16	17	18	19	20
A	A	D	B	B	C	C	C	D	C
21	22	23	24	25	26	27	28	29	30
A	D	B	A	C	D	C	A	B	C
31	32	33	34	35	36	37	38	39	40
B	C	B	D	A	D	B	D	B	D

Paper 2



- (ii) Positive. More aqueous ions produced and thus more ways that energy can be distributed in the system through the motion of ions. [1]

1 (b)



M1	[1/2] voltmeter and salt bridge
	[1/2] a single water bath or hot plate (not separate)
M2	Correct Fe ³⁺ /Fe ²⁺ half cell: [1/2] electrode + [1/2] solutions (with correct concentration)
M3	Correct Cu ²⁺ /Cu half cell: [1/2] electrode + [1/2] solution (with correct concentration)
M4	[1/2] 5.56 g of solid [1/2] details for weighing – electronic balance, weighing bottle/beaker, reweigh <u>or</u> tare and rinse out all solid
M5	<u>Preparation of acidified FeSO₄ solution:</u> [1/2] adding acid <u>before</u> topping up to 100 cm ³ mark [1/2] 100 cm ³ volumetric flask
M6	<u>Preparation of FeSO₄ solution:</u> • Transfer solid to beaker • Dissolve solid in beaker • Transfer solution to volumetric flask

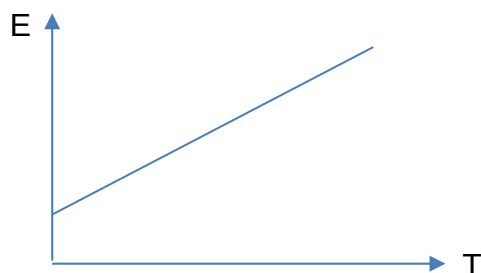
	• Transfer washings to volumetric flask • Top up volumetric flask • Shake [1/2] any 3 – 5 points [1] all 6 points
M7	[1/2] measure volumes of solutions used for both half-cells (minimum volume of electrolyte in each half-cell: 20 cm³) [1/2] use appropriate apparatus e.g. measuring cylinder for measurement of solutions for both half-cells
M8	[1/2] measure temperature using thermometer or set temperature of thermostatically controlled water bath [1/2] range of temperature used at least 30 °C – should have at least 5 readings with at least 5 °C intervals (lowest temperature should not be below 20 °C)
M9	Sketch of graph: [1/2] Correct choice of axes – E vs T (ignore units) [1/2] Linear graph with positive gradient Allow a plot of ΔG vs T. In this case, a linear graph with negative gradient would be obtained. Candidate needs to explain clearly how ΔG can be obtained.
M10	[1] explain how entropy change could be obtained from the graph – e.g. Gradient = $\Delta S / nF$ (for E vs T graph) Gradient = $-\Delta S$ (for ΔG vs T graph)

Sample procedure

1. Using an electronic weighing balance, weigh accurately 5.56g of FeSO₄·7H₂O in a weighing bottle.
2. Transfer this solid into a 100 cm³ beaker. Reweigh the weighing bottle to account for any residual solid. Record the mass of the solid used.
3. Dissolve the solid using about 20 cm³ of 0.50 mol dm⁻³ H₂SO₄(aq).
4. Transfer this solution into a 100 cm³ volumetric flask. Rinse the beaker thoroughly and transfer all washings into the flask. Top up to the mark with deionised water/H₂SO₄(aq) and shake well to obtain a homogeneous solution. Label this solution as FA1.

5. Transfer 15 cm³ of FA1 and 15 cm³ of 0.20 mol dm⁻³ FeCl₃ into a 100 cm³ beaker using separate burettes.
6. Transfer 30 cm³ of 0.10 mol dm⁻³ CuSO₄ into a 100 cm³ beaker using a burette.
7. Set up the apparatus as shown in the diagram above.
8. Ensure that the water bath is maintained at 25°C by measuring the temperature with a thermometer.
9. Record the cell potential using a voltmeter.
10. Record the cell potential at different temperatures: 30°C, 35°C, 40°C, 45°C, 50°C, 55°C.

Plot a graph of E against T.



$$\Delta S = \text{gradient of the graph} \times F \times n$$

2 (a) (i) ½m each:

- ✓ O atom has more protons (or higher nuclear charge than C atom)
- ✓ shielding effect is similar (or almost the same)
- ✓ O has higher effective nuclear charge
- ✓ its outer electrons are pulled (or attracted) more closely to the nucleus

(ii) 1m: S atom has 1 more occupied quantum shell than O and C.

2 (b) (i) 1m: blood red

(ii) ½m each:

- ✓ [Fe(CN)₆]³⁻ has (much) higher K_{stab} than [Fe(H₂O)₅(SCN)]²⁺
- ✓ SCN⁻ (and H₂O) unable to replace CN⁻ as the ligands attached to Fe³⁺ i.e. no ligand exchange

(iii) 1m:

[Fe(edta)]⁻ has (much) higher K_{stab} than [Fe(edta)]²⁻.

So [Fe(edta)]⁻ is less likely to be reduced to [Fe(edta)]²⁻.

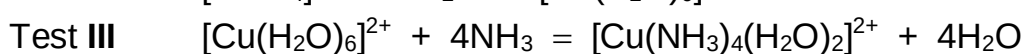
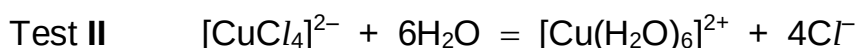
OR reduction equilibrium [Fe(edta)]⁻ + e⁻ ⇌ [Fe(edta)]²⁻ lies more to the left.

OR edta ligand stabilises +3 oxidation state of Fe relative to +2 state.
 $\therefore$ reduction potential for Fe(III)/Fe(II) with edta as ligands or for $[\text{Fe}(\text{edta})]^-/[\text{Fe}(\text{edta})]^{2-}$ would be lower than +0.77 V.

2 (c) (i) $\frac{1}{2}$ m each:

- ✓ yellow solution: $[\text{CuCl}_4]^{2-}$
- ✓ blue solution: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- ✓ pale blue ppt: $\text{Cu}(\text{OH})_2$ or $[\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4]$
- ✓ dark blue solution: $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

(ii) 1m each:



Accept $\rightarrow$

2 (d) (i) $\frac{1}{2}$ m each:

- ✓ $E^\circ(\text{H}_2\text{O}/\text{H}_2) = -0.83 \text{ V}$ and $E^\circ(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$
or $E^\circ(\text{H}^+/\text{H}_2) = 0 \text{ V}$ and $E^\circ(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$
- ✓ $E^\circ(\text{H}_2\text{O}/\text{H}_2)$ is higher or less negative, so H_2O would be preferentially reduced to H_2 , Al^{3+} would not be reduced to give Al .
or $E^\circ(\text{H}^+/\text{H}_2)$ is higher or less negative, so H^+ would be preferentially reduced to H_2 , Al^{3+} would not be reduced to give Al .

(ii) 1m: $2\text{AlO}_2^- \rightarrow \text{Al}_2\text{O}_3 + \frac{1}{2}\text{O}_2 + 2\text{e}^-$
or $4\text{AlO}_2^- \rightarrow 2\text{Al}_2\text{O}_3 + \text{O}_2 + 4\text{e}^-$

(iii) 1m: calculates no. of moles of electrons
1m: calculates time in hours

$$\text{Amount of Al deposited} = \frac{1000 \times 10^3}{27} = 3.704 \times 10^4 \text{ mol}$$

$$\text{Amount of electrons passed} = 3 \times 3.704 \times 10^4 = 1.111 \times 10^5 \text{ mol}$$

$$Q = It = 1.111 \times 10^5 \times 96500 = 1.072 \times 10^{10} \text{ C}$$

$$t = \frac{1.072 \times 10^{10}}{10^4} = 1.072 \times 10^6 \text{ s} = 298 \text{ h} \quad (\text{or } 297.8 \text{ h})$$

2 (e) 1m: concludes +6

1m: calculates 0.00225 mol XeF_2 and 0.00150 mol Cr(III)

1m: explains how to conclude +6, e.g. 1 mol Cr(III) loses 3 mol electrons

Sample working:

$$\text{Amount of XeF}_2 = \frac{15.2}{1000} \times \frac{25}{169} = 0.002249 \text{ mol}$$

XeF₂ reduced to Xe, oxidation state of Xe changes from +2 to 0

$$\text{Amount of electrons transferred} = 2 \times 0.002249 = 0.004497 \text{ mol}$$

$$\text{Amount of Cr(III)} = \frac{10}{1000} \times 0.150 = 0.00150 \text{ mol}$$

$$\frac{0.004497}{0.00150} = 3 \text{ mol of electrons lost from 1 mol of Cr(III)}$$

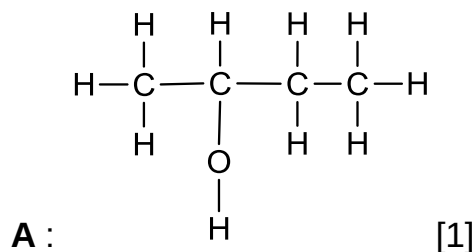
∴ oxidation state of Cr increases by 3 units

∴ oxidation state of Cr is +6 after reaction

- 3 (a) The carbon atom of the reactant (but-2-ene) in the C=C bond is sp² hybridised [1/2] and the bond angle around the carbon atom is 120° [1/2].

The carbon atom of the product (butane) in the C–C bond is sp³ hybridised [1/2], and the bond angle around the carbon atom is 109.5°.
(accept 109°) [1/2]

- (b) (i) Steam, 300°C, 70 atm (or 60 atm), (conc) H₃PO₄ [1]
OR conc H₂SO₄ followed by warming with water.



- (ii) Both but-2-ene and alcohol are simple covalent compounds /simple, discrete molecules /have simple molecular structure. [1/2]

For but-2-ene, there are weak dispersion forces between its molecules. For alcohol **A** (butan-2-ol) with polar O–H bond, there are strong intermolecular hydrogen bonding between its molecules. [1/2]

More energy is required to overcome the stronger intermolecular hydrogen bonding in alcohol **A** than the weak dispersion forces in but-2-ene which is therefore in gaseous state. [1/2]

OR

the energy provided by room temperature is insufficient to overcome the strong hydrogen bonds between alcohol **A** molecules,

Hence alcohol **A** exists as a liquid at room temperature and but-2-ene exists as gas. [1/2]

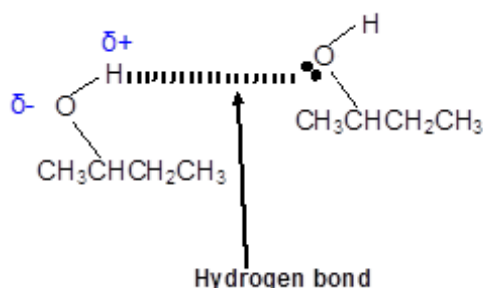
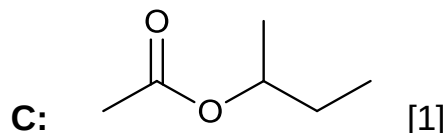
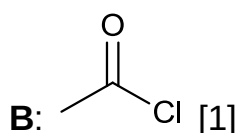


Diagram [1]

- showing correct hydrogen bond (must be oxygen atom and the H atom from the OH group)
- labelling hydrogen bond
- showing lone pair of electrons on oxygen
- labelling $\delta+$ and $\delta-$ for the O–H group forming H bond.

Each mistake minus 1/2 mark

(iii)

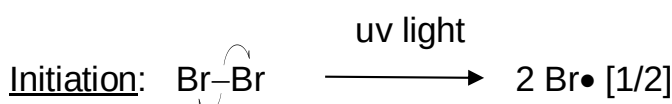


3 (c) (i) Ratio of 1-bromobutane : 2-bromobutane = 1 : 3 [1]

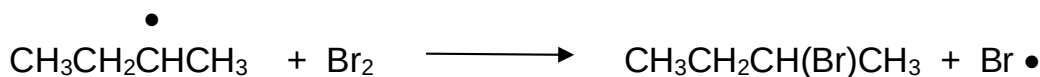
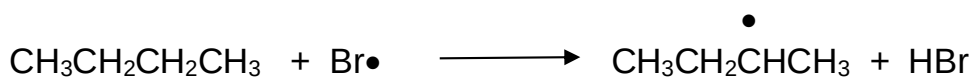
In 1-bromobutane: there are 6 possible primary (1°) H atoms for substitution and in 2-bromobutane: there are only 4 secondary (2°) H atoms for substitution [1/2]

Relative rate of substitution suggests that the mole ratio of 1-bromobutane : 2-bromobutane = $1 \times 6 : 4.5 \times 4 = 6 : 18$ [1/2] for working

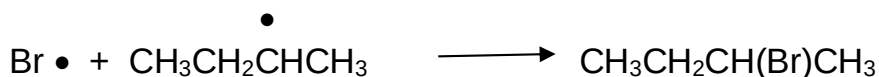
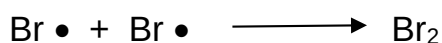
(ii) Type of mechanism: Free radical substitution [1]

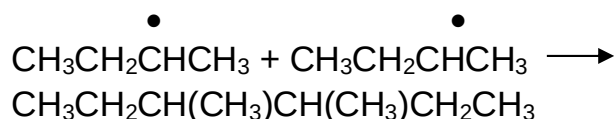


Propagation: [1]



Termination [1/2]





- 4 (a) The thermal stability of the hydrogen halides **decreases** down the group [1/2] as the **bond energy of H–X** decreases accordingly from +562 (HF) to +431 (HCl) to +366 (HBr) to +299 kJ mol^{–1} (HI) [1/2].

Down the group, **less energy is required** to break the bond [1/2] as the **bond strength decreases** [1/2].

- (b) Step 1: To 1 cm³ of each reagent in separate test tubes, add a few drops of **aqueous lead(II) nitrate** and shake. [1/2]
If yellow ppt (of PbI₂) is obtained, the test tube contains NaI. If white ppt is obtained, the test tube contains KBr or KCl. [1]

Step 2: To 1 cm³ of each reagent that gave white ppt in step 1, add a few drops of **acidified sodium chlorate(I)** OR **Cl₂(aq)** and shake. [1/2]
If the solution turned yellow-orange, the test tube contains KBr. If the solution remained colourless, the test tube contains KCl. [1]

OR

Step 1: To 1 cm³ of each reagent in separate test tubes, add a few drops of **acidified sodium chlorate(I)** OR **Cl₂(aq)**, followed by 1 cm³ of **hexane**. Shake well and leave to stand. [1]

If both layers remained colourless, the test tube contains KCl.

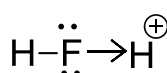
If the aqueous layer turned yellow-orange, while the organic layer turned reddish-brown, the test tube contains KBr.

If the aqueous layer turned brown, while the organic layer turned violet, the test tube contains KI. [3 obs correct:2m; 2 obs correct:1m]

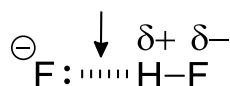
- 4 (c) (i) $2\text{HF} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HF}_2^-$ [1]
 $K = K_1 \times K_2 = (1.1 \times 10^{-3})(2.6 \times 10^{-1}) = 2.86 \times 10^{-4}$ [1]

- (ii) NaOH, Na₂CO₃, etc. Base reacts with acid, lowers [H₃O⁺] and shifts position of equilibrium forward. [2]

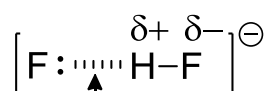
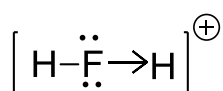
- (d) (i)



hydrogen bonding



OR



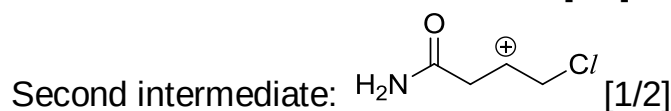
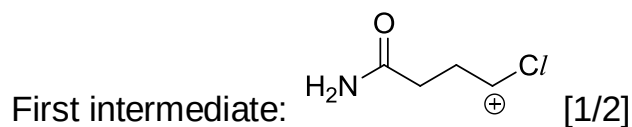
hydrogen bonding [1] x 2

(ii) $[H_2F^+] = [HF_2^-] = \sqrt{(8.0 \times 10^{-12})} = 2.83 \times 10^{-6} \text{ mol dm}^{-3}$ [1]
 $[HF] = \frac{1.002 \times 10^3}{1.0 + 19.0} = 50.1 \text{ mol dm}^{-3}$

The auto-dissociation causes a negligible change in [HF], hence the

requested fraction is $\frac{[H_2F^+]}{[HF]} = \frac{2.83 \times 10^{-6}}{50.1} = 5.65 \times 10^{-8}$ [1]

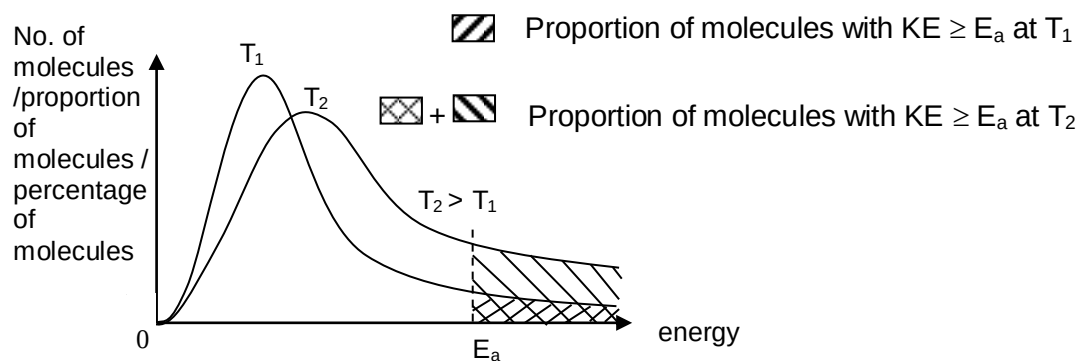
5 (a) (i)



Product formed is from the first intermediate which is less stable than second intermediate. [1/2]

This is because the positive charge is intensified by electron withdrawing chlorine through inductive effect. [1/2]

(ii) Boltzmann distribution diagram: [1]



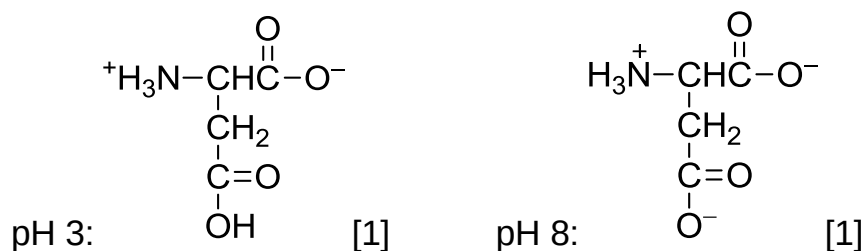
At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to activation energy increases [1].

Thus, frequency of effective collision increases [0.5], reaction rate increases [0.5]

(iii) The prolinamide is synthesised as a racemic mixture containing equal proportions of two enantiomers. [1/2]

Hence only 50% of the synthesised prolinamide can fit into / would possess the correct 3D shape to bind to the active site of the enzyme. [1/2]

5 (b) (i)



(ii)

aspartic acid	lysine	Ionic interaction
isoleucine	phenylalanine	dispersion forces / van der Waals interaction
serine	asparagine	Hydrogen bond

3 correct = [2], 2 correct = [1], 1 correct = [1/2]

(iii) Mercury ion disrupts the disulfide bridge by binding tightly with –SH of cysteine residue

OR

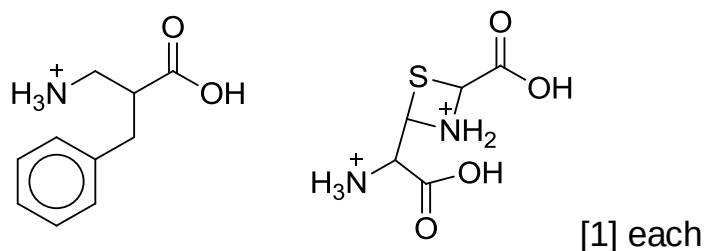
Mercury ion disrupts the ionic interaction by forming ionic interaction with –CO₂[–] side chain of aspartic acid. [1]

The tertiary structure / shape of the enzyme is altered, and hence its function is lost. [1]

5 (c) Asp-lys-ser-phe-lys-gly-cys-asn-phe [1]

(d) (i) Glycine [1/2], cysteine [1/2]

(d) (ii)



Paper 3

- 1 (a) 1-bromobutane has a higher boiling than 1-chlorobutane. Both 1-bromobutane and 1-chlorobutane are simple molecular. Since 1-bromobutane has a larger electron cloud size [1], there is stronger dispersion forces between its molecules as compared to 1-chlorobutane. Hence, more energy [1] is needed to break the stronger dispersion forces for 1-bromobutane.

- (b) (i) Standard enthalpy change of combustion is the heat evolved when one mole of the substance is completely burnt in excess oxygen at 298 K and 1 atm. [1]

- (ii) Heat absorbed by water $q = (200)(4.18)(45.0) = 37620 \text{ J}$
 $= 37.6 \text{ kJ}$ [1]

$$\text{Enthalpy change of combustion} = [100/80 \times 37.62] / (2.35/136.9)$$
$$= -2.74 \times 10^3 \text{ kJ mol}^{-1}$$
 [1]

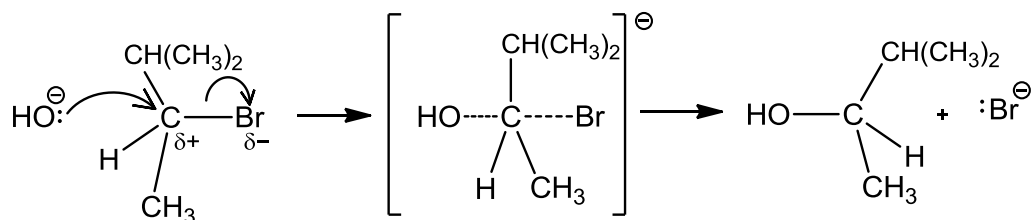
- (c) (i) Comparing Expt 1 and 2,
(Total volume in Expt 2 is half that of Expt 1.)
Concentration of 2-bromo-3-methylbutane is constant, when concentration of NaOH increases 4/3 times, rate increases 4/3 times. Hence, the reaction is 1st order with respect to NaOH [1]

Comparing Expt 2 & 3,
(Total volume in Expt 2 and 3 are the same)
When concentration of 2-bromo-3-methylbutane increases 2 times and concentration of NaOH decreases 4 times, the rate decreases 2 times. Since the reaction is first order with respect to NaOH, the reaction is thus 1st order with respect to 2-bromo-3-methylbutane [1]

[Calculation method also accepted]

$$\text{Rate} = k [\text{2-bromo-3-methylpentane}][\text{NaOH}] \quad [1] \text{ ecf}$$

- (ii) S_N2 Nucleophilic substitution [1]



2 m for mechanism

(iii) Rate = k [2-bromo-3-methylbutane][NaOH]

To obtain the numerical value for k , substitute the rate and the respective concentrations into the rate equation.

$$7.40 \times 10^{-7} = k \left[\frac{\left(\frac{10}{1000} \right) (0.0100)}{\left(\frac{10.0+30.0+60.0}{1000} \right)} \right] \left[\frac{\left(\frac{30}{1000} \right) (0.0100)}{\left(\frac{10.0+30.0+60.0}{1000} \right)} \right]$$

$$k = 0.247 \quad \text{[1] Calculation}$$

To derive the units,

$$\text{mol dm}^{-3} \text{ s}^{-1} = k (\text{mol dm}^{-3})^2$$

$$k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad \text{[1] Units}$$

(d) (i) Test 1: **S_N1** mechanism

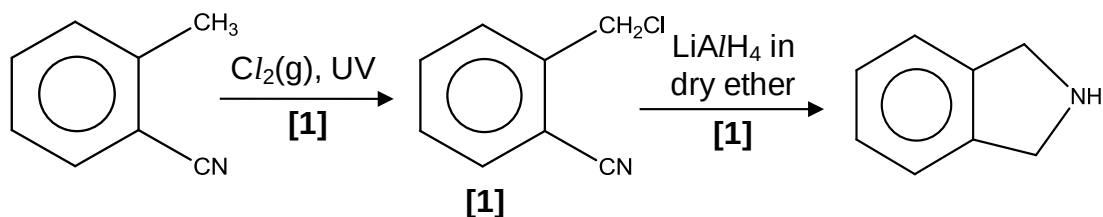
Test 2: **S_N2** mechanism [1]

(ii) In Test 1, the rate of reaction is the fastest for the tertiary bromoalkane. The carbocation formed from the tertiary bromoalkane is stabilised by three electron-donating alkyl groups, hence it undergoes S_N1 rapidly. [1]

In Test 2, the rate of reaction is the fastest for the primary bromoalkane as there is least steric hindrance when the nucleophile attacks the electron deficient carbon atom of the primary bromoalkane, hence it undergoes S_N2 rapidly. [1]

(iii) The carbocation formation is favoured as ethanol can form ion-dipole interactions with the carbocation intermediate thereby stabilising it [1].

(e)



For the second step, accept H_2 , Ni, high temp and high pressure. Also accept if split up last step to show reduction followed by nucleophilic substitution with heat for last step.

2 (a) (i)

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}$$

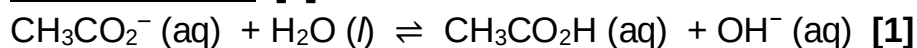
$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]}$$

[1]

$$\begin{aligned} K_a \times K_b &= \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} \times \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} \\ &= [H^+][OH^-] \\ &= K_w \text{ (ionic product of water), which is a constant. } [1] \end{aligned}$$

(ii) CH_3CO_2H is a weak acid so its conjugate base $CH_3CO_2^-$ is a stronger base than water.

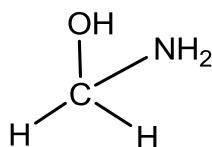
So $CH_3CO_2^-$ undergoes hydrolysis forming OH^- ions, forming an alkaline solution. [1]



(iii) As $[CH_3CO_2H] = [CH_3CO_2^-]$, this is a maximum capacity buffer;

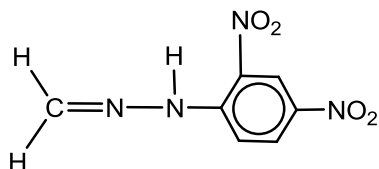
$$\begin{aligned} \text{so } pH &= pK_a \\ &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 [1] \end{aligned}$$

(b) (i) A [1]



(ii) B = 2,4-dinitrophenylhydrazine [1]

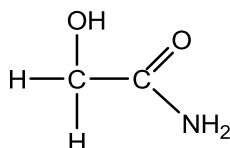
C [1]



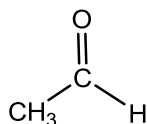
(iii) addition [1]

(iv) Dilute H₂SO₄ / HNO₃ / HCl, heat [1]

(v) D [1]



(vi) E [1]



(vii) Reaction III [1]

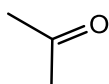
The imine is trigonal planar about the imine carbon atom. The nucleophile can thus attack this δ^+ carbon atom in equal probability from the top as well as the bottom [1], resulting in forming equal proportions of the two optical isomers / racemic mixture.

(c) (i) Functional group level of C in CH₄ = 0; in CO₂ = 4 [1]

(ii) Functional group level of circled C at the start = 3; at the end= 1 [1]

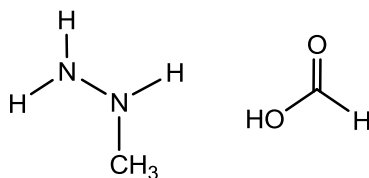
As the functional group level decreases, the reaction is reduction. [1]

(iii)



F

1m each



G / H

3 (a) (i) [1] Americium (Am)

(ii) Ts lies below astatine in Group VII, following the trend of increasing melting point down the group [1], it should be a solid [1] like iodine or astatine.

(iii) [1] Group II.

[0.5]: Effervescence of hydrogen gas with water => Group I or II metal or

Basic oxide hydrolyses to give metal hydroxide in water => Group I or II metal

[0.5]: Sulfate insoluble => Group II metal as Group I sulfates all soluble. Or Group II sulfate solubility decreases down the group.

(b) (i) Titanium is able to form ions with incomplete d-subshell, Ti^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ or Ti^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ [1]

but

zinc forms only the Zn^{2+} ion which has $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ configuration with a fully filled d-subshell [1].

(ii) No. of moles of titanium = no. of moles of $\text{TiO}_2 = 2.99 \times 10^{-3}$ mol

No. of moles of chloride = $1.72 / 143.5 = 0.0120$ mol

Ratio of chloride ions to titanium = $0.0120 / 2.99 \times 10^{-3} = 4.01 = 4$ [1]

1st mark can be awarded if student is able to provide an answer that clearly recognises from TiO_2 that the complex is formed from a Ti(IV) center [0.5] and since complex is electrically neutral, there must be 4 chloride ions [0.5]

Mass of titanium and chloride in 1 g sample = $2.99 \times 10^{-3} \times 189.9 = 0.568$ g

Mass of coordinated THF molecules in 1 g sample = 0.432 g

$0.432 / (72.1 \times n) = 2.99 \times 10^{-3}$

No. of THF molecules coordinated = $0.432 / (2.99 \times 10^{-3} \times 72.1) = 2.00 = 2$ [1] (*working for no. of THF ligands must be shown*)

Coordination number = 6 [1] (*this answer must be based on an actual no. of chloride and THF ligands stated earlier*)

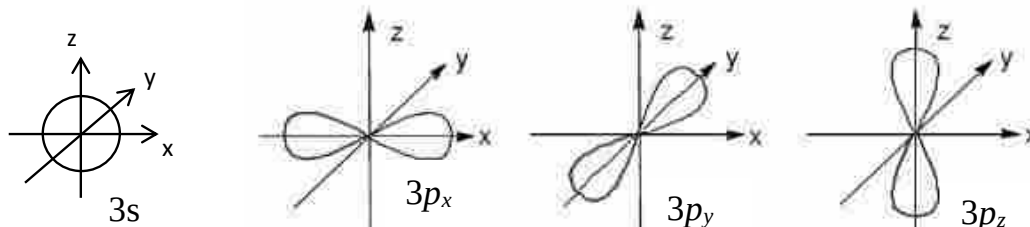
Allow ecf from errors in number or chloride and THF ligands calculated, rounded up to whole numbers.

(c) (i) The 3rd ionization energy of Ca ($+4940 \text{ kJ mol}^{-1}$) is much higher than the 2nd ($+1150 \text{ kJ mol}^{-1}$) as the 3rd electron in Ca is removed from an inner quantum shell [1] which requires a lot of energy. Thus, Ca^{3+} compounds do not exist.

For Ti, the 2nd and 3rd ionisation energies (+1310, +2720 kJ mol⁻¹) do not differ greatly as 4s and 3d electrons are close in energy [1]. Thus, Ti³⁺ can be formed.

[1]: some comparison/discussion of ionisation energies for Ca and Ti pertaining to the high 3rd ionisation energy for Ca compared to Ti.

(ii)

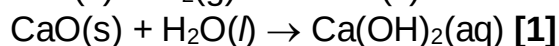
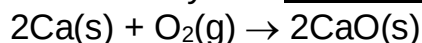


[2]

(iii) In calcium, only the 4s electrons are donated to the sea of delocalised electrons, while in titanium, both the 4s and 3d electrons are involved (idea of more electrons contributed towards metallic bonding). **OR** Titanium cations have higher charge/ smaller ionic radius / greater charge density than calcium cations. [1]

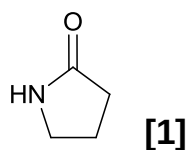
This leads to titanium having stronger metallic bond strength and more energy is needed to overcome the metallic bonds [1] and hence a higher melting point.

(iv) Burns slowly with brick-red flame, leaving a white residue [1]

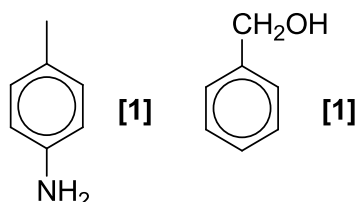


Ca(OH)₂ dissolves / gives a colorless solution in water to give an alkaline solution of pH = 12 [1] (Accept any value above 7)

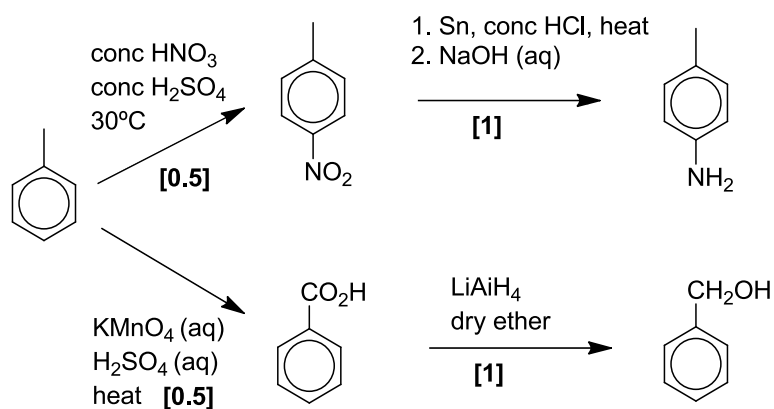
4 (a) (i)



(ii)

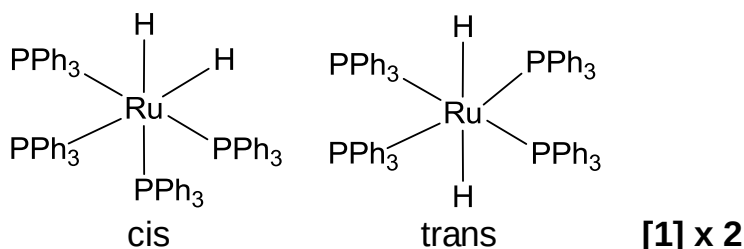


(iii)



accept Cl_2 (g), UV or heat, followed NaOH (aq), heat to get phenylmethanol.

(b)



(c) +1 [1]

(d) (i) The complex is chiral as the two optical isomers are non-superimposable mirror images of each other. [1]

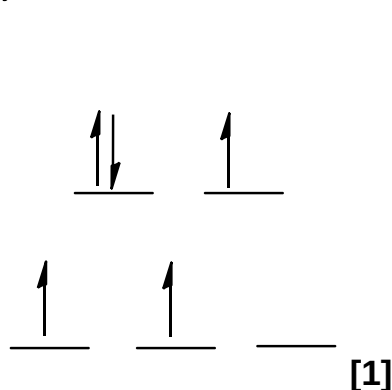
(ii) ΔS is positive [0.5] as the number of product particles is greater than the number of reactant particles therefore the number of ways to distribute energy in the system increases. [1]

$$\Delta G = \Delta H - T\Delta S.$$

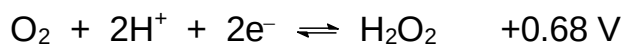
As $\Delta H = 0$ and $\Delta G = -T\Delta S$ [1]. Thus, ΔG is negative [0.5]

(e) (i) The wavelength of light (complementary of yellow) absorbed by $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ is of a lower wavelength than that for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ [1]. Therefore, the energy gap between the d-orbitals must be larger in $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ [1].

(ii) Energy

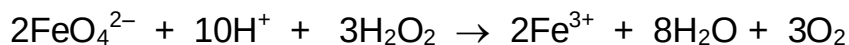


(f) (I)



$$E^\ominus_{\text{cell}} = +2.20 - (0.68)$$

$$= +1.52 \text{ V} > 0 \quad \text{reaction is feasible}$$



Observations: Red solution turns pale yellow, as FeO_4^{2-} is reduced to Fe^{3+} . Effervescence of O_2 OR effervescence of a colourless and odourless gas that rekindles a glowing splint. [3]

(II)



$$E^\ominus_{\text{cell}} = +1.52 - (2.20) < 0 \quad \text{reaction is not feasible}$$

Solution remains purple [1]

5 (a) (i) $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$
 $= (2.57 \times 10^{-4})^2(2.57 \times 10^{-4}/2) = 8.49 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

[1m for numerical answer; 1m for units]

(ii) $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$
 $8.49 \times 10^{-12} = [\text{Ag}^+]^2 \times (2.50 \div (23 \times 2 + 12 + 16 \times 3) \div (100/1000))$
 $[\text{Ag}^+] = 6.00 \times 10^{-6} \text{ mol dm}^{-3}$ [1]
Solubility of $\text{Ag}_2\text{CO}_3 = \frac{1}{2} \times 6.00 \times 10^{-6} = 3.00 \times 10^{-6} \text{ mol dm}^{-3}$ [1]

(b) 4-hydroxybenzoic acid, benzoic acid, 2-hydroxybenzoic acid [1]

4-hydroxybenzoic acid is a weaker acid than benzoic acid because the –OH group attached to the benzene ring is electron-donating (lone pair of electrons on O atom is delocalised into the benzene ring), hence intensifying the negative charge on the carboxylate anion and reducing its stability. [1]

2-hydroxybenzoic acid is a stronger acid than benzoic acid because its conjugate base can be stabilised by intramolecular hydrogen bonding/ion-dipole interactions. [1]

(c) Add $\text{AgNO}_3(\text{aq})$ at room temperature [1]
Q : White ppt of AgCl formed immediately
P: No white ppt formed [1]

OR

Add $\text{K}_2\text{Cr}_2\text{O}_7$, dilute H_2SO_4 , heat [1]
Q : Orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green
P: Orange $\text{K}_2\text{Cr}_2\text{O}_7$ remains orange [1]

OR

Add water [1]

Q: Dense white fumes evolved

P: No white fumes evolved [1]

(d) (i) $PV = nRT$

$$M_r = (\text{mass} \times R \times T) / PV$$

$$(0.219 \times 8.31 \times 423) / (125 \times 10^3 \times 70 \times 10^{-6}) = 88.0 \text{ [1]}$$



(ii) **A**, $C_{13}H_{14}O_3$, and **B**, C_8H_8O have high C:H ratio $\Rightarrow$ Benzene ring present in **A** and **B**

A undergoes acidic hydrolysis with dilute H_2SO_4 to form **B** and **C** $\Rightarrow$ **A** contains an ester group

B undergoes electrophilic substitution and electrophilic addition with aqueous bromine to form **D**, $C_8H_7O_2Br_3 \Rightarrow$ **B** contains phenol and alkene respectively.

B undergoes oxidative cleavage with acidified $KMnO_4$ to form 4-hydroxybenzoic acid and CO_2 in a 1:1 mole ratio $\Rightarrow$ **B** contains a terminal alkene

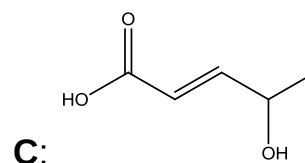
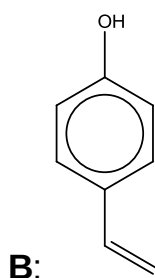
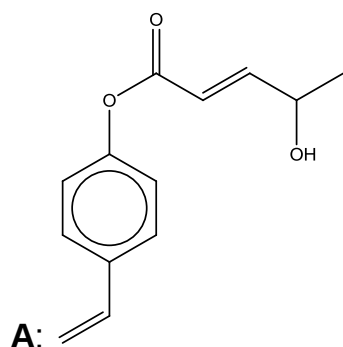
C undergoes oxidative cleavage with acidified $KMnO_4$ to form **E**, $C_3H_4O_3$, and carbon dioxide gas in a 1:2 mole ratio $\Rightarrow$ **C** contains alkene and possibly forms ethanedioic acid (further oxidised to form 2 CO_2) upon oxidation

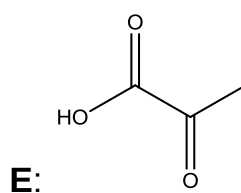
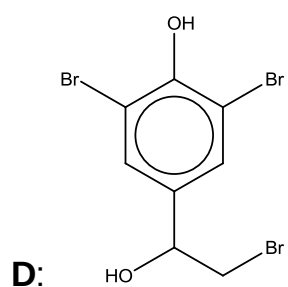
C and **E** undergo oxidation / forms CHI_3 yellow ppt / gave positive iodoform test with warm aqueous alkaline iodine

$\Rightarrow$ **C** contains $-CO(CH_3)$ or $-CH(CH_3)(OH)$ group or **E** contains $-CO(CH_3)$ group

E undergoes acid-base reaction with Na_2CO_3

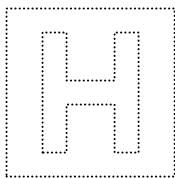
$\Rightarrow$ **E** contains a carboxylic acid group





4m max for explanations
1m for each structure

[9m]



INNOVA JUNIOR COLLEGE

JC 2 PRELIMINARY EXAMINATION

in preparation for General Certificate of Education Advanced Level

Higher 2

CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9647/01

Paper 1 Multiple Choice

30 August 2016

1 hour

Additional Materials: Data Booklet
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

This document consists of **17** printed pages and **1** blank page.

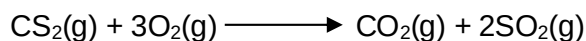


Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 Carbon disulfide, CS_2 , is a volatile liquid used in the production of cellophane which is used for food packaging.

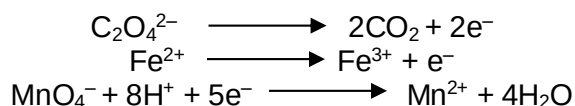
On combustion, CS_2 is oxidised as follows:



A 20 cm^3 sample of carbon disulfide vapour is ignited with 100 cm^3 of oxygen. The final volume of gas after burning is treated with an excess of aqueous alkali.

Which percentage of this final volume dissolves in alkali? (All volumes are measured at room temperature and pressure.)

- A 20%
 - B 40%
 - C 60%
 - D 80%
- 2 Consider the following half-equations



What volume of 0.01 mol dm^{-3} potassium manganate(VII) is needed to completely oxidise 25.0 cm^3 of an acidified solution of 0.01 mol dm^{-3} FeC_2O_4 ?

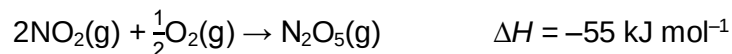
- A 5 cm^3
 - B 7.5 cm^3
 - C 10 cm^3
 - D 15 cm^3
- 3 Which electronic configuration represents an element that forms a simple ion with a charge of -3 ?
- A $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^1$
 - B $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^3$
 - C $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^1 4\text{s}^2$
 - D $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^3 4\text{s}^2$

- 4 Carbon dioxide is a gas at room temperature while silicon dioxide is a solid because
- A carbon dioxide contains double covalent bonds while silicon dioxide contains single covalent bonds.
 - B instantaneous dipole – induced dipole attractions are weaker than permanent dipole – permanent dipole attractions.
 - C carbon-oxygen bonds are less polar than silicon-oxygen bonds.
 - D van der Waals' forces are much weaker than covalent bonds.

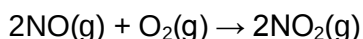
- 5 Under which conditions will the behaviour of a gas be **most** ideal?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

- 6 The enthalpy changes involving some oxides of nitrogen are given below:



What is the enthalpy change, in kJ mol^{-1} , of the following reaction?



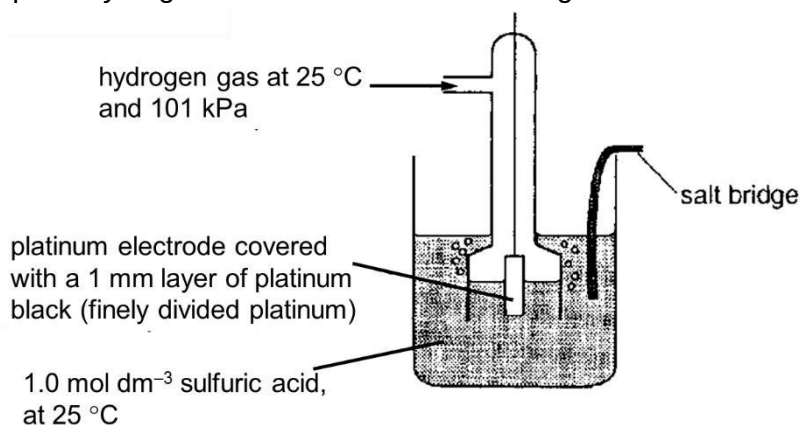
- A -114 B +114 C -136 D +136
- 7 A typical protein forms hundreds of hydrogen bonds and thousands of van der Waals' forces in folding from primary to tertiary structures.
- Which of the following thermodynamic state functions of the protein best represents the folding process?

	$\Delta G / \text{kJ mol}^{-1}$	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J K}^{-1} \text{mol}^{-1}$
A	–	–	–
B	+	–	+
C	–	+	–
D	+	+	–

- 8 When 1 mole of carbon dioxide gas solidifies as dry ice, 25.2 kJ of heat energy is evolved. The sublimation temperature of carbon dioxide is $-78.5\text{ }^{\circ}\text{C}$.

What is the entropy change when 132 g of carbon dioxide gas solidifies at this temperature?

- A $+130\text{ J K}^{-1}$
B -130 J K^{-1}
C $+389\text{ J K}^{-1}$
D -389 J K^{-1}
- 9 A student set up the hydrogen electrode shown in the diagram below.

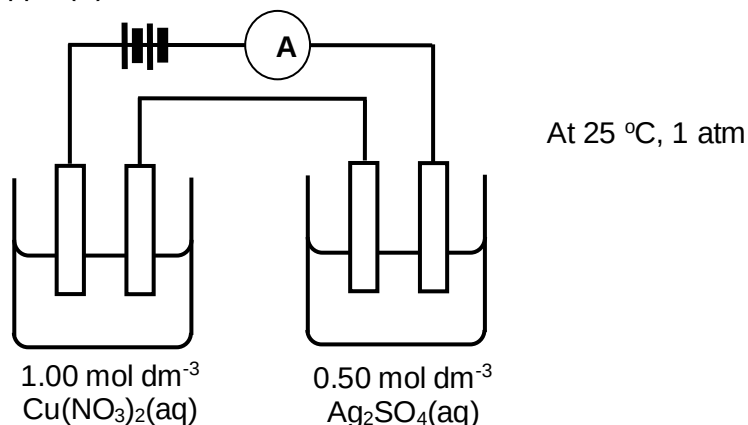


What would have to be changed to make this a standard hydrogen electrode?

- A the acid solution used
B the temperature of the gas and of the acid solution
C the pressure of the gas
D the metal comprising the electrode

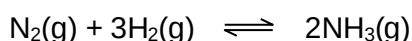
- 10 Use of the Data Booklet is relevant to this question.

Using inert electrodes, a current was passed through two beakers containing aqueous silver sulfate and aqueous copper(II) nitrate, connected in series under standard conditions.



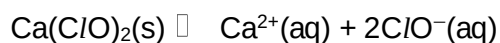
What is the ratio of the mass of silver to copper deposited after the current was passed for t minutes?

- A 0.59 B 0.85
C 1.70 D 3.40
- 11 A nitrogen-hydrogen mixture, initially in the mole ratio of 1:3, reached equilibrium with ammonia when 50% of the nitrogen had reacted. The total equilibrium pressure was p .



What was the partial pressure of ammonia in the equilibrium mixture?

- A $\frac{p}{3}$ B $\frac{p}{4}$ C $\frac{p}{6}$ D $\frac{2p}{7}$
- 12 Solid calcium hypochlorite pellets, $\text{Ca}(\text{ClO})_2(\text{s})$, are added to swimming pools to form $\text{HClO}(\text{aq})$, which kills disease-causing bacteria and algae.



What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH decreases?

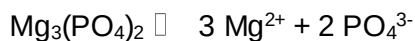
	solubility of calcium hypochlorite	effect on bacterial growth
A	decreases	more favourable
B	decreases	less favourable
C	increases	more favourable
D	increases	less favourable

- 13** The dissociation constant, K_w , for the ionisation of water, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$, at different temperatures is given below.

temperature / °C	K_w
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

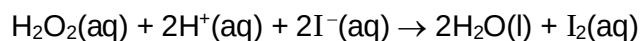
- A** Only at 25 °C are $[\text{H}^+]$ and $[\text{OH}^-]$ equal.
B The equilibrium lies furthest to the right at 0°C.
C The forward reaction is exothermic.
D The pH of water decreases as temperature increases.
- 14** A sparingly soluble salt, $\text{Mg}_3(\text{PO}_4)_2$ dissociates in aqueous solution as follows:



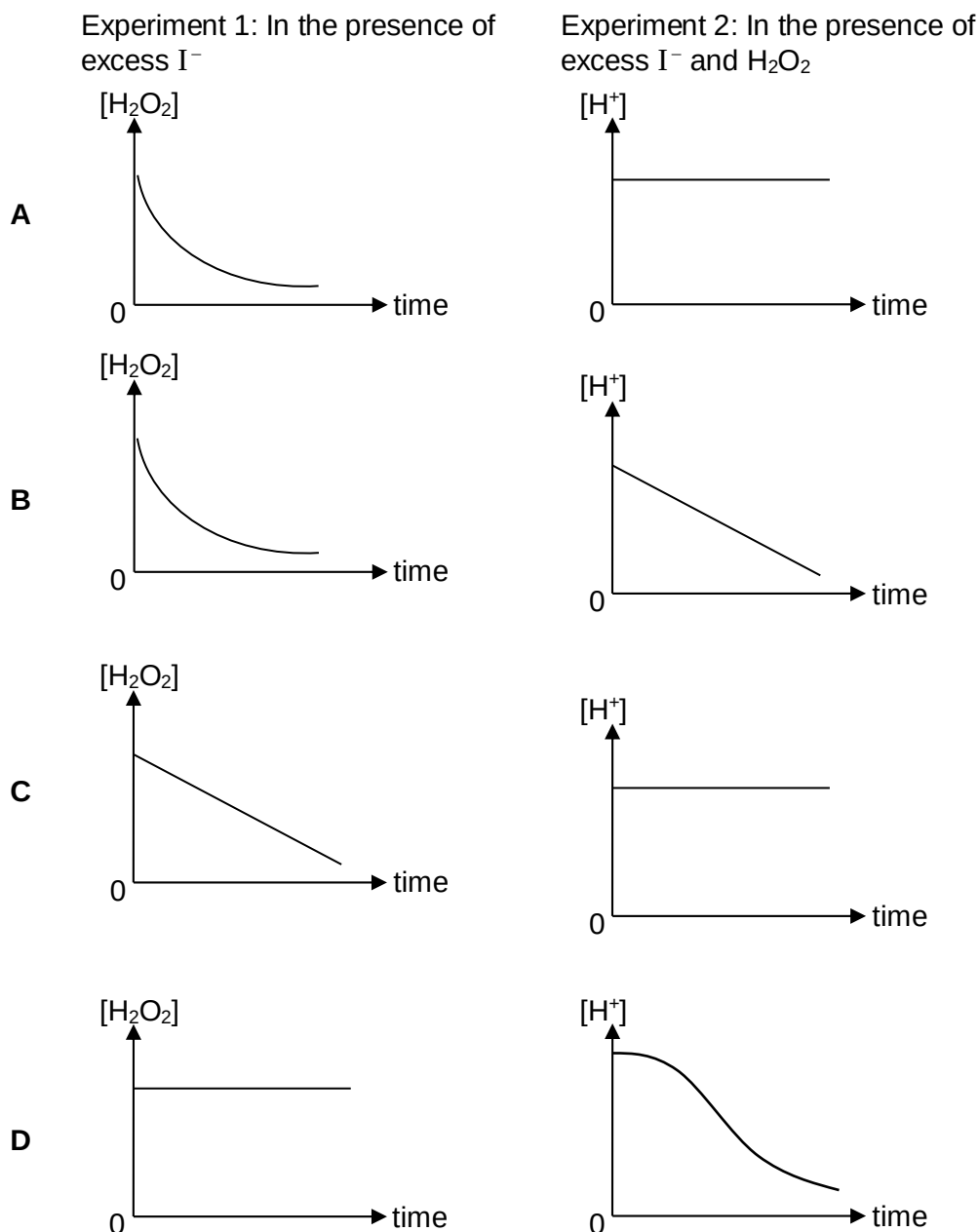
Given that the solubility product, K_{sp} of $\text{Mg}_3(\text{PO}_4)_2$ is Q , what is the value of $[\text{Mg}^{2+}]$ in a saturated solution?

- A** $\left(\frac{9Q}{4}\right)^{\frac{1}{5}}$ **B** $\left(\frac{Q}{27}\right)^{\frac{1}{3}}$ **C** $\left(\frac{Q}{108}\right)^{\frac{1}{5}}$ **D** $\left(\frac{9Q}{64}\right)^{\frac{1}{3}}$

15. The reaction of hydrogen peroxide with iodide ions in an acidic solution is first order with respect to hydrogen peroxide as well as iodide ions, and zero order with respect to hydrogen ions.



Two experiments were carried out. Which pair of diagrams represents the variation of $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$ with time?



16 Aluminium is an element in the third period, Na to Ar, of the Periodic Table.

What is true for aluminium?

- A** Aluminium has the highest melting point of the elements in this period.
- B** Aluminium is the only element in this period whose chloride reacts with water to form an acidic solution.
- C** Aluminium is the only element in this period which can exist, at room temperature and pressure, as solid and conduct electricity.
- D** Aluminium is the only element in this period whose oxide reacts with both acids and bases.

17 Which of the following statements regarding Group II elements or their compounds is **correct**?

- A** Magnesium chloride has a higher melting point than barium chloride.
- B** Magnesium is a stronger reducing agent than strontium.
- C** Calcium hydroxide is more thermally stable than barium hydroxide.
- D** Strontium reacts more readily with oxygen than radium.

18 Which of the following statements about astatine, the element below iodine in Group VII of the periodic table, is **incorrect**?

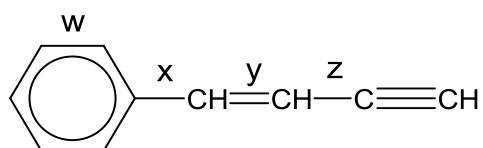
- A** Silver astatide is insoluble in aqueous ammonia.
- B** Hydrogen astatide is less stable to heat than hydrogen iodide.
- C** Sodium astatide and hot concentrated sulfuric acid react to form astatine.
- D** Astatine and aqueous potassium chloride react to form aqueous potassium astatide and chlorine.

- 19** When copper(II) chloride is dissolved in water it gives a blue solution. When this solution is treated with an excess of concentrated hydrochloric acid it turns yellow.

What are the formulae of the copper species in the blue and yellow solution?

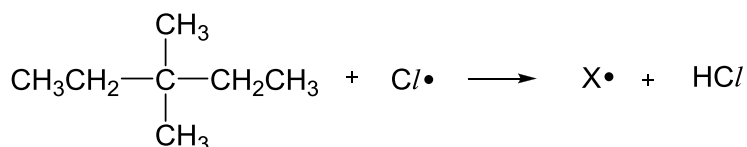
	blue	yellow
A	CuCl_2	$[\text{CuCl}_4]^{2-}$
B	$\text{CuCl}_2(\text{H}_2\text{O})_4$	$[\text{CuCl}_6]^{4-}$
C	$\text{Cu}(\text{OH})_2$	$\text{CuCl}_2(\text{H}_2\text{O})_4$
D	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	$[\text{CuCl}_4]^{2-}$

- 20** Four carbon-carbon bonds are labelled in the diagram.



Which bonds are made up of an $\text{sp}^2\text{-sp}^2$ overlap?

- A** w and y only
B w, x and y only
C w, x, y and z
D x and y only
- 21** When heated with chlorine, the hydrocarbon 3,3-dimethylpentane undergoes free radical substitution. In the propagation step, the free radical $\text{X}^\bullet$ is formed by the loss of one hydrogen atom.



How many different forms of $\text{X}^\bullet$ are theoretically possible?

- A** 2 **B** 3 **C** 4 **D** 5

- 22 Bromoethene, $\text{CH}_2=\text{CHBr}$, is unreactive to nucleophiles whereas 3-bromopropene, $\text{CH}_2=\text{CHCH}_2\text{Br}$ is very reactive by comparison.

What explains the lack of reactivity of $\text{CH}_2=\text{CHBr}$?

- A Substituted alkenes undergo only electrophilic addition.
 - B The $\text{C}=\text{C}$ double bond and the Br atom are both electron withdrawing which stabilises $\text{CH}_2=\text{CHBr}$.
 - C The electrons on the Br atom delocalise into the π bond.
 - D The presence of the π bond prevents free rotation of the C-Br bond this decreasing the reactivity.
- 23 Phosgene, COCl_2 , is a colourless gas that gained infamy as a chemical weapon during World War I. It is formed when trichloromethane, CHCl_3 , is left exposed to the atmosphere.

Below is a reaction scheme that involves trichloromethane and phosgene:



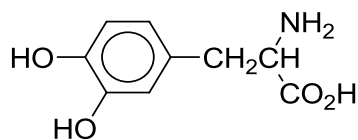
Which of the following type of reaction is **not** being observed in the reaction scheme?

- A oxidation
 - B elimination
 - C electrophilic addition
 - D nucleophilic substitution
- 24 A chlorine-containing organic compound, **X**, undergoes an elimination reaction when treated with hot ethanolic potassium hydroxide solution.

What is **X**?

- A CH_2Cl_2
- B C_2Cl_6
- C $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$
- D $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$

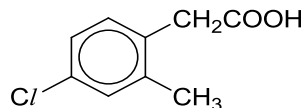
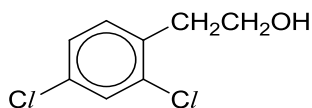
- 25 Dopamine is an important organic chemical that helps control the brain's reward and pleasure centres. It also helps regulate movement and emotional responses.



dopamine

Which of the following statements about dopamine is **incorrect**?

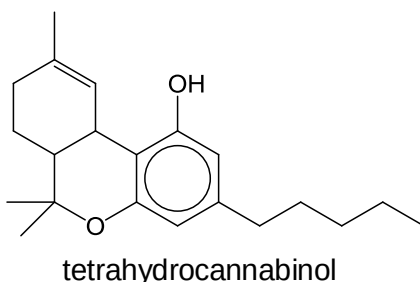
- A It is able to rotate plane-polarized light.
 - B It is soluble in water due to zwitterion formation.
 - C It migrates to the negative electrode of an electrolytic cell at pH 14.
 - D The acidity of dopamine will increase when aqueous bromine is added.
- 26 Two bottles containing the following reagents had their labels removed.



Which one of the following reagents can be used to distinguish between them?

- A sodium metal
- B sodium hydroxide
- C hot acidified potassium manganate(VII)
- D hot acidified potassium dichromate

- 27** Marijuana (cannabis) is the most widely used illegal drug in many developed countries. Medical studies have shown that the active ingredient in marijuana, tetrahydrocannabinol, might provide medical benefits to some patients.



In the following reactions, the tetrahydropyran remains unaltered.

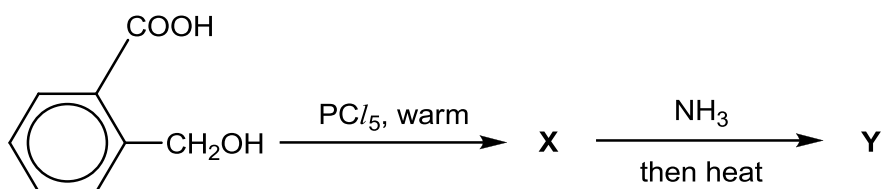
Which reaction will tetrahydrocannabinol undergo?

- A** It reacts with aqueous bromine to incorporate up to 2 atoms of bromine in each molecule.
- B** It reacts with hot acidified potassium dichromate(VI) to form a green solution.
- C** It reacts with dilute nitric acid to form a substitution product.
- D** It reacts with ethanoic acid to form a sweet-smelling product.
- 28** A student carried out an experiment to study the ease of hydrolysis of a series of chlorinated compounds, and recorded the observations based on the addition of acidified silver nitrate solution.

Which of the following gives the expected results?

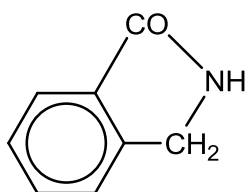
	time taken for precipitate to appear			
	shortest	—————→		longest
A	$\text{C}_6\text{H}_5\text{Cl}$	$\text{CH}_2\text{ClCONH}_2$	CH_3COCl	COCl_2
B	$\text{CH}_2\text{ClCONH}_2$	$\text{C}_6\text{H}_5\text{Cl}$	COCl_2	CH_3COCl
C	CH_3COCl	COCl_2	$\text{C}_6\text{H}_5\text{Cl}$	$\text{CH}_2\text{ClCONH}_2$
D	COCl_2	CH_3COCl	$\text{CH}_2\text{ClCONH}_2$	$\text{C}_6\text{H}_5\text{Cl}$

- 29 In the following two-step synthesis, **Y** a solid which is insoluble in water, is one of the components in the final reaction mixture.

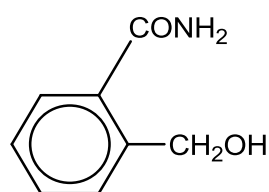


What is **Y**?

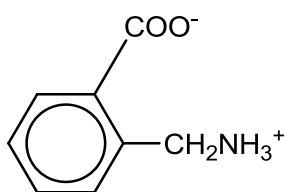
A



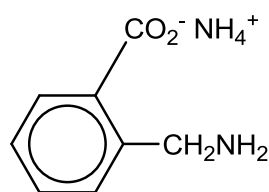
C



B



D



- 30 Benzylamine has the formula $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

- A** It decolourises aqueous Br_2 .
B It can be produced by reduction of $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$.
C It reacts with CH_3COOH to form $\text{C}_6\text{H}_5\text{CH}_2\text{NHCOCH}_3$.
D It reacts with excess $\text{CH}_3\text{CH}_2\text{Cl}$ to form the compound, $\text{C}_{13}\text{H}_{22}\text{NCl}$.

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31** Gaseous particle **Y** has a proton (atomic) number n and a charge of +1.

Gaseous particle **Z** has a proton (atomic) number of $n+1$ and is isoelectronic with **Y**.

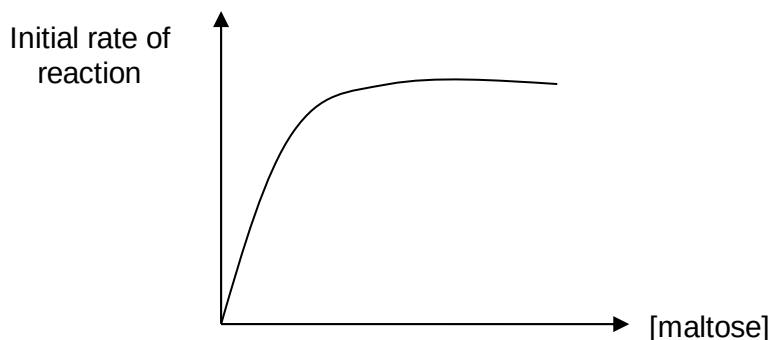
Which statement correctly describes **Y** and **Z**?

- 1** **Y** has a larger radius than **Z**.
- 2** **Y** requires more energy than **Z** when a further electron is removed from each particle.
- 3** **Y** releases more energy than **Z** when an electron is added to each particles.

- 32** Which of the following molecules will form a hydrogen bond with another of its own molecules?

- 1** CH_3NH_2
- 2** CH_3CHO
- 3** $\text{CH}_3\text{CH}_2\text{F}$

- 33 The graph below shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied but that of amylase was kept constant.



Which conclusions can be deduced from these results?

- 1 When [maltose] is low, the rate is first order with respect to [maltose].
 - 2 When [maltose] is high, the rate is independent of [maltose].
 - 3 When [maltose] is high, the rate is independent of [amylase].
- 34 With reference to the *Data Booklet* and the data below, deduce which of the following statements are correct.

Half-equation	E^θ/V
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.00
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.34
$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-0.26

- 1 An excess of zinc is capable of reducing $\text{VO}_2^+(\text{aq})$ to $\text{V}^{2+}(\text{aq})$ in acidic conditions.
- 2 $\text{Fe}^{3+}(\text{aq})$ is capable of oxidising $\text{V}^{2+}(\text{aq})$ to $\text{VO}_2^+(\text{aq})$ in acidic conditions.
- 3 $\text{Zn}^{2+}(\text{aq})$ ions will oxidise $\text{V}^{2+}(\text{aq})$ ions to $\text{V}^{3+}(\text{aq})$ ions.

- 35** The working range and colour change of chlorophenol red is given below.

indicator	working pH range	colour change	
		Acid	Alkali
chlorophenol red	4.8 – 6.4	Yellow	Red

Two drops of this indicator are added to each of the three aqueous solutions listed below.

Which solution has its colour correctly stated?

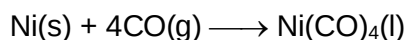
	solution	colour
1	aluminium oxide added to water	Red
2	0.1 mol dm ⁻³ of CH ₃ COOH ($K_a = 1.8 \times 10^{-5}$ mol dm ⁻³)	Yellow
3	solution of sodium ethanoate and ethanoic acid in 1:2 proportion [pK_a of ethanoic acid = 4.7]	Orange

- 36** Use of the Data Booklet is relevant to this question.

Which statements about the trends in properties of the hydrogen halides are correct?

- Volatility decreases in the order: HF > HCl > HBr > HI.
- Thermal stability increases in the order: HI < HBr < HCl < HF.
- Ease of oxidation increases in the order: HF < HCl < HBr < HI.

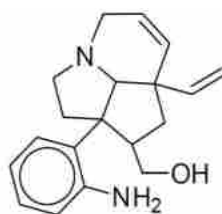
- 37** Nickel is purified by a method called the Mond process. The equation of the first step of the purification is shown below.



Which of the following statements are correct?

- CO is a monodentate ligand.
- Ni in Ni(CO)₄ has a co-ordination number of 4.
- The oxidation number of Ni in Ni(CO)₄ is zero.

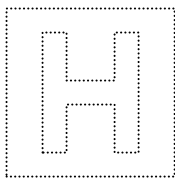
- 38** Compound **X** is a synthetic precursor of *meloscine*, an alkaloid isolated from the New Caledonian plant *Melodinus Scandens* Forst.



compound **X**

Which of the following statements about its reactions are correct?

- 1 1 mol of **X** reacts with 2 mol of HBr(g) when heated.
 - 2 1 mol of **X** reacts with 4 mol of Br₂(aq) at room temperature.
 - 3 1 mol of **X** reacts with 2 mol of CH₃COCl at room temperature.
- 39** Which of the following reactions give products that does not rotate the plane of polarised light?
- 1 1-bromobutane refluxed with aqueous KOH
 - 2 butanone reacted with HCN, trace amount of NaOH
 - 3 but-1-ene reacted with bromine dissolved in organic solvent
- 40** Which of the following could result in the loss of the tertiary structure of a protein?
- 1 addition of weak acid
 - 2 addition of alcohol
 - 3 addition of AgNO₃ solution



INNOVA JUNIOR COLLEGE

JC 2 PRELIMINARY EXAMINATION 2

in preparation for General Certificate of Education Advanced Level

Higher 2

CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9647/01

Paper 1 Multiple Choice

30 August 2016

1 hour

Additional Materials: Data Booklet
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

This document consists of **16** printed pages and **0** blank page.

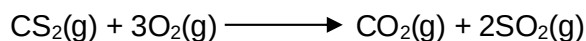


Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 Carbon disulfide, CS_2 , is a volatile liquid used in the production of cellophane which is used for food packaging.

On combustion, CS_2 is oxidised as follows.



A 20 cm^3 sample of carbon disulfide vapour is ignited with 100 cm^3 of oxygen. The final volume of gas after burning is treated with an excess of aqueous alkali.

Which percentage of this final volume dissolves in alkali? (All volumes are measured at room temperature of pressure.)

- A** 20%
B 40%
C 60%
D 80%

Answer: C

1 mole of CS_2 reacts with 60 cm^3 of O_2 , remaining volume of $\text{O}_2 = 40 \text{ cm}^3$

produces 1 mole of CO_2

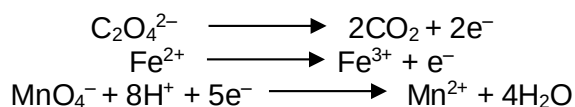
20 cm^3 of CS_2 produces 20 cm^3 of CO_2 and 40 cm^3 of SO_2

Total volume of gases at the end of reaction = $40 + 20 + 40 = 100 \text{ cm}^3$

Both CO_2 and SO_2 are acidic gases which will react with NaOH

Hence % of final volume dissolved in alkali $60/100 \times 100\% = 60\%$

- 2 Consider the following half-equations



What volume of 0.01 mol dm^{-3} potassium manganate(VII) is needed to completely oxidise 25.0 cm^3 of an acidified solution of 0.01 mol dm^{-3} FeC_2O_4 ?

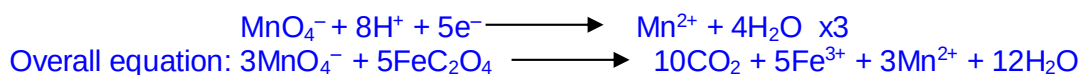
- A** 5 cm^3
B 7.5 cm^3
C 10 cm^3
D 15 cm^3

Answer: D

Combining eqns:



3



Amount of $\text{FeC}_2\text{O}_4 = 25/100 \times 0.01 = 0.00025 \text{ mol}$

Mole ratio of $\text{FeC}_2\text{O}_4 : \text{MnO}_4^- = 5 : 3$

Amount of $\text{MnO}_4^- = 3/5 \times 0.00025 = 0.00015 \text{ mol}$

Volume of $\text{MnO}_4^- = 0.00015 / 0.01 = 0.015 \text{ dm}^3 = 15 \text{ cm}^3$

- 3 Which electronic configuration represents an element that forms a simple ion with a charge of -3 ?

A $1s^2 2s^2 2p^6 3s^2 3p^1$

B $1s^2 2s^2 2p^6 3s^2 3p^3$

C $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

D $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Answer: B

A : Group III element : $+3$ ion

B: Group V : -3 ion

C and D are transition elements – forms positively charged ions

- 4 Carbon dioxide is a gas at room temperature while silicon dioxide is a solid because

- A carbon dioxide contains double covalent bonds while silicon dioxide contains single covalent bonds.
B instantaneous dipole – induced dipole attractions are weaker than permanent dipole – permanent dipole attractions.
C carbon-oxygen bonds are less polar than silicon-oxygen bonds.
D van der Waals' forces are much weaker than covalent bonds.

Answer D

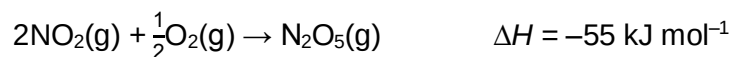
Carbon dioxide is a simple molecules with weak van der waal's forces of attraction between molecules while silicon dioxide is a giant covalent structure with strong covalent bonds. Thus, less amt of energy is required to overcome the weaker VDW forces of attraction between CO_2 molecules, resulting in lower boiling point.

Answer: C

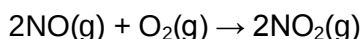
At high temperatures, particles have sufficient energy to overcome the intermolecular forces of attraction.

At low pressures, particles are very far apart. The volume of the particles is negligible to the volume of container which they moves in; intermolecular forces of attraction is negligible.

- 6** The enthalpy changes involving some oxides of nitrogen are given below:

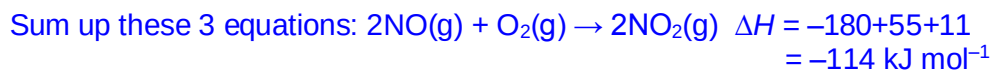
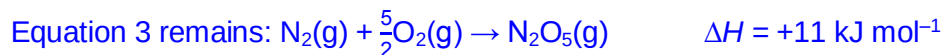
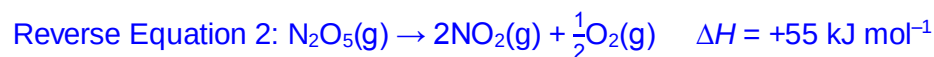
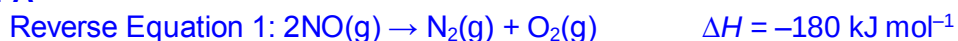


What is the enthalpy change, in kJ mol^{-1} , of the following reaction?



- A** -114 **B** +114 **C** -136 **D** +136

Answer: A



- 7 A typical protein forms hundreds of hydrogen bonds and thousands of van der Waals' forces in folding from primary to tertiary structures.

Which of the following thermodynamic state functions of the protein best represents the folding process?

	$\Delta G / \text{kJ mol}^{-1}$	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J K}^{-1} \text{mol}^{-1}$
A	–	–	–
B	+	–	+
C	–	+	–
D	+	+	–

Answer: A

When hydrogen bonds and van der Waals' forces are formed, heat will be released. Thus ΔH is negative.

When the protein is folded from primary to tertiary structures, the system becomes less disordered. Thus ΔS is negative.

The process of protein folding is spontaneous. Thus, ΔG is negative.

- 8 When 1 mole of carbon dioxide gas solidifies as dry ice, 25.2 kJ of heat energy is evolved. The sublimation temperature of carbon dioxide is -78.5°C .

What is the entropy change when 132 g of carbon dioxide gas solidifies at this temperature?

- A** +130 J K⁻¹
B -130 J K⁻¹
C +389 J K⁻¹
D -389 J K⁻¹

Answer: D

This is a phase change reaction. $\Delta G = 0$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

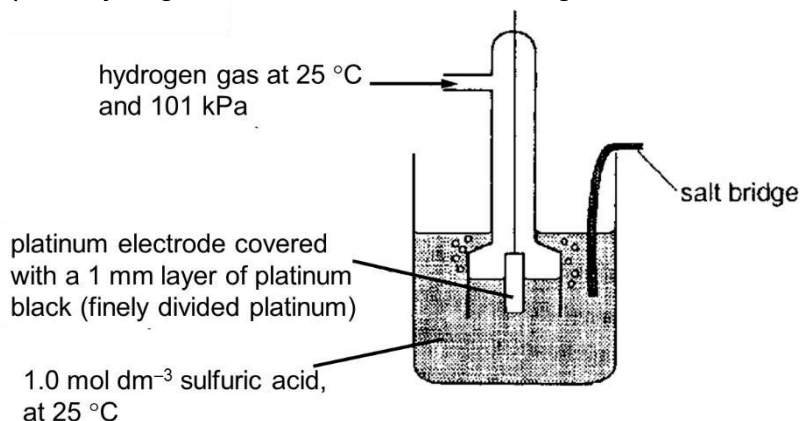
$$\Delta S = \frac{-25200 - 0}{-78.5 + 273}$$

$$\Delta S = \frac{-25200}{194.5}$$

$$\Delta S = -129.56 \text{ J K}^{-1}$$

$$\Delta S \text{ when 132 g of carbon dioxide gas solidifies} = -129.56 \times \frac{132}{44} = -389 \text{ J K}^{-1}$$

- 9 A student set up the hydrogen electrode shown in the diagram below.



What would have to be changed to make this a standard hydrogen electrode?

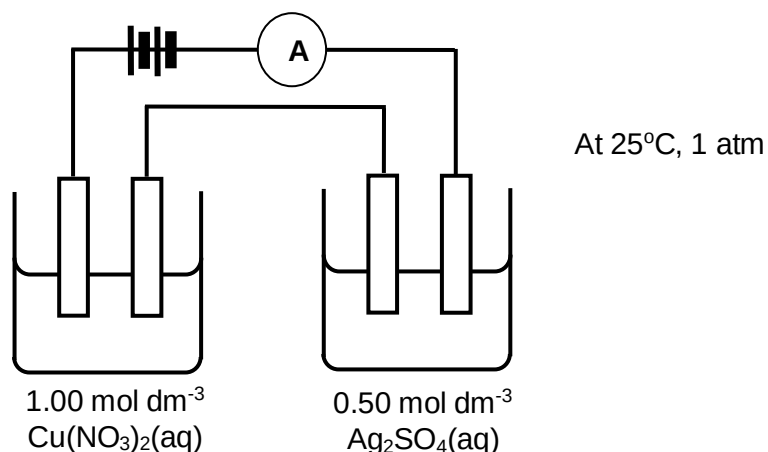
- A** the acid solution used
- B** the temperature of the gas and of the acid solution
- C** the pressure of the gas
- D** the metal comprising the electrode

Answer: A

In 1.0 mol dm⁻³ sulfuric acid, $[H^+] = 2.0 \text{ mol dm}^{-3}$. To make the electrode a standard hydrogen electrode, either change the acid to a 1.0 mol dm⁻³ monoprotic acid (option **A**), or halve the concentration of sulfuric acid used.

- 10 Use of the Data Booklet is relevant to this question.

Using inert electrodes, a current was passed through two beakers containing aqueous silver sulfate and aqueous copper(II) nitrate, connected in series under standard conditions.



What is the ratio of the mass of silver to copper deposited after the current was passed for t minutes?

- A** 0.59
- B** 0.85
- C** 1.70
- D** 3.40

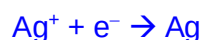
Answer: D

$$It = n_e F$$

$$n_e \text{ transferred} = \frac{It}{F}$$



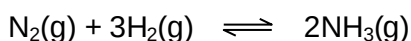
$$n_{\text{Cu}} = \frac{It}{2F}$$



$$n_{\text{Ag}} = \frac{It}{F}$$

$$\frac{\text{mass of Ag formed}}{\text{mass of Cu formed}} = \frac{\text{Ar} \times \text{no. of moles of Ag formed}}{\text{Ar} \times \text{no. of moles of Cu formed}} = \frac{108 \times \frac{It}{F}}{63.5 \times \frac{It}{2F}} = 3.40$$

- 11 A nitrogen-hydrogen mixture, initially in the mole ratio of 1:3, reached equilibrium with ammonia when 50% of the nitrogen had reacted. The total equilibrium pressure was p .



What was the partial pressure of ammonia in the equilibrium mixture?

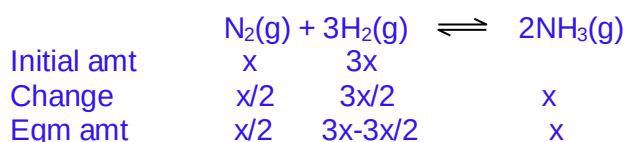
A $\frac{p}{3}$

B $\frac{p}{4}$

C $\frac{p}{6}$

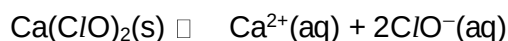
D $\frac{2p}{7}$

Ans A



Total final pressure = sum of eqm partial pressure = $x/2 + (3x - 3x/2) + x = p$
 $3x = p \rightarrow x = p/3$

- 12 Solid calcium hypochlorite pellets, $\text{Ca}(\text{ClO})_2(\text{s})$, are added to swimming pools to form $\text{HClO}(\text{aq})$, which kills disease-causing bacteria and algae.



What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH decreases?

	Solubility of calcium hypochlorite	Effect on bacterial growth
A	decreases	more favourable
B	decreases	less favourable
C	increases	more favourable
D	increases	less favourable

Answer: D

When pH decreases, $[H^+]$ increases and $[OH^-]$ decreases, equilibrium position of second equation shift to the right and $[HC/O]$ increases. Bacterial growth will be less favourable.

When $[ClO^-]$ decreases, equilibrium position of first equation shift to the right and solubility of calcium hypochlorite increases.

- 13** The dissociation constant, K_w , for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

temperature / °C	K_w
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

- A** Only at 25 °C are $[H^+]$ and $[OH^-]$ equal.
- B** The equilibrium lies furthest to the right at 0°C.
- C** The forward reaction is exothermic.
- D** The pH of water decreases as temperature increases.

Answer: D

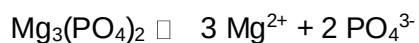
Option A is wrong as $[H^+]$ and $[OH^-]$ are equal at all temperature for pure water.

Option B is wrong as the equilibrium lies furthest to the right at 50°C (as shown by K_w value).

Option C is wrong as the forward reaction is endothermic. When temperature increases, K_w increases. This shows that equilibrium lies to the right.

Option D is correct as the forward reaction is endothermic. When temperature increases, K_w increases. This shows that equilibrium lies to the right. $[H^+]$ increases and this leads to decrease in pH.

- 14 A sparingly soluble salt, $\text{Mg}_3(\text{PO}_4)_2$ dissociates in aqueous solution as follows:



Given that the solubility product, K_{sp} of $\text{Mg}_3(\text{PO}_4)_2$ is Q , what is the value of $[\text{Mg}^{2+}]$ in a saturated solution?

- A** $\left(\frac{9Q}{4}\right)^{\frac{1}{5}}$ **B** $\left(\frac{Q}{27}\right)^{\frac{1}{3}}$ **C** $\left(\frac{Q}{108}\right)^{\frac{1}{5}}$ **D** $\left(\frac{9Q}{64}\right)^{\frac{1}{3}}$

Answer: A



Change	$-x$	$+3x$	$+2x$
Equilibrium		$3x$	$2x$

$$K_{\text{sp}} = [\text{Mg}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

$$Q = (3x)^3 (2x)^2$$

$$Q = (27x^3) (4x^2)$$

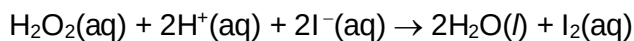
$$x = \left(\frac{Q}{108}\right)^{\frac{1}{5}}$$

$$[\text{Mg}^{2+}] = 3 \times \left(\frac{Q}{108}\right)^{\frac{1}{5}}$$

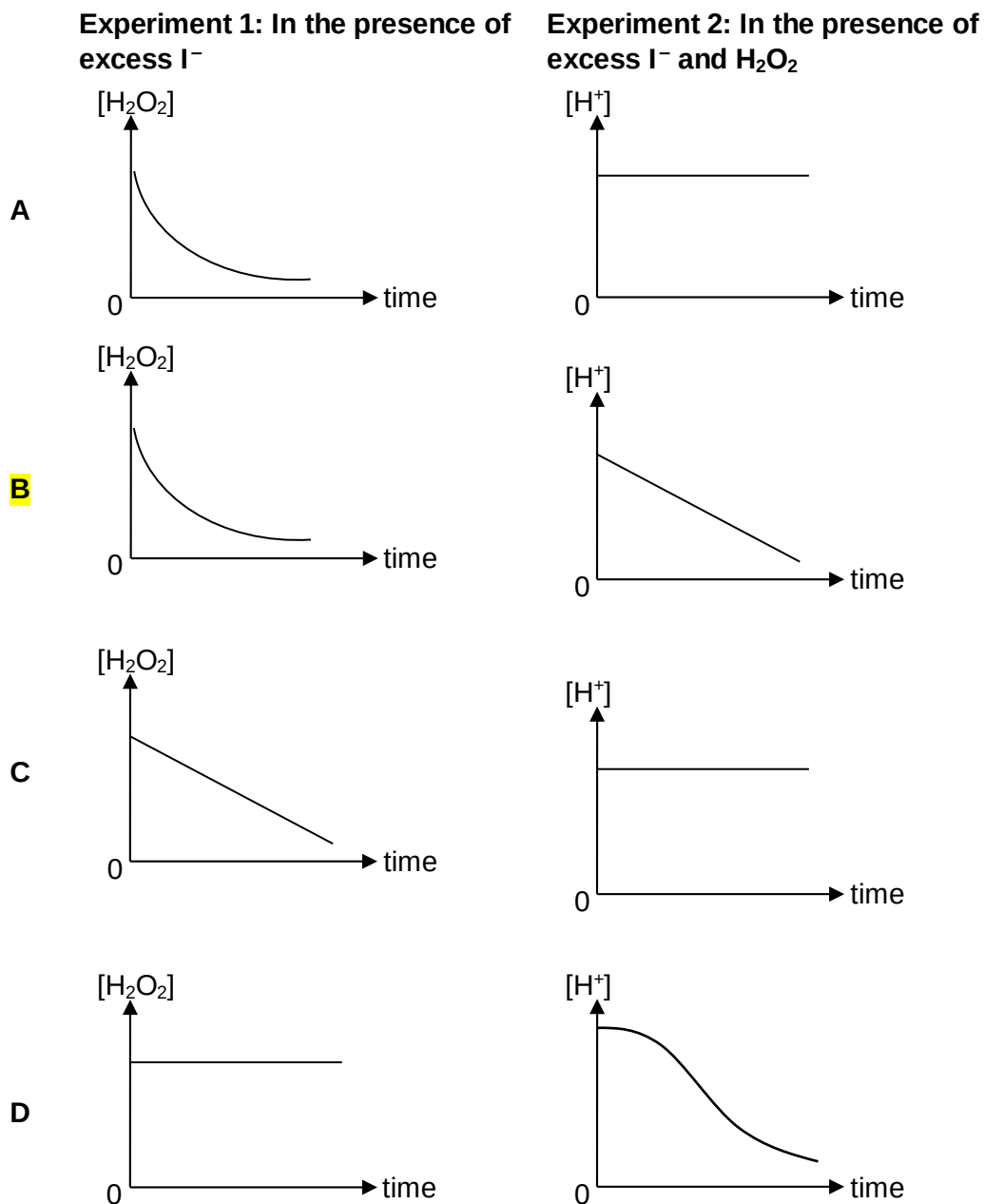
$$= \left(\frac{243Q}{108}\right)^{\frac{1}{5}}$$

$$= \left(\frac{9Q}{4}\right)^{\frac{1}{5}}$$

15. The reaction of hydrogen peroxide with iodide ions in an acidic solution is first order with respect to hydrogen peroxide as well as iodide ions, and zero order with respect to hydrogen ions.



Two experiments were carried out. Which pair of diagrams represents the variation of $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$ with time?



Ans B

Given in question: Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$,

For expt 1: $[\text{I}^-]$ is first order

The graph of $[\text{H}_2\text{O}_2]$ against time is a downward sloping curve with decreasing gradient.

Rate = $k'[\text{H}_2\text{O}_2]$ where $k' = k[\text{I}^-]$

For expt 2:

$[\text{H}^+]$ is zero order. The graph of $[\text{H}^+]$ against time is a decreasing straight line with a constant gradient.

Rate = k' where $k' = k[\text{I}^-][\text{H}_2\text{O}_2]$

- 16 Aluminium is an element in the third period, Na to Ar, of the Periodic Table.

What is true for aluminium?

- A Aluminium has the highest melting point of the elements in this period.
- B Aluminium is the only element in this period whose chloride reacts with water to form an acidic solution
- C Aluminium is the only element in this period which can exist, at room temperature and pressure, as solid and conduct electricity.
- D Aluminium is the only element in this period whose oxide reacts with both acids and bases.

Answer: D

Period 3 trends

Aluminium is the only amphoteric oxide in third period.

- 17 Which of the following statements regarding Group II elements or their compounds is **correct**?

- A Magnesium chloride has a higher melting point than barium chloride.
- B Magnesium is a stronger reducing agent than strontium.
- C Calcium hydroxide is more thermally stable than barium hydroxide.
- D Strontium reacts more readily with oxygen than radium.

Answer:

MgCl_2 has a larger magnitude of lattice energy than BaCl_2 since ionic radius of Mg^{2+} is smaller than that of Ba^{2+} ion.

Mg is a weaker reducing agent or undergoes oxidation less readily than Sr since $E^\ominus(\text{Mg}^{2+}/\text{Mg})$ is less negative than $E^\ominus(\text{Sr}^{2+}/\text{Sr})$.

$\text{Ca}(\text{OH})_2$ is less thermally stable than $\text{Ba}(\text{OH})_2$ as Ca^{2+} has a higher charge density than Ba^{2+} (due to the smaller ionic radius of Ca^{2+} . Ca^{2+} polarises the electron cloud of OH^- ions and weakens the O-H bond in the hydroxide ions to a greater extent, thus less energy is required for the decomposition of $\text{Ca}(\text{OH})_2$).

The reactivity of Group II metals increases down the group due to increasing reducing power of the metals down the Group. Since Sr is above Ra in Group II, Sr is expected to react less readily with oxygen than Ra.

- 18 Which of the following statements about astatine, the element below iodine in Group VII of the periodic table, is **incorrect**?

- A Silver astatide is insoluble in aqueous ammonia.
 B Hydrogen astatide is less stable to heat than hydrogen iodide.
 C Sodium astatide and hot concentrated sulfuric acid react to form astatine.
 D Astatine and aqueous potassium chloride react to form aqueous potassium astatide and chlorine.

Answer:

AgI is insoluble in both dilute and concentrated NH_3 and since K_{sp} of AgX decreases down the group, AgAt is expected to be less soluble in both dilute and concentrated NH_3 than AgI. H-At bond is weaker than H-I bond since At atom is bigger and more diffuse leading to less effective orbital overlap in H-At bond.

Since reducing power of the halides increases down the group and NaI reacts with conc H_2SO_4 to give I_2 , NaAt is similarly expected to react with conc H_2SO_4 to give I_2 .

At_2 cannot undergo displacement reaction with KCl since At_2 is a weaker oxidising agent (or less likely to undergo reduction) than Cl_2 as oxidising power of halogen decreases down the group.

- 19 When copper(II) chloride is dissolved in water it gives a blue solution. When this solution is treated with an excess of concentrated hydrochloric acid it turns yellow.

What are the formulae of the copper species in the blue and yellow solution?

	blue	yellow
A	CuCl_2	$[\text{CuCl}_4]^{2-}$
B	$\text{CuCl}_2(\text{H}_2\text{O})_4$	$[\text{CuCl}_6]^{4-}$
C	$\text{Cu}(\text{OH})_2$	$\text{CuCl}_2(\text{H}_2\text{O})_4$
D	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	$[\text{CuCl}_4]^{2-}$

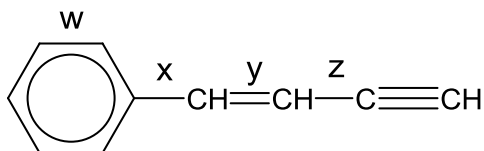
Answer: D

When copper(II) chloride dissolves in water, it dissociates into Cu^{2+} and Cl^- ions. The Cu^{2+} ions exist in the hydrated form, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, which is blue in colour.

When excess conc HCl is added, ligand exchange occurs, where the Cl^- ligand displace the H_2O ligands to form $[\text{CuCl}_4]^{2-}$, according to the following equation.



- 20 Four carbon-carbon bonds are labelled in the diagram.



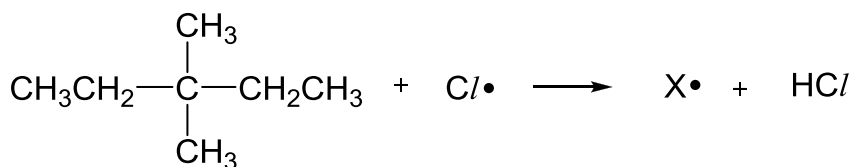
Which bonds are made up of an sp^2-sp^2 overlap?

- A w and y only
- B w, x and y only
- C w, x, y and z
- D x and y only

Answer: B

All the carbons are sp^2 , except the bond for z where the carbon in $C\equiv C$ is sp hybridized.

- 21 When heated with chlorine, the hydrocarbon 3,3-dimethylpentane undergoes free radical substitution. In the propagation step, the free radical $X^\bullet$ is formed by the loss of one hydrogen atom.

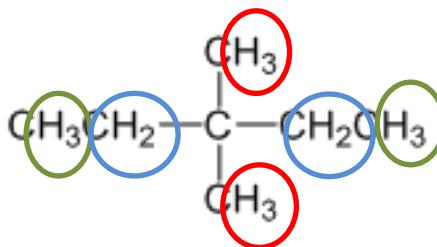


How many different forms of $X^\bullet$ are theoretically possible?

- A 2
- B 3
- C 4
- D 5

Answer: B

There are 3 types of Hydrogen atoms that can be lost.



- 22 Bromoethene, $\text{CH}_2=\text{CHBr}$, is unreactive to nucleophiles whereas 3-bromopropene, $\text{CH}_2=\text{CHCH}_2\text{Br}$ is very reactive by comparison.

What explains the lack of reactivity of $\text{CH}_2=\text{CHBr}$?

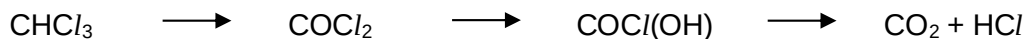
- A Substituted alkenes undergo only electrophilic addition.
- B The C=C double bond and the Br atom are both electron withdrawing which stabilises $\text{CH}_2=\text{CHBr}$.
- C The electrons on the Br atom delocalise into the π bond.
- D The presence of the π bond prevents free rotation of the C-Br bond this decreasing the reactivity.

Answer: C

For halogen-containing organic compounds, reactivity to nucleophiles (such as OH^-) depends on the bond strength of C-X bonds. The unreactivity of bromoethene with nucleophile possibly suggest stronger C-Br bonds, as a result of the p orbital of Br overlapping with π bonds, hence having partial double-bond character.

- 23 Phosgene, COCl_2 , is a colourless gas that gained infamy as a chemical weapon during World War I. It is formed when trichloromethane, CHCl_3 , is left exposed to the atmosphere.

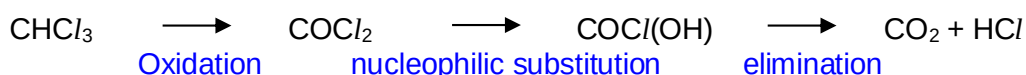
Below is a reaction scheme that involves trichloromethane and phosgene:



Which of the following type of reaction is **not** being observed in the reaction scheme?

- A Oxidation
- B Elimination
- C Electrophilic addition
- D Nucleophilic substitution

Ans: C



- 24 A chlorine-containing organic compound, **X**, undergoes an elimination reaction when treated with hot ethanolic potassium hydroxide solution.

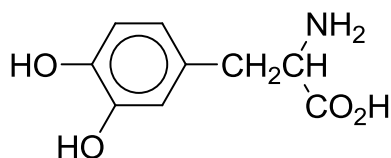
What is **X**?

- A CH_2Cl_2
- B C_2Cl_6
- C** $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$
- D $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$

Answer: C

To undergo elimination, there must be a hydrogen atom on the carbon atom adjacent to the carbon atom bearing the halogen atom. Only option C fulfils this criterion.

- 25 Dopamine is an important organic chemical that helps control the brain's reward and pleasure centres. It also helps regulate movement and emotional responses.



Dopamine

Which of the following statements about dopamine is **incorrect**?

- A It is able to rotate plane-polarized light.
- B It is soluble in water due to zwitterion formation.
- C It migrates to the negative electrode of an electrolytic cell at pH 14.**
- D The acidity of dopamine will increase when aqueous bromine is added.

Ans: C

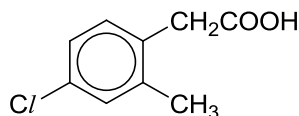
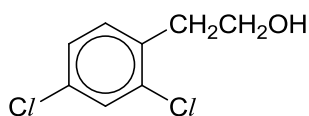
Option A: Dopamine indeed contains a chiral carbon and exhibits optical activity

Option B: Dopamine is able to exist as a zwitterion $\text{RCH}(\text{NH}_3^+)(\text{COO}^-)$ which is able to form ion-dipole interactions with water.

Option C: At pH 14, the COOH group is deprotonated. The predominant form is the anionic form, which should migrate to the positive electrode instead of the negative electrode.

Option D: When aqueous bromine is added, electrophilic substitution occurs with the introduction of Br into the benzene ring. Br is electron withdrawing and is able to disperse the negative charge on the oxygen atoms in the anion, thus increasing the acidity of the compound.

26 Two bottles containing the following reagents had their labels removed.



Which one of the following reagents can be used to distinguish between them?

A sodium metal

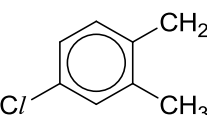
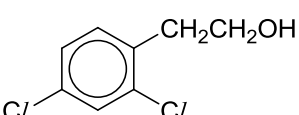
C hot acidified potassium manganate(VII)

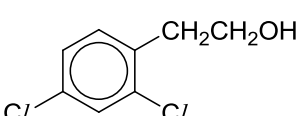
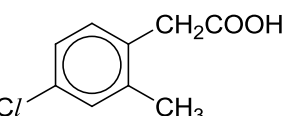
B sodium hydroxide

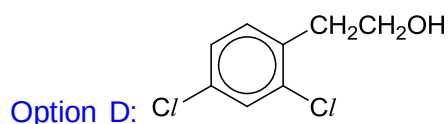
D hot acidified potassium dichromate

Ans: D

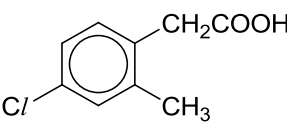
Option A: Both compounds react with Na . Effervescence will be seen for both compounds. Gas evolved will extinguish lighted splint with a 'pop' sound.

Option B:  can react with NaOH but not . However, the reaction is not easily visible.

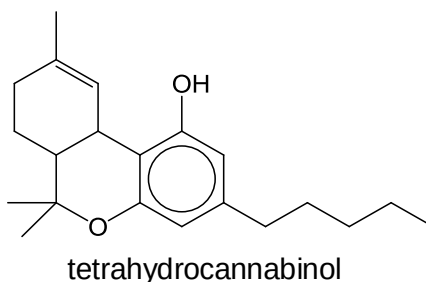
Option C: Both  and  reacts with hot acidified KMnO_4 via side chain oxidation. Hence purple KMnO_4 will decolourise for both compounds and effervescence will be seen for both. Gas evolved will form white ppt with $\text{Ca}(\text{OH})_2$.

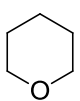


reacts with hot acidified $K_2Cr_2O_7$ via oxidation of primary

alcohol (orange solution turns green).  does not undergo side chain oxidation as $K_2Cr_2O_7$ is a weaker oxidizing agent than $KMnO_4$.

- 27 Marijuana (cannabis) is the most widely used illegal drug in many developed countries. Medical studies have shown that the active ingredient in marijuana, tetrahydrocannabinol, might provide medical benefits to some patients.



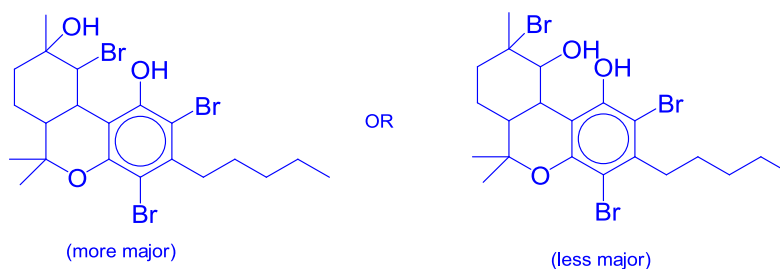
In the following reactions, the  remains unaltered.

Which reaction will tetrahydrocannabinol undergo?

- A** It reacts with aqueous bromine to incorporate up to 2 atoms of bromine in each molecule.
- B** It reacts with hot acidified potassium dichromate(VI) to form a green solution.
- C** It reacts with dilute nitric acid to form a substitution product.
- D** It reacts with ethanoic acid to form a sweet-smelling product.

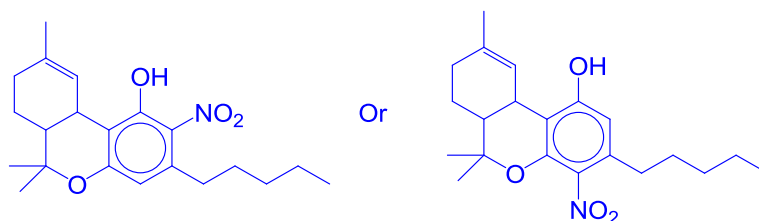
Ans: C

Option **A** is incorrect because both alkene group and phenol group will react with aqueous Br_2 to incorporate **3 Br atoms**, forming the following products:



Option **B** is incorrect. $K_2Cr_2O_7$ is not strong enough to oxidise side-chain of benzene and alkene. Phenol is not oxidised as well.

Option **C** is correct. Dilute nitric acid reacts with phenol functional group via electrophilic substitution to form the following product:



Option **D** is incorrect. Phenol functional group does not react readily with ethanoic acid (even in the presence of conc. H_2SO_4 as catalyst). Hence, no ester will be formed. (To form the ester, the phenol should be treated with aq. NaOH to generate a stronger phenoxide ion before added into ethanoyl chloride)

- 28** A student carried out an experiment to study the ease of hydrolysis of a series of chlorinated compounds, and recorded the observations based on the addition of acidified silver nitrate solution.

Which of the following gives the expected results?

	time taken for precipitate to appear			
	shortest	→		longest
A	$\text{C}_6\text{H}_5\text{Cl}$	$\text{CH}_2\text{Cl}/\text{CONH}_2$	CH_3COCl	COCl_2
B	$\text{CH}_2\text{Cl}/\text{CONH}_2$	$\text{C}_6\text{H}_5\text{Cl}$	COCl_2	CH_3COCl
C	CH_3COCl	COCl_2	$\text{C}_6\text{H}_5\text{Cl}$	$\text{CH}_2\text{Cl}/\text{CONH}_2$
D	COCl_2	CH_3COCl	$\text{CH}_2\text{Cl}/\text{CONH}_2$	$\text{C}_6\text{H}_5\text{Cl}$

Ans: **D**

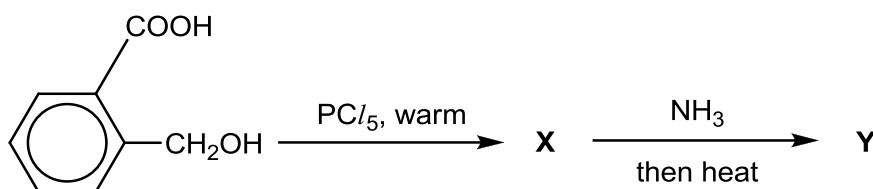
COCl_2 and CH_3COCl more reactive as the highly electronegative O and Cl atoms that are bonded to acyl carbon make it more electron deficient (or more δ^+ charged), thus attract nucleophiles more readily. COCl_2 hydrolyses more rapidly than CH_3COCl as the former has its acyl carbon more electron deficient due to its additional Cl atom.

In addition, the acyl carbon atoms are sp^2 hybridised, so they have trigonal planar arrangement with respect to C, resulting in less steric hindrance for the approach of nucleophiles compared to the sp^3 C atom (that is bonded to Cl in $\text{CH}_2\text{Cl}/\text{CONH}_2$).

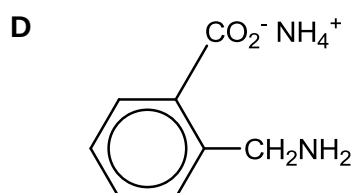
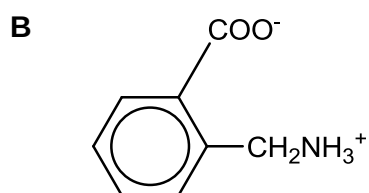
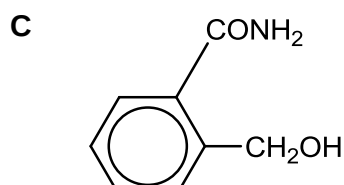
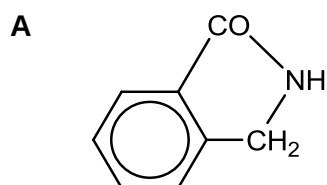
$\text{CH}_2\text{Cl}/\text{CONH}_2$ is the next most reactive as the C atom bonded to only one highly electronegative Cl atom is less electron deficient (or less δ^+ charged) compared to COCl_2 and CH_3COCl .

$\text{C}_6\text{H}_5\text{Cl}$ is a halogenoarene (or aryl halide) where its Cl atom is bonded directly to benzene ring. The p orbital of Cl overlaps with the π electron cloud of benzene ring resulting its lone pair being delocalized into benzene and double bond character in its C-Cl bond. Since its C-Cl is most difficult to break, nucleophilic substitution (or hydrolysis) cannot occur.

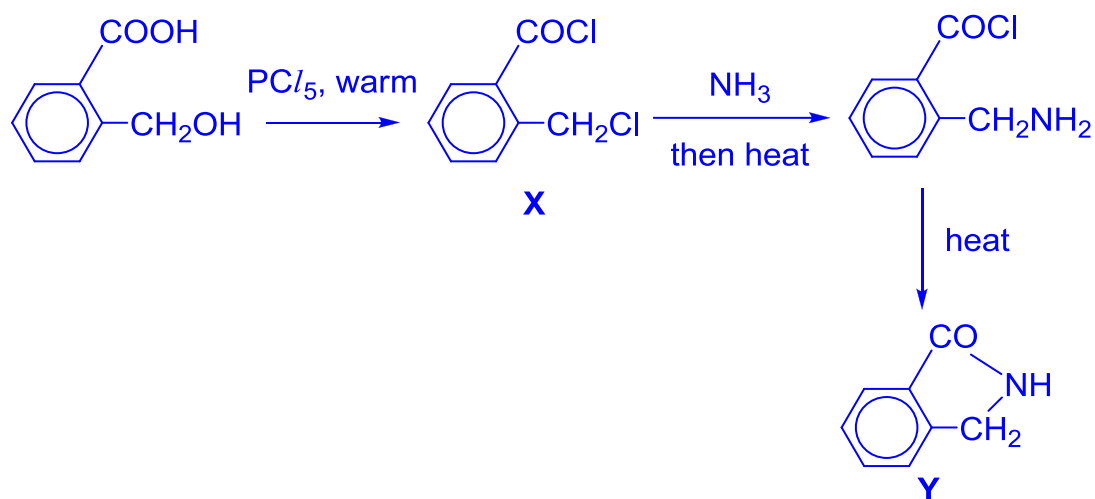
- 29 In the following two-step synthesis, **Y** a solid which is insoluble in water, is one of the components in the final reaction mixture.



What is **Y**?



Ans: A



The reaction of **X** with NH_3 produces a mixture of products. O=C(Cl)c1ccccc1CCN is one of the products which contains an amine group and an acyl chloride group. The amine group is nucleophilic and undergo intramolecular reaction with the electron-deficient C of the acyl chloride to form a cyclic product.

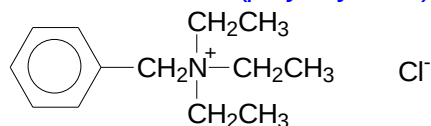
Since reaction with PCl_5 converts $-\text{COOH}$ to $-\text{COCl}$ and $-\text{CH}_2\text{OH}$ to $-\text{CH}_2\text{Cl}$ (as shown in **X**), the product should not contain $-\text{COO}-$ or $-\text{CH}_2\text{OH}$ group. Hence, by elimination of options, B, C and D are incorrect.

- 30 Benzylamine has the formula $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

- A** It decolourises aqueous Br_2 .
B It can be produced by reduction of $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$.
C It reacts with CH_3COOH to form $\text{C}_6\text{H}_5\text{CH}_2\text{NHCOCH}_3$.
D It reacts with excess $\text{CH}_3\text{CH}_2\text{Cl}$ to form the compound, $\text{C}_{13}\text{H}_{22}\text{NCl}$.

- (A) $-\text{CH}_2\text{NH}_2$ group is not strongly activating, hence benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, cannot undergo easy electrophilic substitution with aqueous Br_2 . This is not to be confused with phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.
 (B) When $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ undergoes reduction, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$ is produced, not $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$.
 (C) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ undergoes acid base reaction, not condensation reaction, with CH_3COOH to give $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+\text{CH}_3\text{COO}^-$. An amide is formed from condensation between a primary or secondary amine and *acyl halide*.
 (D) A quaternary ammonium salt (shown below) is formed from successive nucleophilic substitutions (polyalkylation).



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31 Gaseous particle **Y** has a proton(atomic) number n and a charge of $+1$.

Gaseous particle **Z** has a proton(atomic) number of $n+1$ and is isoelectronic with **Y**.

Which statement correctly describes **Y** and **Z**?

- 1** **Y has a larger radius than Z.**
2 **Y** requires more energy than **Z** when a further electron is removed from each particle.
3 **Y** releases more energy than **Z** when an electron is added to each particles.

Ans: D

Statement 1 (correct) Y (less protons) and isoelectronic with Z has a lower nuclear charge and has a larger radius.

Statement 2: (wrong) Z has a higher nuclear charge and hold electrons more strongly (stronger attraction) and hence requires more energy.

- 32 Which of the following molecules will form a hydrogen bond with another of its own molecules?

- 1 CH_3NH_2
- 2 CH_3CHO
- 3 $\text{CH}_3\text{CH}_2\text{F}$

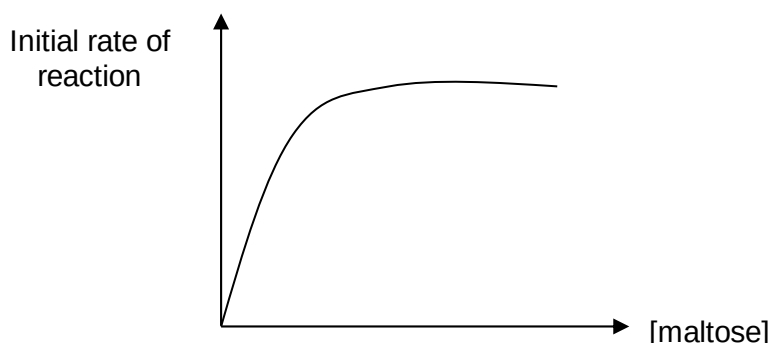
Answer: D

Option 1: There is H-bonding between CH_3NH_2 .

Option 2: No H-bonding as O is not directly bonded to H atom.

Option 3: No H-bonding as F is not directly bonded to H atom.

- 33 The graph below shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied but that of amylase was kept constant.



Which conclusions can be deduced from these results?

- 1 When [maltose] is low, the rate is first order with respect to [maltose].
- 2 When [maltose] is high, the rate is independent of [maltose].
- 3 When [maltose] is high, the rate is independent of [amylase].

Answer: B

Answer: B

Option 1:

At **low substrate concentration** [maltose], not all of the active sites are occupied.

- $\text{rate} \propto [\text{maltose}] \Rightarrow$ reaction is **first order** with respect to the maltose.

Option 2:

At **high** [maltose], all the active sites are occupied, i.e. the active sites of the enzyme [amylase] become **saturated** with maltose.

- Any increase in [maltose] will not have any effect on the reaction rate.
- The reaction is **zero order** with respect to the maltose.

Option 3: If substrate is not the limiting factor, increasing enzyme amylase concentration **will increase** the rate of reaction, as there will be more active sites of enzyme.

- 34** With reference to the *Data Booklet* and the data below, deduce which of the following statements are correct.

Half-equation	E^θ/V
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.00
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.34
$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-0.26

- 1** An excess of zinc is capable of reducing $\text{VO}_2^+(\text{aq})$ to $\text{V}^{2+}(\text{aq})$ in acidic conditions.
- 2** $\text{Fe}^{3+}(\text{aq})$ is capable of oxidising $\text{V}^{2+}(\text{aq})$ to $\text{VO}_2^+(\text{aq})$ in acidic conditions.
- 3** $\text{Zn}^{2+}(\text{aq})$ ions will oxidise $\text{V}^{2+}(\text{aq})$ ions to $\text{V}^{3+}(\text{aq})$ ions.

Answer: D

Answer: D

Half-equation	E^θ/V
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76

Option 1:

Excess Zn is the reducing agent which can reduce $\text{VO}_2^+(\text{aq})$ to $\text{VO}^{2+}(\text{aq})$

$$E_{\text{cell}} = +1.00 - (-0.76) = 1.76\text{V} > 0$$

Excess Zn can further reduce $\text{VO}^{2+}(\text{aq})$ to $\text{V}^{3+}(\text{aq})$:

$$E_{\text{cell}} = +0.34 - (-0.76) = 1.10\text{V} > 0$$

Excess Zn can further reduce $\text{V}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{V}^{2+}(\text{aq})$:

$$E_{\text{cell}}: -0.26 - (-0.76) = 0.50\text{V} > 0$$

Quick thinking for MCQ:

Since $E_{\text{cell}} = E_{\text{red}} - E_{\text{oxi}} > 0$ for reaction to proceed (Zn is oxidised),
 $E_{\text{red}} - (-0.76) > 0$
 $E_{\text{red}} > -0.76$ for reaction to proceed

Option 2: wrong

Quick thinking for MCQ:

Since $E_{\text{cell}} = E_{\text{red}} - E_{\text{oxi}} > 0$ for reaction to proceed
 (Fe³⁺ is reduced to Fe²⁺),
 $+0.77 - E_{\text{oxi}} > 0$
 $E_{\text{oxi}} < +0.77$ for reaction to proceed

Fe³⁺ can oxidise V²⁺ to VO²⁺ but not VO₂⁺

$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.00
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77

$$E_{\text{cell}} = +0.77 - 1.00 = -0.23\text{V} < 0$$

Another factor: Fe³⁺ is not in excess, successive oxidation of vanadium compounds may not occur.

35 The working range and colour change of Chlorophenol red is given below.

Indicator	Working pH range	Colour change	
		Acid	Alkali
Chlorophenol red	4.8 – 6.4	Yellow	Red

Two drops of this indicator are added to each of the three aqueous solutions listed below.

Which solution has its colour correctly stated?

	Solution	Colour
1	Aluminium oxide added to water	Red
2	0.1 mol dm ⁻³ of CH ₃ COOH (K _a = 1.8 × 10 ⁻⁵ mol dm ⁻³)	Yellow
3	Solution of sodium ethanoate and ethanoic acid in 1:2 proportion [pK _a of ethanoic acid = 4.7]	Orange

Answer: B

Option 1 is correct.

Aluminium oxide does not dissolve in water and it gives a pH 7 solution. According to the working pH range of this indicator, the color is red.

Option 2 is correct.

$$\begin{aligned}
 [\text{H}^+] &= \sqrt{K_a[\text{acid}]} \\
 &= \sqrt{1.8 \times 10^{-5} [0.1]} \\
 &= 1.342 \times 10^{-3} \text{ mol dm}^{-3}
 \end{aligned}$$

$$\therefore \text{pH} = -\log_{10} (1.342 \times 10^{-3}) = \underline{2.87}$$

According to the working pH range of this indicator, the color shown for a solution of pH 2.87 is yellow.

Option 3 is incorrect.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.7 + \log 0.5 = 4.7 - 0.3 = 4.4$$

According to the working pH range of this indicator, the color shown for a solution of pH 4.4 is yellow and not orange.

36 Use of the Data Booklet is relevant to this question.

Which statements about the trends in properties of the hydrogen halides are correct?

1 Volatility decreases in the order: HF > HCl > HBr > HI.

2 Thermal stability increases in the order: HI < HBr < HCl < HF.

3 Ease of oxidation increases in the order: HF < HCl < HBr < HI.

Ans: C

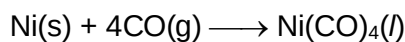
Option 1: Volatility is inversely proportional to the boiling point. The higher the boiling point, the less volatile the substance. HF has stronger intermolecular hydrogen bonding that requires more energy to break while the strength of instantaneous dipole-induced dipole interaction increases from HCl to HBr to HI due to increasing polarizability of electron cloud of the molecules. Thus the correct trend of volatility is HF < HI < HBr < HCl.

Option 2: Thermal stability of hydrogen halides depend on the bond strength of H-X. The stronger the H-X bond, the more thermally stable the hydrogen halides. Down the group, the valence orbital is more diffused, as there is less effective orbital overlap between the valence orbitals of hydrogen and halogen OR down the group, as the atomic size of halogen increases,

the H-X bond length increases. As such, the H-X bond strength is weaker, and less thermally stable. Therefore, the trend of increasing thermal stability ($\text{HI} < \text{HBr} < \text{HCl} < \text{HF}$) is correct.

Option 3: The ease of oxidation or reducing power of the halides increases down the group due to the less positive $E^\circ(\text{X}_2/\text{X}^-)$ down the group. Hence, the trend is correct.

- 37 Nickel is purified by a method called the Mond process. The equation of the first step of the purification is shown below.



Which of the following statements are correct?

- 1 CO is a monodentate ligand.
- 2 Ni in Ni(CO)_4 has a co-ordination number of 4.
- 3 The oxidation number of Ni in Ni(CO)_4 is zero.

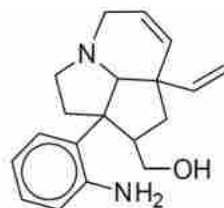
Ans: A

CO is a monodentate ligand as it forms one dative bond (using the lone pair of electron on the carbon atom) per formula unit.

Ni in Ni(CO)_4 has 4 dative or coordinate bonds formed with 4 CO ligands, thus its coordination number is 4.

Since the charges of the complex compound, Ni(CO)_4 and CO ligands are zero, the charge of Ni is zero too.

- 38 Compound X is a synthetic precursor of *meloscine*, an alkaloid isolated from the New Caledonian plant *Melodinus Scandens* Forst.



compound X

Which of the following statements about its reactions are correct?

- 1 1 mol of X reacts with 2 mol of HBr(g) when heated.
- 2 1 mol of X reacts with 4 mol of $\text{Br}_2(\text{aq})$ at room temperature.
- 3 1 mol of X reacts with 2 mol of CH_3COCl at room temperature.

Ans: C

Option 1: Incorrect. 1 mol of X reacts with 3 mol of HBr.

Each $\text{C}=\text{C}$ will undergo electrophilic addition with HBr. 1° alcohol will undergo nucleophilic substitution with HBr, heat.

Option 2: Correct

Each $\text{C}=\text{C}$ will undergo electrophilic addition with $\text{Br}_2(\text{aq})$. Phenylamine will undergo electrophilic substitution with 2 mol of Br_2 to form the di-substituted product.

Option 3: Correct

1° alcohol will undergo condensation reaction with CH_3COCl to form an ester. Phenylamine will undergo condensation reaction with 1 mol of CH_3COCl to form amide.

39 Which of the following reactions give products that **does not** rotate the plane of polarised light?

- 1 1-bromobutane refluxed with aqueous KOH
- 2 Butanone reacted with HCN, trace amount of NaOH
- 3 But-1-ene reacted with bromine dissolved in organic solvent

Ans: A

Option 1: 1-bromobutane is a 1° halogenoalkane hence it will react with aq KOH via S_N2 mechanism. Since the product does not contain a chiral carbon, it is unable to rotate plane of polarised light.

Option 2: Butanone reacts with HCN via nucleophilic addition. As the nucleophiles can attack the carbonyl carbon (trigonal planar in shape) either from the top or the bottom of the plane with equal chance, it results in a racemic mixture. Hence, even though the products are chiral, they are unable to rotate plane of polarised light.

Option 3: But-1-ene reacts with bromine via electrophilic addition. As the electrophile can attack the C atom of the carbocation intermediate is trigonal planar in shape, either from the top or the bottom of the plane with equal chance, it results in a racemic mixture. Hence, even though the products are chiral, they are unable to rotate plane of polarised light.

40 Which of the following could result in the loss of the tertiary structure of a protein?

- 1 Addition of weak acid
- 2 Addition of alcohol
- 3 Addition of $AgNO_3$ solution

Ans: A

Note: The tertiary structure of proteins refers to the 3D arrangement of the protein due to the folding of a polypeptide chain. Folding is due to R group (side chain) interactions.

Option 1: Addition of weak acid pH can change the ionic charges on amino acid residues (i.e. groups containing acidic $COOH$ or basic NH_2 groups) and hence disrupt the ionic interactions.

⇒ In acidic conditions, protonation occurs, i.e. $-COO^-$ is converted to $-COOH$.

Option 2: Alcohol can disrupt the original hydrogen bonds between polar R groups thereby disrupting their normal folding.

Option 3: Metal ions (Ag^+) are positively charged cations. They compete with positively charged groups (e.g. $-NH_3^+$) for attraction to negatively charged groups (e.g. $-COO^-$), hence disrupting the original ionic interactions.

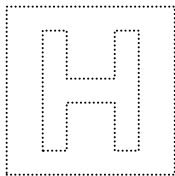
1	C	6	A	11	A	16	D	21	B	26	D	31	D	36	C
2	D	7	A	12	D	17	A	22	C	27	C	32	D	37	A
3	B	8	D	13	D	18	D	23	C	28	D	33	B	38	C
4	D	9	A	14	A	19	D	24	C	29	A	34	D	39	A
5	C	10	D	15	B	20	B	25	C	30	D	35	B	40	A

A = 10

B = 6

C = 9

D = 15



INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9647/02

Paper 2 Structured Questions

18 August 2016

Candidates answer on the Question Paper

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.
A Data Booklet is provided.

You are advised to show all working in calculations.
You are reminded of the need for good English and
clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

The number of marks is given in brackets [] at the end of each
question or part question.

At the end of the examination, fasten all your work
securely together.

For Examiner's Use	
Section A	
1	12
2	17
3	10
4	18
5	15
Significant figures	
Handwriting	
Total	72

This document consists of **17** printed pages and **1** blank page.



Answer ALL questions on the spaces provided.

1 Planning

Using the information below, you are to write a plan for determining number of molecules of water of crystallisation, n , in barium chloride crystals, $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$ where $n = 1, 2$ or 3 . The basis of this investigation is a technique known as *precipitation titration* with the use of silver nitrate solution, $\text{AgNO}_3(\text{aq})$.

AgCl , Ag_2CrO_4 and BaCrO_4 are sparingly soluble salts and relevant information about these salts are given in the table below.

compound	colour	numerical value of K_{sp} at 25°C
AgCl	white	2.0×10^{-10}
Ag_2CrO_4	red	2.0×10^{-12}
BaCrO_4	yellow	1.0×10^{-10}

Some barium chloride crystals, $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$, is dissolved to make up 250.0 cm^3 of standard solution. Approximately 10 cm^3 of 0.2 mol dm^{-3} of reagent **X** solution is added to a portion of this standard solution to precipitate the barium ions *before* a few drops of K_2CrO_4 indicator solution is added. A titration is then carried out on this portion of solution against silver nitrate solution, $\text{AgNO}_3(\text{aq})$. Ag_2CrO_4 would just precipitate only when almost all of the Cl^- ions have been precipitated as AgCl . The titration is repeated until a more reliable average value, $V\text{ cm}^3$, can be determined.

(a) (i) Identify reagent **X**.

..... [1]

(ii) A student suggested that BaCrO_4 is more soluble than Ag_2CrO_4 as BaCrO_4 has larger numerical value of K_{sp} than Ag_2CrO_4 .

Suggest whether this student's claim is valid.

.....

 [1]

(iii) Suggest why reagent **X** is added *before* a few drops of K_2CrO_4 indicator solution is added.

.....

 [1]

(b) You may assume that you are provided with

- 0.10 mol dm^{-3} silver nitrate
- 0.2 mol dm^{-3} of reagent **X** solution
- 10 g of barium chloride crystals, $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$
- Potassium chromate solution, $\text{K}_2\text{CrO}_4(\text{aq})$
- The equipment and materials normally found in a school or college laboratory.

Your plan should include the following

- brief, but specific details of the apparatus you would use, bearing in mind the levels of precision they offer
- details, including quantities, for preparation of 250.0 cm^3 of BaCl_2 solution from barium chloride crystals, $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$
- essential details of the titration procedure
- an outline of how the results obtained, including $V \text{ cm}^3$, would be used to determine n , in barium chloride crystals ($\text{BaCl}_2 \cdot n\text{H}_2\text{O}$)

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[illegible]

..... [8]

- (c) Explain why this titration cannot be conducted under acidic *or* alkaline medium.

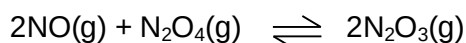
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..... [1]

[Total: 12]

6

- 2 This question is about the oxides of nitrogen and its reactions. Oxides of nitrogen constitute air pollutants originating from emission of car exhaust that cause acid rain and photochemical smog.

The two gases of NO and N₂O₄ slowly react to form the blue compound, N₂O₃ according to the following equation.



- (a) (i) Draw the dot and cross diagrams of the two molecules, NO and N₂O₃.
The N₂O₃ molecule contains a N–N bond.

[2]

- (ii) From your answer in (a)(i), suggest why the forward reaction is likely to occur.

.....
.....
..... [1]

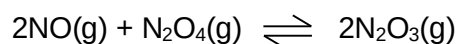
- (b) In an experiment, a mixture containing NO and N₂O₄ was introduced into a 1.48 dm³ evacuated vessel was allowed to reach equilibrium at 280 K. The equilibrium pressure is 98.9 kPa.

Calculate the total number of moles of gases at equilibrium, assuming the gases behave ideally.

[2]

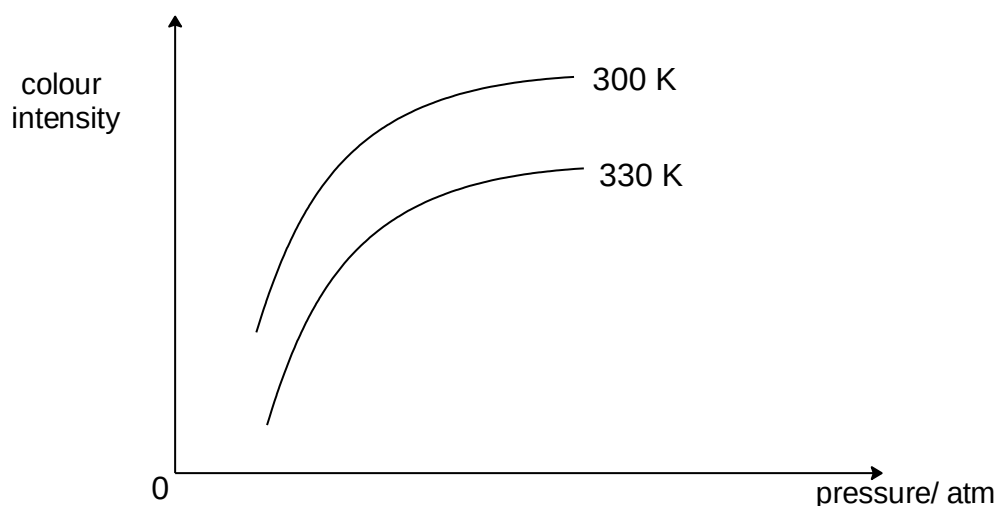
7

- (c) Two colourless gases NO and N₂O₄ slowly react to form the blue compound, N₂O₃ according to the following equation.



Equimolar mixtures of NO and N₂O₄ are mixed at varying pressure P but at two different temperatures of 300 K and 330 K, and the variation in colour intensity was monitored over a period of time.

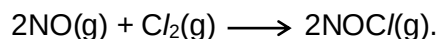
The graphs below show the variation of the colour intensity with pressure at temperatures of 300 K and 330 K.



- (i) What is the significance of the colour intensity in this reaction?
-
- [1]
- (ii) Explain why colour intensity of the reaction mixture increases with increasing pressure.
-
-
- [1]
- (iii) Using information from the graphs, state and explain whether the formation of N₂O₃ from NO and N₂O₄ is an exothermic reaction.
-
-
-
-
- [2]

8

- (d) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:



In an experiment, the amount of $\text{Cl}_2\text{(g)}$ was kept in *large excess* while the initial partial pressure of NO(g) was varied at constant temperature of 500K. The table below shows the experimental results obtained.

time / s	$P_{\text{NO}} / \text{atm}$	(Rate / P_{NO}) / s^{-1}	(Rate / $(P_{\text{NO}})^2$) / $(\text{atm}^{-1} \text{s}^{-1})$
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	1.127×10^{-4}

- (i) Suggest why the amount of $\text{Cl}_2\text{(g)}$ was kept in *large excess*.

.....
 [1]

- (ii) Using the data from the table above, deduce the order of reaction with respect to NO(g) .

.....
 [1]

- (iii) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with $\text{Cl}_2\text{(g)}$ at a constant temperature of 500 K. The partial pressure of $\text{Cl}_2\text{(g)}$ was recorded at time intervals of 30 s. The data obtained are tabulated below.

time / s	partial pressure of $\text{Cl}_2\text{(g)}$ / atm	time / s	partial pressure of $\text{Cl}_2\text{(g)}$ / atm
0	0.78	300	0.49
30	0.76	330	0.46
60	0.72	360	0.44
90	0.70	390	0.42
120	0.66	420	0.39
150	0.63	450	0.38
180	0.59	480	0.36
210	0.57	510	0.34
240	0.54	540	0.33
270	0.52	570	0.32

9

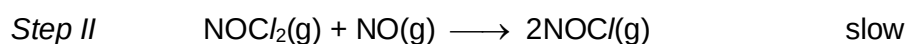
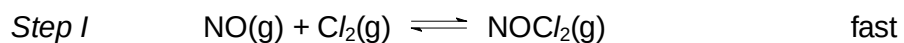
Using the data but without the plotting of any graph, deduce the order of reaction with respect to $\text{Cl}_2(\text{g})$.

.....
.....
..... [1]

- (iv) Write the rate equation for this reaction.
Hence, calculate the rate constant, including its units

[3]

- (v) One possible mechanism of the reaction is given below.



Explain whether it is consistent with the observed kinetics data in (d)(iv).

.....
.....
.....
.....
..... [2]

[Total: 17]

- 3** Organic compounds can undergo combustion. Chemical companies produce containers filled with butane for use by campers.

The enthalpy change of combustion of butane is $-3000 \text{ kJ mol}^{-1}$.

- (a) (i)** Define the term *standard enthalpy of combustion of butane*.

.....
..... [1]

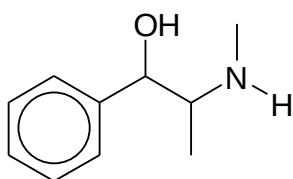
- (ii)** Calculate the mass of water at 25°C that could be brought to the boiling point by the combustion of 1.2 dm^3 of butane gas. Assume 75 % of the heat from the butane is absorbed by the water.

[2]

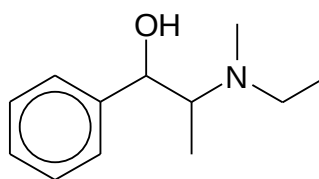
- (b)** Explain in terms of structure and bonding, why butanone has a higher boiling point than pentane.

.....
.....
.....
.....
.....
..... [2]

- (c) Organic compounds are also widely used for pharmaceutical purposes such as ephedrine which is an anti-asthmatic and stimulant. Ephedrine can be converted into ethylephedrine via a S_N2 reaction.



Ephedrine



Ethylephedrine

- (i) Suggest the reagent that can be used to perform this conversion.
[1]
- (ii) Explain why an S_N2 mechanism is favoured for this reaction.

[1]
- (d) Complete hydrolysis of proteins produces individual units of amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments. Partial hydrolysis of a tetrapeptide (containing four amino acid residues) produces the following three dipeptides, as well as the individual amino acids.



- (i) Define the *primary structure* of a protein.

 [1]
- (ii) Deduce the order in which the amino acids are bonded together in the tetrapeptide.

 [1]
- (iii) Suggest suitable reagents and conditions to hydrolyse the tetrapeptide into its individual amino acids.

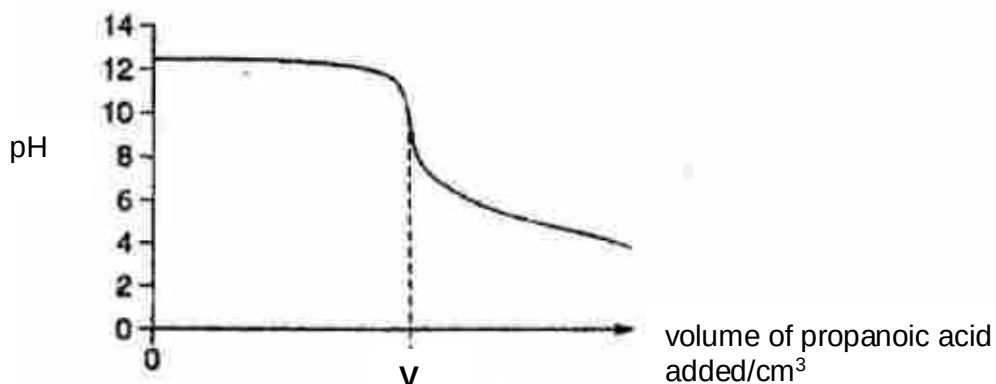
 [1]

[Total: 10]

- 4 (a) A $0.031 \text{ mol dm}^{-3}$ solution of a base, MOH, has a pH of 12.5. (M is a metal.)

25 cm^3 of the solution of MOH was titrated with $0.025 \text{ mol dm}^{-3}$ propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, at 25°C . The pH of the solution was followed using a pH meter and the following titration curve was obtained.

pK_a of propanoic acid = $1.29 \times 10^{-5} \text{ mol dm}^{-3}$



- (i) Calculate the concentration of hydroxide ions present in the sample of MOH and use it to explain whether it is a strong or weak base.

.....

[1]

- (ii) Calculate the value of V .

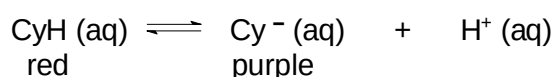
[1]

- (iii) Explain, with the aid of an equation, why the pH when $V \text{ cm}^3$ of propanoic acid was added, is greater than 7.

.....

 [2]

- (b) The colour of blackberries is due to a compound known as cyanidin. Cyanidin is a weak organic acid which may be represented by CyH . In aqueous solution, CyH dissociates slightly:



The colours of CyH and Cy^- are indicated in the above equation.
 Acid dissociation constant, K_a , of CyH is $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ at 25°C .

A glass of blackberry juice has a pH of 3.00 at 25°C . Calculate the ratio of the red to purple form in the juice, and hence predict its colour.

[3]

- (c) When chlorine is bubbled through cold sodium hydroxide solution and acidified silver nitrate solution, only half of the chlorine that has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five-sixth of the chlorine can be precipitated. Explain the observations, giving balanced equations where appropriate.

.....

..... [3]

- (d) The table below gives data about some physical properties of the elements calcium, nickel and copper.

	calcium	nickel	copper
atomic radius / nm	0.197	0.124	0.128
electronic configuration	[Ar]4s ²	[Ar]3d ⁸ 4s ²	[Ar]3d ¹⁰ 4s ¹

- (i) What do you understand by the term *transition element*?

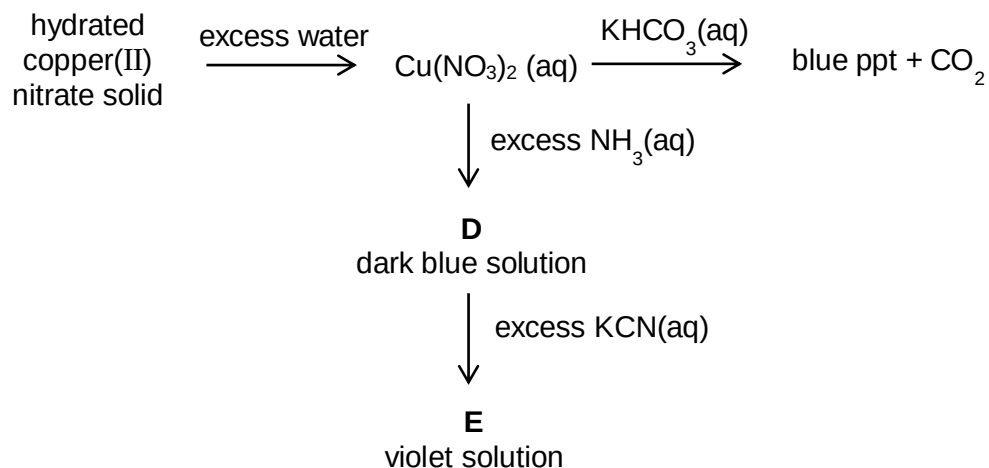
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- (ii) Although the nickel and copper atoms have more electrons than the calcium atom, the atomic radii of nickel and copper are smaller than that of calcium.

Suggest an explanation for this.

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..... [3]

- (e) The following are some reactions involving copper(II) nitrate.



- (i) Explain why carbon dioxide is evolved when $\text{KHCO}_3(\text{aq})$ is added to aqueous copper(II) nitrate. Include any relevant equations with state symbols in your answer.

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.....[2]

- (ii) Suggest a formula for the complex ion present in **D**.

..... [1]

- (iii) The metal ion in complex **E** is known to have a coordination number of four. Suggest a formula for complex ion **E**.

..... [1]

[Total: 18]

- 5 Benzene reacts with propanoyl chloride and 1-phenylpropan-1-one is formed in the reaction.

- (a) State the reagents and conditions needed to convert 1-phenylpropan-1-one into compound **Q**. Show the structure of the intermediate in the box provided.



Reagents and conditions

Step 1

Step 2

[3]

- (b) Describe the mechanism in Step 1 in part (a). In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

- (c) The 2,4-D weed killer, $C_8H_6Cl_2O_2$, is widely used on cereal crops, pastures and orchards. Compound **R** is an isomer of the weed killer under development to improve its properties. It is an aromatic compound which contains **three** functional groups.

The following tests are carried out in the order given. In **each** case, state **all** deductions about the compound **R** you can make at **that** stage. When identifying the functional groups, your answers should be unambiguous.

- (i) When Compound **R** is treated with Na, $C_8H_5Cl_2O_2Na$ is formed.

deduction(s).....

.....[1]

- (ii) When Fehling's solution is added to Compound **R**, red brick precipitate is obtained.

deduction(s).....

.....[1]

- (iii) When 1 mole of Compound **R** is boiled with ethanolic silver nitrate, 287 g of white precipitate is formed.

deduction(s).....

.....

.....

.....[2]

- (iv) When Compound **R** is treated with concentrated nitric acid, $C_8H_3Cl_2N_3O_8$ is formed.

1. What type of reaction takes place?

.....

2. Name the functional group present in Compound **R** that is confirmed by this reaction.

.....

[2]

- (v) You now have enough information to determine the structural formula of **R**.

1. Draw the fully displayed structure of **R**.

2. Explain clearly why you have placed each of the aromatic substituent groups in their particular positions.

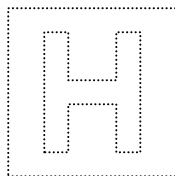
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in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

26 August 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Begin each question on a fresh sheet of paper.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [] at the end of each question or part question.

This document consists of **12** printed pages.

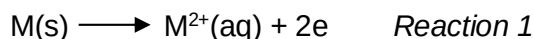


Answer any **four** questions.

- 1 Data concerning the elements of group II of the Periodic Table, at 298K, are given in the table. Further data may be found in the *Data Booklet*. M refers to elements of group II.

	1 st and 2 nd IE of M / kJ mol ⁻¹	$\Delta H_{\text{atom of M}}$ / kJ mol ⁻¹	$\Delta H_{\text{hydration of M}^{2+}}$ / kJ mol ⁻¹	E° / V
Ca	1740	178	-1650	-2.87
Sr	1608	164	-1480	-2.89

- (a) The electrode reduction potential E° of Group II elements gives an indication of the ease with which the following reaction occurs:



The *enthalpy change of reaction 1* can be related to the following factors:

- *first and second ionisation energy* of the element
- *enthalpy change of atomisation* and
- *enthalpy change of hydration* of its gaseous ion.

- (i) Construct an energy cycle relating the factors above, and use the values given above to calculate the enthalpy change of *Reaction 1* for calcium. [3]
- (ii) By quoting appropriate data from *Data Booklet*, explain the difference in enthalpy change of hydration of calcium and strontium ions. [2]

- (b) Calcium oxide is the key ingredient for the process of making cement.

When calcium is burned in oxygen, calcium oxide is produced.

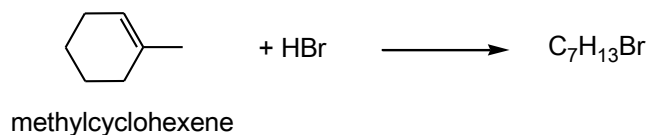
When 1.50 g calcium is burned in air, a mixture of ionic solids calcium oxide and red brown solid is formed.

The red brown solid has the following composition by mass: Ca, 81.1%; N, 18.9%.

Adding water to the red brown solid produces calcium hydroxide and 19.2 cm³ of ammonia gas at room temperature and pressure.

- (i) Calculate the formula of the red brown solid. [1]
- (ii) Write an equation for the reaction between red brown solid with water. [1]
- (iii) Write equations for the reactions of calcium with air and use them to calculate the mass of CaO formed when 1.5 g of calcium is burnt in air. [3]
- (c) Calcium oxide is normally made by heating calcium carbonate to a temperature above 825°C. A gas which turns lime water chalky is produced in the process.
- (i) Write an equation for the decomposition of CaCO₃. [1]
- (ii) Explain why barium carbonate decomposes at a higher temperature than calcium carbonate. [2]

(d) Methylcyclohexene reacts with hydrogen bromide to form alkyl bromides.

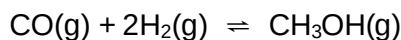


- (i) The above reaction could produce two isomers with molecular formula $C_7H_{13}Br$. However, when the reaction is carried out, mainly one product is formed. Give the structural formula of the major product, explaining your answer. [2]
- (ii) Describe the mechanism of the reaction between hydrogen bromide and methylcyclohexene, $C_6H_9CH_3$, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]
- (iii) Unsymmetrical dihalides reacts with alkene in a similar way as hydrogen halides. Predict the structure of the product when IBr reacts with methylcyclohexene, and explain your answer by considering the polarity within the molecule IBr . [2]

[Total: 20]

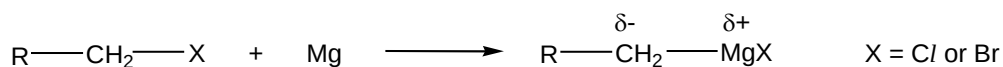
- 2 Alcohols and carboxylic acids have many scientific, medical and industrial uses worldwide.

(a) Methanol is made from the following gaseous reaction.

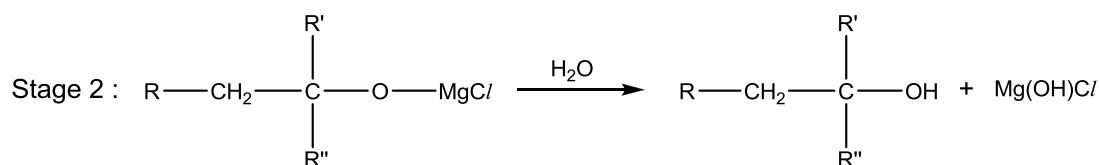
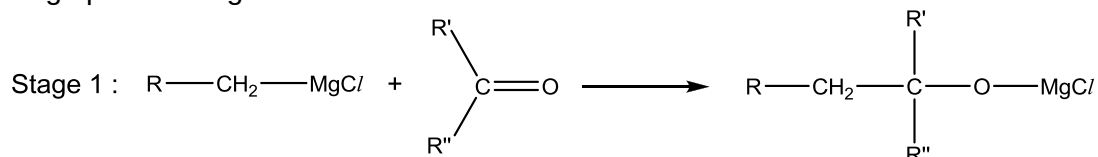


A 1:2 mixture of CO and H₂ was pumped into a sealed reactor at 6 atm and then heated to 227 °C and maintained at this temperature for some time. When equilibrium was reached, the partial pressure of CH₃OH was found to be 1.6 atm.

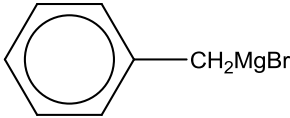
- (i) Write an expression for K_p for the reaction. Hence, determine the value of K_p stating its units. [3]
- (ii) Suggest the effect on the position of equilibrium and value of K_p when methanol is removed from the reaction vessel. Explain your answer. [2]
- (b) Grignard reagent, RMgX, is an important reagent in organic synthesis. Grignard reagents are prepared by the addition of activated magnesium on an alkyl halide or aryl halide in non-polar solvents such as ether in anhydrous conditions.



An example of a Grignard reagent reacting with a ketone to form an alcohol via a two stage process is given below:



R' and R'' could be alkyl / aryl group / H atoms

- (i) Suggest the type of reaction occurred between the Grignard reagent and the carbonyl compound in Stage 1 and 2. [2]
- (ii) Suggest the structural formula of the final organic product formed when  is reacted with propanone, CH₃COCH₃, in a similar two-step process. [1]

- (iii) Deduce the structures of a suitable Grignard reagent, RMgBr, and a suitable carbonyl compound, R'R''CO, to synthesize the following alcohol, (CH₃)₂CHCH₂CH(OH)CH₂CH₂CH₃. [2]

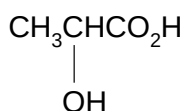
- (iv) The Grignard reagent $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula of the organic product formed. [1]

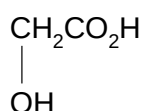
- (v) The product formed by using Grignard reagent in (b) (iii) does not rotate the plane polarised light. Explain your reasoning. [2]

- (c) Describe and explain the relative acidities of phenol, benzoic acid and phenylmethanol. [3]

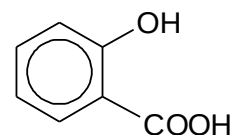
- (d) Lactic acid, glycolic acid and salicylic acid are three organic acids commonly used in chemical peel.



lactic acid



glycolic acid



salicylic acid

Suggest a simple chemical test that can be used to distinguish each of the following pairs. State what you would observe for each chemical test.

- lactic acid from glycolic acid, and
- glycolic acid from salicylic acid.

[4]

[Total: 20]

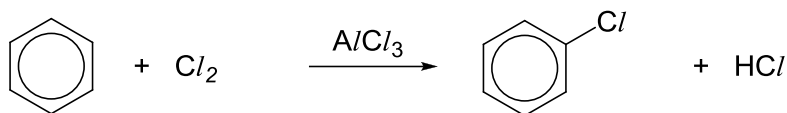
- 3 Aluminium, is the third most abundant element (after oxygen and silicon) found in the Earth's crust. Aluminium reacts readily with carbon to form aluminium carbide, Al_4C_3 .

(a) Aluminium carbide can react with protic reagents such as hydrochloric acid to produce methane gas and aluminium(III) chloride.

(i) Write a balanced equation for the reaction between aluminium carbide and hydrochloric acid. [1]

(ii) Using the equation in (a)(i), calculate the maximum volume of methane gas that can be produced when 12.0 g of aluminium carbide reacts with 250 cm^3 of 2.0 $mol\ dm^{-3}$ hydrochloric acid at standard temperature and pressure. [3]

(b) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.



The reaction occurs in several steps.

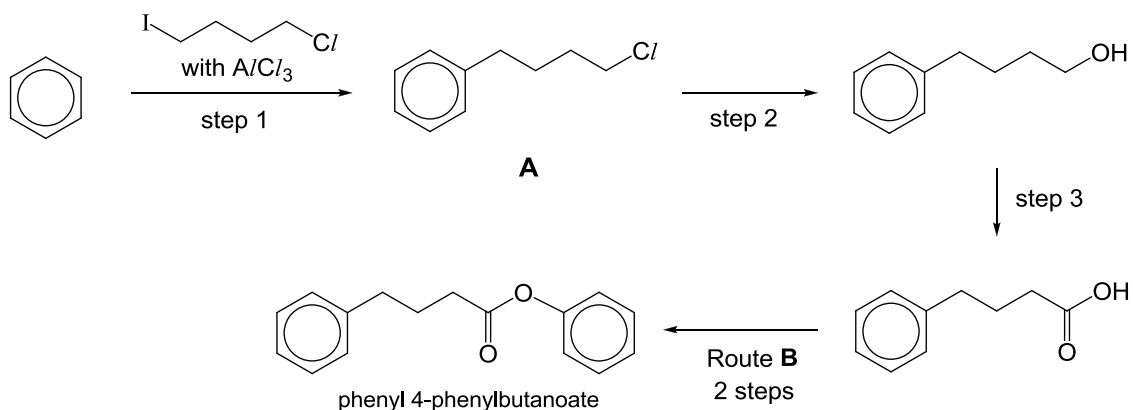
- The first step is the reaction between Cl_2 and AlCl_3 .



- The benzene ring is then attacked by the Cl^+ cation in the second step.

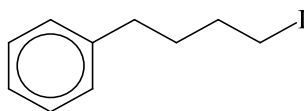
AlCl_3 reacts in a similar way with halogenoalkanes and acyl chlorides, producing a carbocation that can then attack a benzene ring.

Using the reactions described above as parts of a synthesis route, a student suggested the following route to form phenyl 4-phenylbutanoate, from benzene.



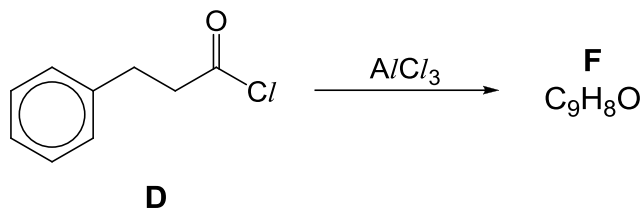
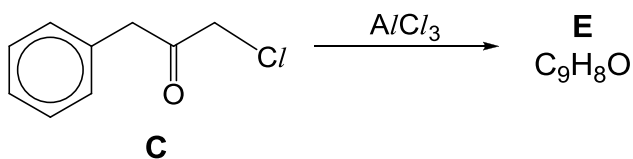
- (i) Explain why step 1 has to be carried out in an anhydrous condition. [1]
- (ii) Draw the carbocation formed in step 1. [1]

- (iii) A student suggested that **A** could have the following structure:



By quoting appropriate data in the *Data Booklet*, explain why the structure suggested by the student is less likely to be formed. [2]

- (iv) Give appropriate reagents and conditions necessary for steps 2 and 3. [2]
- (v) Suggest the reagents and conditions for each of the two steps in route **B**. [2]
- (vi) Predict the structure of the product of each of the following reactions. Both compounds **E** and **F** react with 2,4-dinitrophenylhydrazine. [2]



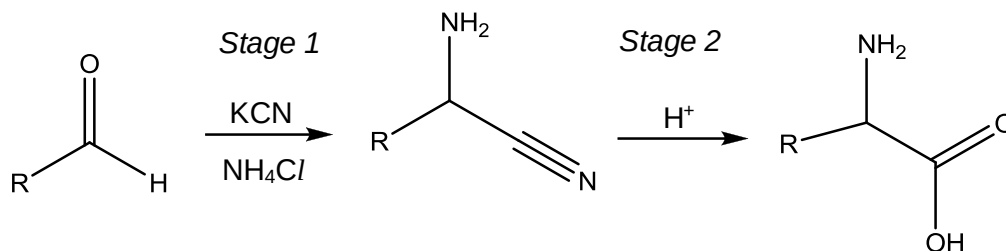
- (vii) Describe and explain the relative ease of hydrolysis of the two compounds **C** and **D**. chloro- [2]
- (c) By considering the structure and bonding, explain why
- (i) the boiling point of aluminium fluoride is higher than that of aluminium chloride. [2]

- (ii) salicylic acid, is less soluble in water than benzoic acid, .

[2]

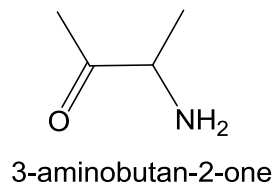
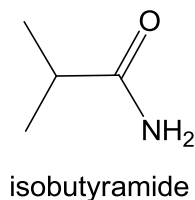
[Total: 20]

- 4 The *Strecker synthesis* is a term used for a series of chemical reactions that synthesize an amino acid from an aldehyde or ketone. This reaction requires acid and HCN is supplied from cyanide salts.

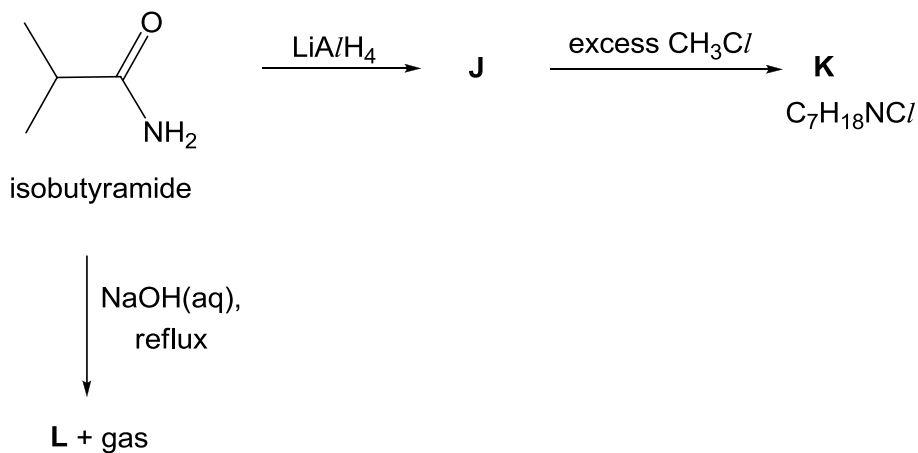


One example of the Strecker synthesis is a multikilogram scale synthesis of amino acids.

- (a) Name the type of reaction occurring in *Stage 2* and state the reagent and conditions used in this reaction. [2]
- (b) In *Stage 1*, ammonia formed from the reaction between KCN and NH_4Cl reacts with the aldehyde.
Suggest an equation for the formation of ammonia from the reaction between KCN and NH_4Cl and describe the role of KCN in stage 1. [2]
- (c) Explain why isobutyramide is less basic than 3-aminobutan-2-one. [2]



- (d) Predict the outcomes of the following reactions starting from isobutyramide, drawing the structures of the intermediate **J** and the products **K** and **L**. [3]

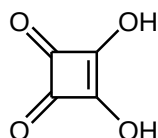


- (e) Compound **P**, $C_9H_{12}O_2$, shows optical activity and does not react with aqueous potassium carbonate. However, it is soluble in aqueous potassium hydroxide. When **P** reacts with hot acidified potassium dichromate(VI), the solution turns from orange to green. **P** also decolourises aqueous bromine to form a white precipitate, **Q**, $C_9H_{10}O_2Br_2$.

Upon heating with concentrated sulfuric acid, **P** gives only compound **R**, $C_9H_{10}O$, which displays geometric isomerism. **R** gives compound **S** and ethanoic acid on reacting with hot acidified potassium manganate(VII) solution.

Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [7]

- (f) The structure of squaric acid is shown below.

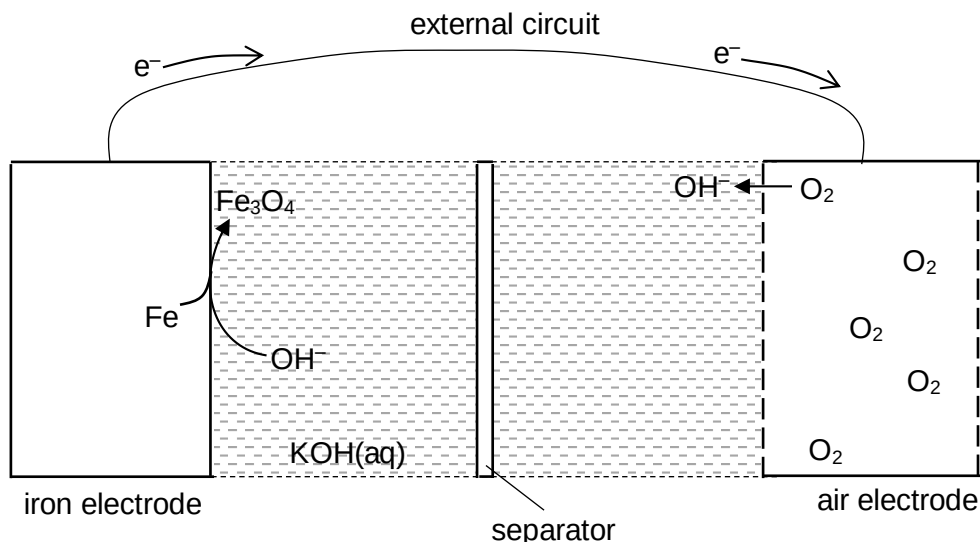


- (i) State the functional groups in squaric acid. [2]
- (ii) Squaric acid is a stable molecule although it has high angle strain associated with a four-membered ring. It is a strong diprotic acid with pK_a values 1.5 and 3.4 respectively. Explain the high acidity of squaric acid. [2]

[Total: 20]

- 5 Iron is, by mass, the most common element on Earth, forming much of Earth's outer and inner core. Iron and its compounds have been used as catalysts in many reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$, to form I_2 and SO_4^{2-} ions.
- (a) (i) Write an equation to represent the **third ionisation energy** of Fe. [1]
- (ii) Write the electronic configuration for Fe^{2+} . Hence, suggest why the third ionisation energy of $_{26}\text{Fe}$ is lower than that of $_{25}\text{Mn}$. [2]
- (iii) State the type of catalysis for the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ that is catalysed by aqueous iron(II) chloride. [1]
- (iv) The reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ can also be catalysed by aqueous cobalt(II) chloride. Using relevant $E^\ominus$ values from the *Data Booklet*, explain why cobalt(II) chloride can be a catalyst for this reaction. [2]
- (b) A green solution of aqueous iron(II) chloride is reacted with acidified potassium manganate(VII). The resultant solution **D** is treated with aqueous sodium carbonate to form a reddish brown precipitate **E**, together with a colourless gas which forms white precipitate in aqueous calcium hydroxide. When aqueous NH_4SCN is added to **D**, a blood red solution is formed.
- (i) Explain why aqueous iron(II) chloride is coloured. [2]
- (ii) Identify precipitate **E**. [1]
- (iii) Suggest the type of reaction that has occurred for the formation of the blood red solution. [1]

- (c) Iron is also used in making iron-air battery which is a low-cost and environmental friendly rechargeable energy source. An iron-air battery comprises of iron electrode, porous carbon-containing air electrode. The electrolyte used is aqueous potassium hydroxide.

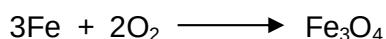


At the iron electrode, iron is oxidised to magnetite, Fe_3O_4 , during discharging, according to the following reaction:



At the air electrode, oxygen is reduced to form hydroxide ions.

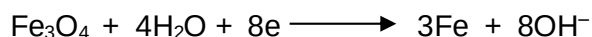
- (i) Write the half-equation for the reaction that occurred at the air electrode during discharging. [1]
- (ii) During discharging, the cell acts as a power source and the overall reaction occurred is as follows:



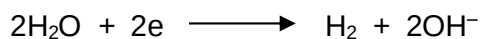
Suggest, with explanation, for the sign of the $\Delta G^\ominus$ for this reaction. [1]

- (iii) The battery is capable of producing an e.m.f. of 1.28V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the $\text{Fe}_3\text{O}_4|\text{Fe}$ electrode reaction. [1]

During charging, at the iron electrode, magnetite and water undergo the following reaction:



At the same electrode, a competing side-reaction occurs where water reacts to form hydrogen gas according to the following reaction:



After a 1-hour charging, the volume of H_2 gas evolved, measured at r.t.p., is 0.652 dm^3 .

(iv) Calculate the amount of electrons that was required to produce H_2 gas. [1]

(v) A current of 9.5 A is supplied to the battery during the 1-hour charging.

Use this information and your answer in (c)(iv) to calculate the amount of iron produced during the charging. [2]

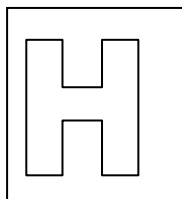
(d) The separator used in the iron-air battery is an organic polymeric membrane, made from compound **X**.

Compound **X** has a molecular formula $\text{C}_3\text{H}_3\text{N}$. On heating with dilute sulfuric acid, **X** forms compound **Y**, $\text{C}_3\text{H}_4\text{O}_2$. Both **X** and **Y** decolourise aqueous bromine, however, only **Y** reacts with sodium carbonate to form gas which forms white precipitate in $\text{Ca}(\text{OH})_2(\text{aq})$.

Suggest structures for compounds **X** and **Y**, giving reasons for your answers. [4]

[Total: 20]

Candidate Name: _____



2016 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY

9647/01

Paper 1 Multiple Choice

21st Sept 2016**1 hour**

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

There are **forty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet provided.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this question paper.

The use of an approved scientific calculator is expected, where appropriate.

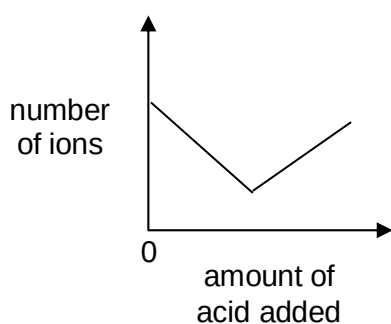
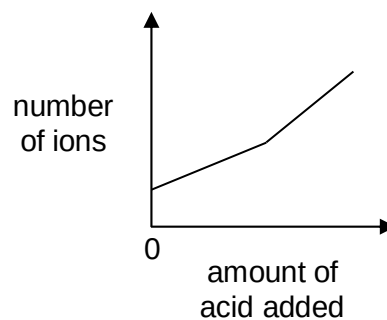
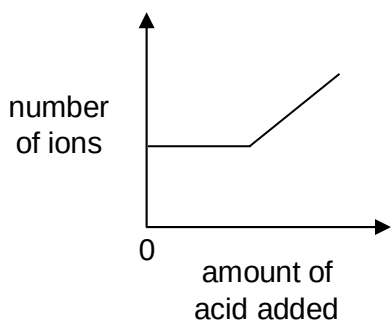
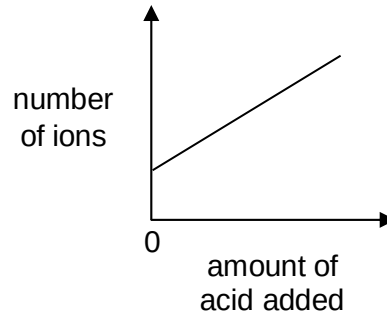
FOR EXAMINER'S USE	
TOTAL (40 marks)	

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1** Gaseous hydrochloric acid was bubbled through a solution of sodium carbonate until the solution turned blue litmus paper red.

How will the total number of ions present in solution in the reaction mixture vary?

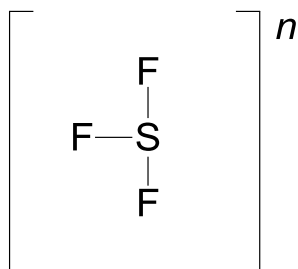
A**B****C****D**

- 2** In winter, ice forms only on the surface of lakes and rivers, allowing aquatic life to survive below the surface.

Which of the following statements about ice does **not** explain this phenomenon?

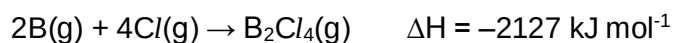
- A** Ice has an open structure.
- B** The water molecules in ice are in an orderly tetrahedral arrangement.
- C** Water molecules can form intermolecular hydrogen bonding in ice.
- D** Water molecules have a much lower energy in ice than in water.

- 3 An ion SF_3^n is T-shaped as shown below.



What is the value of n ?

- A** -2 **B** -1 **C** +1 **D** +2
- 4 What is the new pressure of a sample of gas, initially at 1 atm, when it is heated from 25 °C to 75 °C at constant volume?
- A** 0.3 atm **B** 0.9 atm **C** 1.2 atm **D** 3.0 atm
- 5 Diboron tetrachloride, B_2Cl_4 , is a colourless liquid at room temperature. The combination of gaseous atoms of boron and chlorine to form $\text{B}_2\text{Cl}_4(\text{g})$ is represented by the equation below.



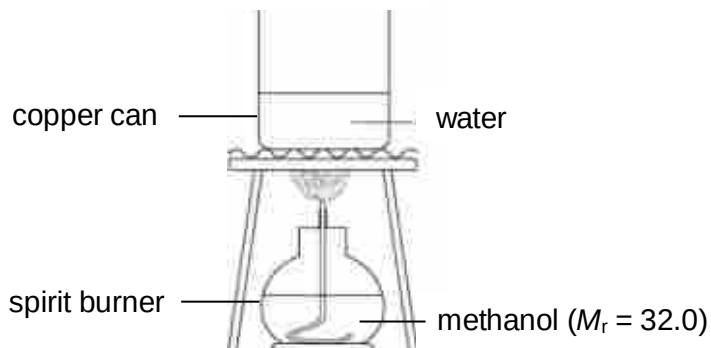
The bond energy of a B–B bond is +303 kJ mol⁻¹.

What is the bond dissociation energy of a B–Cl bond?

- A** -608 kJ mol⁻¹ **B** -456 kJ mol⁻¹ **C** +456 kJ mol⁻¹ **D** +608 kJ mol⁻¹

- 6 Use of the Data Booklet is relevant to this question.

A student carried out an experiment to determine the heat capacity of a copper can using the setup below.



The following data was recorded by the student:

Initial temperature of water / °C	25 °C
Final temperature of water / °C	42 °C
Mass of spirit burner before burning / g	220.00 g
Mass of spirit burner after burning / g	219.50 g
Volume of water / cm ³	150 cm ³

Given that the enthalpy change of combustion of methanol is -715 kJ mol^{-1} , determine the heat capacity of the copper can.

- A** 30.2 J K⁻¹ **B** 43.8 J K⁻¹ **C** 626 J K⁻¹ **D** 655 J K⁻¹

- 7 The following reaction is thermodynamically feasible **only** at a high temperature.



What are the signs of ΔH and ΔS for the reaction?

	ΔH	ΔS
A	–	–
B	+	–
C	–	+
D	+	+

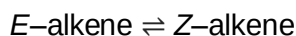
- 8 The mechanism involved in the formation of compound **Z** is as follows:

Step I: $\text{W} + \text{X} \rightleftharpoons \text{Y}$ (fast)

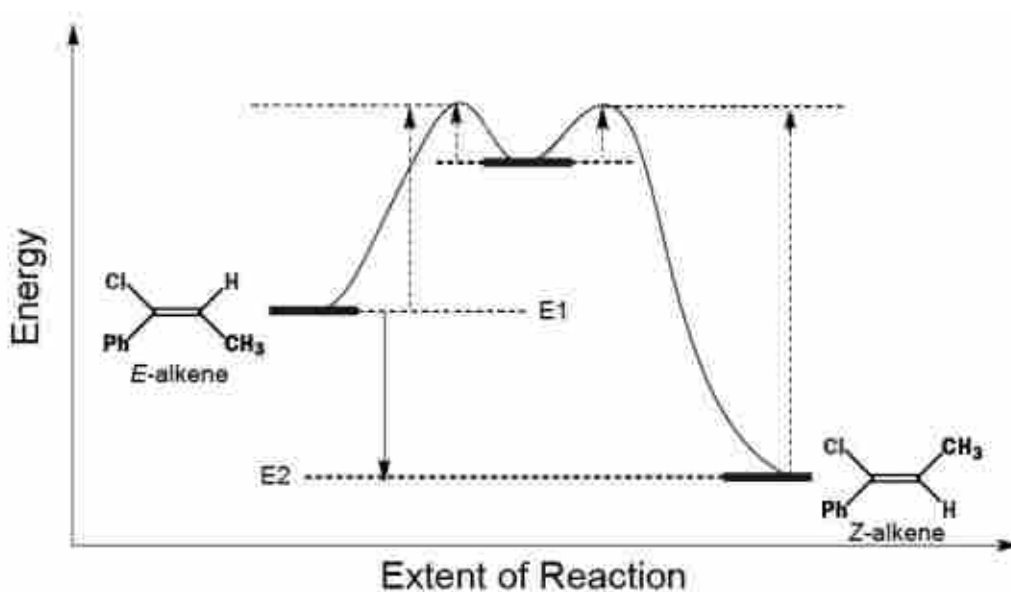
Step II: $\text{W} + \text{Y} \rightarrow \text{Z}$ (slow)

What is the rate equation for this reaction?

- A Rate = $k[\text{W}][\text{X}]$
 B Rate = $k[\text{W}][\text{Y}]$
 C Rate = $k[\text{W}][\text{Y}]^2$
 D Rate = $k[\text{W}]^2[\text{X}]$
- 9 Alkenes in an acidic medium can isomerise in the presence of Al_2O_3 catalyst.



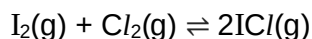
The energy profile diagram of the reaction is shown below.



Which of the following statements is correct?

- A (E1 – E2) corresponds to the enthalpy change of the forward reaction.
 B Leaving pure *E*-alkene to isomerise for a long duration yields mainly *Z*-alkene.
 C The isomerisation produces more *Z*-alkene at high temperatures and produces more *E*-alkene at low temperatures.
 D There are 2 intermediates in the isomerisation process.

- 10** At 313 K, iodine monochloride exists in equilibrium with iodine and chlorine.



When a mixture of iodine and chlorine in the mole ratio of 1:1 is heated at 313 K and a constant pressure of 1 atm, the mole fraction of iodine monochloride present at equilibrium is 0.23.

What is the equilibrium constant, K_p ?

- A** 0.299 **B** 0.357 **C** 0.597 **D** 1.55
- 11** The concentration of Sr^{2+} ions in a 0.5 dm^3 solution is $2.0 \times 10^{-2} \text{ mol dm}^{-3}$. Na_2CO_3 solid was added to the solution in excess until the concentration of CO_3^{2-} ions remained at $2.5 \times 10^{-6} \text{ mol dm}^{-3}$.

Given that the K_{sp} of SrCO_3 is 1.6×10^{-9} , what mass of SrCO_3 was precipitated?

- A** 0.0472 g
B 0.0944 g
C 1.43 g
D 2.86 g
- 12** Halogens T_2 , U_2 and V_2 were added to separate aqueous solutions containing T^- , U^- and V^- ions and observations recorded in the table below.

	$\text{T}^-(\text{aq})$	$\text{U}^-(\text{aq})$	$\text{V}^-(\text{aq})$
T_2	no reaction	U_2 formed	V_2 formed
U_2	no reaction	no reaction	no reaction
V_2	no reaction	U_2 formed	no reaction

In which sequence is reducing power of the halides arranged in increasing order?

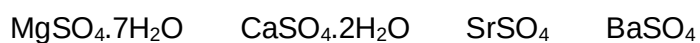
- A** $\text{T}^- < \text{V}^- < \text{U}^-$
B $\text{U}^- < \text{T}^- < \text{V}^-$
C $\text{U}^- < \text{V}^- < \text{T}^-$
D $\text{V}^- < \text{U}^- < \text{T}^-$

- 13** It is known that lithium and magnesium have similar chemical properties.

Which property of the following lithium compounds is likely to be wrong?

- A** Li_2CO_3 undergoes thermal decomposition to produce carbon dioxide as the only gas.
- B** LiNO_3 produces oxygen as the only gas upon heating.
- C** Li_2O dissolves in water to form a solution of pH greater than 7.
- D** LiSO_4 is soluble in water.

- 14** The following Group II elements form sulfates with the following crystalline forms:



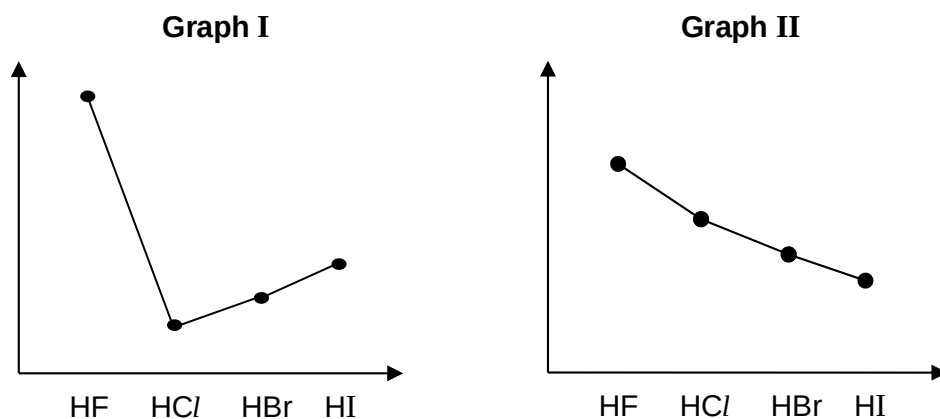
Which of the following explains the observed trend in number of moles of water of crystallisation?

- A** Atomic radius of the elements increases down the group.
- B** Ionic character of sulfates increases down the group.
- C** Ionisation energy of the elements decreases down the group.
- D** Radius of the cations increases down the group.

- 15** What are the products formed when chlorine gas is bubbled into cold aqueous sodium hydroxide?

- A** NaCl and NaClO
- B** NaCl and NaClO_3
- C** NaClO only
- D** NaClO_3 only

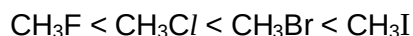
- 16 The graphs below show the variation of two properties of the halogen hydrides.



Which properties are illustrated in **Graphs I** and **II**?

	Graph I	Graph II
A	Boiling point	Thermal stability
B	pH of solution	Thermal stability
C	Thermal stability	Melting point
D	Thermal stability	pH of solution

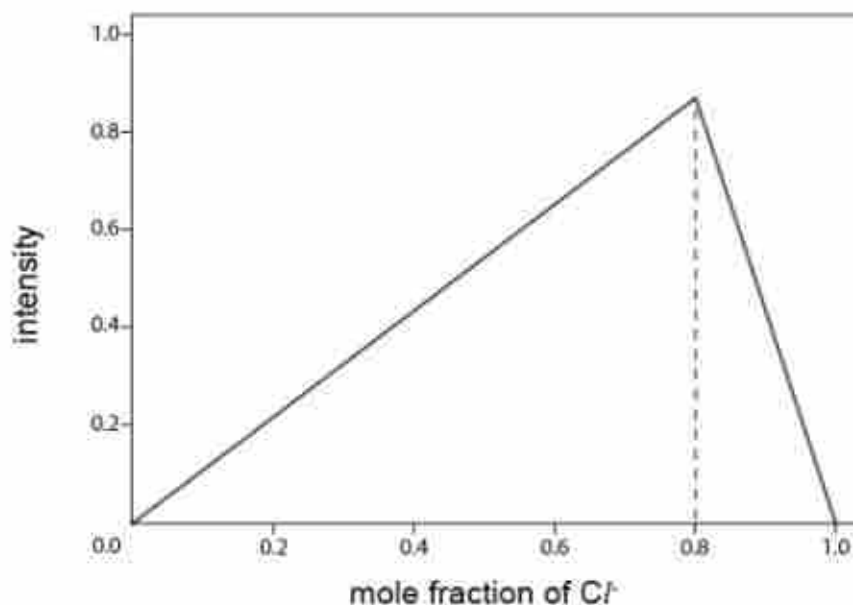
- 17 When halogenomethanes are warmed in aqueous NaOH followed by acidified AgNO₃, the rate of formation of precipitate is observed to be in the order:



Which of the following best explains this observation?

- A** Anionic radius increases from F to I.
- B** Bond energy decreases from C–F to C–I.
- C** Bond polarity decreases from C–F to C–I.
- D** Charge density decreases from F[–] to I[–].

- 18** The Co^{2+} ion forms a blue complex with Cl^- ions. Various samples containing different amounts of Co^{2+} and Cl^- were prepared, and their colour intensities measured using a colorimeter. The following graph was obtained.



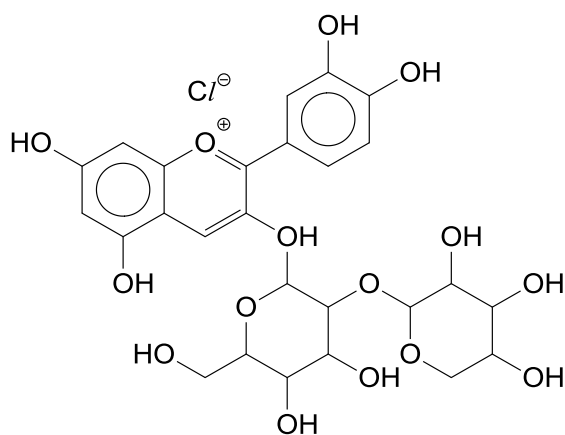
Which statement about the complex ion formed is correct?

- A** The complex ion absorbs blue light.
 - B** The co-ordination number of the Co^{2+} ion is 4.
 - C** The geometry of the complex ion is octahedral about Co^{2+} .
 - D** The overall charge of the complex ion is 2+.
- 19** A compound with the molecular formula C_5H_{10} reacts with hot acidified KMnO_4 to form products that give a white precipitate with limewater and a yellow precipitate with aqueous alkaline iodine.

What is the identity of the compound?

- A** $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
- B** $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$
- C** $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$
- D** $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$

- 20 The deep purple colour of elderberries originates from cyanidin 3-sambubioside.

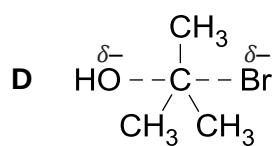
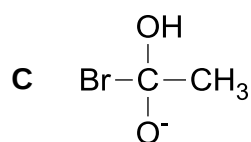
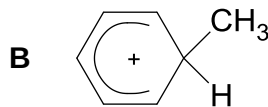
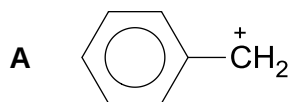


cyanidin 3-sambubioside

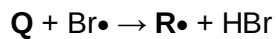
How many optical isomers does cyanidin 3-sambubioside have?

- A 2^6 B 2^8 C 2^9 D 2^{11}

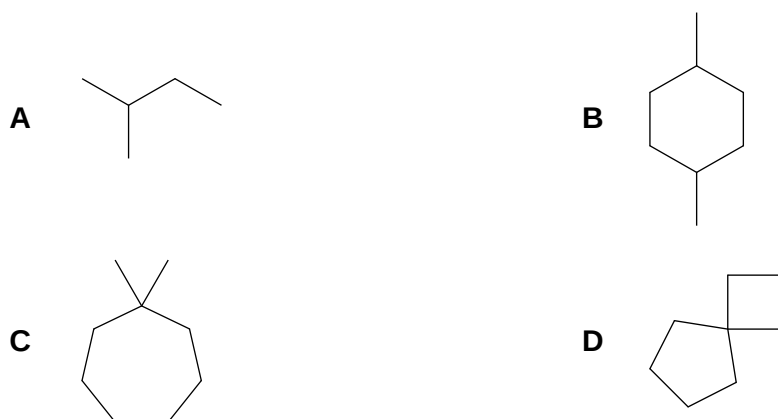
- 21 Which species could be an intermediate in an S_N1 substitution?



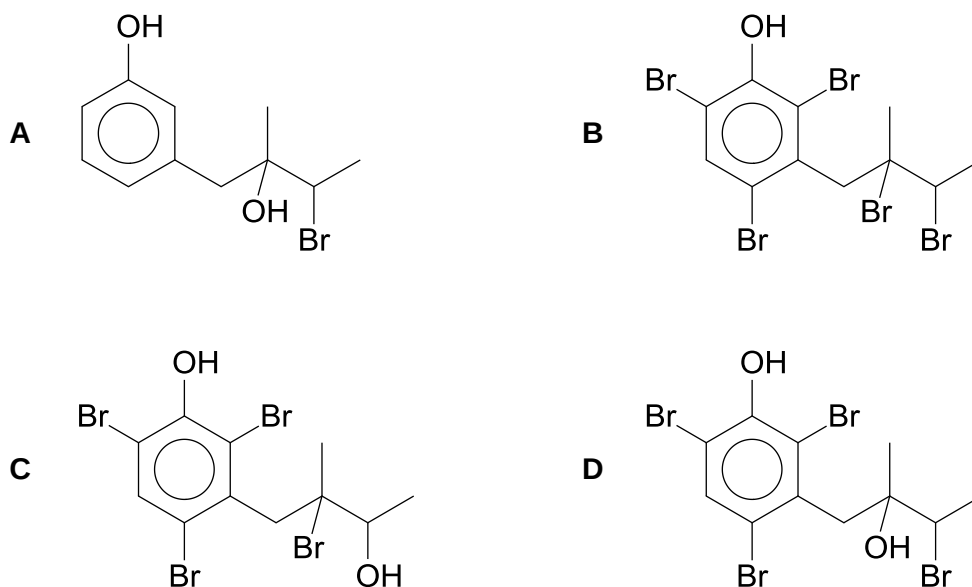
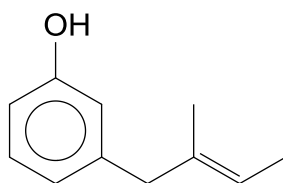
- 22 When heated with bromine, hydrocarbon **Q** undergoes free radical substitution. In the propagation step, free radical **R•** is formed.



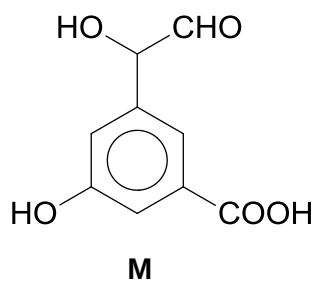
If there are exactly three possible structures of **R•**, which of the following is a possible structure of **Q**?



- 23 What is the major organic product formed when excess aqueous bromine is added to the following compound?



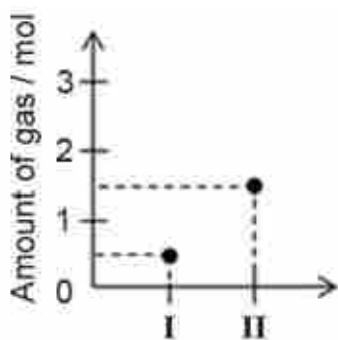
- 24 Which graph shows the amounts of gases evolved when 1 mol of compound **M** is subjected to reagents **I** and **II** separately?



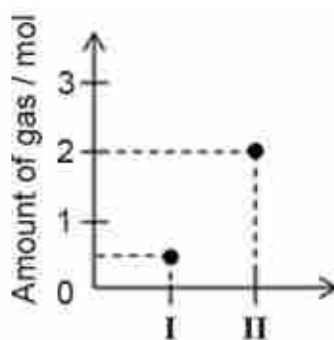
I: $\text{Na}_2\text{CO}_3(\text{s})$ in excess

II: $\text{Na}(\text{s})$ in excess

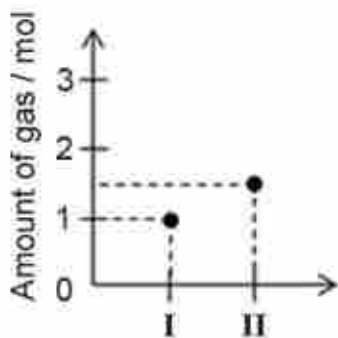
A



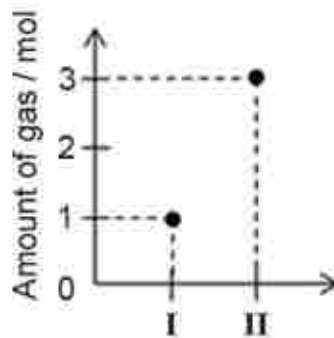
B



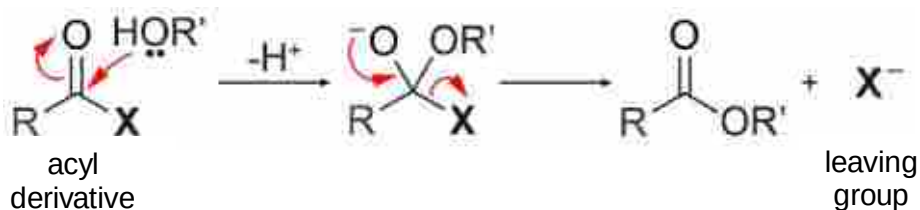
C



D



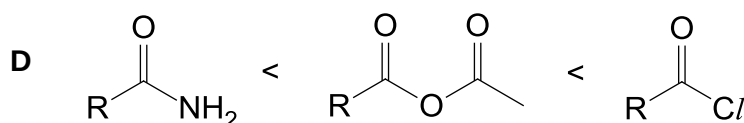
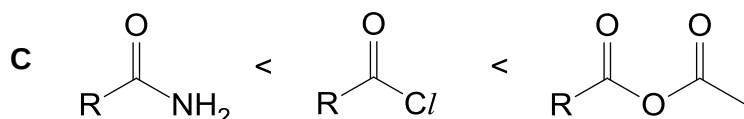
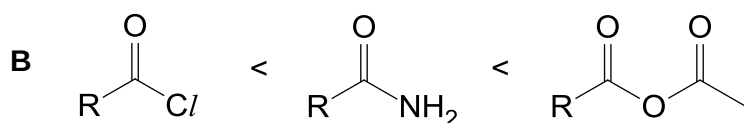
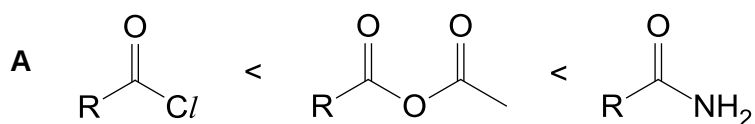
- 25 The mechanism of esterification with acyl derivatives in base is as follows, where R'OH is the alcohol and X⁻ is the leaving group.



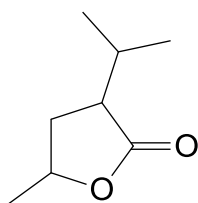
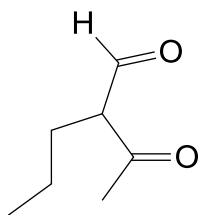
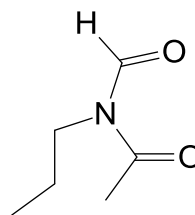
The rate of esterification is known to increase with better leaving group ability, which is related to basicity. The less basic the leaving group, the better its ability to leave.

Which of the following is the reactivity of acyl derivatives arranged in increasing order?

Acyl derivative



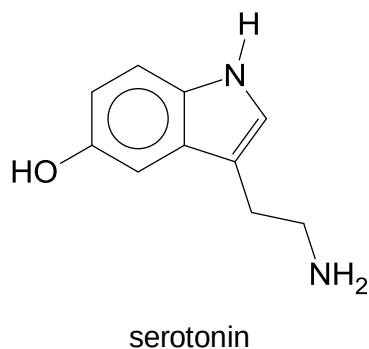
26 Compounds **K**, **L** and **M** have the following structures.

**K****L****M**

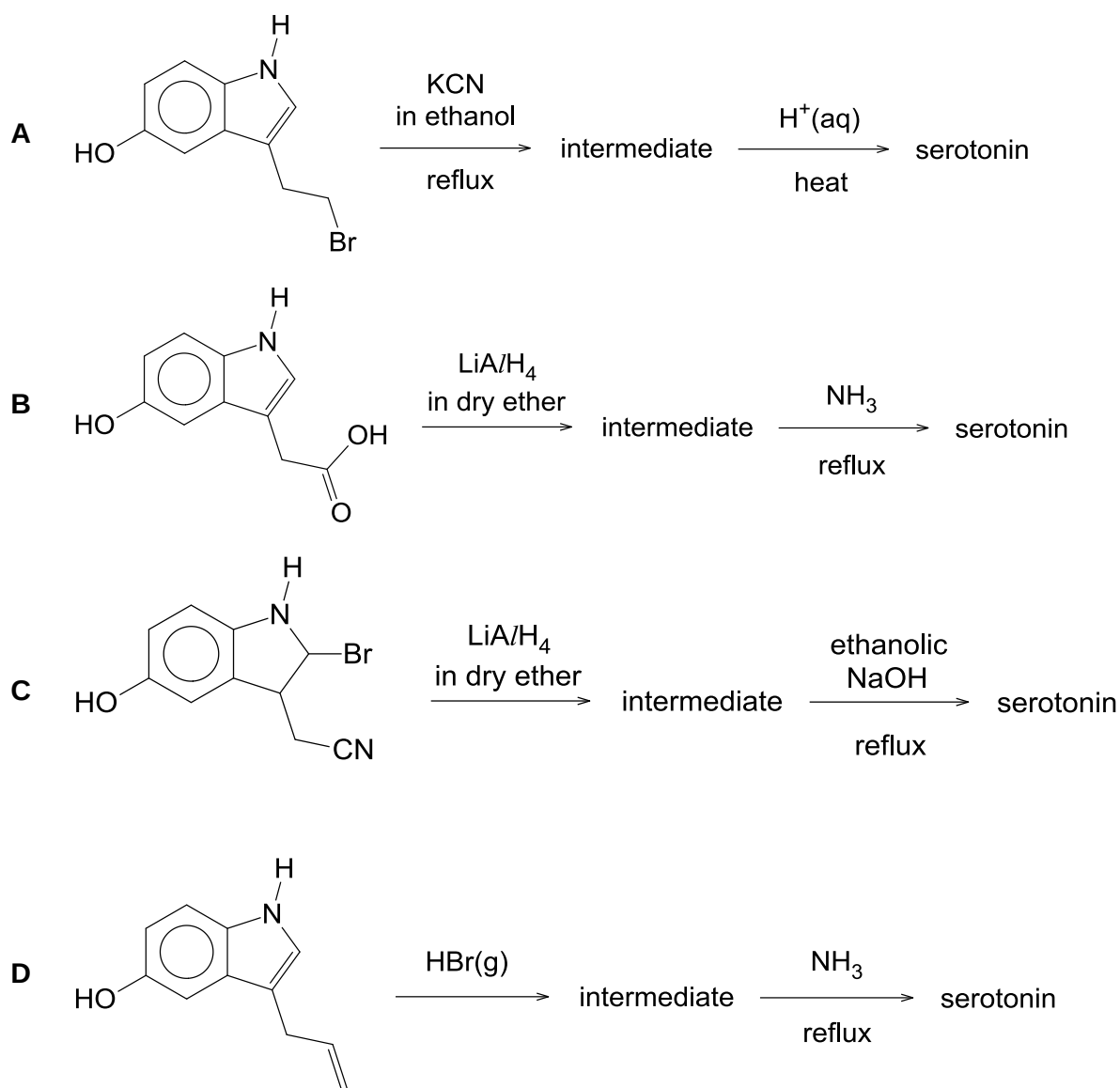
Which pair of statements about the properties of **K**, **L** and **M** are correct?

	gives a red precipitate with Fehling's solution	gives a yellow precipitate with hot alkaline aqueous iodine
A	K , L and M	L only
B	L and M only	L and M only
C	L only	L only
D	L only	K and L only

- 27 Serotonin is a neurotransmitter found in the central nervous system of humans.

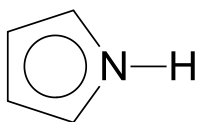


Which of the following could be used to synthesise serotonin?



- 28** Huckel's rule dictates that when there are 6 delocalised π -electrons, the compound has additional stability and is considered to be aromatic. Benzene is one such aromatic compound.

Pyrrole and pyridine are two nitrogen containing aromatic compounds with 6 delocalised π -electrons.



pyrrole

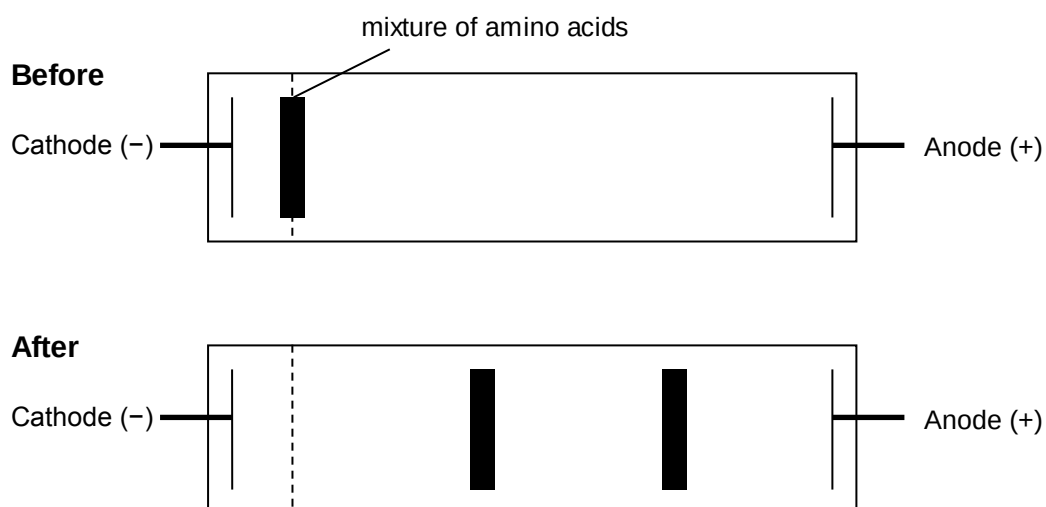


pyridine

How many electrons do the nitrogen atoms in pyrrole and pyridine contribute to their delocalised π -electron cloud respectively?

	pyrrole	pyridine
A	1	1
B	1	2
C	2	1
D	2	2

- 29 A mixture of two amino acids, leucine and aspartic acid, were run on a gel electrophoresis plate. The following results were obtained:

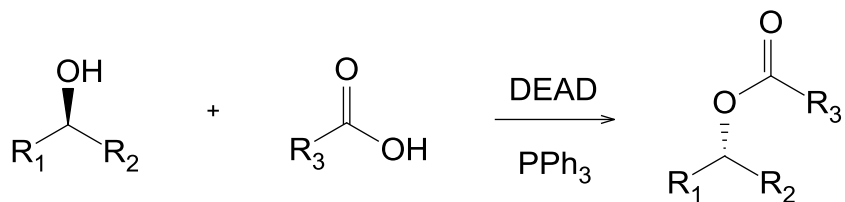


Amino acid	Side chain	pK_a		
		$-\text{COOH}$	$-\text{NH}_3^+$	Side chain
Leucine	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$	2.3	9.7	—
Aspartic acid	$-\text{CH}_2\text{COOH}$	2.0	9.9	3.9

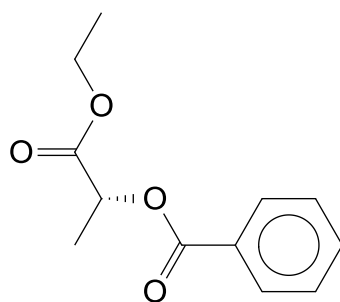
What pH was the gel likely to be buffered at?

- A** 1.5 **B** 3.9 **C** 9.8 **D** 10.5

- 30** The Mitsunobu reaction is a procedure that allows for the conversion of primary and secondary alcohols into esters with the addition of a carboxylic acid and a DEAD catalyst. The reaction is highly useful as the stereochemistry at the chiral carbon is completely inverted.



Which pair of alcohol and carboxylic acid could give compound **E**?

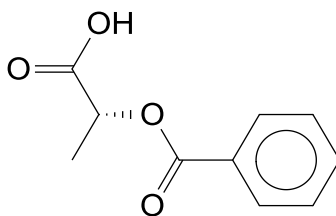


Compound **E**

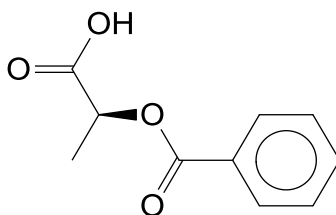
alcohol

carboxylic acid

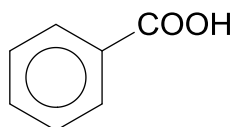
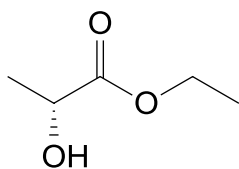
A



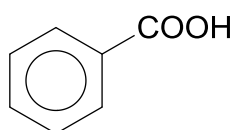
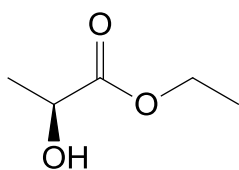
B



C



D



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Which properties of beryllium chloride are related to its electron-deficient Be atom?

- 1** its tendency to polymerise
- 2** its covalent character
- 3** its acidity in aqueous solution

32 The following diagram illustrates the energy changes of a set of reactions.



Which of the following can be deduced from the diagram?

- 1** The first electron affinity of **X** is -581 kJ mol^{-1} .
- 2** The enthalpy change from $\text{X}(\text{g}) \rightarrow \text{X}^-(\text{aq})$ is exothermic.
- 3** The enthalpy change for the reaction $\frac{1}{2}\text{X}_2(\text{standard state}) \rightarrow \text{X}(\text{g})$ is $+112 \text{ kJ mol}^{-1}$.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

33 *Use of Data Booklet is relevant to this question.*

A voltaic cell is set up using a $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ half-cell and a $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell. What are the features of the above set up?

- 1** Electrons flow in the external circuit from zinc to copper.
- 2** Reduction takes place at the copper terminal and the copper electrode increases in mass over time.
- 3** The zinc electrode is the negative electrode.

34 Three elements **H**, **I** and **J** belong to the same period of the Periodic Table.

The oxide of **H** reacts with both strong acids and bases. The oxide of **I** gives a solution of $\text{pH} > 7$ in water and the oxide of **J** gives a solution $\text{pH} < 7$ in water.

Which statements about elements **H**, **I** and **J** are always correct?

- 1** Element **H** has the highest electrical conductivity.
- 2** The ionic radius decreases in the order **I**, **H**, **J**.
- 3** The electronegativity of the elements decreases in the order **I**, **H**, **J**.

35 Samples of strontium and barium are burnt in air.

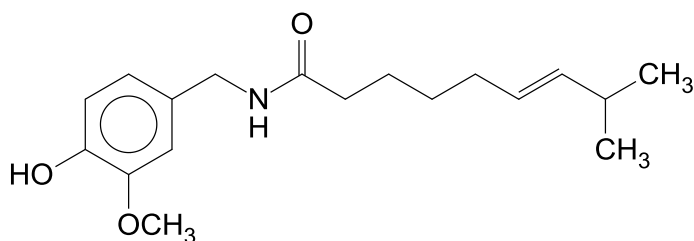
Which of the following flame colours are observed?

- 1** pale green
- 2** orange-red
- 3** lilac

36 Which of the following titanium compounds are likely to exist?

- 1 Ti_2O_5
- 2 TiBr_4
- 3 $\text{K}_2\text{Ti}_2\text{O}_3$

37 Capsaicin is the chemical found in chillies that gives rise to the sensation of spiciness.



Capsaicin

Which of the following statements about capsaicin are correct?

- 1 Capsaicin decolourises cold alkaline potassium manganate(VII).
- 2 Capsaicin gives a positive FeCl_3 test.
- 3 Capsaicin gives an orange precipitate with 2,4-dinitrophenylhydrazine.

38 Bromobenzene is unreactive to nucleophiles while 3-bromopropene is very reactive in comparison.

What could be reasons for the lack of reactivity of bromobenzene with nucleophiles?

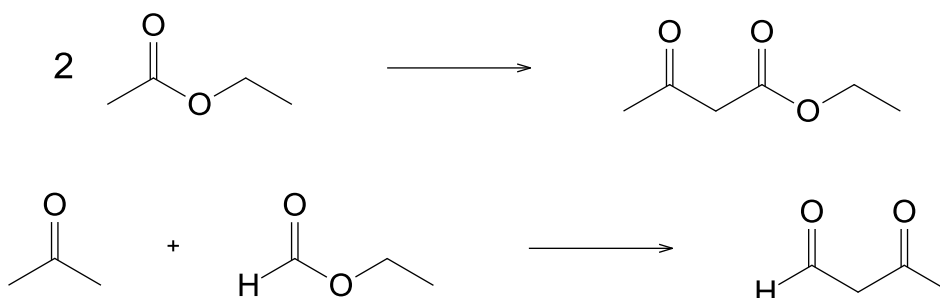
- 1 The π electrons repel incoming attacking nucleophiles.
- 2 The C-Br bond in bromobenzene is stronger than the C-Br bond in 3-bromopropene.
- 3 The C-Br bond is unable to rotate freely.

The responses **A** to **D** should be selected on the basis of

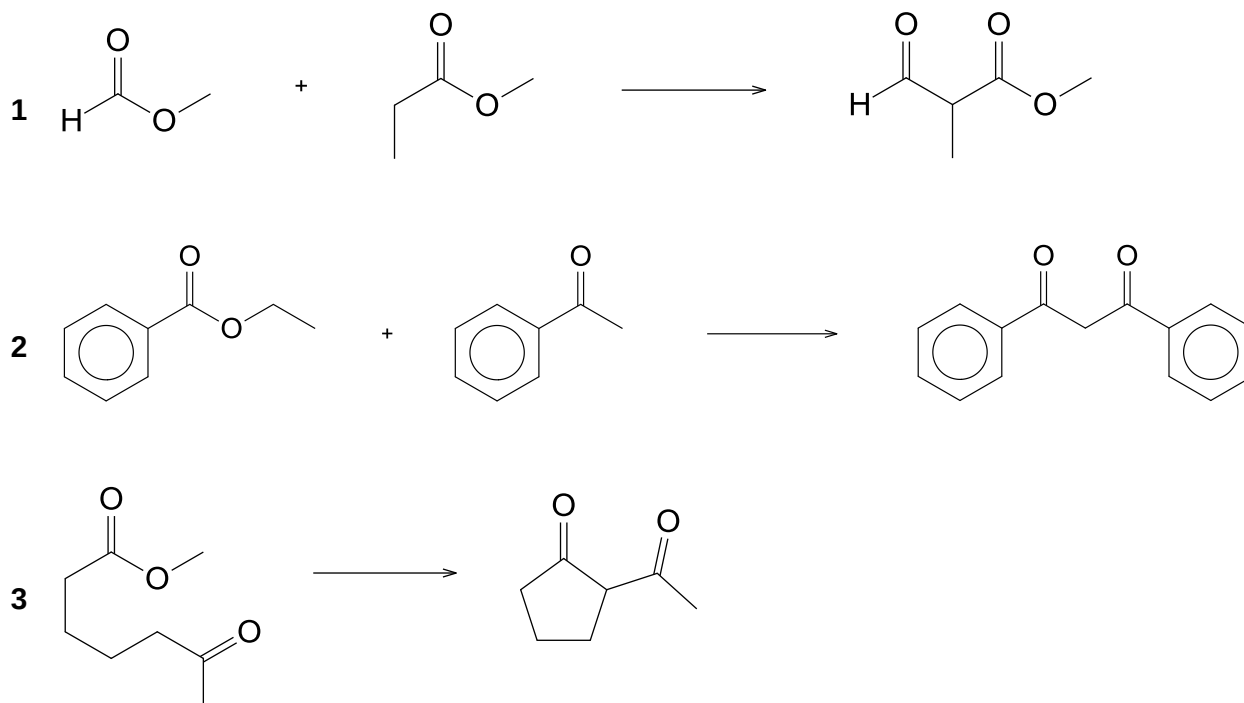
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 39** The Claisen Condensation is a reaction that occurs between two esters, or between one ester and another carbonyl compound.



Which of the following are examples of the Claisen Condensation reaction?



- 40** Hair contains chains of the protein keratin, which comprises amino acids forming interactions with other keratin chains. Hair can be treated in many ways to achieve a desired hair style.

Which of the following treatments will produce the desired styles?

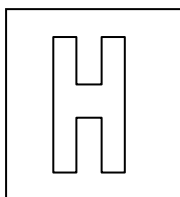
- 1** Heating hair with steam can help to elongate it.
- 2** The curling of hair requires both reducing and oxidising agents.
- 3** Usage of ammonia causes hair to soften and uncurl.

END OF PAPER

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Candidate Name: _____

Class Adm No



2016 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY

Paper 2 Structured

9647/02

15th Sept 2016

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** the questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

Question	1	2	3	4	5	6	Total
Marks	12	12	7	16	11	14	72

Answer ALL questions on the spaces provided.

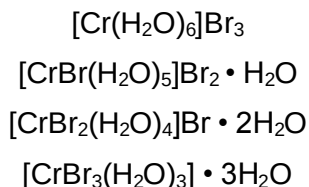
1 Planning

A student found a bottle of solid transition metal complex, **X**, in the laboratory. The label on the bottle showed that the molecular formula of **X** is $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ and that the cation of complex **X** is octahedral in shape. The label also showed that **X** is soluble in water.

- (a) State the oxidation state of Cr in complex **X** and hence the full electronic configuration of the Cr ion in **X**.

.....[2]

The student researched online and found out that **X** could have any of the four structural formulae below:



The student wanted to determine the structural formula of **X** using precipitation and gravimetric analysis. Gravimetric analysis involves the measurement of mass of the precipitate collected after a suspension is filtered.

In order to perform the experiment, a 100 cm^3 standard solution of $0.100 \text{ mol dm}^{-3}$ of $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ needs to be prepared.

- (b) Write a plan to prepare the standard solution. In your plan, provide details of calculation of mass of solid **X** used. You may assume you are provided with:

- solid **X**
- distilled water
- apparatus normally found in a school laboratory.

.....

.....

.....

.....

For
examiner's
use

.....[3]

(c) You are to design an experiment to help the student determine the structural formula of **X** using the method of precipitation of silver bromide followed by gravimetric analysis.

- standard solution prepared in **(b)**
- aqueous silver nitrate of concentration 2.0 mol dm^{-3}
- apparatus normally found in a school laboratory.

- the quantity of the reagents used
- the procedure for the precipitation and gravimetric analysis
- an outline of how the experimental data would be used to determine the structural formula of **X**.

.....

.....

.....

For
examiner's
use

[5]

- (d) In an experiment using a different sample of $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$, it was found that the mole ratio of $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ to AgBr formed is 1: 1. Given that the shape of the cation of this sample is also octahedral and that it can exhibit geometric isomerism, draw the structures of the two isomers of the cation.

For
examiner's
use

[2]

[Total: 12]

- 2 (a) This question is about the chemistry of crown ethers.

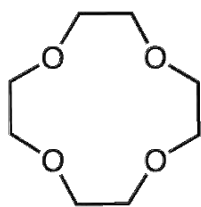
For
examiner's
use

Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e. $-\text{CH}_2\text{CH}_2\text{O}-$. The term “crown” refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person’s head.

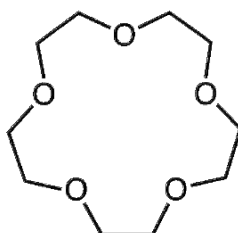
The first number in a crown ether’s name refers to the number of atoms in the ring, and the second number refers to the number of oxygen atoms in the crown ether.

Crown ethers strongly bind to certain cations, forming complexes. The oxygen atoms are well situated to coordinate with a cation located at the interior of the ring, whereas the exterior of the ring is hydrophobic.

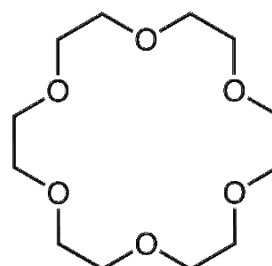
Structures of common crown ethers are shown below.



12-crown-4



15-crown-5



Q

- (i) Name the crown ether Q.

.....[1]

- (ii) Predict and explain whether crown ethers are soluble in water.

.....

.....[2]

Crown ethers are *size-selective*, as they form the most stable complexes with metal ions that fit best into the ring. The metal cation sits in the centre of the ring and interacts with lone pairs from all of the oxygen atoms.

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use

Q forms stable complexes with K^+ metal ion.

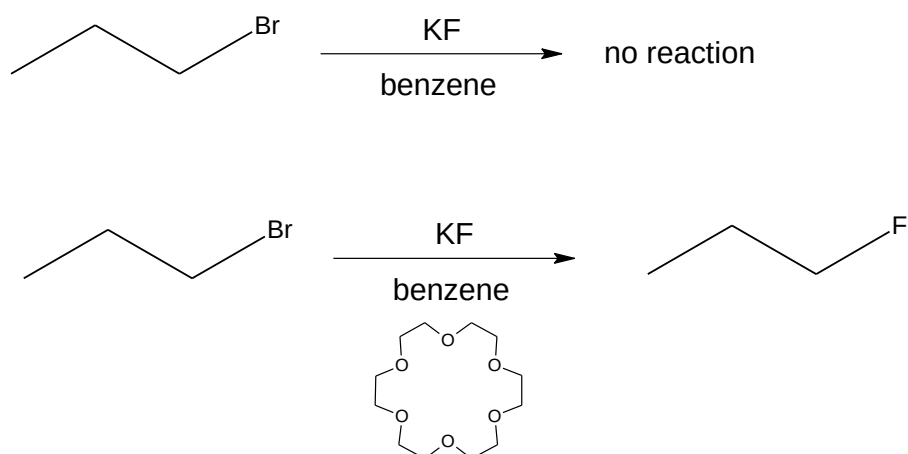
- (iii) Illustrate how K^+ metal ion binds to **Q** with an aid of a diagram. State the type of bonding between the crown ether and the metal ion.

[2]

- (iv) Suggest the identity of a Group I cation which would be most suitable to bind with 15-crown-5.

.....[1]

- (v) When propyl bromide is treated with KF in benzene, no reaction takes place. But when the crown ether **Q** is added to the reaction mixture, the desired propyl fluoride is produced.



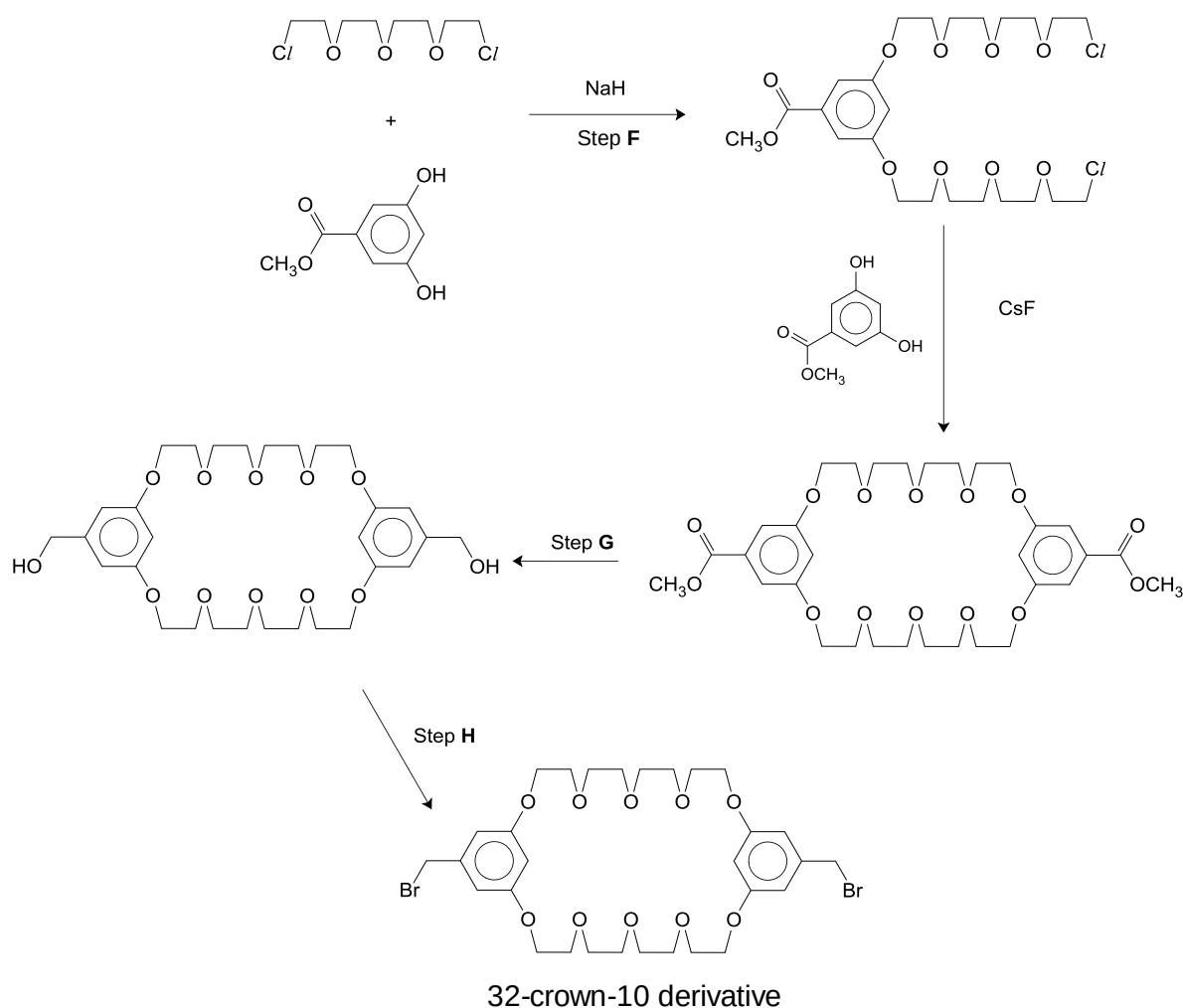
Explain why this is so.

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[Turn over

.....[2]

- (b) Crown ethers are generally synthesised involving the Williamson ether syntheses between excess dichloride derivatives of the appropriate ethylene glycols and the appropriate bishydroxy benzenes. The synthesis scheme for the synthesis of difunctionalised 32-crown-10 derivative is shown below.



- (i) Suggest the roles of NaH and CsF in the reaction scheme.

.....[1]

- (ii) State the type of reaction occurring in step F.

.....[1]

- (iii) State the reagents and conditions required for steps G and H.

Step **G**:.....

Step **H**:.....

[2]

[Total: 12]

- 3** In the Periodic Table, there is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table exemplified by lithium and magnesium.

An element **R** is related to aluminium by such a relationship and **R** also has the highest first ionisation energy of its group.

- (a) (i)** Identify **R** and explain the similarity in polarising powers of the cations of **R** and Al^{3+} .

.....

.....[2]

- (ii)** Predict and explain the pH of the solution formed when the chloride of **R** dissolves in water.

.....

.....[2]

- (b)** Another class of chlorides, acid chlorides, can react with alcohols to form esters which are sweet-smelling. Esters have been used as flavourings in food and perfumes. For example, ethyl propanoate is an ester with pineapple-like smell.

The kinetics of the hydrolysis of ethyl propanoate in alkaline medium at **T** K was studied.

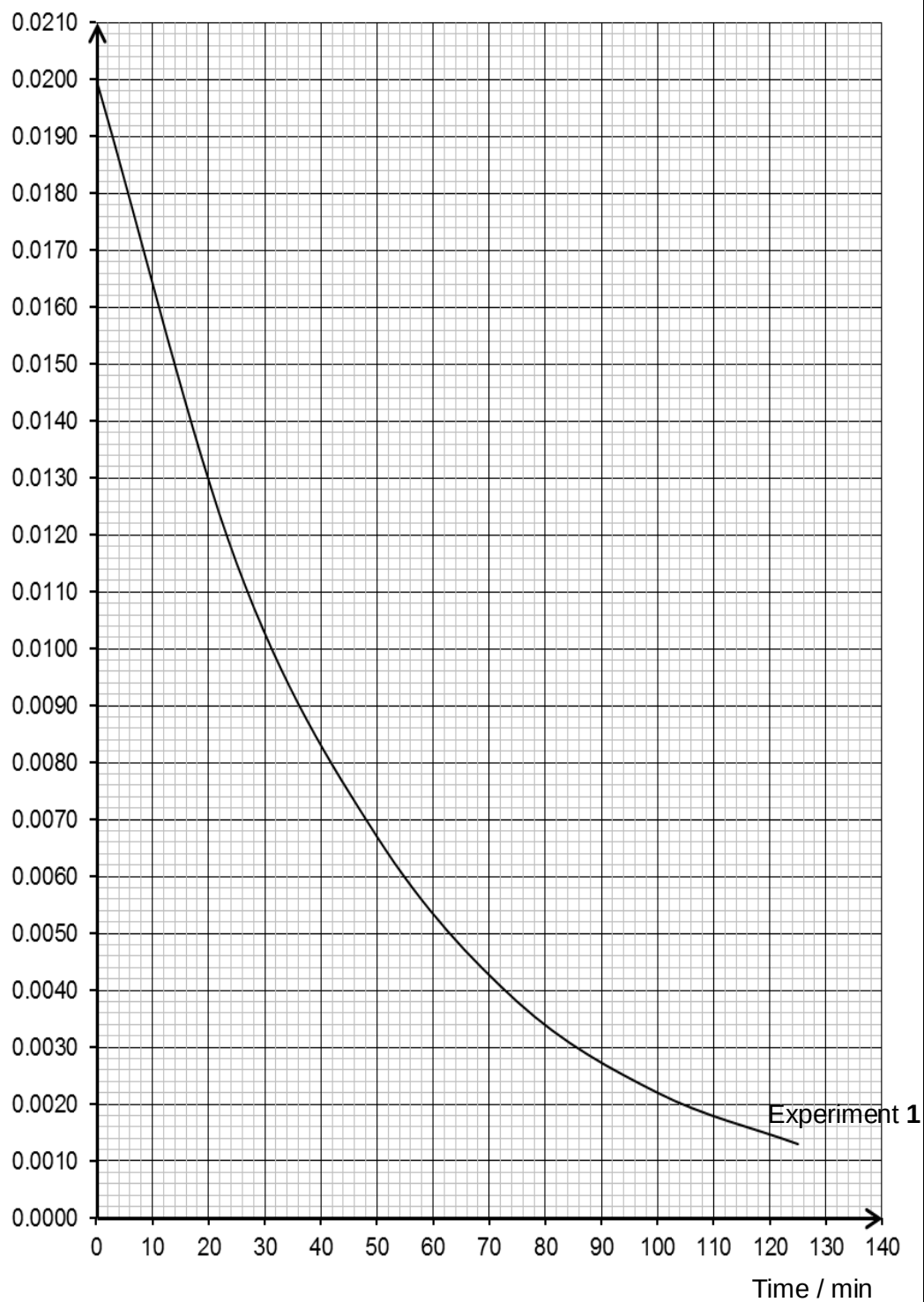
Two separate experiments were carried out with varying concentrations of aqueous sodium hydroxide solution. For each experiment, the concentration of ethyl propanoate was determined at regular time intervals.

The graph below shows the results of Experiment **1** with $[\text{NaOH}] = 2.0 \text{ mol dm}^{-3}$.

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[Turn over

$[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3] / \text{mol dm}^{-3}$



The results of Experiment 2 with $[\text{NaOH}] = 1.0 \text{ mol dm}^{-3}$ are shown below.

Time / min	Experiment 2 with $[\text{NaOH}] = 1.0 \text{ mol dm}^{-3}$ $[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3] / \text{mol dm}^{-3}$
0	0.0200
25	0.0152
50	0.0115
75	0.0088
100	0.0067
125	0.0051

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examiner's
use

- (i) Plot the results of Experiment 2 on the same graph above. Label your graph clearly. [1]
- (ii) Use the two graphs to determine the order of reaction with respect to $[\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3]$ and $[\text{NaOH}]$, showing your working clearly.

[2]

[Total: 7]

[Turn over

- 4 2-propanol is a colourless, flammable liquid with a strong odour. It is widely used as a solvent in many industrial applications.

(a) 2-propanol can be used as a fuel in the fuel cell. At the anode of the cell, 2-propanol is oxidised to carbon dioxide. The electrons pass around the external circuit to the cathode. The protons formed from the oxidation move through the conducting polymer electrolyte to the cathode, where they react with oxygen to produce water.

- (i) Construct ion-electron equations for the reactions at the anode and cathode respectively.

Anode:.....

Cathode:.....[2]

- (ii) Hence construct the equation for the overall reaction.

.....[1]

- (iii) The cell is capable of producing an e.m.f. of 1.56 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the $\text{CO}_2/\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ electrode reaction.

[2]

- (iv) Suggest a possible advantage of using the 2-propanol fuel cell compared to a hydrogen fuel cell.

.....

.....[1]

- (b) 2-propanol reacts with hot excess concentrated sulfuric acid to form propene. The reaction follows a 3-step mechanism as described below:

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use

Step 1	The oxygen atom on 2-propanol is protonated by H_2SO_4 forming intermediate A and HSO_4^- in an exothermic reaction. $\begin{array}{c} \text{H} \\ \\ ^+\text{O}-\text{H} \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array}$ Intermediate A
Step 2	The C-O bond in intermediate A breaks, forming a carbocation B and water. This step is endothermic and is the rate determining step.
Step 3	The carbocation is then deprotonated in an exothermic reaction, forming propene. H_2SO_4 is regenerated.

- (i) State the type of reaction undergone when 2-propanol reacts with hot excess concentrated sulfuric acid.

.....[1]

- (ii) Use the information given in the table above to draw out the full mechanism for the reaction between 2-propanol and concentrated sulfuric acid, indicating the movement of electrons using curly arrows and showing clearly the lone pair of electrons involved in the mechanism. You are advised to use structural formulae for all species, so that it is clear which bonds are broken and which are formed.

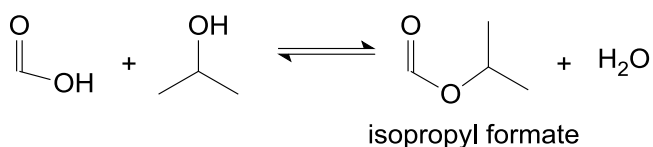
[3]

- (iii) Using the information given in the table in (b), sketch a fully labelled energy profile diagram of the reaction between 2-propanol and concentrated sulfuric acid.

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examiner's
use

[2]

- (c) 2-propanol reacts with methanoic acid in the presence of concentrated sulfuric acid, producing an ester, isopropyl formate, and water. The equilibrium below is set up during the reaction:



If 0.500 mol of methanoic acid and 0.300 mol of 2-propanol were mixed with a small amount of concentrated sulfuric acid and allowed to reach equilibrium, the equilibrium mass of isopropyl formate was found to be 16.64 g.

- (i) Write an expression for the equilibrium constant, K_c , for the reaction.

[1]

- (ii) Calculate a value for K_c .

For
examiner's
use

[2]

- (iii) A molecular sieve is a crystalline substance with pores of molecular dimensions which permits the passage of very small molecules such as water. The use of molecular sieves in the reaction above increases the yield of isopropyl formate. Suggest a reason for the increase in yield.

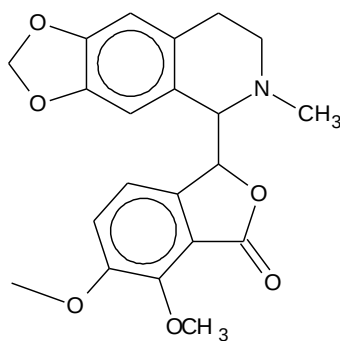
.....

.....[1]

[Total: 16]

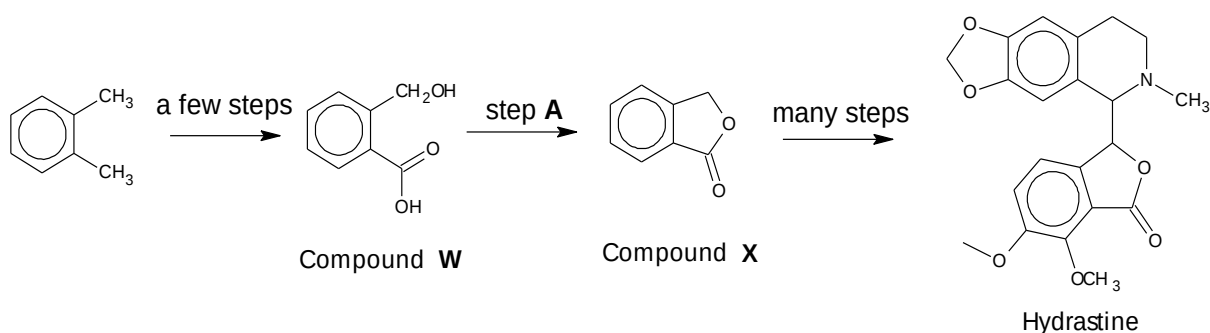
- 5 Hydrastine is a nitrogen containing drug used in the treatment of memory-related disorders such as Alzheimer's disease and schizophrenia and has the structure shown below.

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use



Hydrastine

A chemist planned a synthetic route to synthesise Hydrastine from 1,2-dimethylbenzene through the intermediates, compounds **W** and **X**, as shown below.



- (a) Hydrastine can be hydrolysed in either

- I acidic or
- II basic conditions.

Draw the structures of the products obtained for **each** case. Assume that the ether group (C-O-C) is inert. [2]

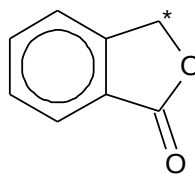
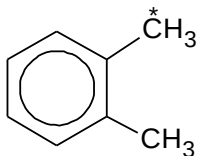
I	II

- (b) Devise a reaction scheme to help him synthesise compound **X** via compound **W** from 1,2-dimethylbenzene. Show clearly the reagents and conditions required for each step.

For
examiner's
use

[4]

- (c) State the oxidation numbers of the carbon atoms, labelled with an *, in 1,2-dimethylbenzene and compound **X**.



Oxidation number of C* in 1,2-dimethylbenzene:.....

Oxidation number of C* in compound **X**:[2]

- (iv) Compare the relative acidity of the alcohol and the carboxylic acid groups present in compound **W**.

.....

.....

.....[3]

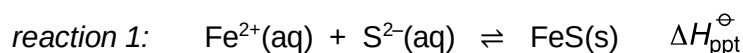
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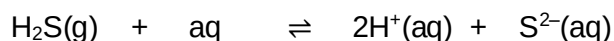
- 6 (a) Boiling raw eggs in hot spring water at pH = 9.2 produces black eggs (kuro tamago) through a chemical reaction with geothermal heat and volcanic gas as iron properties adhere to the porous shells. The black colour of iron sulfide is a result of a reaction with hydrogen sulfide, and it produces boiled eggs with black shells.

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use

Iron sulfide is precipitated according to the following reaction.



Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid.



In a saturated solution of hydrogen sulfide,

$$[\text{H}^+]^2[\text{S}^{2-}] = 1.0 \times 10^{-23} \text{ mol}^3 \text{ dm}^{-9}$$

- (i) Calculate the maximum concentration of sulfide ions present in hot spring water.

[2]

- (ii) Hence, calculate the minimum concentration of Fe^{2+} that must be present in hot spring water in order for precipitation to occur.

$$(K_{\text{sp}} \text{ of FeS} = 4.9 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6})$$

[1]

- (iii) Use the following data, together with relevant data from the *Data Booklet*, to calculate $\Delta H_{\text{ppt}}^{\ominus}$ for reaction 1 with the aid of an energy cycle.

For
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use

standard enthalpy change of formation of FeS(s)	-102 kJ mol^{-1}
standard enthalpy change of atomisation of Fe(s)	$+415 \text{ kJ mol}^{-1}$
standard enthalpy change of atomisation of S(s)	$+279 \text{ kJ mol}^{-1}$
sum of first two electron affinities of S(g)	$+337 \text{ kJ mol}^{-1}$
enthalpy change of hydration of $\text{Fe}^{2+}(\text{g})$	$-1981 \text{ kJ mol}^{-1}$
enthalpy change of hydration of $\text{S}^{2-}(\text{g})$	$-1372 \text{ kJ mol}^{-1}$

[4]

- (b) When a precipitate is formed, $\Delta G_{\text{ppt}}^{\ominus}$, in J mol^{-1} , is given by the following expression.

$$\Delta G_{\text{ppt}}^{\ominus} = 2.303RT \log K_{\text{sp}}$$

- (i) Use the data given in (a)(ii) to calculate $\Delta G_{\text{ppt}}^{\ominus}$, in kJ mol^{-1} , for FeS.

[1]

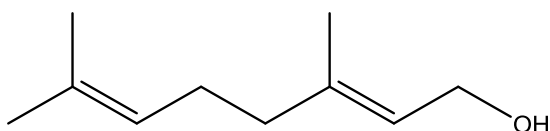
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- (ii) Use your answer in (a)(iii) and (b)(i) to calculate $\Delta S_{\text{ppt}}^{\ominus}$, in $\text{J mol}^{-1} \text{K}^{-1}$, for the formation of the precipitate FeS(s) at 298 K.

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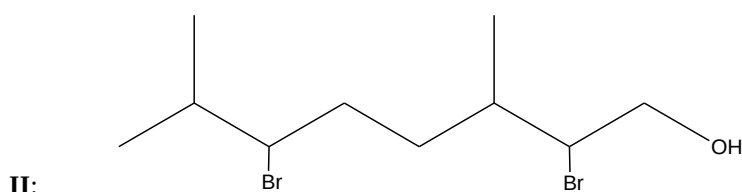
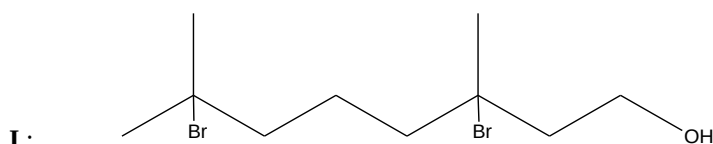
[1]

- (c) Geraniol ($\text{C}_{10}\text{H}_{18}\text{O}$) appears as a clear to pale-yellow oil that is insoluble in water but soluble in most common organic solvents. It has a rose-like scent and is commonly used in perfumes.



Geraniol

Geraniol reacts with HBr(g) to form the two possible products:



- (i) State which of the products would be the major product. Explain your answer.

.....

.....

.....[3]

- (ii) Draw a diagram to illustrate the bonding in C=C bond in geraniol in terms of orbital overlap.

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[2]

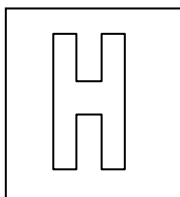
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Candidate Name: _____

Class Adm No



2016 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY

9647/03

Paper 3 Free Response

19th Sept 2016

2 hours

Candidates answer on separate paper.

Additional materials: Cover Page

Answer Paper

Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

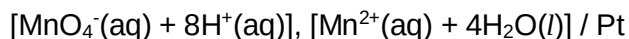
The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

- 1 (a) At room temperature, the electrode potential E for the system



is given by the equation

$$E = E^\ominus + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-(\text{aq})] [\text{H}^+(\text{aq})]^8}{[\text{Mn}^{2+}(\text{aq})]}$$

where $E^\ominus = +1.51 \text{ V}$. E values at various pH are given below when $[\text{MnO}_4^-(\text{aq})] = 0.01 \text{ mol dm}^{-3}$ and $[\text{Mn}^{2+}(\text{aq})] = 0.0001 \text{ mol dm}^{-3}$.

pH	E / V
0	+1.52
3	+1.24
7	+0.83

- (i) Define what the symbol $E^\ominus$ refers to. [1]
- (ii) Calculate the electrode potential of the cell at pH 1, when the manganate(VII) ion concentration is 0.01 mol dm^{-3} and the manganese(II) ion concentration is $0.001 \text{ mol dm}^{-3}$. [2]
- (iii) Predict at which pH value (0, 3 or 7) the solution is the most oxidising. [1]

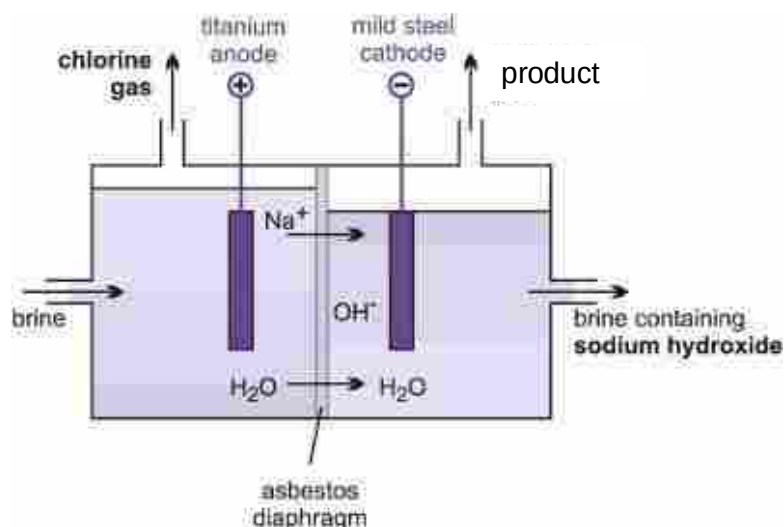
The electrolytic conductivity, κ , of a solution in a cell is given by the following formula:

$$\kappa = \frac{(c)(l)}{a}$$

where c is the conductance of the cell and a is the cross-sectional area of the electrodes, separated by a distance l .

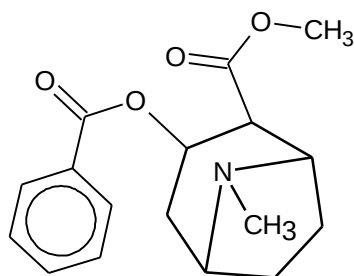
- (iv) Often the term $\frac{l}{a}$ is replaced by a cell constant K . Calculate the cell constant of a particular cell if it was found that the conductance of the cell containing $\text{Mn}^{2+}(\text{aq})$ of concentration $0.100 \text{ mol dm}^{-3}$ is $0.022 \Omega^{-1}$ and the electrolytic conductivity, κ , was $0.011 \Omega^{-1} \text{ cm}^{-1}$. State the units of K . [2]

- (b) A diaphragm cell consisting brine solution, concentrated NaCl , is used in the commercial electrolytic production of chlorine and sodium hydroxide.



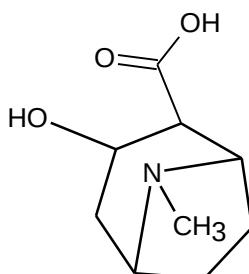
- (i) Write the ion-electron equations for the reactions occurring at the cathode and at the anode. [2]
- (ii) The chlorine gas is collected separately at the anode to prevent a side reaction that will occur with one of the products formed. Write a balanced equation for this side reaction that occurs at room conditions. State the oxidation numbers of chlorine in all the products formed. [2]
- (iii) In an electrolytic experiment using this diaphragm cell, 1.0 mol of gas is produced at the cathode. Calculate the mass of chlorine gas that is produced in the same experiment. [1]
- (c) Chlorine contains electrons which occupy the $n = 2$ principal quantum shell. Draw all the possible shapes of orbitals at the energy level, $n = 2$. [2]
- (d) Explain why aqueous manganese(II) ions are coloured. [3]

- (e) Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant and its structure is shown below.



Cocaine

Student **X** was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound **A**.

Compound **A**

Student **X** suggested the following steps:

Step 1	Methylbenzene is oxidised with hot, acidified $KMnO_4(aq)$ to give benzoic acid.
Step 2	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step 1 with thionyl chloride.
Step 3	Benzoyl chloride is reacted with compound A at room temperature.
Step 4	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid.

- (i) Give two reasons why the method suggested would not work. [2]
- (ii) Draw the **aromatic** organic product formed when cocaine undergoes acidic hydrolysis. [1]

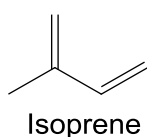
Cocaine is smuggled and inhaled as its protonated hydrochloride salt, known as cocaine hydrochloride. Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is hence converted back to cocaine before smoking. This is also done as the salt will decompose before it vapourises.

- (iii) Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine. [1]

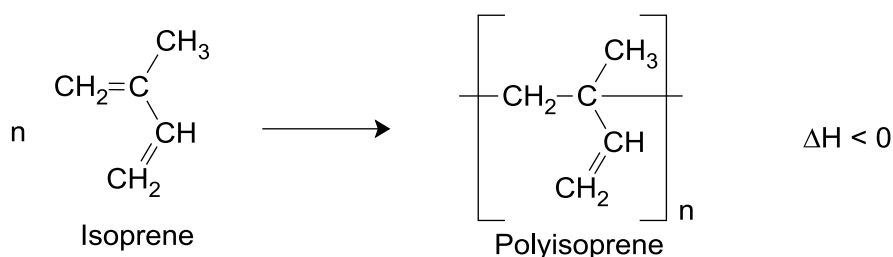
[Total: 20]

- 2 Researchers at the Max Planck Institute of Chemistry conducted a study to determine whether the chemicals emitted by human beings via their breath and their skin vary in response to audiovisual stimulus. In one of the experiments carried out during the screening of The Hunger Games 2 in a cinema, the researchers detected that there were spikes of emission of a diene, isoprene, twice; when the heroine's dress caught fire and when the final battle began. Isoprene is associated with muscle contraction, hence the spikes in emission could be due to unconscious muscle twitching as the audience empathised with the heroine.

The structure of isoprene is shown below. In its pure form, it exists as a colourless volatile liquid.



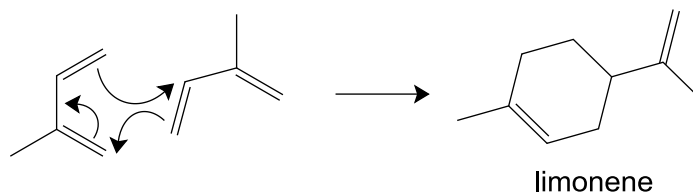
- (a) Isoprene reacts with gaseous HBr at room temperature.
- (i) Draw the structure of the major product of the reaction and hence state the IUPAC name of the major product. [2]
 - (ii) Name and illustrate with a diagram the type of stereoisomerism exhibited by the major product of the reaction. [2]
- (b) Polyisoprene, a polymer of isoprene, is the primary chemical constituent of natural rubber.



- (i) Predict, with a reason, the sign of the entropy change of the polymerisation process of isoprene. [1]
- (ii) With reference to your answer in (b)(i), state and explain if the polymerisation is more spontaneous or less spontaneous at higher temperatures. [2]

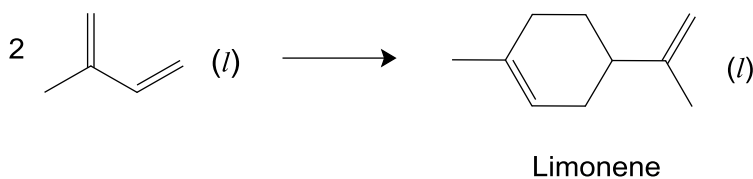
(iii) Natural rubber is insoluble in water. With reference to the structure of polyisoprene, explain why. [2]

(c) In a Diels-Alder reaction, 2 moles of isoprene react to form 1 mole of limonene. Limonene is a colourless liquid which possesses a strong smell of oranges. The mechanism of the reaction proceeds as follow.



The enthalpy changes of vaporisation of isoprene and limonene are $+26.4 \text{ kJ mol}^{-1}$ and $+39.4 \text{ kJ mol}^{-1}$ respectively.

Using the data given and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change for the reaction below.



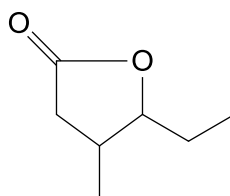
You may use C_5H_8 and $\text{C}_{10}\text{H}_{16}$ in your energy cycle to represent isoprene and limonene respectively. [3]

- (d) Compound **P** is an isomer of limonene. When **P** is oxidised by hot acidified potassium manganate(VII), **Q**, $C_3H_4O_3$, and **R**, $C_7H_{12}O_3$, are formed.

Both **Q** and **R** give orange precipitate with 2,4-dinitrophenylhydrazine and give effervescence when reacted with solid calcium carbonate. Only **Q** gives a yellow precipitate with warm alkaline iodine.

When **Q** reacts with $NaBH_4$ in methanol, **S** is formed. 1 mole of **S** gives 1 mole of $H_2(g)$ upon reaction with excess sodium metal.

R reacts with phosphorus pentachloride, giving white fumes and **T**, $C_7H_{11}ClO_2$. When **T** reacts with ethereal $LiAlH_4$, **U**, as shown below is formed.

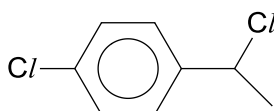


compound **U**

Deduce the structures for compounds **P** – **T**, explaining the chemistry involved. [8]

[Total: 20]

- 3 Compound **U** reacts with aqueous hydroxide ions when heated under reflux.

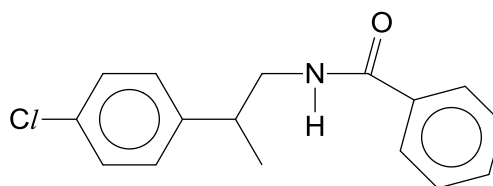


Compound **U**

The product of the reaction between **U** and hot aqueous hydroxide ions does not have optical activity.

- (a) (i) Describe the full mechanism of the reaction. [3]
- (ii) Explain why the product of the reaction does not exhibit optical activity. [2]
- (b) When $0.100 \text{ mol dm}^{-3}$ of hydroxide ions react with $0.00100 \text{ mol dm}^{-3}$ of compound **U** at 90°C , the half-life of compound **U** is 25 s.
- (i) Define the term *half-life*. [1]
- (ii) Using your answer in (a)(i), state the rate equation of the reaction. [1]
- (iii) Calculate the rate constant at 90°C , stating its units. [1]
- (iv) If the reaction is repeated using $0.100 \text{ mol dm}^{-3}$ of hydroxide ions and $0.00200 \text{ mol dm}^{-3}$ of **U** at the same temperature, state the half-life of **U** in the new experiment. [1]
- (v) With the aid of a clearly labelled Boltzmann distribution curve, explain why the rate of the reaction decreases when the temperature of the reaction decreases. [2]
- (c) 0.450 g of **U** was reacted completely with excess hot aqueous sodium hydroxide. The reaction mixture was cooled and acidified with excess $\text{HNO}_3(\text{aq})$. Calculate the mass of silver chloride formed when an excess of $\text{AgNO}_3(\text{aq})$ was added. [2]

- (d) Compound **V** can be formed from compound **U** in 3 steps.



compound **V**

Propose a 3-step synthesis of **V** from **U**, indicating clearly all reagents and conditions used. Draw the structures of all intermediates. [5]

- (e) Compound **W** is an isomer of **U**.



compound **W**

When **W** is boiled with aqueous sodium hydroxide, it immediately loses water to form an organic compound **X** which gives a yellow precipitate with a medicinal smell when reacted with warm iodine in KOH(aq).

Suggest the structure of **X** and write a balanced chemical equation for the reaction of **X** with warm iodine in KOH(aq). [2]

[Total: 20]

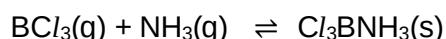
- 4 (a) Boron is a metalloid chemical element in Group III. However due to its smaller size compared to other Group III elements, its charge over mass ratio is closer to that of silicon. Hence it resembles silicon in many reactions.

(i) Predict the pH of the solution when BCl_3 is added into water. Hence write an equation for the reaction. [2]

(ii) Explain why CCl_4 does not undergo the same reaction as BCl_3 when it is added to water. [1]

(iii) The oxide of boron reacts with NaOH the same way SiO_2 reacts with NaOH . One of the products of the reaction is Na_3BO_3 . Propose a chemical equation for the reaction between the oxide of boron and NaOH . [1]

- (b) The following equilibrium exists when $\text{BCl}_3(\text{g})$ is mixed with $\text{NH}_3(\text{g})$.



(i) Draw a dot-and-cross diagram of the Cl_3BNH_3 molecule showing clearly its co-ordinate (dative covalent) bonds. [1]

(ii) Suggest the shape and the bond angle of the BCl_3 molecule. [1]

(iii) Predict the effect of decreasing the temperature on the above equilibrium. Explain your answer. [3]

(iv) At a total initial pressure of 3 atm, a 1 : 2 mixture of BCl_3 and NH_3 was allowed to reach equilibrium at 60°C . It was found that the equilibrium partial pressure of BCl_3 was 0.68 atm.

Determine the value of the equilibrium constant, K_p , for this reaction at 60°C , stating its units. [2]

- (c) Keratin is a fibrous protein that acts as the key structural component of hair. The amino acid content of keratin in hair of human varies slightly with ethnicity. The hair sample of an Asian was analysed. Eight of the amino acids in a keratin molecule present in the hair are listed below.

Amino acid	Formula of side chain (R in $\text{RCH}(\text{NH}_2)\text{COOH}$)	Number of amino acid residues per molecule of keratin
cysteine	$-\text{CH}_2\text{SH}$	1200
glutamic acid	$-\text{CH}_2\text{CH}_2\text{COOH}$	1026
serine	$-\text{CH}_2\text{OH}$	990
threonine	$-\text{CH}(\text{OH})\text{CH}_3$	572
leucine	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$	520
aspartic acid	$-\text{CH}_2\text{COOH}$	478
glycine	$-\text{H}$	464
valine	$-\text{CH}(\text{CH}_3)_2$	456

- (i) Use **any three** of the above amino acids to construct the displayed formula of a possible section of the protein chain of keratin. [2]
- (ii) Describe how a polypeptide chain of keratin is held in the shape of an α -helix. [2]
- (iii) The cysteine residues in the keratin molecule can form *disulfide bridges*. Illustrate this process by means of a balanced equation.
- Assuming all the disulfide bridges are intramolecular, what is the maximum number of bridges which could be formed within each keratin molecule? [2]
- (iv) Apart from the disulfide bridges mentioned in (c)(iii), describe, by means of diagrams, **two** other types of side-chain interaction, using suitable pairs of amino acids from the table above. [2]
- (v) Glutamic acid has three pK_a values: 2.1, 4.1 and 9.5. Suggest the structure of the major species present in solutions of glutamic acid at pH 7. [1]

[Total: 20]

- 5 Fluorine is a highly toxic pale yellow diatomic gas under standard conditions. As the most electronegative element, it is highly reactive.

Hydrogen fluoride is also a highly toxic gas which forms corrosive hydrofluoric acid upon contact with water.

- (a) State and explain which gas, fluorine or hydrogen fluoride, displays greater deviation from ideal gas behaviour. [2]

- (b) Fluorine reacts with hydrogen to form hydrogen fluoride.

Write an equation with state symbols for the reaction and describe how you would expect the reaction of hydrogen with fluorine to differ from that of hydrogen with chlorine. [2]

- (c) Hydrofluoric acid is a weak acid. It forms a buffer solution with salts containing its conjugate base.

Calculate the mass of solid sodium fluoride required to be added into a 250 cm^3 solution of $0.00420 \text{ mol dm}^{-3}$ of HF to form a buffer solution of pH 5.6.

$[K_a \text{ of HF} = 7.20 \times 10^{-4} \text{ mol dm}^{-3}]$ [2]

- (d) Hydrofluoric acid is a poison with greater hazards than strong acids even though it is a weak acid. It can react with calcium in the blood leading to hypocalcemia and potentially causing death through cardiac arrhythmia. This is due to the formation of sparingly soluble calcium fluoride in the body.

- (i) The solubility of calcium fluoride in water is $2.707 \times 10^{-4} \text{ mol dm}^{-3}$. Calculate the solubility of calcium fluoride in a solution of $0.00200 \text{ mol dm}^{-3}$ of aqueous NaF. [2]

- (ii) Explain briefly how the presence of NaF affects the solubility of calcium fluoride. [1]

(e) HCl is a reagent often used in organic reactions.

- (i) For each of the following types of reaction, write a balanced equation for a reaction involving HCl as a reagent or as a catalyst. You may use any organic compound as the starting material for each reaction.

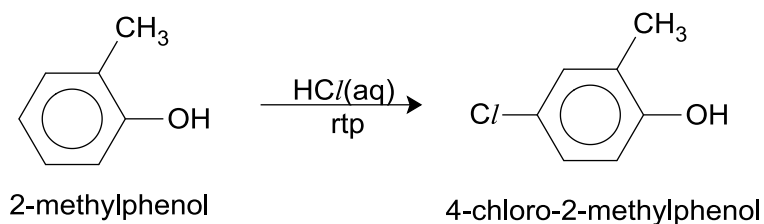
I Hydrolysis

II Neutralisation

III Addition

[3]

- (ii) A student proposed the following reaction for the conversion of 2-methylphenol to 4-chloro-2-methylphenol using aqueous hydrochloric acid as the reagent.

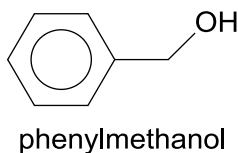


Explain why the reaction he proposed is not likely to work, and suggest how the student can improve the conversion.

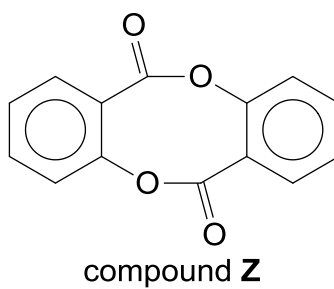
[3]

- (iii) Suggest a simple chemical test to distinguish between 2-methylphenol and phenylmethanol. State clearly the reagent and conditions used as well as the observations expected.

[2]



- (iv) Compound **Z** can be formed from 2-methylphenol in two steps.



Propose a two-step synthesis of **Z** from 2-methylphenol, stating the reagents and conditions for each step and showing the structure of the intermediate.

Your synthesis should involve 2-methylphenol as the only organic reactant. [3]

[Total: 20]

END OF PAPER

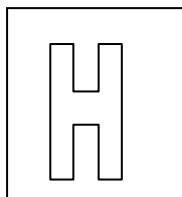
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2016 PU3 H2 CHEM PRELIM 2 EXAM**ANSWER SHEET (H2)**

<i>Question Number</i>	<i>Key</i>	<i>Question Number</i>	<i>Key</i>
1	B	21	A
2	D	22	B
3	B	23	D
4	C	24	A
5	C	25	D
6	A	26	D
7	D	27	C
8	D	28	C
9	B	29	D
10	B	30	D
11	C	31	D
12	A	32	C
13	B	33	A
14	D	34	D
15	A	35	D
16	A	36	C
17	B	37	B
18	B	38	B
19	D	39	A
20	C	40	A

Candidate Name: _____

Class Adm No



2016 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY

Paper 2 Structured Questions

9647/02

15 Sept 2016

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** the questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

Question	1	2	3	4	5	6	Total
Marks	12	12	7	16	11	14	72

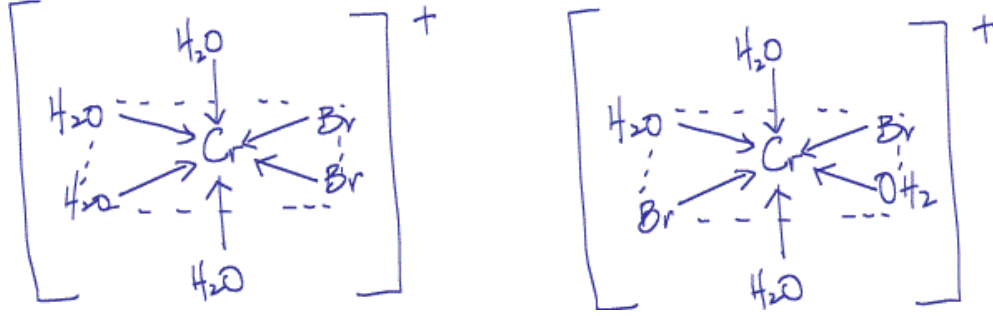
This question paper consists of **17** printed pages and **1** blank page.

Answer ALL questions on the spaces provided.

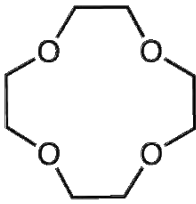
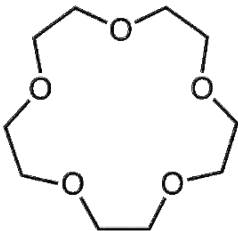
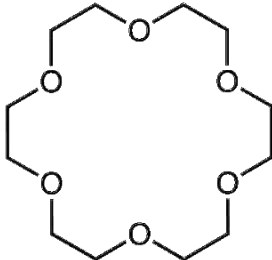
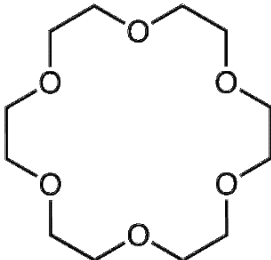
For
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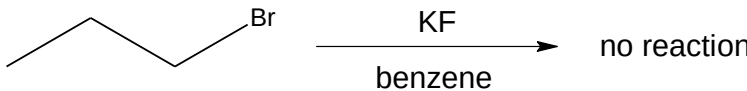
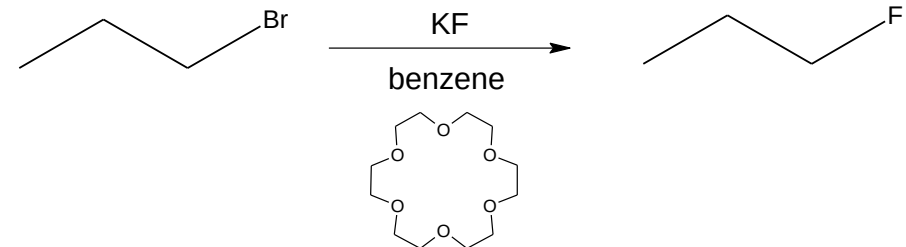
1	Planning
	A student found a bottle of solid transition metal complex, X , in the laboratory. The label on the bottle showed that the molecular formula of X is $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ and that the cation of complex X is octahedral in shape. The label also showed that X is soluble in water.
	(a) State the oxidation state of Cr in complex X and hence the full electronic configuration of the Cr ion in X . [2]
	+3 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
	The student researched online and found out that X could have any of the four structural formulae below: $\begin{aligned} &[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3 \\ &[\text{CrBr}(\text{H}_2\text{O})_5]\text{Br}_2 \cdot \text{H}_2\text{O} \\ &[\text{CrBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O} \\ &[\text{CrBr}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O} \end{aligned}$ The student wanted to determine the structural formula of X using precipitation and gravimetric analysis. Gravimetric analysis involves the measurement of mass of the precipitate collected after a suspension is filtered. In order to perform the experiment, a 100 cm^3 standard solution of $0.100 \text{ mol dm}^{-3}$ of $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ needs to be prepared.
	(b) Write a plan to prepare the standard solution. In your plan, provide details of calculation of mass of solid X used. You may assume you are provided with: • solid X • distilled water • apparatus normally found in a school laboratory. [3]
	Mass of X needed = $(100/1000) \times 0.100 \times 399.7 = 3.997\text{g}$ • Using a mass balance, weigh accurately 3.997g of solid X in a weighing bottle. • Transfer the solid into a 250cm^3 beaker, rinsing the weighing bottle with distilled water and pouring the washing into the beaker. Dissolve the solid with distilled water.

		- Transfer the solution into a 100cm³ volumetric flask, making sure all washing goes into the volumetric flask. - Add distilled water into the volumetric flask and top up to the mark. - Stopper the volumetric flask and shake well to form a homogeneous solution.										
	With the standard solution of X prepared, the student wanted to carry out an experiment to determine the structural formula of X .											
	(c)	You are to design an experiment to help the student determine the structural formula of X using the method of precipitation of silver bromide followed by gravimetric analysis. You may assume that you are provided with: - standard solution prepared in (b) - aqueous silver nitrate of concentration 2.0 mol dm⁻³ - apparatus normally found in a school laboratory. Your plan should include: - the quantity of the reagents used - the procedure for the precipitation and gravimetric analysis - an outline of how the experimental data would be used to determine the structural formula of X. [5]										
		- Using a pipette, transfer 10.0 cm³ of the standard solution of X into a beaker. - Add aqueous silver nitrate until in excess and stir with a glass rod. Stop adding when the cream precipitate formed does not increase in mass (or at least 3 times the amount of X in 10 cm³). - Using a filter funnel, filter the mixture to obtain the residue. - Transfer the residue to a pre-weighed dry evaporating dish and heat the residue to dryness by placing the evaporating dish on top of a Bunsen burner with tripod. - Cool and reweigh the evaporating dish to obtain mass of the residue. - Repeat the heating, cooling and weighing until a constant mass is obtained. - Amount of X used = (10/1000) × 0.100 = 0.00100 mol Amount of residue formed = mass of residue / 187.9 = y <table><tr><th>Mol ratio of X to AgBr</th><th>Structural formula</th></tr><tr><td>1 : 0</td><td>[CrBr₃(H₂O)₃] • 3H₂O</td></tr><tr><td>1 : 1</td><td>[CrBr₂(H₂O)₄]Br • 2H₂O</td></tr><tr><td>1 : 2</td><td>[CrBr(H₂O)₅]Br₂ • H₂O</td></tr><tr><td>1 : 3</td><td>[Cr(H₂O)₆]Br₃</td></tr></table>	Mol ratio of X to AgBr	Structural formula	1 : 0	[CrBr ₃ (H ₂ O) ₃] • 3H ₂ O	1 : 1	[CrBr ₂ (H ₂ O) ₄]Br • 2H ₂ O	1 : 2	[CrBr(H ₂ O) ₅]Br ₂ • H ₂ O	1 : 3	[Cr(H ₂ O) ₆]Br ₃
Mol ratio of X to AgBr	Structural formula											
1 : 0	[CrBr ₃ (H ₂ O) ₃] • 3H ₂ O											
1 : 1	[CrBr ₂ (H ₂ O) ₄]Br • 2H ₂ O											
1 : 2	[CrBr(H ₂ O) ₅]Br ₂ • H ₂ O											
1 : 3	[Cr(H ₂ O) ₆]Br ₃											

	(d)	In an experiment using a different sample of $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$, it was found that the mole ratio of $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ to AgBr formed is 1: 1. Given that the shape of the cation of this sample is also octahedral and that it can exhibit geometric isomerism, draw the structures of the two isomers of the cation. [2]
		
		[Total: 12]

2	(a)	This question is about the chemistry of crown ethers. Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e. $-\text{CH}_2\text{CH}_2\text{O}-$. The term “crown” refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person’s head. The first number in a crown ether’s name refers to the number of atoms in the ring, and the second number refers to the number of oxygen atoms in the crown ether. Crown ethers strongly bind to certain cations, forming complexes. The oxygen atoms are well situated to coordinate with a cation located at the interior of the ring, whereas the exterior of the ring is hydrophobic. Structures of common crown ethers are shown below.

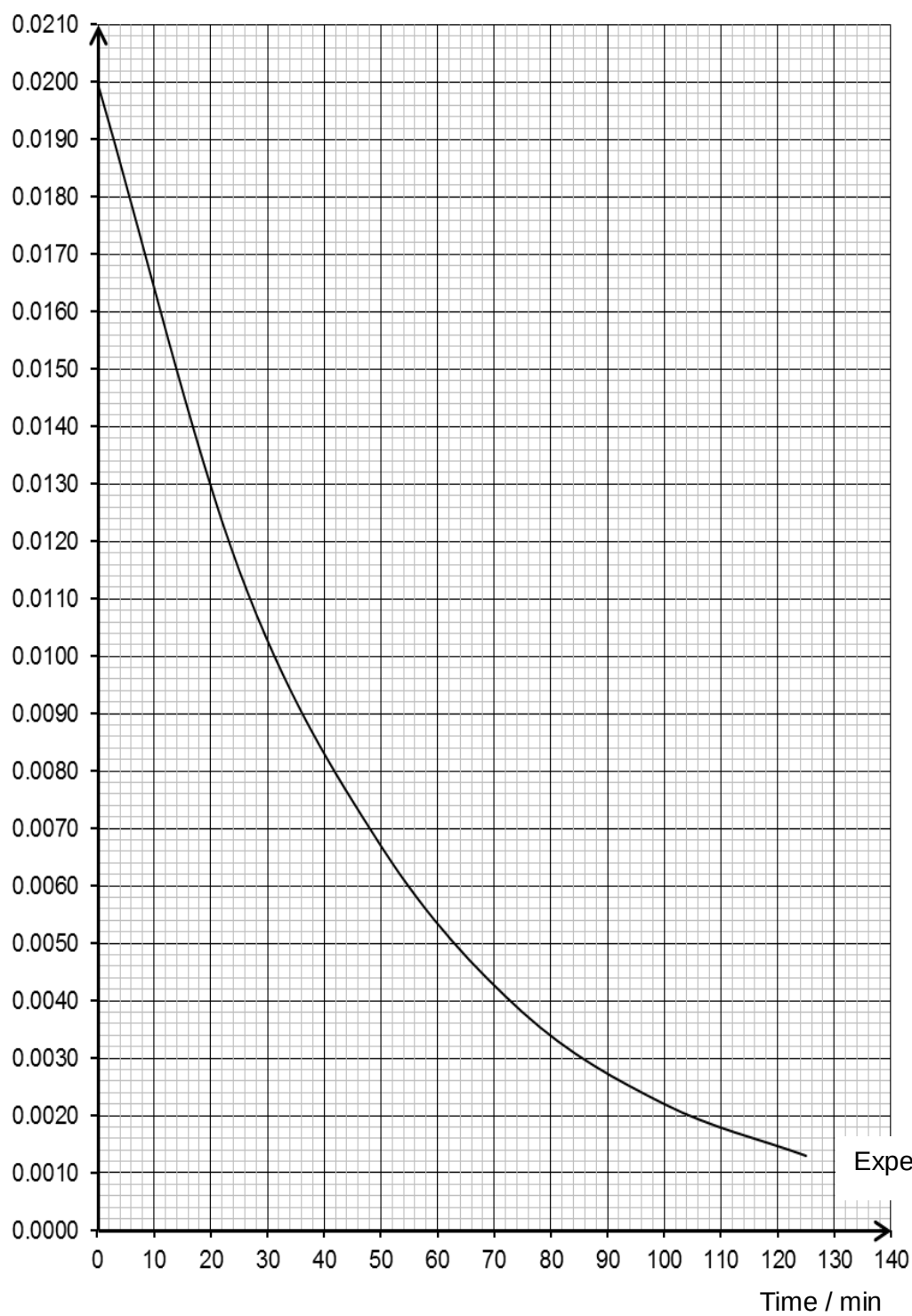
		 12-crown-4  15-crown-5  Q
	(i)	Name the crown ether Q. [1]
		18-crown-6
	(ii)	Predict and explain whether crown ethers are soluble in water. [2]
		Crown ethers are generally insoluble in water because the hydrogen bonds formed between crown ethers and water are not exothermic enough to break the temporary dipole-induced dipole interactions between crown ether molecules and hydrogen bonds between water molecules.
		Crown ethers are <i>size-selective</i>, as they form the most stable complexes with metal ions that fit best into the ring. The metal cation sits in the centre of the ring and interacts with lone pairs from all of the oxygen atoms. Q forms stable complexes with K^+ metal ion.
	(iii)	Illustrate how K^+ metal ion binds to Q with an aid of a diagram. State the type of bonding between the crown ether and the metal ion. [2]
		 Coordinate / Dative bonding
	(iv)	Suggest the identity of a Group I cation which would be most suitable to bind with 15-crown-5. [1]
		Na^+
	(v)	When propyl bromine is treated with KF in benzene, no reaction takes place. But when the crown ether Q is added to the reaction mixture, the desired propyl fluoride is produced.

			 <chem>CCCCBr</chem> $\xrightarrow[\text{benzene}]{\text{KF}}$ no reaction
			 <chem>CCCCBr</chem> $\xrightarrow[\text{benzene}]{\text{KF}}$ <chem>CCCCF</chem>
			Explain why this is so. [2]
			KF is insoluble in benzene, so F^- is unavailable to attack the propyl bromine. When 18-crown-6 is added, the crown ether surrounds the K^+ ion, allowing the F^- ion to be formed for nucleophilic substitution, so the reaction can proceed
	(b)		Crown ethers are generally synthesised involving the Willaimsen ether syntheses between excess dichloride derivatives of the appropriate ethylene glycols and the appropriate bishydroxy benzenes. The synthesis scheme for the synthesis of difunctionalised 32-crown-10 derivative is shown below.

		The reaction scheme shows the synthesis of a macrocyclic crown ether. It begins with 1,6-dichlorohexane and 4-methoxyphenol reacting in Step F with NaH to form a dimeric intermediate. This intermediate then reacts with 2,4,6-trimethylphenol in Step G with CsF to form a macrocyclic crown ether. Finally, in Step H, the crown ether is brominated to form a dibrominated product.		
	(i)	Suggest the roles of NaH and CsF in the reaction scheme.	[1]	
		They act as bases, abstracting a proton from phenol.		
	(ii)	State the type of reaction occurring in step F.	[1]	
		Nucleophilic Substitution (S_N2)		
	(iii)	State the reagents and conditions required for Steps G and H.	[2]	
		Step G: LiAlH_4 dry ether, rtp Step H: PBr_3 / SOBr_2 , rtp		
			[Total: 12]	

3	In the Periodic Table, there is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table exemplified by lithium and magnesium. An element R is related to aluminium by such a relationship and R also has the highest first ionisation energy of its group.		
	(a)	(i)	Identify R and explain the similarity in polarising powers of the cations of R and Al^{3+} . [2]
			R is beryllium. Polarising power is directly proportional to charge density (q/r). Although Al^{3+} is of a higher charge than Be^{2+}, Al^{3+} is also larger in size. The two ions have similar charge densities and hence, similar polarising powers.
		(ii)	Predict and explain the pH of the solution formed when the chloride of R dissolves in water. [2]
			pH = 3 (accept any value from 1 to 4) Due to the high charge density of Be^{2+}, it undergoes hydrolysis whereby it weakens and breaks the O-H bond in H_2O, readily donating a proton. Hence the solution becomes acidic.
	(b)	Another class of chlorides, acid chlorides, can react with alcohols to form esters which are sweet-smelling. Esters have been used as flavourings in food and perfumes. For example, ethyl propanoate is an ester with pineapple-like smell. The kinetics of the hydrolysis of ethyl propanoate in alkaline medium at T K was studied. Two separate experiments were carried out with varying concentrations of aqueous sodium hydroxide solution. For each experiment, the concentration of ethyl propanoate was determined at regular time intervals as the reaction proceeded. The graph below shows the results of Experiment 1 with $[NaOH] = 2.0 \text{ mol dm}^{-3}$. The results of Experiment 2 with $[NaOH] = 1.0 \text{ mol dm}^{-3}$ are shown below.	

$[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3] / \text{mol dm}^{-3}$

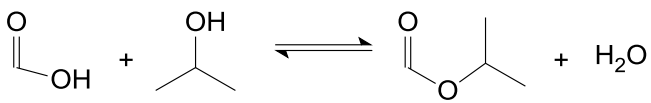


Experiment 1

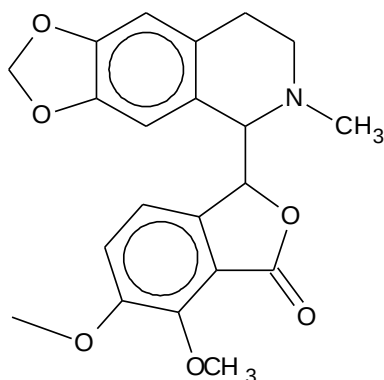
			<table><tr><th>Time / min</th><th>Experiment 2 with [NaOH] = 1.0 mol dm⁻³ [CH₃CH₂COOCH₂CH₃] / mol dm⁻³</th></tr><tr><td>0</td><td>0.0200</td></tr><tr><td>25</td><td>0.0152</td></tr><tr><td>50</td><td>0.0115</td></tr><tr><td>75</td><td>0.0088</td></tr><tr><td>100</td><td>0.0067</td></tr><tr><td>125</td><td>0.0051</td></tr></table>	Time / min	Experiment 2 with [NaOH] = 1.0 mol dm ⁻³ [CH ₃ CH ₂ COOCH ₂ CH ₃] / mol dm ⁻³	0	0.0200	25	0.0152	50	0.0115	75	0.0088	100	0.0067	125	0.0051	
Time / min	Experiment 2 with [NaOH] = 1.0 mol dm ⁻³ [CH ₃ CH ₂ COOCH ₂ CH ₃] / mol dm ⁻³																	
0	0.0200																	
25	0.0152																	
50	0.0115																	
75	0.0088																	
100	0.0067																	
125	0.0051																	
		(i)	Plot the results of Experiment 2 on the same graph above. Label your graph clearly. [1]															
		(ii)	Use the two graphs to determine the order of reaction with respect to CH ₃ CH ₂ CO ₂ CH ₂ CH ₃ and NaOH, showing your working clearly. [2]															
			<u>To find the order of reaction with respect to the ester.</u> Consider the graph for experiment 1. 1st t_{1/2} = 31.0 min (with construction lines shown on the graph) 2nd t_{1/2} = 32.0 min (with construction lines shown on the graph) Since t_{1/2} is almost constant, order of reaction with respect to ethyl propanoate = 1 <u>Alternative answer</u> Can also use the graph for experiment 2 to find two t_{1/2} values. 1st t_{1/2} = 63.0 min (with construction lines shown on the graph) 2nd t_{1/2} = 63.0 min (with construction lines shown on the graph) Since t_{1/2} is constant, order of reaction with respect to ethyl propanoate = 1 <u>To find the order of reaction with respect to NaOH.</u> For experiment 1, initial rate = 0.010/24.0 = 4.17 × 10⁻⁴ mol dm⁻³ min⁻¹ For experiment 2, initial rate = 0.010/48.0 = 2.08 × 10⁻⁴ mol dm⁻³ min⁻¹ When [NaOH] is doubled, initial rate is also doubled (4.17×10⁻⁴/2.08×10⁻⁴ = 2). Hence order of reaction with respect to NaOH = 1 <u>Alternative answer</u> Consider the graph for experiment 2. t_{1/2} = 63.0 min ⇒ t_{1/2} for experiment 2 = (2)(t_{1/2} for experiment 1) ⇒ reaction rate is halved when [NaOH] is halved. Hence order of reaction with respect to NaOH = 1															
			[Total: 7]															

4	2-propanol is a colourless, flammable liquid with a strong odour. It is widely used as a solvent in many industrial applications.	
	(a)	2-propanol can be used as a fuel in the fuel cell. At the anode of the cell, 2-propanol is oxidised to carbon dioxide. The electrons pass around the external circuit to the cathode. The protons formed from the oxidation move through the conducting polymer electrolyte to the cathode, where they react with oxygen to produce water.
	(i)	Construct ion-electron equations for the reactions at the anode and cathode respectively. [2]
		Anode: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + 5\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^-$ Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
	(ii)	Hence construct the equation for the overall reaction. [1]
		$2\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + 9\text{O}_2 \rightarrow 6\text{CO}_2 + 8\text{H}_2\text{O}$
	(iii)	The cell is capable of producing an e.m.f. of 1.56 V. By using suitable data from the <i>Data Booklet</i> , suggest a value for the $E^\ominus$ of the $\text{CO}_2/\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ electrode reaction. [2]
		$1.56 = +1.23 - E^\ominus_{\text{anode}}$ $E^\ominus_{\text{anode}} = -0.33\text{V}$
	(iv)	Suggest a possible advantage of using the 2-propanol fuel cell compared to a hydrogen fuel cell. [1]
		2-propanol is a liquid but hydrogen is a gas at rtp. 2-propanol is easier to store and transport.
	(b)	2-propanol reacts with hot excess concentrated sulfuric acid to form propene. The reaction follows a 3-step mechanism as described below:
	Step 1	The oxygen atom on 2-propanol is protonated by H_2SO_4 forming intermediate A and HSO_4^- in an exothermic reaction. $ \begin{array}{c} \text{H} \\ \\ ^+\text{O}-\text{H} \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array} $ Intermediate A
	Step 2	The C-O bond in intermediate A breaks, forming a carbocation B and water. This step is endothermic and is the rate determining step.

		Step 3	The carbocation is then deprotonated in an exothermic reaction, forming propene. H_2SO_4 is regenerated.	
		(i)	State the type of reaction undergone when 2-propanol reacts with hot excess concentrated sulfuric acid. [1]	
			Elimination	
		(ii)	Use the information given in the table above to draw out the full mechanism for the reaction between 2-propanol and concentrated sulfuric acid, indicating the movement of electrons using curly arrows and showing clearly the lone pair of electrons involved in the mechanism. You are advised to use structural formulae for all species, so that it is clear which bonds are broken and which are formed. [3]	
			$\begin{array}{c} \text{H}-\text{O} \cdot \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array} + \text{H}-\text{O}-\text{S}(=\text{O})_2-\text{OH} \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}^+-\text{CH}_3 \\ \\ \text{H} \end{array} + \text{HSO}_4^-$ $\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}^+-\text{CH}_3 \\ \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array} + \text{H}_2\text{O}$ $\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}^+-\text{CH}_3 \\ \\ \text{H} \end{array} + \text{HSO}_4^- \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{SO}_4$	
		(iii)	Using the information given in the table above, sketch a fully labelled energy profile diagram of the reaction between 2-propanol and concentrated sulfuric acid. [2]	

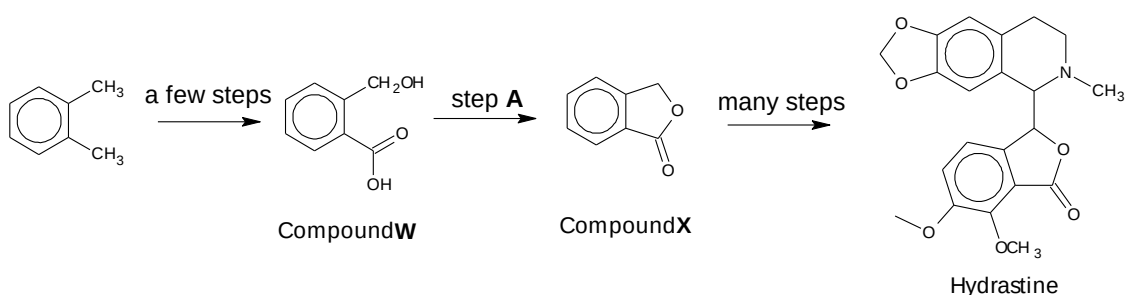
	(c) 2-propanol reacts with methanoic acid in the presence of concentrated sulfuric acid, producing an ester, isopropyl formate, and water. The equilibrium below is set up during the reaction:  isopropyl formate If 0.500 mol of methanoic acid and 0.300 mol of 2-propanol were mixed with a small amount of concentrated sulfuric acid and allowed to reach equilibrium, the equilibrium mass of isopropyl formate was found to be 16.64 g.																																
	(i) Write the expression for K_C. [1]																																
	$K_C = \frac{[\text{isopropyl formate}][\text{H}_2\text{O}]}{[\text{methanoic acid}][2\text{-propanol}]}$																																
	(ii) Calculate a value for K_C. [2]																																
	Amount of isopropyl formate = 16.64 / 88 = 0.189 mol <table border="1"><thead><tr><th></th><th>acid</th><th>+</th><th>alcohol</th><th>$\rightleftharpoons$</th><th>ester</th><th>+</th><th>water</th></tr></thead><tbody><tr><td>Initial amount / mol</td><td>0.500</td><td></td><td>0.300</td><td></td><td>0</td><td></td><td>0</td></tr><tr><td>Change / mol</td><td>-0.189</td><td></td><td>-0.189</td><td></td><td>+0.189</td><td></td><td>+0.189</td></tr><tr><td>Egm amount / mol</td><td>0.311</td><td></td><td>0.111</td><td></td><td>0.189</td><td></td><td>0.189</td></tr></tbody></table> $K_C = \frac{\left(\frac{0.189}{V}\right)\left(\frac{0.189}{V}\right)}{\left(\frac{0.311}{V}\right)\left(\frac{0.111}{V}\right)} = 1.03$		acid	+	alcohol	$\rightleftharpoons$	ester	+	water	Initial amount / mol	0.500		0.300		0		0	Change / mol	-0.189		-0.189		+0.189		+0.189	Egm amount / mol	0.311		0.111		0.189		0.189
	acid	+	alcohol	$\rightleftharpoons$	ester	+	water																										
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Change / mol	-0.189		-0.189		+0.189		+0.189																										
Egm amount / mol	0.311		0.111		0.189		0.189																										
	(iii) A molecular sieve is a crystalline substance with pores of molecular dimensions which permits the passage of very small molecules such as water. The use of molecular sieves in the reaction above increases the yield of isopropyl formate. Suggest a reason for the increase in yield. [1]																																
	The molecular sieve removes water, causing concentration of water to decrease. By LCP, equilibrium will then shift to the right to replenish water, hence increasing the yield.																																
	[Total: 16]																																

- 5 (a) Hydrastine is a nitrogen containing drug used in the treatment of memory-related disorders such as Alzheimer's disease and schizophrenia and has the structure shown below.



Hydrastine

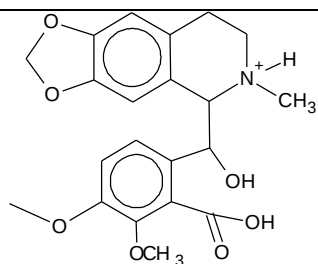
A chemist planned a synthetic route to synthesise Hydrastine from 1,2-dimethylbenzene through the intermediates, compounds **W** and **X**, as shown below.



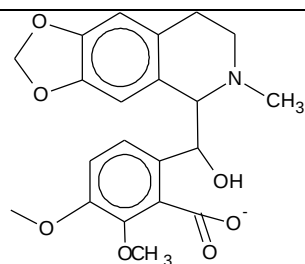
- (i) Hydrastine can be hydrolysed in either

- I** acidic or
II basic conditions.

Draw the structures of the products obtained for **each** case. Assume that the ether group (C-O-C) is inert. [2]



Acidic conditions

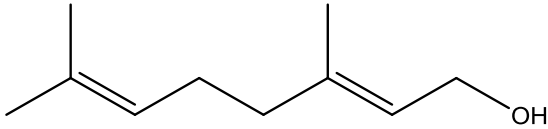
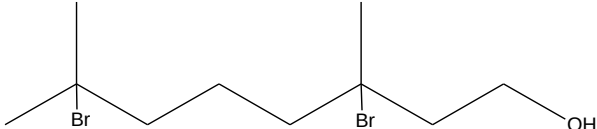
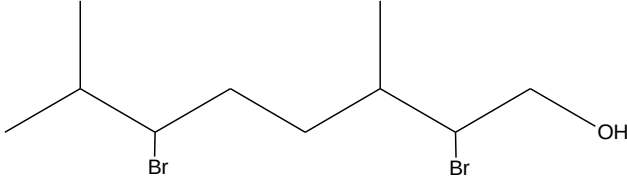


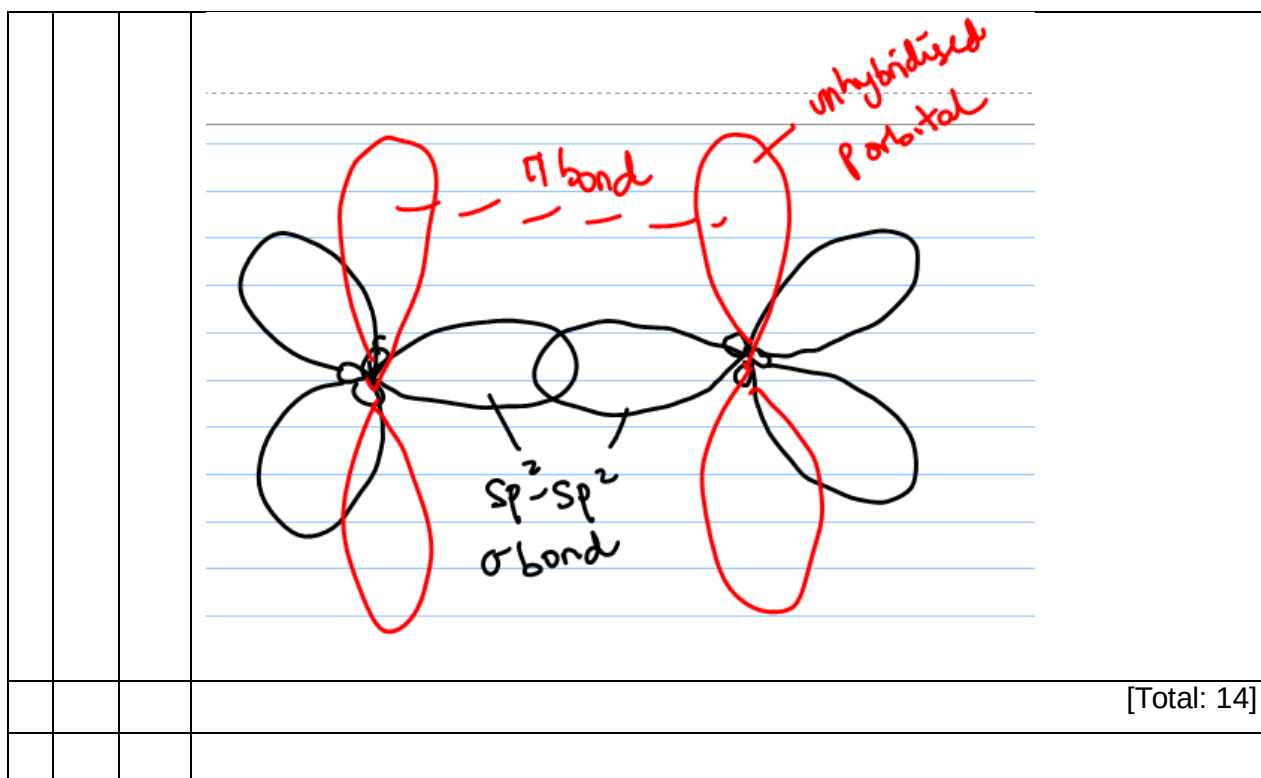
basic conditions

		(ii)	Devise a reaction scheme to help him synthesise compound X via compound W from 1,2-dimethylbenzene. Show clearly the reagents and conditions required for each step.	[4]
			<chem>Cc1ccccc1C</chem> $\xrightarrow[\text{heat}]{\text{KMnO}_4, \text{H}_2\text{SO}_4}$ <chem>OC(=O)c1ccccc1C(=O)O</chem> $\xrightarrow[\text{dry ether}]{\text{limited LiAlH}_4}$ <chem>OC(=O)c1ccccc1CO</chem> $\xrightarrow[\text{heat}]{\text{Conc. H}_2\text{SO}_4}$ <chem>O=C1OC(=O)c2ccccc12</chem>	
		(iii)	State the oxidation numbers of the carbon atoms, labelled with an *, in 1,2-dimethylbenzene and compound X .	[2]
			In 1,2-dimethylbenzene, C = -3 In compound X , C = -1	
		(iv)	Compare the relative acidity of the alcohol and the carboxylic acid groups present in compound W .	
			The R-CH ₂ OH is less acidic as compared to R-COOH; The electron donating R group intensifies the negative charge on the oxygen atom of the conjugate base, making the conjugate base less stable; The R-COOH is more acidic because the negative charge on the oxygen atom can undergo resonance and disperse the –ve charge among the 3 atoms of the carboxylate group, thus making the conjugate base more stable;	
			[Total: 11]	

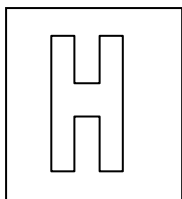
6	(a)	Boiling raw eggs in hot spring water at pH = 9.2 produces black eggs (kuro tamago) through a chemical reaction with geothermal heat and volcanic gas as iron properties adhere to the porous shells. The black colour of iron sulfide is a result of a reaction with hydrogen sulfide, and it produces boiled eggs with black shells. Iron sulfide is precipitated according to the following reaction. reaction 1: $\text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightleftharpoons \text{FeS}(\text{s}) \quad \Delta H_{\text{ppt}}^{\ominus}$ Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid. $\text{H}_2\text{S}(\text{g}) + \text{aq} \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$ In a saturated solution of hydrogen sulfide, $[\text{H}^+]^2[\text{S}^{2-}] = 1.0 \times 10^{-23} \text{ mol}^3 \text{ dm}^{-9}$
	(i)	Calculate the maximum concentration of sulfide ions present in hot spring water. [2]
		$[\text{H}^+] = 10^{-9.2}$ $= 6.31 \times 10^{-10} \text{ mol dm}^{-3}$ $[\text{S}^{2-}] = \frac{1.0 \times 10^{-23}}{(6.31 \times 10^{-10})^2} = 2.51 \times 10^{-5} \text{ mol dm}^{-3}$
	(ii)	Hence, calculate the minimum concentration of Fe^{2+} present in hot spring water in order for precipitation to occur. (K_{sp} of FeS = $4.9 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}$) [1]
		$K_{\text{sp}} = [\text{Fe}^{2+}][\text{S}^{2-}]$ $[\text{Fe}^{2+}] = \frac{4.9 \times 10^{-18}}{2.51 \times 10^{-5}} = 1.95 \times 10^{-13} \text{ mol dm}^{-3}$
	(iii)	Use the following data, together with relevant data from the <i>Data Booklet</i>, to calculate $\Delta H_{\text{ppt}}^{\ominus}$ for reaction 1 with the aid of an energy cycle.

			<table><tr><td>standard enthalpy change of formation of FeS(s)</td><td>−102 kJ mol^{−1}</td></tr><tr><td>standard enthalpy change of atomisation of Fe(s)</td><td>+415 kJ mol^{−1}</td></tr><tr><td>standard enthalpy change of atomisation of S(s)</td><td>+279 kJ mol^{−1}</td></tr><tr><td>sum of first two electron affinities of S(g)</td><td>+337 kJ mol^{−1}</td></tr><tr><td>enthalpy change of hydration of Fe²⁺(g)</td><td>−1981 kJ mol^{−1}</td></tr><tr><td>enthalpy change of hydration of S^{2−}(g)</td><td>−1372 kJ mol^{−1}</td></tr></table>	standard enthalpy change of formation of FeS(s)	−102 kJ mol ^{−1}	standard enthalpy change of atomisation of Fe(s)	+415 kJ mol ^{−1}	standard enthalpy change of atomisation of S(s)	+279 kJ mol ^{−1}	sum of first two electron affinities of S(g)	+337 kJ mol ^{−1}	enthalpy change of hydration of Fe ²⁺ (g)	−1981 kJ mol ^{−1}	enthalpy change of hydration of S ^{2−} (g)	−1372 kJ mol ^{−1}	[4]
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			$-102 = 415 + 279 + 337 + 762 + 1560 - 1981 - 1372 + \Delta H_{\text{ppt}}^{\ominus}$ $\Delta H_{\text{ppt}}^{\ominus} = -102 \text{ kJ mol}^{-1}$													
		(b)	When a precipitate is formed, $\Delta G_{\text{ppt}}^{\ominus}$, in J mol ^{−1} , is given by the following expression.													
			$\Delta G_{\text{ppt}}^{\ominus} = 2.303RT \log K_{\text{sp}}$													
		(i)	Use the data given in (a)(ii) to calculate $\Delta G_{\text{ppt}}^{\ominus}$, in kJ mol ^{−1} , for FeS.	[1]												
			$\Delta G_{\text{ppt}}^{\ominus} = 2.303 \times 8.31 \times 298 \times \lg(4.9 \times 10^{-18})$ $= -98.7 \text{ kJ mol}^{-1}$													
		(ii)	Use your answer in (a)(iii) and (b)(i) to calculate $\Delta S_{\text{ppt}}^{\ominus}$, in J mol ^{−1} K ^{−1} , for the formation of the precipitate FeS(s) at 298 K.	[1]												
			$\Delta G_{\text{ppt}}^{\ominus} = \Delta H_{\text{ppt}}^{\ominus} - T \Delta S_{\text{ppt}}^{\ominus}$ $-98.7 = -102 - 298 \Delta S_{\text{ppt}}^{\ominus}$ $\Delta S_{\text{ppt}}^{\ominus} = \frac{-102 + 98.7}{298}$ $= -11.1 \text{ J mol}^{-1} \text{ K}^{-1}$													

		(c) Geraniol ($C_{10}H_{18}O$) appears as a clear to pale-yellow oil that is insoluble in water but soluble in most common organic solvents. It has a rose-like scent and is commonly used in perfumes.  Geraniol Geraniol reacts with $HBr(g)$ to form the two possible products: I:  II: 
		(i) State which of the products would be the major product. Explain your answer. [3]
		I would be the major product. This is due to the fact that by Markovnikov's rule, the tertiary carbocation intermediate formed after the addition of H is more stable than that of II, which forms a secondary carbocation, due to more electron donating alkyl groups attached to the carbocation which stabilises the cation more.
		(ii) Draw a diagram to illustrate the bonding in any of the $C=C$ bond in geraniol in terms of orbital overlap. [2]



Candidate Name: _____



2016 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY**9647/03**

Paper 3 Free Response

19th Sept 2016**2 hours**

Candidates answer on separate paper.

Additional materials: Cover Page

Answer Paper

Data Booklet

READ THESE INSTRUCTIONS FIRST**Do not turn over this question paper until you are told to do so**

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

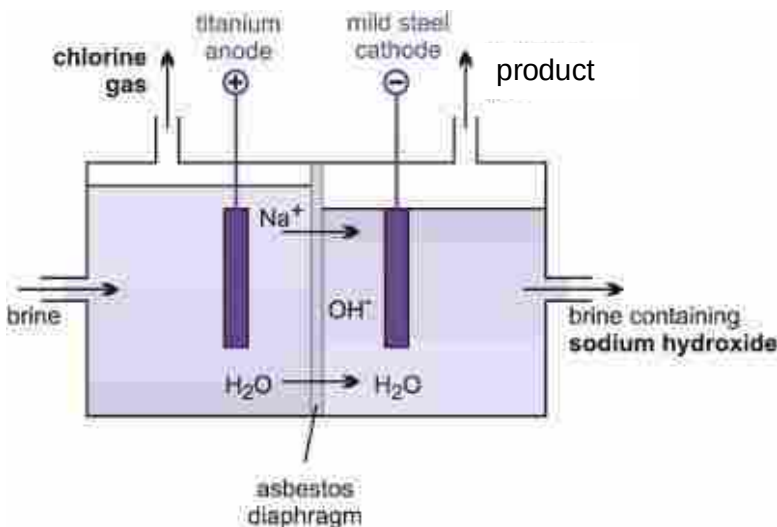
The use of an approved scientific calculator is expected, where appropriate.

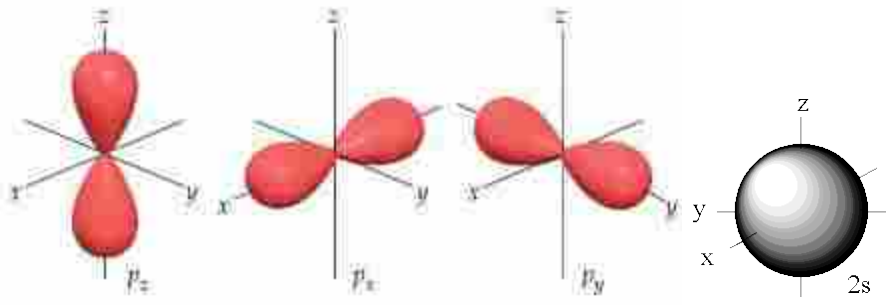
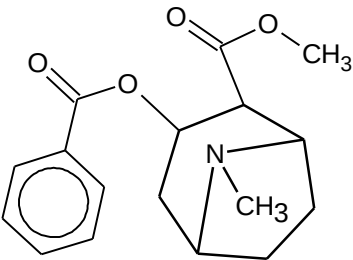
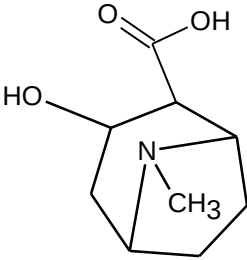
You are reminded of the need for good English and clear presentation in your answers.

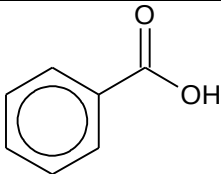
At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

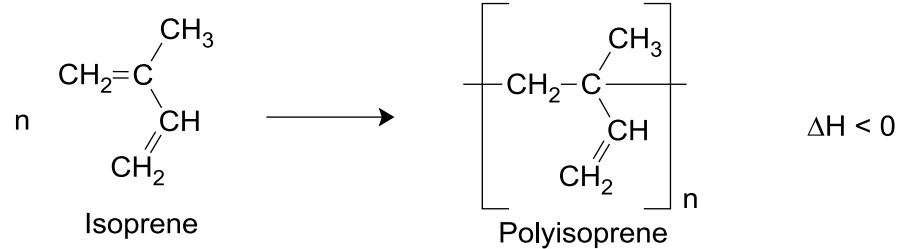
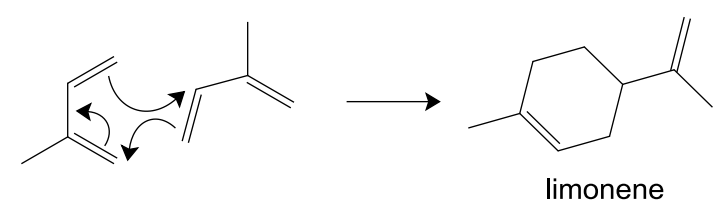
1	(a)	At room temperature, the electrode potential E for the system $[\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq})], [\text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})] / \text{Pt}$ is given by the equation $E = E^\ominus + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-(\text{aq})] [\text{H}^+(\text{aq})]^8}{[\text{Mn}^{2+}(\text{aq})]}$ where $E^\ominus = +1.51 \text{ V}$. E values at various pH are given below when $[\text{MnO}_4^-(\text{aq})] = 0.01 \text{ mol dm}^{-3}$ and $[\text{Mn}^{2+}(\text{aq})] = 0.0001 \text{ mol dm}^{-3}$ <table><tr><th>pH</th><th>E / V</th></tr><tr><td>0</td><td>+1.52</td></tr><tr><td>3</td><td>+1.24</td></tr><tr><td>7</td><td>+0.83</td></tr></table>		pH	E / V	0	+1.52	3	+1.24	7	+0.83
pH	E / V										
0	+1.52										
3	+1.24										
7	+0.83										
	(i)	Define what the symbol $E^\ominus$ refers to.	[1]								
		It refers to the standard electrode potential under standard conditions of 298K, 1 atm and 1 mol dm ⁻³ electrolyte used.									
	(ii)	Calculate the electrode potential of the cell at pH 1, when the manganate(VII) ion concentration is 0.01 mol dm ⁻³ and the manganese(II) ion concentration is 0.001 mol dm ⁻³ .	[2]								
		$pH = 1$ $[\text{H}^+] = 10^{-1} = 0.100 \text{ mol dm}^{-3}$ $E = +1.51 + \frac{0.059}{5} \log \frac{(0.01)[0.1]^8}{[0.001]} = +1.43 \text{ V}$									
	(iii)	Predict at which pH value, from the table above, the solution is the most oxidising.	[1]								
		At pH=0									
		The electrolytic conductivity $\mathcal{K}$ of a solution in a cell is given by the following formula: $\mathcal{K} = \frac{(c)(l)}{a}$ where c is the conductance of the cell and a is the cross-sectional area of the electrodes, separated by a distance l .									
	(iv)	Often the term $\frac{l}{a}$ is replaced by a cell constant K . Calculate the cell constant of a particular cell if it was found that the conductance of the cell									

		containing $\text{Mn}^{2+}(\text{aq})$ of concentration $0.100 \text{ mol dm}^{-3}$ is $0.022 \Omega^{-1}$ and the electrolytic conductivity, K , was $0.011 \Omega^{-1} \text{ cm}^{-1}$. State the units of K . [2]
		$0.011 = K (0.022)$ $K = 0.500 \text{ cm}^{-1}$
	(b)	A diaphragm cell consisting brine solution, concentrated NaCl, is used in the commercial electrolytic production of chlorine and sodium hydroxide. 
	(i)	Write the ion-electron equations for the reactions occurring at the cathode and at the anode. [2] Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$
	(ii)	The chlorine gas is collected separately at the anode to prevent a side reaction that will occur with one of the products formed. Write a balanced equation for this side reaction that occurs at room conditions. State the oxidation numbers of chlorine in all the products formed. [2] $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$ Oxidation no. of Cl in $\text{Cl}^- = -1$ Oxidation no of Cl in $\text{ClO}^- = +1$
	(iii)	In an electrolytic experiment using this diaphragm cell, 1.0 mol of gas is produced at the cathode. Calculate the mass of chlorine gas that is produced in the same experiment. [1] $1 \text{ mol of H}_2 \text{ produced} \equiv 1 \text{ mol of Cl}_2 \text{ produced}$ Mass of Cl_2 produced = $1 \times 71.0 = 71.0 \text{ g}$

	(c) Chlorine contains electrons which occupy the $n=2$ principal quantum shell. Draw all the possible shapes of orbitals at the energy level, $n=2$. [2]
	
	(d) Explain why aqueous manganese(II) ions are coloured. [3]
	• Mn^{2+} has partially-filled d-orbitals. When the ligands approach the central metal ion, splitting of the d-orbitals occurs. • The energy gap, ΔE, between the non-degenerate orbitals corresponds to the wavelength of light in the visible region of the electromagnetic spectrum. • When an electron from a lower energy d orbital is promoted to a higher energy d orbital (d-d electron transition), radiation corresponding to ΔE is absorbed. The complementary colour will be seen as the colour of the complex.
	(e) Cocaine, $\text{C}_{17}\text{H}_{21}\text{NO}_4$, was first used as a local anaesthetic. It is also a powerful stimulant and its structure is shown below.  Cocaine Student X was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound A.  Compound A Student X suggested the following steps:

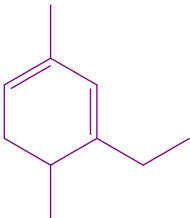
		Step 1	Methylbenzene is oxidised with hot, acidified KMnO_4 to give benzoic acid.
		Step 2	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step 1 with thionyl chloride.
		Step 3	Benzoyl chloride is reacted with compound A at room temperature.
		Step 4	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid.
		(i)	Give two reasons why the method suggested would not work. [2]
			1. In step 2, thionyl chloride will hydrolyse in the presence of aqueous solution 2. The final product will be the protonated form of cocaine since it is prepared in an acidic medium. 3. Heat is required for step 4.
		(ii)	Draw the aromatic organic product formed when cocaine undergoes acidic hydrolysis. [1]
			
		Cocaine is smuggled and inhaled as its protonated hydrochloride salt, known as cocaine hydrochloride. Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is hence converted back to cocaine before smoking. This is also done as the salt will decompose before it vapourises.	
		(iii)	Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine. [1]
			Dilute NaOH
		[Total: 20]	

2	Researchers at the Max Planck Institute of Chemistry conducted a study to determine whether the chemicals emitted by human beings via their breath and their skin vary in response to audiovisual stimulus. In one of the experiments carried out during the screening of The Hunger Games 2 in a cinema, the researchers detected that there were spikes of emission of a diene, isoprene, twice; when the heroine's dress catches fire and when the final battle begins. Isoprene is associated with muscle contraction, hence the spikes in emission could be due to unconscious muscle twitching as the audience empathises with the heroine. The structure of isoprene is shown below. In its pure form, it exists as a colourless volatile liquid. Isoprene	
(a)	Isoprene reacts with gaseous HBr at room temperature.	
	(i)	Draw the structure of the major product of the reaction and hence state the IUPAC name of the major product. [2]
		2,3-dibromo-2-methylbutane
	(ii)	Name and illustrate with a diagram the type of stereoisomerism exhibited by the major product of the reaction. [2]
		Optical isomerism
(b)	Polyisoprene, a polymer of isoprene, is the primary chemical constituent of natural rubber.	

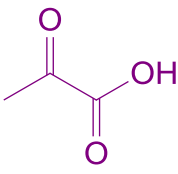
		 Isoprene Polyisoprene
	(i)	Predict, with a reason, the sign of the entropy change of the polymerisation process of isoprene. [1]
		Negative, because the system becomes less disorderly as the number of molecules decrease, hence having less way to arrange
	(ii)	With reference to your answer in (b)(i), state and explain if the polymerisation is more spontaneous or less spontaneous at higher temperatures. [2]
		$\Delta G = \Delta H - T\Delta S$ ΔH and ΔS are both negative. At high temperature, magnitude of $T\Delta S$ is larger than magnitude of ΔH hence ΔG is more positive. Less spontaneous
	(iii)	Natural rubber is insoluble in water. With reference to the structure of polyisoprene, explain why. [2]
		Energy evolved from the formation of H-bonds between polyisoprene and water is not sufficient to overcome the hydrogen bonds between water molecules.
(c)		In a Diels-Alder reaction, 2 moles of isoprene react to form 1 mole of limonene. Limonene is a colourless liquid which possesses a strong smell of oranges. The mechanism of the reaction proceeds as follow.  limonene The enthalpy changes of vaporisation of isoprene and limonene are $+26.4 \text{ kJ mol}^{-1}$ and $+39.4 \text{ kJ mol}^{-1}$ respectively. Using the data given and relevant data from the <i>Data Booklet</i>, construct an energy cycle to calculate the enthalpy change for the reaction below.

	Limonene You may use C_5H_8 and $C_{10}H_{16}$ in your energy cycle to represent isoprene and limonene respectively. [3]
	$\begin{array}{ccc} 2 C_5H_8 (l) & \xrightarrow{\Delta H} & C_{10}H_{16} (l) \\ \downarrow 2 \times (+26.4) & & \downarrow +39.4 \\ 2 C_5H_8 (g) & \xrightarrow{\Delta H_1} & C_{10}H_{16} (g) \end{array}$ Using bond energy, $\Delta H_1 = 2 \times BE(C=C) - 4 \times BE(C-C) = 2(610) - 4(350) = -180 \text{ kJ mol}^{-1}$ By Hess' Law, $\Delta H = 2(+26.4) + (-180) - (+39.4) = -166.6 \approx -167 \text{ kJ mol}^{-1}$
(d)	Compound P is an isomer of limonene. When P is oxidised by hot acidified potassium manganate(VII), Q, $C_3H_4O_3$, and R, $C_7H_{12}O_3$, are formed. Both Q and R give orange precipitate with 2,4-dinitrophenylhydrazine and give effervescence when reacted with solid calcium carbonate. Only Q gives a yellow precipitate with warm alkaline iodine. When Q reacts with $NaBH_4$ in methanol, S is formed. 1 mole of S gives 1 mole of $H_2(g)$ upon reaction with excess sodium metal. R reacts with phosphorus pentachloride, giving white fumes and T, $C_7H_{11}ClO_2$. When T reacts with ethereal $LiAlH_4$, U, as shown below is formed. compound U Deduce the structures for compounds P – T, explaining the chemistry involved. [8]

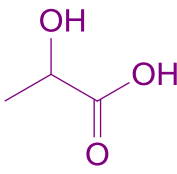
Information	Deduction
Both Q and R give orange precipitate with 2,4-dinitrophenylhydrazine and give effervescence when reacted with solid calcium carbonate.	Q and R are ketones. Q and R has carboxylic acid group.
Only Q gives a yellow precipitate with warm alkaline iodine.	Q has the structure $\text{CH}_3\text{CO}-$
When Q reacts with NaBH_4 in methanol, S is formed.	Reduction of ketone. S is secondary alcohol.
1 mole of S gives 1 mole of $\text{H}_2(\text{g})$ upon reaction with excess sodium metal.	Acid-metal reaction S has two $-\text{OH}$ groups
R reacts with phosphorus pentachloride, giving white fumes and T , $\text{C}_7\text{H}_{11}\text{ClO}_2$.	Substitution reaction T has acyl chloride
When T reacts with ethereal LiAlH_4 , U is formed.	Reduction of ketone to secondary alcohol Followed by nucleophilic substitution to form ester.



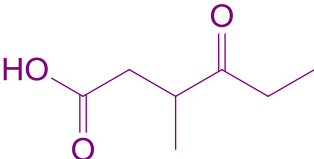
P



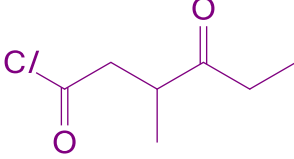
Q



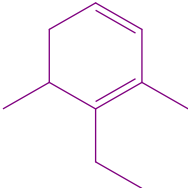
S



R

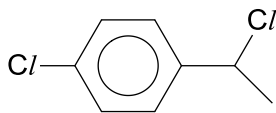
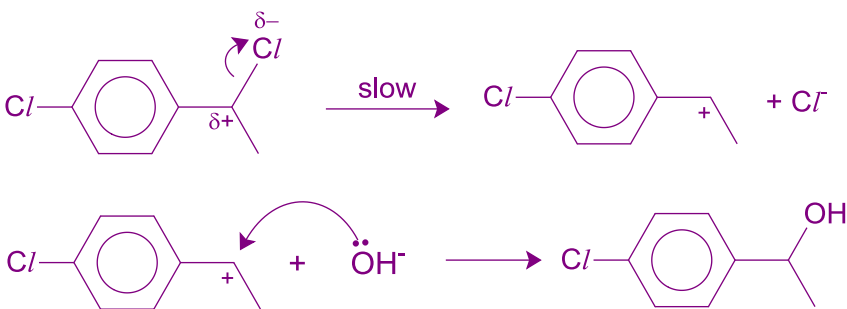
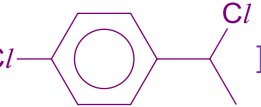


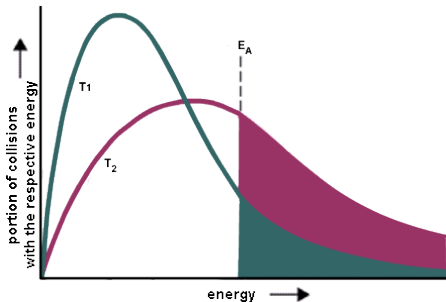
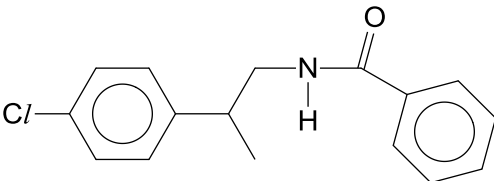
T

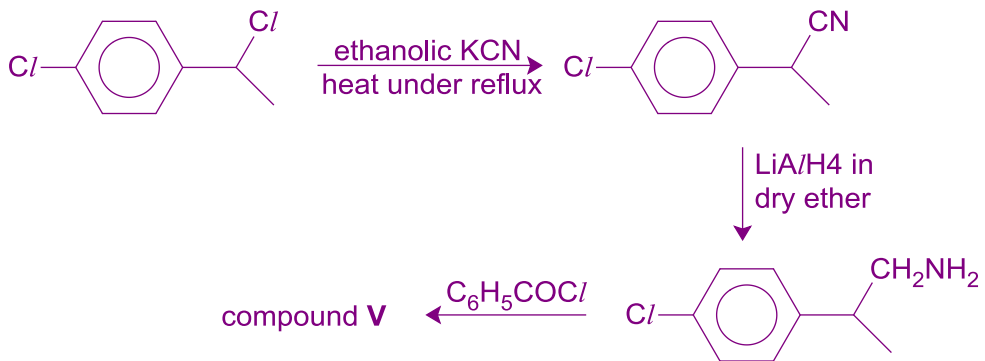
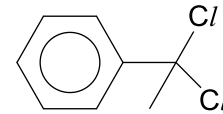
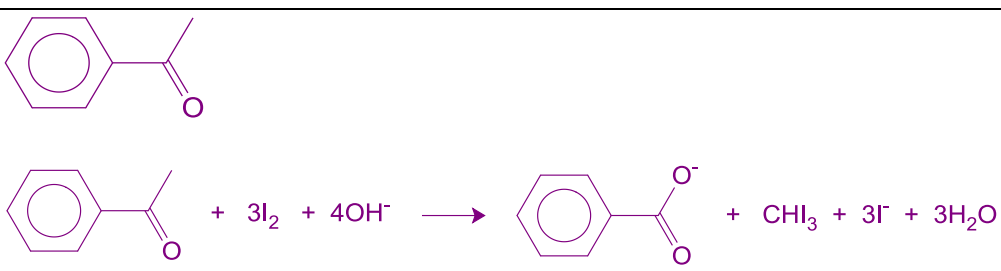


Alternative answer for **P**:

[Total: 20]

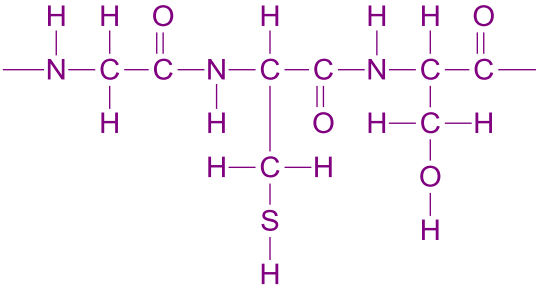
3	Compound U reacts with aqueous hydroxide ions when heated under reflux.	
	 Compound U The product of the reaction between U and hot aqueous hydroxide ions does not have optical activity.	
(a)	(i)	Describe the full mechanism of the reaction. [3]
		Nucleophilic substitution 
	(ii)	Explain why the product of the reaction does not exhibit optical activity. [2]
		The intermediate formed in the first step is trigonal planar at the C with the positive charge. The nucleophile can attack the carbon from the top or the bottom of the plane. A racemic mixture is formed.
(b)	When 0.100 mol dm ⁻³ of hydroxide ions react with 0.00100 mol dm ⁻³ of compound U at 90°C, the half-life of compound U is 25 s.	
	(i)	Define the term <i>half-life</i> . [1]
		Half-life is the time taken for the concentration of a reactant to reduce to half its original value.
	(ii)	Using your answer in (a)(i), state the rate equation of the reaction. [1]
		Rate = $k[\text{Cl}-\text{C}_6\text{H}_4-\text{CH}(\text{Cl})\text{CH}_3]$ 
	(iii)	Calculate the rate constant at 90°C, stating its units. [1]
		$k = \frac{\ln 2}{\text{half life}} = \frac{\ln 2}{25} = 0.0277 \text{ s}^{-1}$
	(iv)	If the reaction is repeated using 0.100 mol dm ⁻³ of hydroxide ions and 0.002 mol dm ⁻³ of U at the same temperature, state the half-life of U in the new experiment. [1]
		25 s

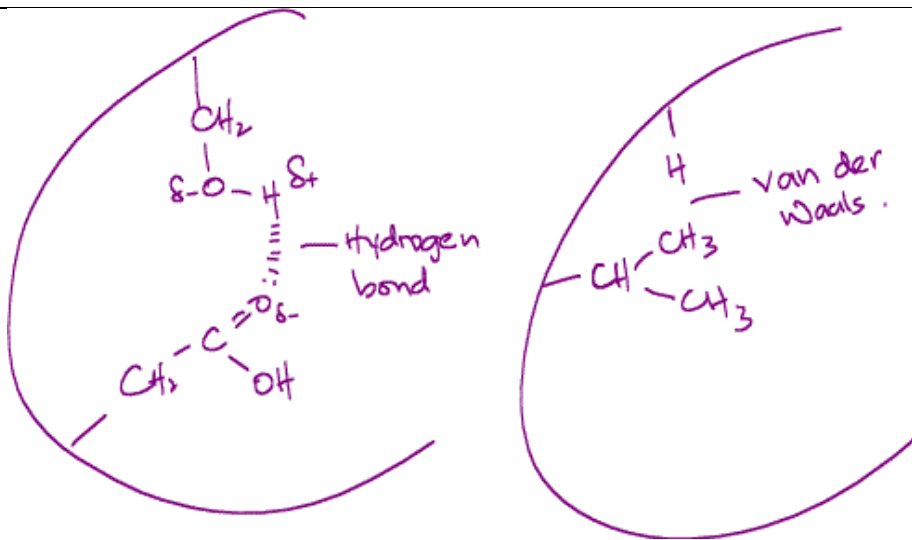
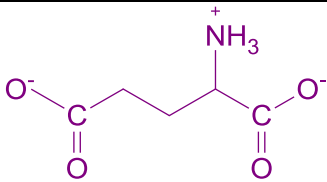
		(v)	With the aid of a clearly labelled Boltzmann distribution curve, explain why the rate of the reaction decreases when the temperature of the reaction decreases. [2]
			 $T_1 < T_2$ At lower temperature, kinetic energy of molecules decreases, less molecules have energy greater than or equal to activation energy. Frequency of effective collision decreases.
	(c)	0.450 g of U was reacted completely with excess hot aqueous sodium hydroxide. The reaction mixture was cooled and acidified with excess HNO_3 . Calculate the mass of silver chloride formed when an excess of $\text{AgNO}_3(\text{aq})$ was added. [2]	
		Amount of U = $0.450 / 175 = 0.002571 \text{ mol}$ Amount of AgCl = 0.002571 mol Mass of AgCl = $0.002571 \times (108 + 35.5) = 0.369 \text{ g}$	
	(d)	Compound V can be formed from compound U in 3 steps.  compound V Propose a 3-step synthesis of V from U, indicating clearly all reagents and conditions used. Draw the structures of all intermediates. [5]	

		 ethanolic KCN heat under reflux LiAlH₄ in dry ether compound V ← C₆H₅COCl
(e)	Compound W is an isomer of U .	 compound W When W is boiled with aqueous sodium hydroxide, it immediately loses water to form an organic compound X which gives a yellow precipitate with a medicinal smell when reacted with warm iodine in KOH(aq). Suggest the structure of X and write a balanced chemical equation for the reaction of X with warm iodine in KOH(aq). [2]
		
		[Total: 20]

4	(a)	Boron is a metalloid chemical element in Group III. However due to its smaller size compared to other Group III elements, its charge over mass ratio is closer to that of silicon. Hence it resembles silicon in many reactions.
	(i)	Predict the pH of the solution when BCl ₃ is added into water. Hence write an equation for the reaction. [2]
		pH 2 (accept between 1 to 2) BCl₃ + 3H₂O → B(OH)₃ + 3HCl Also accept: 2BCl₃ + 3H₂O → B₂O₃ + 6HCl

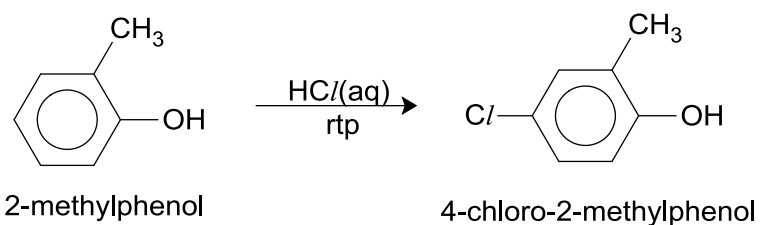
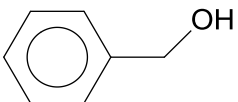
		(ii)	Explain why CCl_4 does not undergo the same reaction as BCl_3 when it is added to water. [1]																								
			B in BCl_3 has energetically accessible empty orbital to accept lone pair from O of H_2O but C in CCl_4 do not.																								
		(iii)	The oxide of boron reacts with NaOH the same way SiO_2 reacts with NaOH . One of the products of the reaction is Na_3BO_3 . Propose a chemical equation for the reaction between the oxide of boron and NaOH . [1]																								
			$\text{B}_2\text{O}_3 + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{BO}_3 + 3\text{H}_2\text{O}$																								
	(b)	The following equilibrium exists when $\text{BCl}_3(\text{g})$ is mixed with $\text{NH}_3(\text{g})$. $\text{BCl}_3(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{Cl}_3\text{BNH}_3(\text{s})$																									
		(i)	Draw a dot-and-cross diagram of the Cl_3BNH_3 molecule including its co-ordinate (dative covalent) bonds. [1]																								
		(ii)	Suggest the shape and the bond angle of the BCl_3 molecule. [1]																								
			trigonal planar 120°																								
		(iii)	Predict the effect of decreasing the temperature on the above equilibrium. Explain your answer. [3]																								
			Reaction is exothermic since it involves formation of dative bonds By LCP, position of equilibrium will shift to the right This is to increase the temperature of the system by favouring the exothermic reaction.																								
		(iv)	At a total initial pressure of 3 atm, a 1 : 2 mixture of BCl_3 and NH_3 was allowed to reach equilibrium at 60°C . It was found that the equilibrium partial pressure of BCl_3 was 0.68 atm. Determine the value of the equilibrium constant, K_p , for this reaction at 60°C , stating its units. [2]																								
			<table><tr><td></td><td>$\text{BCl}_3(\text{g})$</td><td>+</td><td>$\text{NH}_3(\text{g})$</td><td>$\rightleftharpoons$</td><td>$\text{Cl}_3\text{BNH}_3(\text{s})$</td></tr><tr><td>Initial partial pressure</td><td>1</td><td></td><td>2</td><td></td><td>0</td></tr><tr><td>Change / atm</td><td>-0.32</td><td></td><td>-0.32</td><td></td><td>+0.32</td></tr><tr><td>Eqm partial pressure</td><td>0.68</td><td></td><td>1.68</td><td></td><td>0.32</td></tr></table> $K_p = \frac{1}{(0.68)(1.68)} = 0.875 \text{ atm}^{-2}$		$\text{BCl}_3(\text{g})$	+	$\text{NH}_3(\text{g})$	$\rightleftharpoons$	$\text{Cl}_3\text{BNH}_3(\text{s})$	Initial partial pressure	1		2		0	Change / atm	-0.32		-0.32		+0.32	Eqm partial pressure	0.68		1.68		0.32
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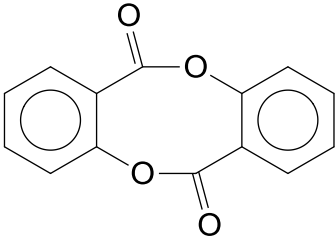
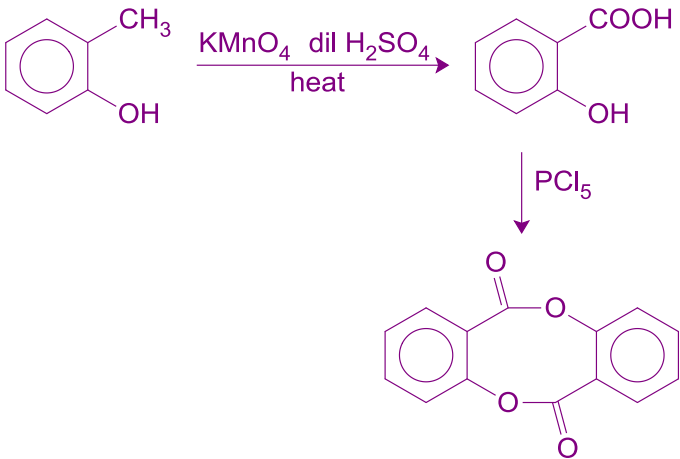
		(c)	Keratin is a fibrous protein that acts as the key structural component of hair. The amino acid content of keratin in hair of human varies slightly with ethnicity. The hair sample of an Asian was analysed. Eight of the amino acids in a keratin molecule present in the hair are listed below.																											
			<table><tr><th>Amino acid</th><th>Formula of side chain (R in RCH(NH₂)COOH)</th><th>Number of amino acid residues per molecule of keratin</th></tr><tr><td>cysteine</td><td>-CH₂SH</td><td>1200</td></tr><tr><td>glutamic acid</td><td>-CH₂CH₂COOH</td><td>1026</td></tr><tr><td>serine</td><td>-CH₂OH</td><td>990</td></tr><tr><td>threonine</td><td>-CH(OH)CH₃</td><td>572</td></tr><tr><td>leucine</td><td>-CH₂CH(CH₃)₂</td><td>520</td></tr><tr><td>aspartic acid</td><td>-CH₂COOH</td><td>478</td></tr><tr><td>glycine</td><td>-H</td><td>464</td></tr><tr><td>valine</td><td>-CH(CH₃)₂</td><td>456</td></tr></table>	Amino acid	Formula of side chain (R in RCH(NH ₂)COOH)	Number of amino acid residues per molecule of keratin	cysteine	-CH ₂ SH	1200	glutamic acid	-CH ₂ CH ₂ COOH	1026	serine	-CH ₂ OH	990	threonine	-CH(OH)CH ₃	572	leucine	-CH ₂ CH(CH ₃) ₂	520	aspartic acid	-CH ₂ COOH	478	glycine	-H	464	valine	-CH(CH ₃) ₂	456
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valine	-CH(CH ₃) ₂	456																												
		(i)	Use any three of the above amino acids to construct the displayed formula of a possible section of the protein chain of keratin. [2]																											
			 or any other combination																											
		(ii)	Describe how a polypeptide chain of keratin is held in the shape of an α-helix. [2]																											
			The α-helix is held in place via <u>hydrogen bonds</u> formed <u>between O of -C=O of a peptide and H of -NH of another peptide</u>.																											
		(iii)	The cysteine residues in the keratin molecule can form <i>disulfide bridges</i>. Illustrate this process by means of a balanced equation. Assuming all the disulfide bridges are intramolecular, what is the maximum number of bridges which could be formed within each keratin molecule? [2]																											
			2 -CH₂SH → -CH₂S-SCH₂- + 2H 600																											

		(iv)	Apart from the disulfide bridges mentioned in (c)(iii), describe, by means of diagrams, two other types of side-chain interaction, using suitable pairs of amino acids from the table above. [2]
			
		(v)	Glutamic acid has three pK_a values: 2.1, 4.1 and 9.5. Suggest the structure of the major species present in solutions of glutamic acid at pH 7. [1]
			
			[Total: 20]

5	Fluorine is a highly toxic pale yellow diatomic gas under standard conditions. As the most electronegative element, it is highly reactive. Hydrogen fluoride is also a highly toxic gas which forms corrosive hydrofluoric acid upon contact with water.
(a)	State and explain which gas, fluorine or hydrogen fluoride, displays greater deviation from ideal gas behaviour. [2]
	Hydrogen fluoride is held by hydrogen bonds and fluorine is held by d-d. Hydrogen fluoride has stronger intermolecular forces of attraction hence has greater deviation from ideal gas behaviour.
(b)	Fluorine reacts with hydrogen to form hydrogen fluoride. Write an equation with state symbols for the reaction and describe how you would expect the reaction of hydrogen with fluorine to differ from that of hydrogen with chlorine. [2]
	$H_2(g) + F_2(g) \rightarrow 2HF(g)$

		Fluorine reacts explosively and more vigorously with hydrogen compared to chlorine with hydrogen.
	(c)	Hydrofluoric acid is a weak acid. It forms a buffer solution with salts containing its conjugate base. Calculate the mass of solid sodium fluoride required to be added into a 250 cm³ solution of 0.00420 mol dm⁻³ of HF to form a buffer solution of pH 5.6. [K_a of HF = 7.20 × 10⁻⁴ mol dm⁻³] [2]
		pH = pK_a + lg ([salt]/[acid]) 5.6 = -lg(7.20 × 10⁻⁴) + lg ([NaF]/0.0042) [NaF] = 1.204 mol dm⁻³ mass of NaF = 1.204 × (250/1000) × (23.0 + 19.0) = 12.6 g
	(d)	Hydrofluoric acid is a poison with greater hazards than strong acids even though it is a weak acid. It can react with calcium in the blood leading to hypocalcemia and potentially causing death through cardiac arrhythmia. This is due to the formation of sparingly soluble calcium fluoride in the body.
	(i)	The solubility of calcium fluoride in water is 2.707 × 10⁻⁴ mol dm⁻³. Calculate the solubility of calcium fluoride in a solution of 0.00200 mol dm⁻³ of aqueous NaF. [2]
		CaF₂(s) ⇌ Ca²⁺(aq) + 2F⁻(aq) K_{sp} = [Ca²⁺][F⁻]² = (2.707 × 10⁻⁴)(2 × 2.707 × 10⁻⁴)² = 7.93 × 10⁻¹¹ mol³ dm⁻⁹ 7.93 × 10⁻¹¹ = y × (2y + 0.002)² ≈ y × (0.002)² y = 1.98 × 10⁻⁵ mol dm⁻³
	(ii)	Explain briefly how the presence of NaF affects the solubility of calcium fluoride. [1]
		CaF₂(s) ⇌ Ca²⁺(aq) + 2F⁻(aq) The presence of NaF increases [F⁻], hence by LCP shifting the equilibrium to the left.
	(e)	HCl is a reagent often used in organic reactions.
	(i)	For each of the following types of reaction, write a balanced equation for a reaction involving HCl as a reagent or as a catalyst. You may use any organic compound as the starting material for each reaction. [3]
		I Hydrolysis
		any correct equation showing hydrolysis of ester, amide or nitrile
		II Neutralisation
		any correct equation showing acid-base reaction of amine or carboxylate salt

			III	Addition
				any correct equation showing addition equation of alkene forming alcohol (must balance equation with water)
		(ii)	A student proposed the following reaction for the conversion of 2-methylphenol to 4-chloro-2-methylphenol using aqueous hydrochloric acid as the reagent.  2-methylphenol $\xrightarrow[\text{rtp}]{\text{HCl(aq)}}$ 4-chloro-2-methylphenol Explain why the reaction he proposed is not likely to work. Hence suggest the correct reagent and conditions for the conversion. [3]	
			The reaction involves electrophilic substitution of benzene. Hence a electrophile Cl^+ is required for the reaction However in HCl, since Cl is more electronegative, Cl^+ is not likely to be formed. Cl_2 in CCl_4 at room temperature	
		(iii)	Suggest a simple chemical test to distinguish between 2-methylphenol and phenylmethanol. State clearly the reagent and conditions used as well as the observations expected. [2]  phenylmethanol	
			$\text{K}_2\text{Cr}_2\text{O}_7$ in dilute H_2SO_4, heat orange solution turns green for phenylmethanol orange solution remains orange for 2-methylphenol OR $\text{Br}_2(\text{aq})$; orange solution decolourises for 2-methylphenol, forming white ppt orange solution remains orange for phenylmethanol, no ppt formed OR neutral FeCl_3 ; violet colouration formed for 2-methylphenol no violet colouration for phenylmethanol	

		(iv)	Compound Z can be formed from 2-methylphenol in two steps.  compound Z Propose a two-step synthesis of Z from 2-methylphenol, stating the reagents and conditions for each step and showing the structure of the intermediate. Your synthesis should involve 2-methylphenol as the only organic reactant. [3]
			
			[Total: 20]

Name: _____ Class: 15S _____ Reg Number: _____



MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9647/01**Paper 1 Multiple-Choice Questions****23 September 2016****1 hour**

Additional Materials: *Data Booklet*
 OMR Answer Sheet

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

There are **forty** questions in this section. Answer **all** questions. For each question, there are four possible answers labelled **A, B, C** and **D**. Choose the **one** you consider correct and record your choice in soft pencil on the OMR answer sheet.

Read very carefully the instructions on the OMR answer sheet.

You are advised to fill in the OMR Answer Sheet as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet.

Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the **OMR sheet**, please follow the given examples:

If your register number is **1**, then shade **01** in the index number column.

If your register number is **21**, then shade **21** in the index number column.

This document consists of **23** printed pages

Answer all questions in this section.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1** Use of the Data Booklet is relevant to this question.

Sodium percarbonate, $(\text{Na}_2\text{CO}_3)_x \cdot y(\text{H}_2\text{O}_2)$, is an oxidising agent in some home and laundry cleaning products.

20.0 cm³ of 0.0500 mol dm⁻³ sodium percarbonate releases 48.0 cm³ of carbon dioxide at room conditions on acidification.

An identical sample, on titration with 0.0500 mol dm⁻³ K₂Cr₂O₇, requires 20.0 cm³ before the first green colour appears. K₂Cr₂O₇ reacts with H₂O₂ in the mole ratio of 1 : 3.

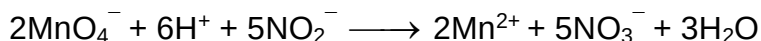
What is the ratio $\frac{y}{x}$?

- A** $\frac{1}{3}$ **B** $\frac{2}{3}$ **C** $\frac{3}{2}$ **D** $\frac{3}{1}$

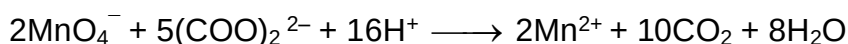
- 2** Magnesium nitrate(V), Mg(NO₃)₂ decomposes on heating to form magnesium oxide, nitrogen dioxide and oxygen, while sodium nitrate(V), NaNO₃ decomposes to form NaNO₂ and oxygen only.



A mixture of magnesium nitrate(V) and sodium nitrate(V) was heated until no more gases were evolved. The water soluble part of the residue was used to prepare 1.00 dm³ of solution. 10.00 cm³ of this solution was reacted with 30.00 cm³ of 0.0200 mol dm⁻³ of acidified potassium manganate(VII) solution.



The excess potassium manganate(VII) solution required 10.00 cm³ of 0.0500 mol dm⁻³ ethanedioic acid solution for complete reaction



What is the mass of sodium nitrate(V) in the mixture?

Given M_r of NaNO₃ = 85.0

- A** 0.85 g **B** 1.36 g **C** 4.25 g **D** 8.50 g

- 3** *Use of the Data Booklet is relevant to this question.*

Dinitrogen tetroxide, N_2O_4 , has a melting point of $-11\text{ }^\circ\text{C}$ and a boiling point of $21\text{ }^\circ\text{C}$.

A sample of 18.4 g of $\text{N}_2\text{O}_4\text{ (s)}$ is placed in a 24 dm^3 vessel under an atmosphere of helium gas chilled to $-20\text{ }^\circ\text{C}$ at a pressure of 1.0 atm . When the vessel is warmed to $25\text{ }^\circ\text{C}$ and the contents are allowed to reach equilibrium, 40% of the $\text{N}_2\text{O}_4\text{ (g)}$ has dissociated into $\text{NO}_2\text{ (g)}$.

What is the total pressure of the gases in the vessel at $25\text{ }^\circ\text{C}$?

- A** 0.28 atm **B** 1.28 atm **C** 1.38 atm **D** 1.46 atm

- 4** *Use of the Data Booklet is relevant to this question.*

The ion X^{4+} contains 46 electrons and 69 neutrons.

Which of the following statements about X^{4+} or X^{2+} is correct?

- A** X^{4+} is deflected to approximately twice the extent as Rb^+ when subjected to an electric field.
- B** X^{4+} has the same electronic configuration as Sr^{2+} .
- C** X^{2+} undergoes hydration in water to a greater extent than X^{4+} .
- D** X^{2+} can be oxidised by Fe^{3+} .

- 5** *Use of the Data Booklet is relevant to this question.*

Which particle contains a single unpaired electron?

- A** a molecule of N_2O
- B** one of the particles formed after the heterolytic fission of a H-Br molecule
- C** the vanadium ion in VO_2
- D** the chromium ion in Cr_2O_3

- 6 Use of the Data Booklet is relevant to this question.

In which of the following pairs of compounds would the first compound have a lower melting point than the second compound?

- A $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ and $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$
B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$
C GaF_3 , GaCl_3
D Na_2S , MgF_2

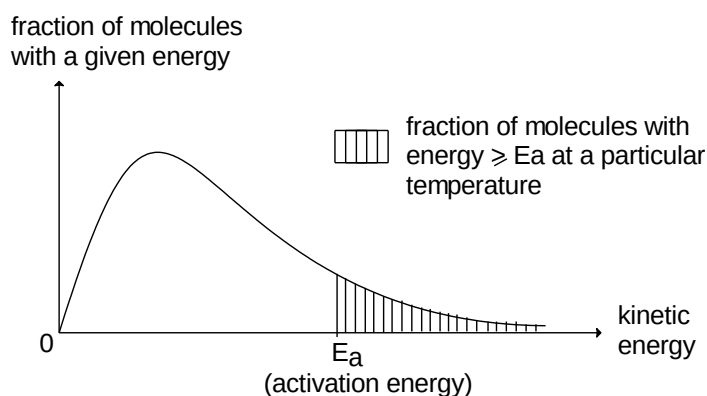
- 7 Compound X has the following properties.

- It is very hard.
- It is a lubricant.
- It can conduct electricity in the solid state.

What is the most likely structure of compound X?

- A simple molecular
B giant molecular
C giant metallic
D giant ionic

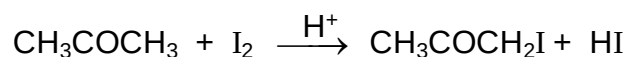
- 8 The *Maxwell–Boltzmann* distribution curve shown below is for a chemical reaction in living systems.



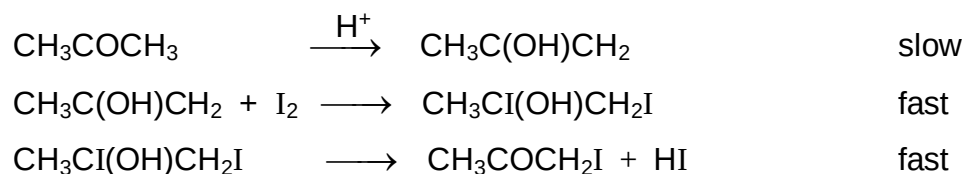
Which statement is **not** true?

- A The total area under the curve is 1.
B The activation energy will decrease with a decrease in temperature.
C When temperature is increased, the peak of the curve becomes lower.
D The shaded area of the curve will decrease when enzymes are denatured.

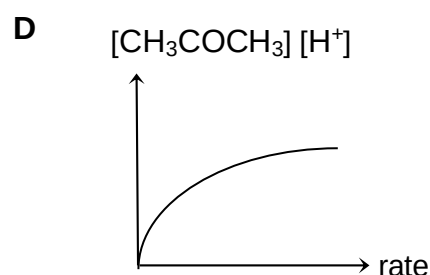
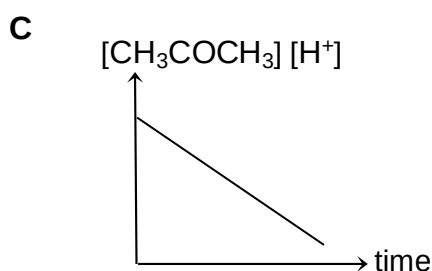
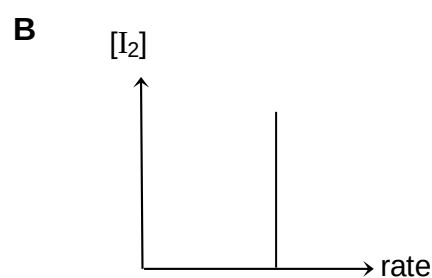
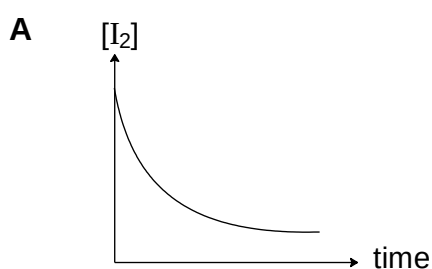
- 9 Propanone reacts with iodine in the presence of an acid:



The mechanism involves the following steps.



Which graph would be obtained?



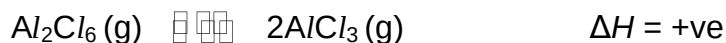
- 10 The following data was obtained from the studies of the reaction between O_2 and NO in a vessel at constant temperature.

Experiment	1	2	3
Initial total pressure of O_2 and NO / atm	1.00	1.30	1.80
Initial partial pressure of O_2 / atm	0.60	0.90	1.20
Initial rate of reaction/ atm s^{-1}	1.08	1.62	4.86

Which of the following statements is correct regarding the above system?

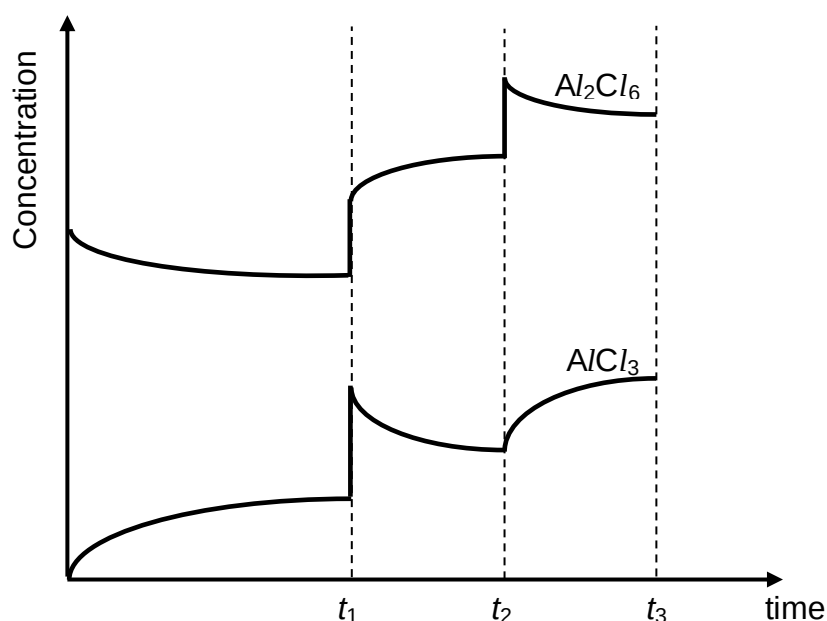
- A** The order of reaction with respect to O_2 is zero.
B The rate constant k has units of $\text{atm}^{-1} \text{s}^{-1}$.
C The rate equation is $\text{rate} = k [\text{NO}][\text{O}_2]^2$.
D The overall order of the reaction is three.

- 11** Aluminium chloride exists in two different forms in the vapour state. When some Al_2Cl_6 was added into a reaction vessel, the following equilibrium is slowly set up.



At different times during the experiment, changes were made to the conditions in the reaction vessel. At each time, there was only one change made to the conditions in the reaction vessel.

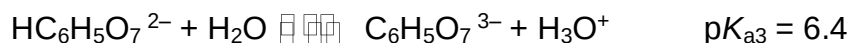
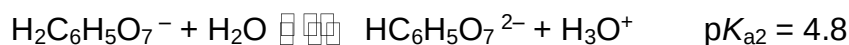
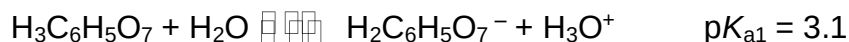
The change in the concentrations in the mixture with time is shown in the graph below.



Which conclusion can be drawn from the graph?

- A** At t_1 , the pressure of the system was increased by increasing the volume.
- B** At t_2 , a catalyst was added to the system.
- C** The temperature of the mixture at t_2 was higher than that at t_1 min.
- D** The equilibrium constant, K_p , remains the same at t_1 and t_3 .

- 12** Citrate buffers are commonly used to control pH in household cleaners and pharmaceuticals.



A citrate buffer with pH 5.1 was prepared by dissolving solid $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ and $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$. The total sodium concentration of the prepared buffer was 1.0 mol dm^{-3} .

What are the concentrations of $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ and $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$ in this buffer?

	$[\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7] / \text{mol dm}^{-3}$	$[\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7] / \text{mol dm}^{-3}$
A	0.10	0.20
B	0.20	0.40
C	0.20	0.10
D	0.40	0.30

- 13** Use of the Data Booklet is relevant to this question.

Excess aqueous $(\text{COOH})_2$ was added to an acidified solution of potassium dichromate(VI) in a conical flask. Effervescence was observed until all $(\text{COOH})_2$ had completely reacted. The resulting solution was then left to stand in air for a long time.

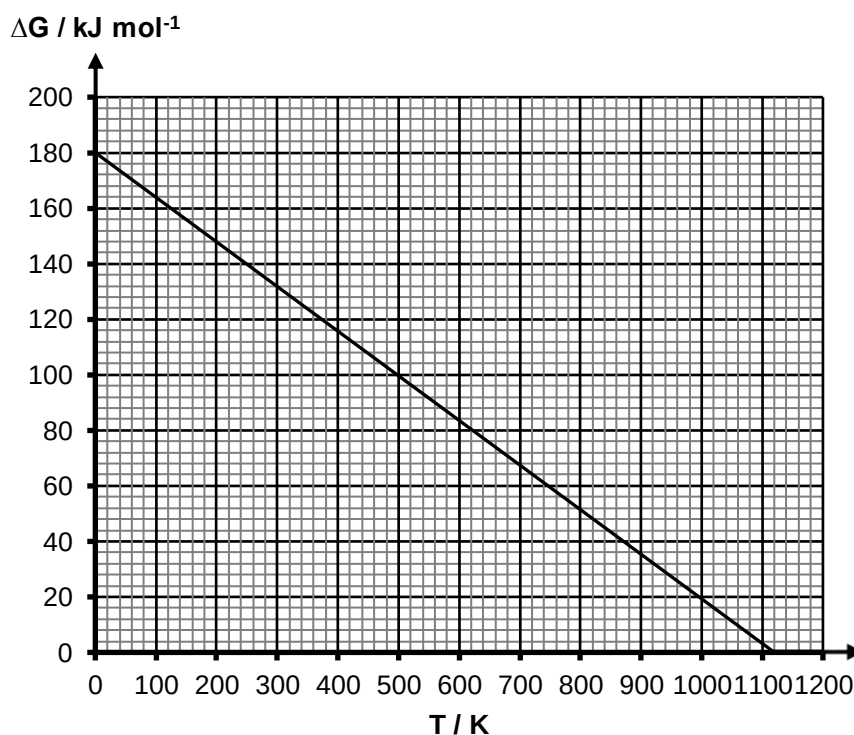


What is the colour of the final solution?

A Blue	B Green
C Yellow	D Orange

- 14** When heated, magnesium carbonate decomposes to form carbon dioxide and magnesium oxide.

A graphical plot of ΔG versus T , describing the change of the Gibbs free energy of the decomposition of magnesium carbonate with respect to temperature, is shown below.

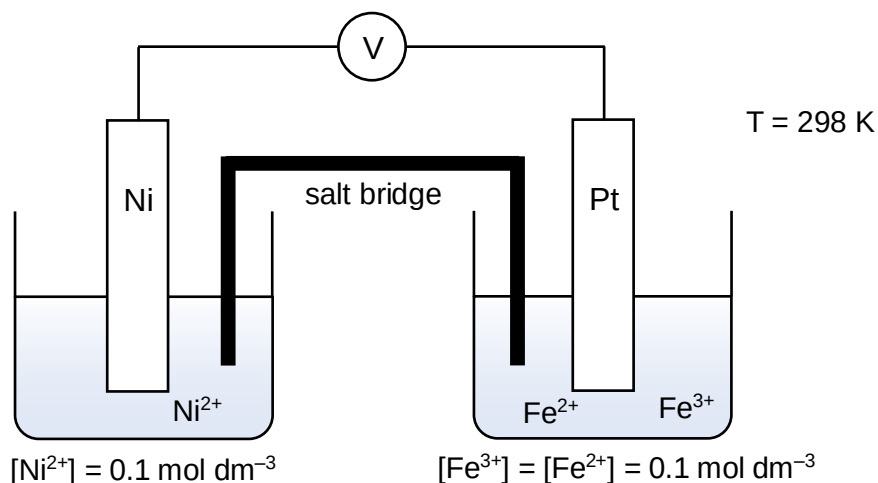


Using the information from the graph, what is the value of $\Delta S^\ominus$ for the decomposition reaction?

A $+ 6.22 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}$	B $+ 6.04 \times 10^2 \text{ J mol}^{-1} \text{ K}^{-1}$
C $+ 1.61 \times 10^2 \text{ J mol}^{-1} \text{ K}^{-1}$	D $+ 1.80 \times 10^6 \text{ J mol}^{-1} \text{ K}^{-1}$

- 15 Use of the Data Booklet is relevant to this question.

An electrochemical cell is set up as shown:



Which statement about the e.m.f. of the above cell is correct?

- A The e.m.f of the cell is +1.02 V.
 - B Addition of water to the $\text{Fe}^{3+} / \text{Fe}^{2+}$ half-cell increases the e.m.f of the cell.
 - C Increasing the mass of the nickel electrode decreases the e.m.f of the cell.
 - D Addition of excess aqueous ammonia to the $\text{Ni}^{2+} / \text{Ni}$ half-cell increases the e.m.f of the cell.
- 16 In which row of the table are all statements comparing calcium and barium as well as their hydroxides correct?

	Melting point		Flame Test		Solubility of hydroxide	
	Calcium	Barium	Calcium	Barium	$\text{Ca}(\text{OH})_2$	$\text{Ba}(\text{OH})_2$
A	higher	lower	green	red	lower	higher
B	higher	lower	red	green	lower	higher
C	higher	lower	white	green	higher	lower
D	lower	higher	red	green	higher	lower

- 17 Element **Z** is in Period 3 of the Periodic Table. The following four statements were made about the properties of element **Z** or its compounds.

Three statements are correct descriptions and one is false.

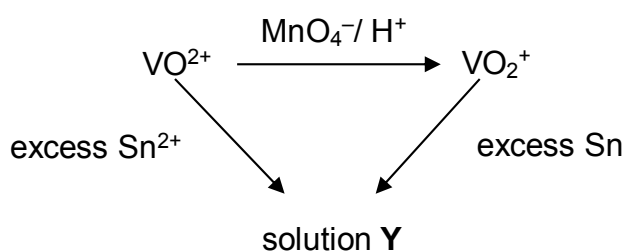
Which statement does **not** fit with the other three?

- A Element **Z** burns in oxygen with a bright white flame.
- B Element **Z** is a solid at room temperature which does not conduct electricity.
- C The oxide of element **Z** reacts with water to form a solution that turns red on addition of Universal Indicator.
- D Adding NaOH (aq) to the solution resulting from the reaction of the chloride of **Z** with water produces a white precipitate which is soluble in an excess of NaOH (aq).

- 18 *Use of the Data Booklet is relevant to this question.*

Paramagnetism is the property of being attracted to a magnetic field. Many transition compounds that contain unpaired electrons tend to be paramagnetic while those that do not contain unpaired electrons tend to be diamagnetic. Some compounds are more paramagnetic than others as they contain more unpaired electrons.

A blue solution of VO^{2+} undergoes the following reactions.

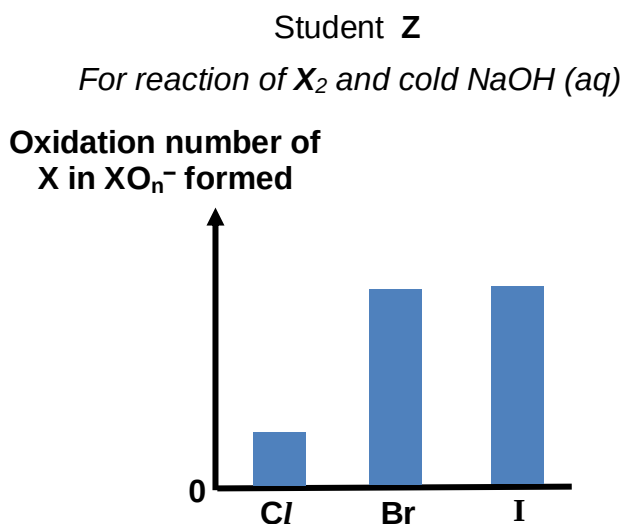
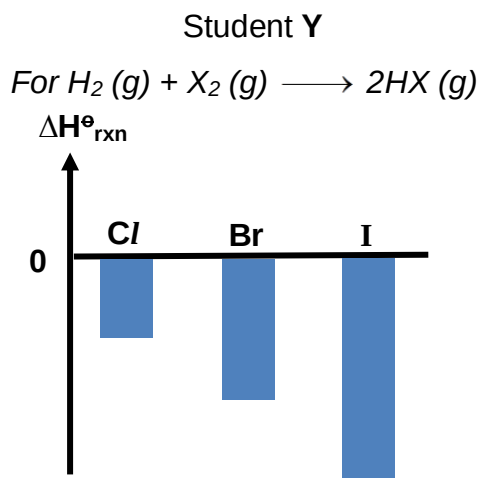
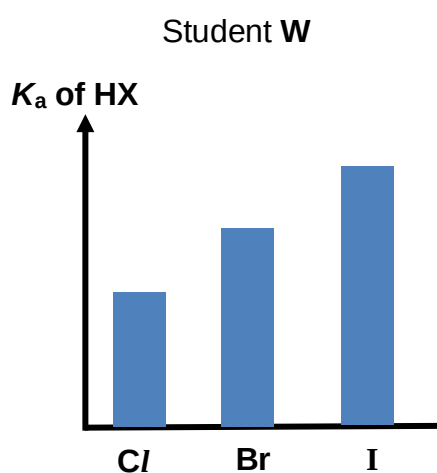


Which of the following statements is **incorrect**?

- A Solution **Y** contains $[\text{V}(\text{H}_2\text{O})_6]^{3+}$.
- B Both Sn^{2+} and Sn act as reducing agents.
- C The reacting ratio of VO^{2+} and MnO_4^- is 5 : 1.
- D VO^{2+} is diamagnetic while VO_2^+ is paramagnetic.

- 19 Three students, **W**, **Y** and **Z**, were asked to draw bar charts to represent how some properties of the halogens and their compounds differ in magnitude.

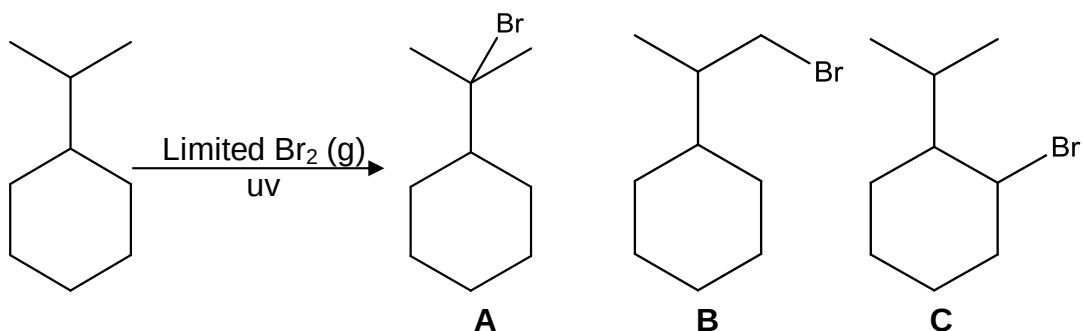
Their diagrams are shown.



Which of the students' diagrams are correct?

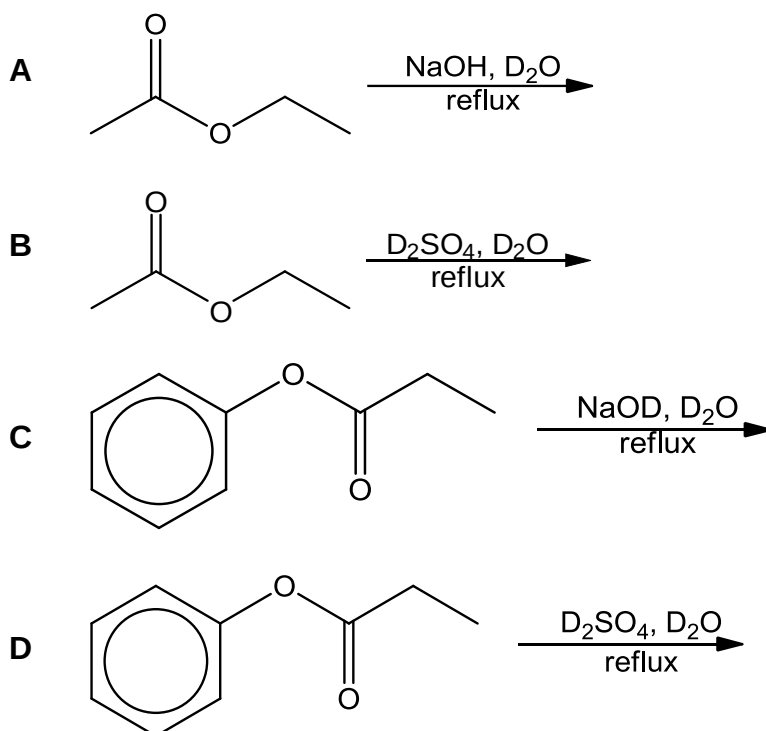
A both W and Z C both Y and Z	B both W and Y D none of the diagrams
- 20 How many isomers (both structural and stereoisomers) are there for a compound with the formula $C_4H_{10}O$ that can react with $Na(s)$?
- | | | | |
|------------|------------|------------|------------|
| A 3 | B 4 | C 5 | D 6 |
|------------|------------|------------|------------|

- 21 Isopropylcyclohexane reacts with bromine gas to form different mono-substituted products. Three of the products are shown below.

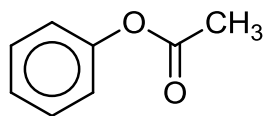


Given that the rate of abstraction of primary, secondary and tertiary hydrogen is 2 : 3 : 6 respectively, what is the expected ratio of the mono-substituted products **A** : **B** : **C** formed?

A 6 : 2 : 3 C 1 : 2 : 2	B 1 : 1 : 1 D 1 : 6 : 4
- 22 Which of the following reactions will **not** incorporate deuterium (D) into any of the organic products formed? (D = ^2_1H , an isotope of hydrogen)



- 23 Phenyl acetate is commonly used in the laboratory as a precursor for organic synthesis.

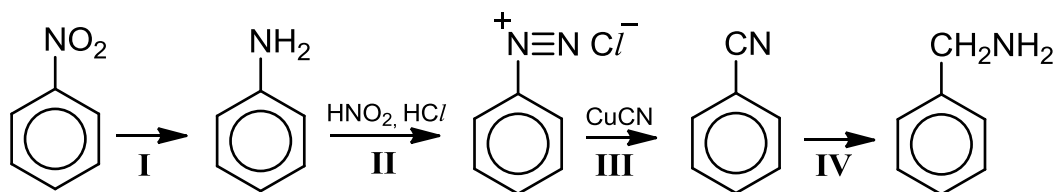


phenyl acetate

Which pair of compounds would produce phenyl acetate in high yield when reacted together?

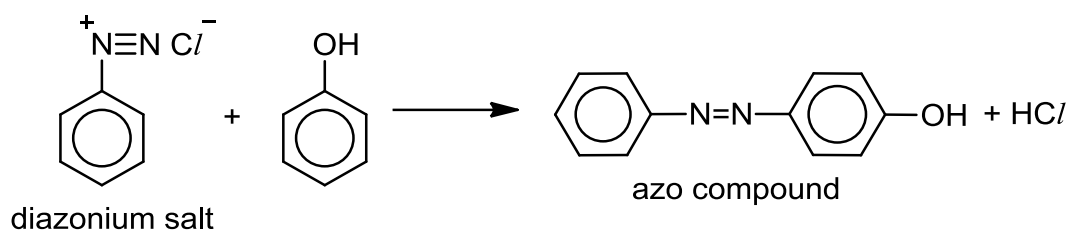
- A
- B
- C
- D

Use of the following reaction scheme is relevant for Q24 and Q25.

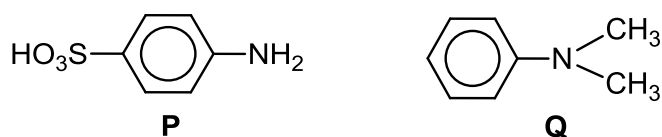


- 24 Which of the following statements is correct about the reaction scheme?
- A The reagent for stage I is LiAlH_4 .
- B Stage II is neutralisation reaction.
- C Stage III is nucleophilic substitution reaction.
- D The reagent for stage IV is hot aqueous NaOH .

- 25 Stage II is the formation of the diazonium salt, which can undergo coupling reactions with other organic compounds, such as phenol, to form azo compounds which are useful dyes.

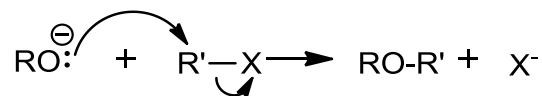


What is the structure of the azo compound formed when **P** and **Q** react together in the presence of HNO_2 and HCl ?

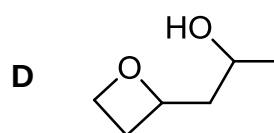
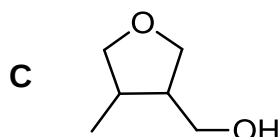
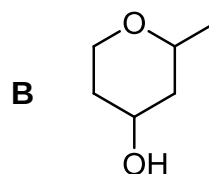
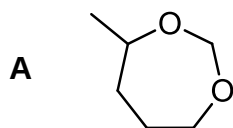
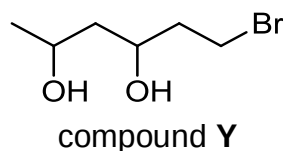


- A**
- B**
- C**
- D**

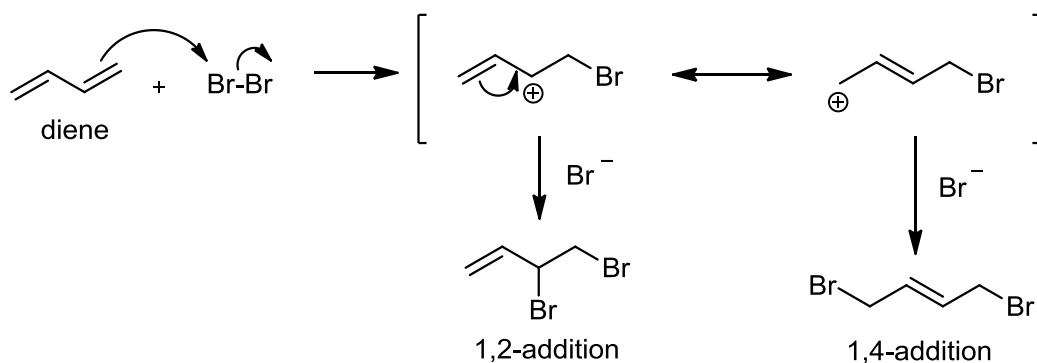
- 26 Williamson ether synthesis is a very useful reaction in the formation of ethers via the S_N2 mechanism shown below.



Which of the following compounds will be formed as a **major** product when compound **Y** undergoes Williamson ether synthesis followed by acidification?



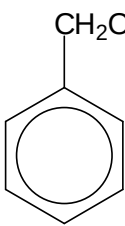
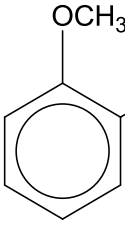
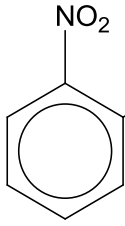
- 27 When a conjugated diene undergoes electrophilic addition with Br_2 , it forms two products through the 1,2-addition and the 1,4-addition, which is shown in the mechanism below.



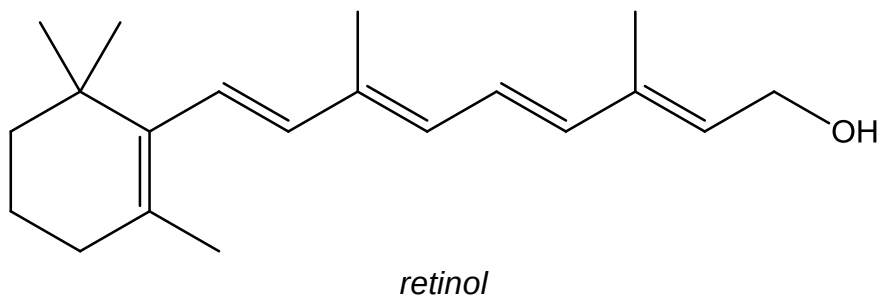
Which of the following statements is **not** correct?

- A** The overall rate law is second order.
- B** The carbocation intermediates are resonance stabilised.
- C** The 1,2-addition product formed when HCl is used is
- D** The 1,4-addition product formed when ICl is used is

- 28 Which of the following shows the given species arranged in order of decreasing K_b values?

$\text{CH}_3\text{CH(I)COO}^-$			
I	II	III	IV

- A I, III, IV, II B I, IV, III, II
 C II, III, IV, I D II, IV, III, I
- 29 The rod cells at the back of the eye contain a primary alcohol called *retinol* which is responsible for their sensitivity to light. *Retinol* is oxidised by an enzyme-catalysed reaction that keeps the double bonds intact, to *retinal*, an aldehyde.



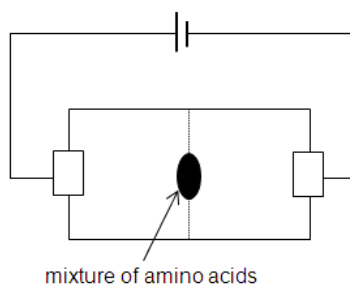
Which of the following is correct?

- A The number of stereoisomers in *retinol* is 32.
 B There are six σ bonds formed by $2sp^2-2sp^3$ overlap in a molecule of *retinol*.
 C In laboratory preparations, *retinal* can be formed from heating *retinol* under reflux with hot potassium dichromate(VI).
 D One mole of *retinol* reacts with 4 moles of hydrogen gas in the presence of palladium catalyst.

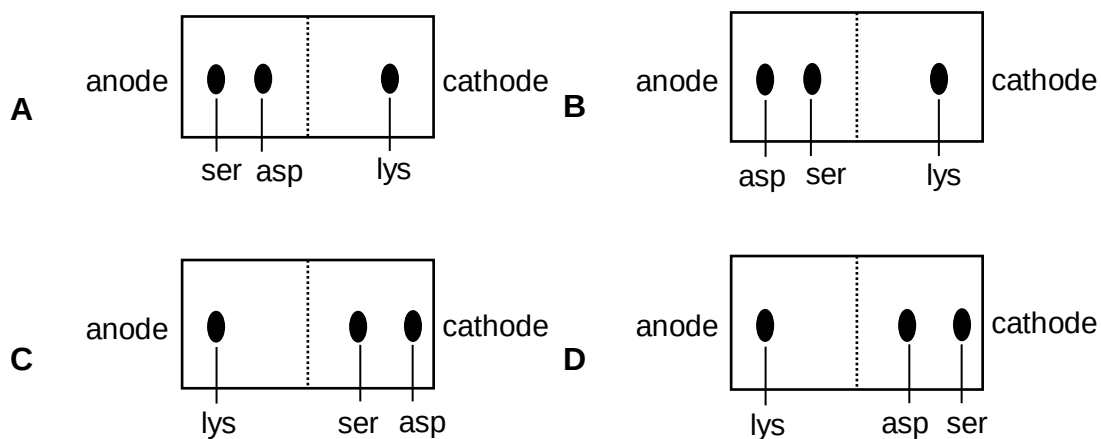
30 The table below gives some information pertaining to three amino acids.

amino acid	structure	isoelectric point
lysine (lys)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ (\text{CH}_2)_4\text{NH}_2 \end{array}$	9.6
serine (ser)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	5.7
aspartic acid (asp)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{COOH} \end{array}$	2.9

A mixture of these three amino acids can be separated by electrophoresis.



Which of the following diagrams shows the result of the separation of the amino acids mixture at pH 7.0?



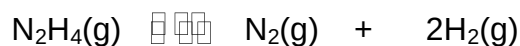
For questions 31 to 40, one or more of the three numbered statements 1 to 3 may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

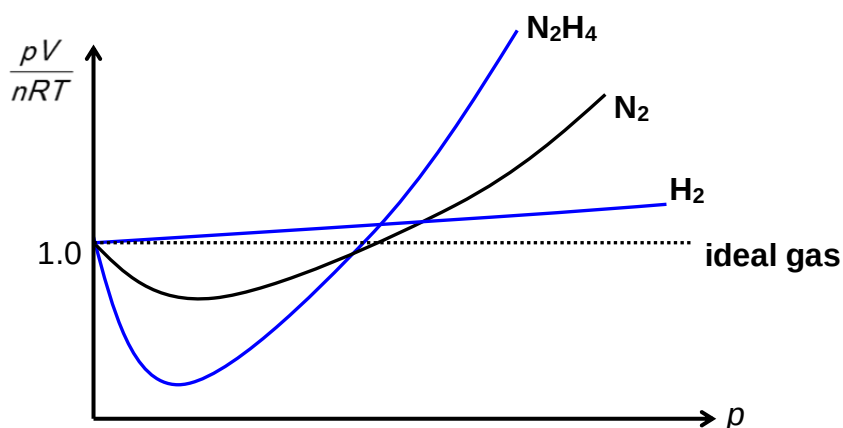
- 31** In a closed reaction vessel of 10 dm³ maintained at a temperature of 150 °C, gaseous hydrazine decomposes into nitrogen and hydrogen. The system reaches equilibrium with a total pressure of 1 atm.



The average M_r of the equilibrium gas mixture in the 10 dm³ vessel is found to be 20.

Which of the following statements are correct?

- 1** In liquid form, both reactants and products flowing from a burette remain undeflected when subjected to close vicinity to a charged rod.
- 2** The mass of the gaseous mixture inside the reaction vessel is 5.75 g.
- 3** The following graphs depicts the correct behaviour of the three gases under standard conditions.



The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 32** Metal thiocyanates have very different industrial uses. For example, calcium thiocyanate, $\text{Ca}(\text{NCS})_2$, is used as a stiffening agent of fabrics.

The following data is provided:

$$\Delta H_{\text{latt}}^{\ominus}(\text{Ca}(\text{NCS})_2) = -2118 \text{ kJ mol}^{-1}$$

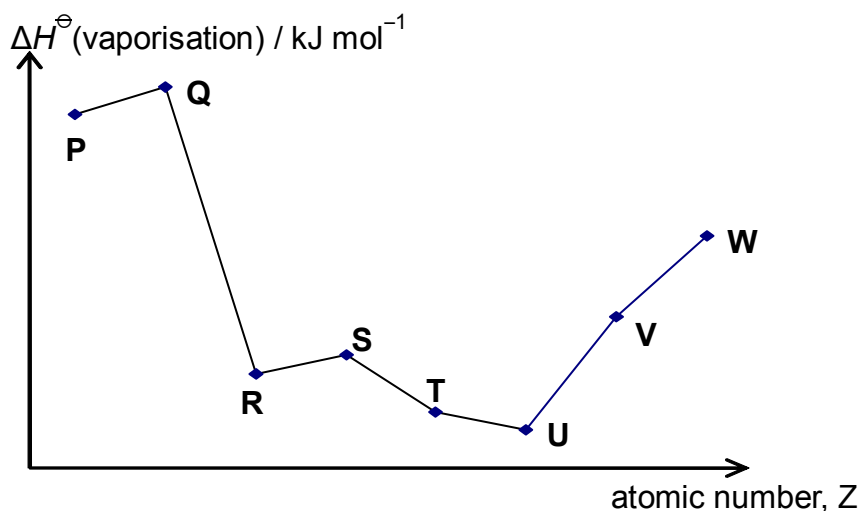
$$\Delta H_{\text{hyd}}^{\ominus}(\text{NCS}^{-}) = -310 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}^{\ominus}(\text{Ca}^{2+}) = -1577 \text{ kJ mol}^{-1}$$

Which of the following statements are correct?

- The magnitude of $\Delta H_{\text{soln}}^{\ominus}$ of $\text{Ca}(\text{NCS})_2$ is 79 kJ mol^{-1} .
- Magnitude of $\Delta H_{\text{latt}}^{\ominus}$ of $\text{Ba}(\text{NCS})_2$ is smaller than that of $\text{Ca}(\text{NCS})_2$.
- $\Delta G_{\text{soln}}^{\ominus}$ of $\text{Ca}(\text{NCS})_2$ is negative at all temperatures.

- 33** The graph below shows the variation in the standard enthalpy change of vaporisation, $\Delta H^{\ominus}(\text{vaporisation})$, for eight consecutive elements in the Periodic Table, all with atomic number, $Z \leq 20$.



Which of the following statements are correct?

- The chloride of element **Q** is acidic in aqueous solution.
- The oxide of element **R** has a higher melting point than that of element **S**.
- Electrical conductivity decreases from element **P** to **W**.

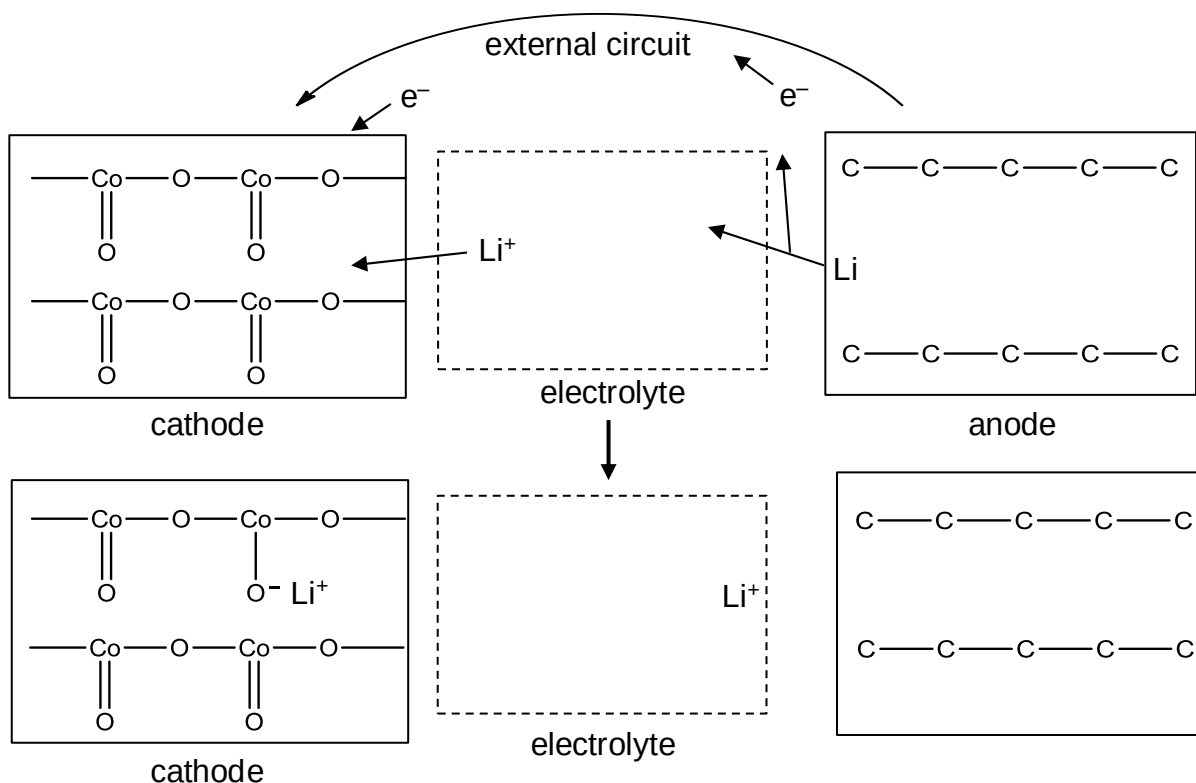
The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 34** A lithium-ion battery consists of: a cathode made from cobalt oxide, CoO_2 ; an anode made from graphite with lithium atoms inserted between the layers.

During discharge, Li atoms at the anode give up electrons to become Li^+ ions. The electrons travel round the external circuit, and are picked up by the cathode. A Li^+ ion from the electrolyte also moves to the cathode. This is illustrated in the following diagram in which C—C—C—C—C is a simplified representation of a layer of carbon atoms in graphite.



Which of the following statements are true?

- The mass of lithium metal that is deposited when a current of 3 A is passed through the battery during the charging process in 1 h 20 min is 1.03 g.
- The oxidation number of cobalt oxide cathode after discharge is +3.
- The bonding between the lithium atoms and the layers of carbon atoms is ionic in nature.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 35** A chemist allowed a halogen, X_2 , to react completely with $S_2O_3^{2-}$ (aq). This resultant acidic solution was treated with an excess of aqueous barium nitrate to produce a white precipitate which is insoluble in dilute nitric acid.

Another halogen, Y_2 , gave a different sulfur-containing product with $S_2O_3^{2-}$ (aq).

Which of the following statements are correct with regards to the chemistry described?

- 1** A possible identity for X_2 is Br_2 .
- 2** A possible identity for Y_2 is I_2 .
- 3** Y_2 is a stronger oxidising agent than X_2 .

- 36** Which statements concerning the first row transition metal ions are **incorrect**?

- 1** Addition of K_2CO_3 (aq) to $CrCl_3$ (aq) produces a green precipitate of $Cr_2(CO_3)_3$.
- 2** Addition of KI (aq) to $Fe_2(SO_4)_3$ (aq) produces a brown precipitate of FeI_3 .
- 3** Addition of $NaOH$ (aq) to K_2CrO_4 (aq) produces an orange solution of $K_2Cr_2O_7$ (aq).

- 37** A catalytic converter is part of the exhaust system of modern cars.

Which reactions occur in a catalytic converter?

- 1** $2C_xH_y + (4x + y) NO \longrightarrow 2x CO_2 + y H_2O + (2x + \frac{y}{2}) N_2$
- 2** $2CO + 2NO \longrightarrow 2CO_2 + N_2$
- 3** $CO_2 + NO \longrightarrow CO + NO_2$

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

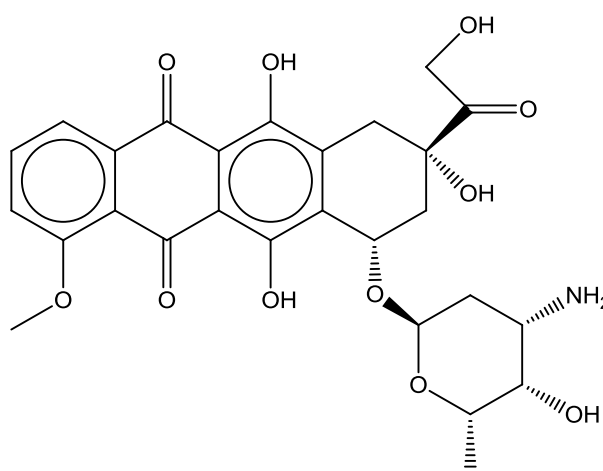
- 38** A non-cyclic organic compound has the molecular formula $C_5H_9O_2N$.

Which pair of functional groups could be present in this molecule?

- 1** one ketone group and one amide group
- 2** one ester group and one nitrile group
- 3** one carboxylic acid group and one nitrile group

- 39** *Doxorubicin* is an anti-cancer drug used to treat a wide range of cancers including blood cancers, like leukaemia and lymphoma.

[The ether group, $R-O-R'$ is inert].



doxorubicin

Which of the following statements about *doxorubicin* are true?

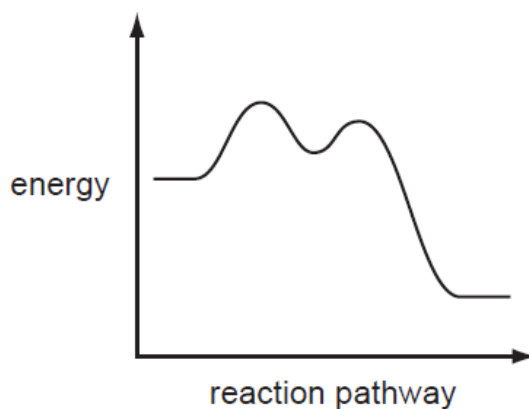
- 1** Addition of sodium boron hydride causes six atoms of hydrogen to be incorporated into the molecule.
- 2** On reacting with ethanoyl chloride, six moles of ethanoyl chloride is used up per mole of *doxorubicin*.
- 3** On reacting with thionyl chloride, five moles of thionyl chloride is used up per mole of *doxorubicin*.

The responses **A** to **D** should be selected on the basis of

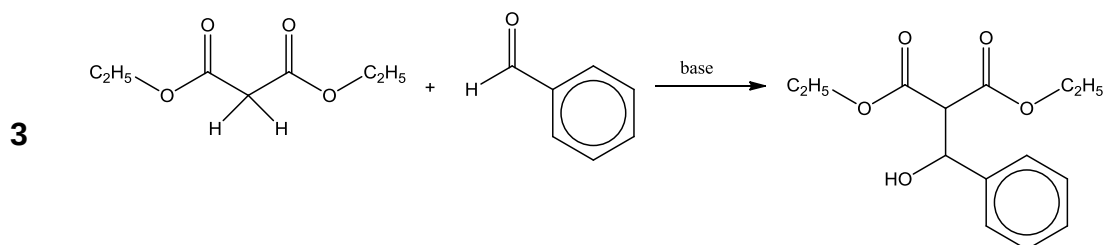
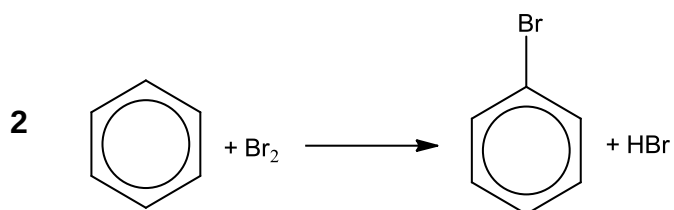
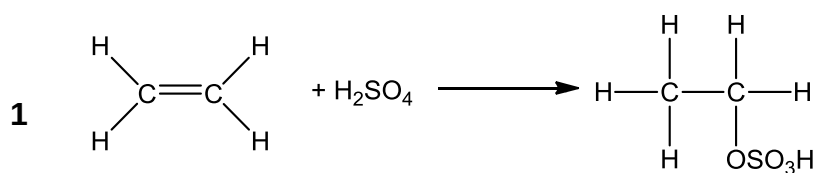
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

40 A reaction pathway diagram is shown.



Which organic reactions could have such a profile?



END OF PAPER

Name: _____ **Class: 15S** _____ **Reg Number:** _____



MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9647/02

Paper 2 Structured Questions

19 September 2016

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [] at the end of each question or part question.

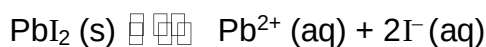
You are reminded of the need for good English and clear presentation in your answers.

Examiner's Use		
Paper 1	MCQ	/ 40
Paper 2	Q1	/ 12
	Q2	/ 17
	Q3	/ 15
	Q4	/ 9
	Q5	/ 7
	Q6	/ 12
	Total	/ 72
Paper 3	/ 80	
Total	/ 192	
Percentage		
Grade		

This document consists of **28** printed pages

1 Planning (P)

Lead iodide, PbI_2 , is a sparingly soluble salt.



One method of determining the relative solubility and an approximate value of the solubility product of the salt, K_{sp} , would be through direct observation. Two standard solutions (one of a soluble lead(II) salt, and the other of a soluble iodide salt) in different proportions are mixed and allowed to stand and reach an equilibrium. In some mixtures, the ionic product of the particular solution exceeds the K_{sp} value and precipitation of PbI_2 crystals will occur. In other mixtures, the final concentrations of lead and iodide ions will be such that precipitation does not occur.

The experimental ionic product can be determined for each solution. In the experiment, the value of K_{sp} lies between the ionic product values for solutions with precipitate and those values for solutions without precipitate. The value for K_{sp} can be given as:

$$\begin{array}{ccc} \text{Maximum ionic product} & & \text{Minimum ionic product} \\ \text{that does not give ppt} & < K_{\text{sp}} < & \text{that gives ppt} \end{array}$$

The value for K_{sp} can be estimated by determining the mean between the above two ionic products. In order for a more precise determination of K_{sp} , the concentration of the solution mixtures should be prepared in a manner that would result in a relatively small range of ionic products.

In the experiment, two standard solutions of lead(II) nitrate and potassium iodide are prepared and then diluted appropriately using relevant volumes of the solutions and water. To avoid localised supersaturation that brings about erroneous precipitation, water has to be mixed in first.

In order to predetermine the concentrations required, a student prepared two solutions, **A** and **B**.

Solution A contains 2.50 cm³ of 0.0100 mol dm⁻³ lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$ with 5.50 cm³ of deionised water added.

Solution B contains 2.00 cm³ of 0.0100 mol dm⁻³ potassium iodide, KI.

Mixing these above solutions (at 25°C) produced the yellow precipitate of PbI_2 . These solutions provide an ionic product which **just exceeds** the K_{sp} of PbI_2 .

- (a) Calculate the ionic product of PbI_2 in this given mixture to determine a rough estimate of the K_{sp} value of PbI_2 .

[1]

- (b) Consider the description of the precipitation experiment given in this question.

Write a plan for such a series of **four** experiments to determine a value for the K_{sp} of PbI_2 . In your plan, you should use the same total volume as described when solutions **A** and **B** are mixed.

Your plan should ensure that

- at least two of your experiments do not produce a precipitate
- the estimated range for the value of K_{sp} is relatively small. ($< 10\%$ deviation from the estimated ionic product in (a)).

You should use the quantities specified in (a) in one of your experiments.

You may assume that you are provided with

- solid lead nitrate, $\text{Pb}(\text{NO}_3)_2$
- $0.0400 \text{ mol dm}^{-3}$ aqueous potassium iodide, KI,
- deionised water,
- the equipment and materials normally found in a school or college laboratory.

Your plan should include the following.

- details, including quantities, for the preparation of a 100 cm^3 stock solution of $0.0100 \text{ mol dm}^{-3}$ of $\text{Pb}(\text{NO}_3)_2$
- details, including quantities for the preparation of a 100 cm^3 stock solution of $0.0100 \text{ mol dm}^{-3}$ of KI
- suitable format summarising appropriate quantities of solutions to be used in each experiment (for four experiments), the corresponding concentrations and calculated ionic products
- outline of all essential experimental procedures
- brief, but specific details on how the K_{sp} value can be estimated from the experiment.

[8]

[illegible]

- (c) Explain how the solubility of PbI_2 would change if PbI_2 is dissolved in a solution of hydroiodic acid, HI.

[1]

- (d) Lead(II) salts are toxic and prolonged exposure affects the mental development in children. Pb^{2+} ions can be removed from contaminated water through precipitation by adding a soluble salt solution containing the appropriate anion.

The solubility products of some sparingly soluble lead(II) salts, at 25 °C are given in the table below.

Salt	K_{sp}
PbCO_3	$7.4 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
$\text{Pb}(\text{IO}_3)_2$	$3.7 \times 10^{-13} \text{ mol}^3 \text{ dm}^{-9}$
$\text{Pb}_3(\text{PO}_4)_2$	$7.9 \times 10^{-43} \text{ mol}^5 \text{ dm}^{-15}$

Calculate the solubility of the above lead(II) salts in mol dm^{-3} at 25°C. Hence, state the most effective anion in removing Pb^{2+} from the contaminated water sample.

[2]

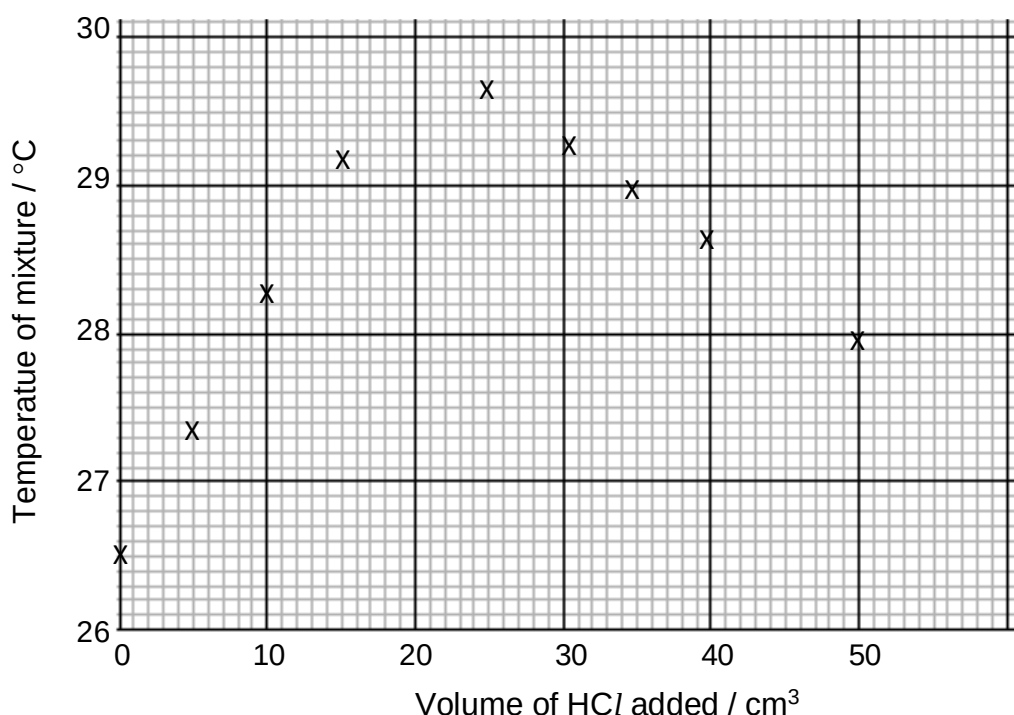
[Total: 12]

- 2 Amines are a class of compounds that are widely used in both the pharmaceutical and agricultural industry. An amine-containing drug, *Tamiflu* is an effective drug against the H1N1 strain of influenza A virus. Another amine, ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, is widely used in the production of herbicides.

(a) In order to determine the standard enthalpy change of neutralisation, 60.0 cm^3 of $0.370 \text{ mol dm}^{-3}$ aqueous ethylamine was placed in a polystyrene cup. Dilute HCl was added and after each addition, the mixture was stirred and the temperature noted.

The highest temperature reached was recorded and plotted on the graph below.

Graph of temperature of mixture against volume of HCl added



- (i) Calculate the initial pH of aqueous ethylamine in the polystyrene cup.

Base dissociation constant of ethylamine is $5.6 \times 10^{-4} \text{ mol dm}^{-3}$.

[1]

(ii) Calculate the concentration of dilute HCl used in the experiment. [1]

(iii) Calculate the enthalpy change of neutralisation for the reaction between HCl and ethylamine.

(You may assume the density of the solutions is 1.00 g cm^{-3} and their specific heat capacity is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.)

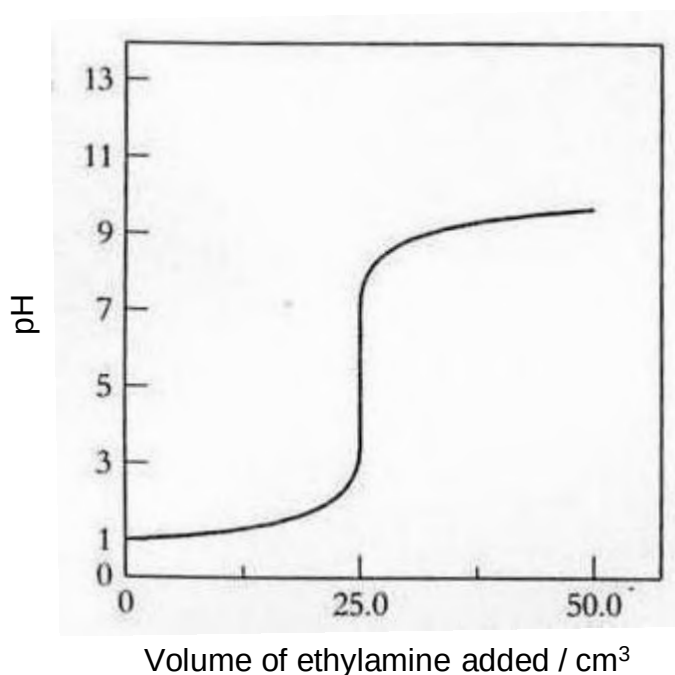
[2]

(iv) With reference to your answer in (a)(iii), explain why the temperature of the mixture was reported to be higher when the above experiment was repeated using an aliquot of aqueous potassium hydroxide of the same concentration as that of the ethylamine sample.

[1]

- (b) In another experiment, a sample of $0.640 \text{ mol dm}^{-3}$ aqueous ethylamine was added to 10.0 cm^3 dilute HNO_3 in a conical flask. The equivalence point can be detected by a distinct colour change brought about by the use of a suitable indicator.

The graph below shows the change in pH of the reaction mixture against the volume of ethylamine added.



- (i) Suggest a suitable indicator for this acid–base titration and state the colour change observed at the equivalence point.

[1]

Indicator: _____

Colour change: _____

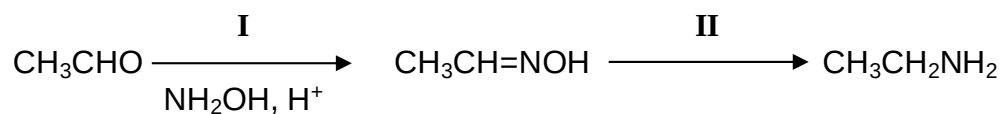
- (ii) Circle clearly on the graph, the region within which the mixture is acting as a buffer.

[1]

- (iii) Write an equation to suggest how the solution in (b) (ii) acts a buffer upon the addition of a small amount of aqueous sodium hydroxide.

[1]

- (c) An agricultural chemist synthesised ethylamine from ethanal in an industrial laboratory via a two-step procedure as shown in the scheme below.



- (i) Suggest the type of reactions for both steps and the reagents and conditions for step II.

[2]

Step	Type of reaction	Reagents and conditions
I		
II		

- (ii) Suggest a chemical test that the chemist can perform to confirm that the procedure is complete.

[1]

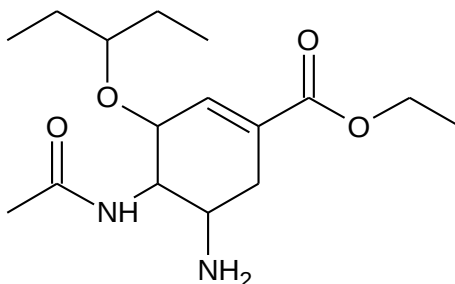
- (d) Use the following data and relevant data from the *Data Booklet* to construct an energy cycle to calculate the enthalpy change of formation of $\text{CH}_3\text{CH}_2\text{NH}_2(l)$.

Enthalpy change of vapourisation of $\text{CH}_3\text{CH}_2\text{NH}_2(l) = +29 \text{ kJ mol}^{-1}$

Enthalpy change of atomisation of $\text{C(s)} = +715 \text{ kJ mol}^{-1}$

[3]

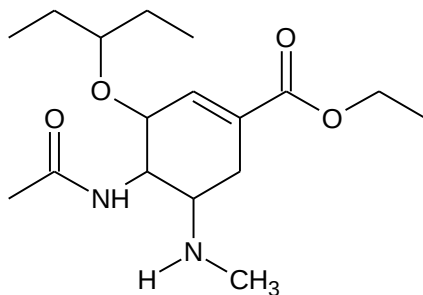
- (e) The structure of *Tamiflu* is shown below.



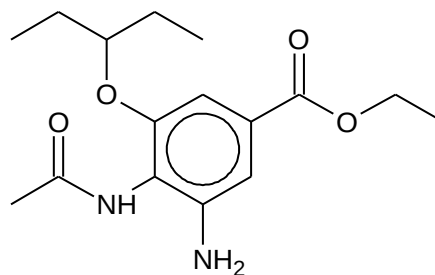
- (i) Name the two nitrogen-containing functional groups present in *Tamiflu*.

[1]

- (ii) Compound **Q** is a derivative of *Tamiflu* while compound **R** is an aromatic compound with similar functional groups as *Tamiflu*.



compound **Q**



compound **R**

Describe and explain the relative basicities of the following compounds:

- Compound **Q** and *Tamiflu*

[1]

- Compound **R** and *Tamiflu*

[1]

3 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) When potassium iodide reacts with concentrated sulfuric acid, violet vapour is observed and a pungent gas is detected.

(i) Write a chemical equation for the reaction to account for the formation of the violet vapour.

[1]

(ii) When potassium bromide reacts with concentrated sulfuric acid, different observations are made.

By quoting suitable values from the *Data Booklet*, explain the difference in the observations.

[2]

(iii) In order to prepare HBr as the only bromine-containing product from KBr, concentrated H_3PO_4 should be used instead of concentrated H_2SO_4 .

Suggest a plausible reason for this. Write a balanced equation for this reaction.

[2]

(b) Precipitates are formed when aqueous silver nitrate is added to separate tubes containing aqueous potassium chloride, aqueous potassium bromide and aqueous potassium iodide.

(i) Describe the effect of adding concentrated NH_3 to **each** of the resulting mixtures.

[1]

Tube containing KCl _____

Tube containing KBr _____

Tube containing KI _____

(ii) Provide a qualitative explanation to substantiate your answer for observations in the tube containing KI .

[2]

- (c) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 20.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions. The remaining solution was made up to 250 cm^3 with distilled water.

A 25.0 cm^3 aliquot of the resultant solution required 40.0 cm^3 of $0.010 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, for complete reaction.

Calculate the value of n .

[2]

(d) When heated in chlorine, magnesium forms magnesium chloride. Magnesium can also be heated in air to give magnesium oxide. Similarly, aluminium and zinc can be vapourised and reacted with air to form the respective oxides.

(i) Describe the reactions, if any, of magnesium chloride and magnesium oxide with water, suggesting the pH of the resulting solutions and writing equations where appropriate.

[3]

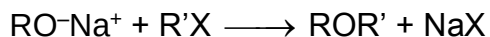
(ii) Zinc oxide has acid–base properties that are similar to aluminium oxide. Write equations for **two** reactions which demonstrate these properties of zinc oxide.

[2]

[Total: 15]

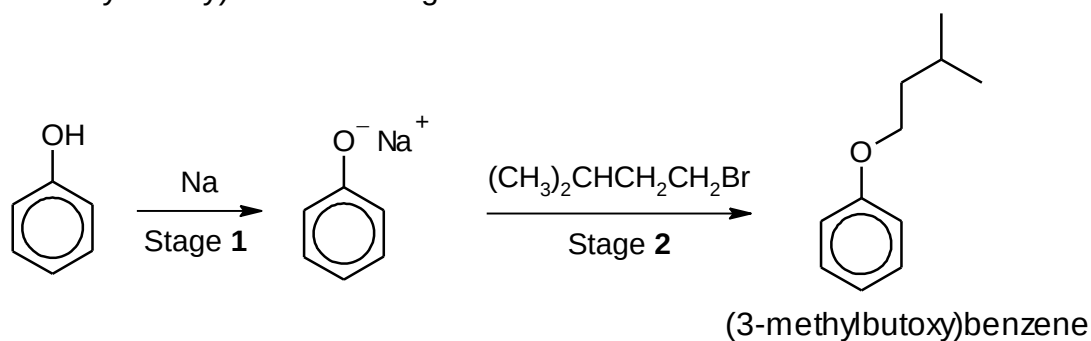
- 4 The *Williamson* reaction is widely used in the laboratory and industrial synthesis of ethers. It is the simplest and most popular method of preparing ethers.

In a typical *Williamson* reaction, an alkoxide ion is prepared *in situ* and is reacted with a halogenoalkane according to the general equation shown below.



where R,R' are alkyl groups and X is Br or Cl.

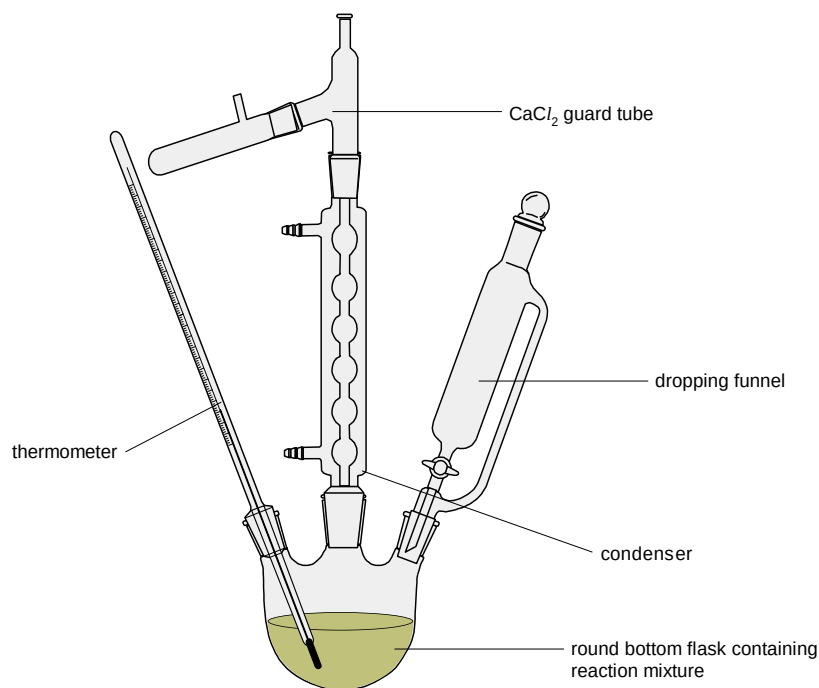
The following experimental procedure details the synthesis of (3-methylbutoxy)benzene using the *Williamson* reaction.



PROCEDURE:

Preparation of (3-methylbutoxy)benzene

- 1 2.90 g of sodium metal is added to a dry round-bottom flask equipped with a dropping funnel and a condenser. This apparatus set-up is shown below. The set-up is protected from atmospheric moisture with the use of a calcium chloride guard tube.



- 2 Prepare an ethanolic solution containing 11.8 g of phenol. Add dropwise to the reaction mixture using the dropping funnel. If the reaction becomes too vigorous, cool the flask with a cold towel until the reaction is again under control.
- 3 Transfer 20.0 cm³ of 1-bromo-3-methylbutane to the dropping funnel and add it to the flask slowly over 3 – 4 minutes.
- 4 Boil the reaction mixture gently over a water bath for 30 minutes.
- 5 Evaporate as much of the ethanol solvent as possible.

Purification of (3-methylbutoxy)benzene

- 6 Add about 20 cm³ of water to the residue in the flask and separate the organic layer using a separating funnel.
- 7 Wash the organic layer with sodium hydroxide.
- 8 Then, wash the organic layer with dilute sulfuric acid and water again.
- 9 Add anhydrous magnesium sulfate to the organic layer.
- 10 Distill the organic layer to purify (3-methylbutoxy)benzene at a suitable temperature.

Table 4: Physical Properties of the reagents and the organic product

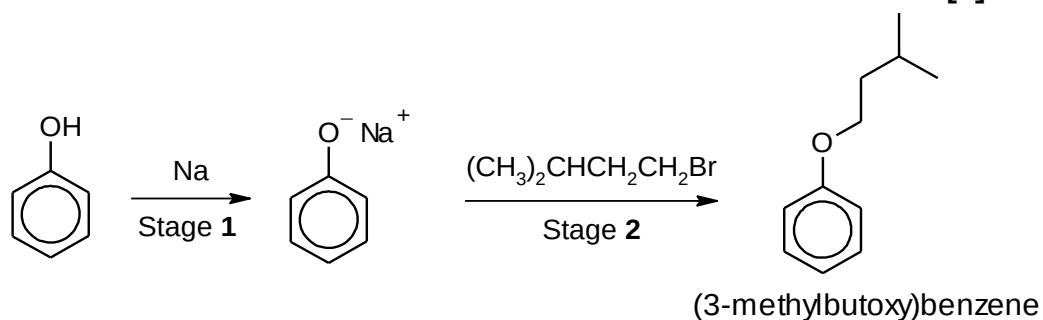
substance	formula	molar mass / g mol ⁻¹	physical state at r.t.p.	density / g cm ⁻³	solubility in water	boiling point / °C
ethanol	C ₂ H ₅ OH	46	liquid	0.789	soluble	78
phenol	C ₆ H ₅ OH	94	solid	1.07	insoluble	182
1-bromo-3-methylbutane	C ₅ H ₁₁ Br	151	liquid	1.21	insoluble	120
(3-methylbutoxy)benzene	C ₁₁ H ₁₆ O	164	liquid	0.91	insoluble	216
sodium bromide	NaBr	103	solid	3.21	soluble	–
water	H ₂ O	18	liquid	1.00	–	100

- (a) (i) Suggest why it is necessary to protect the apparatus set-up from moisture using the calcium chloride guard tube in step 1.

[1]

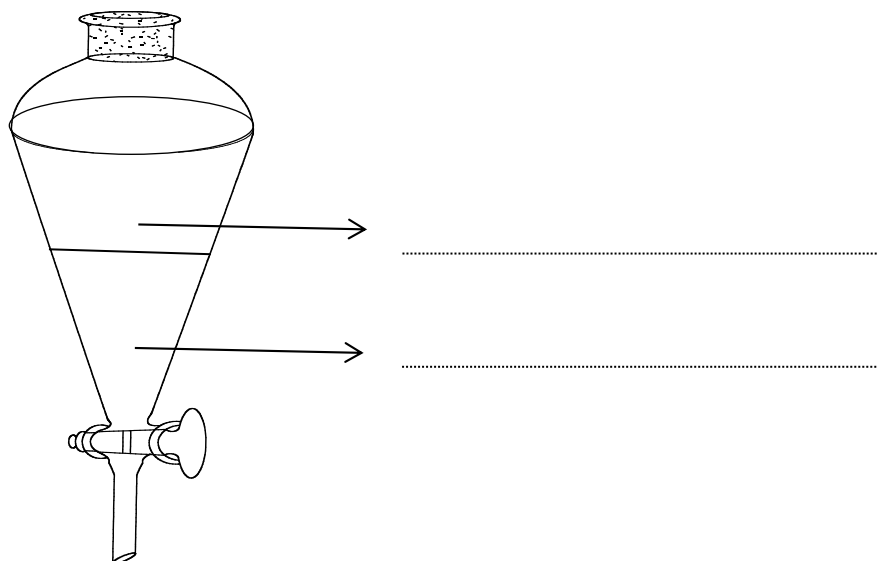
- (ii) Determine the theoretical yield (in g) of (3-methylbutoxy)benzene for this reaction. You may assume that the reaction between sodium and phenol to form phenoxide in stage 1 is complete.

[2]



- (iii) On the diagram of the separating funnel below, label the two layers that will be observed after step 6.

[1]



- (b)** Other than the crude product, the organic layer (Step **6**) also contains several impurities. These impurities comprises of unreacted reactants, by-products or products from undesired reactions.

In the purification of the crude product (Steps **6 – 9**), the impurities are removed from the crude product with each subsequent addition of chemicals.

- (i)** Suggest the impurity removed by each of the chemicals below.

[1]

1 sodium hydroxide _____

2 anhydrous magnesium sulfate _____

- (ii)** With reference to the data provided in **Table 4**, account for the observed boiling points of ethanol and the product, (3–methylbutoxy)benzene.

In your answer, you should state the predominant type of interactions present in the two compounds.

[2]

- (iii)** The final stage in the purification process is the distillation of the crude product (Step **10**).

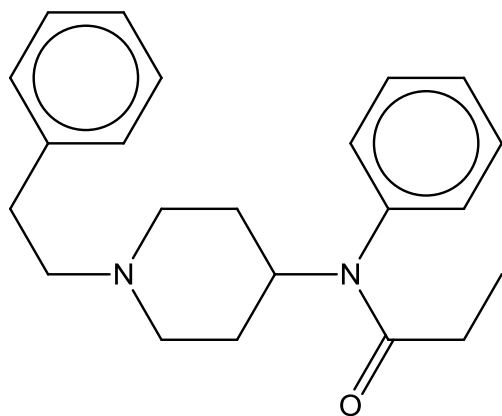
Suggest why distillation is a suitable technique to obtain a pure sample of (3-methylbutoxy)benzene. Propose a suitable range of temperature for the distillation set-up.

[2]

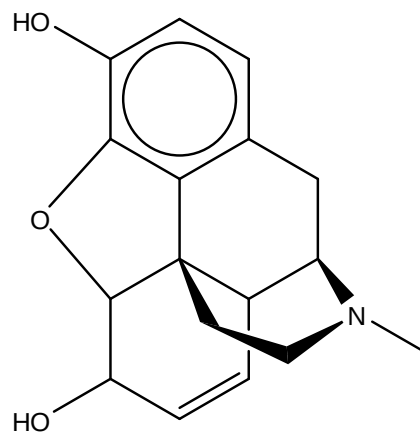
[Total: 9]

- 5 On 21st April 2016, famed American pop artiste, Prince Rogers Nelson died of an accidental overdose of the drug, *fentanyl*.

Fentanyl, an opioid analgesic was first synthesised in 1960. It was primarily used for pain relief in clinical practice. Its efficacy is about 100 times that of *morphine*.

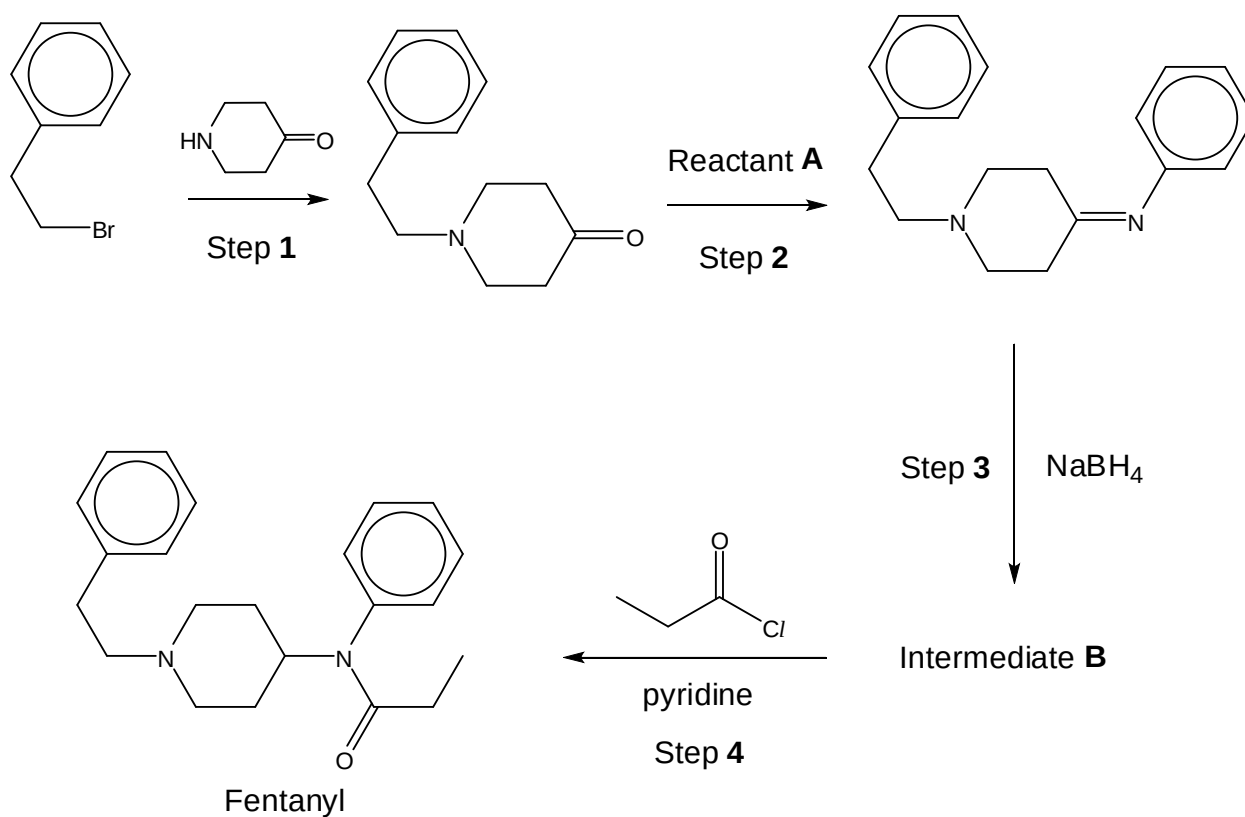


Fentanyl



Morphine

Fentanyl can be synthesised from 2-bromoethylbenzene following the reaction scheme below.



- (a)** Name and outline the mechanism for the reaction in step **1**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

- (b)** Suggest the displayed formula of reactant **A** in Step **2**.

[1]

- (c)** Propose the structure of intermediate **B**.

[1]

- (d)** Propanyl chloride is used in step 4 in the synthesis of *fentanyl*.

Explain why the use of propanoic acid as a replacement in step 4 is not suitable.

[1]

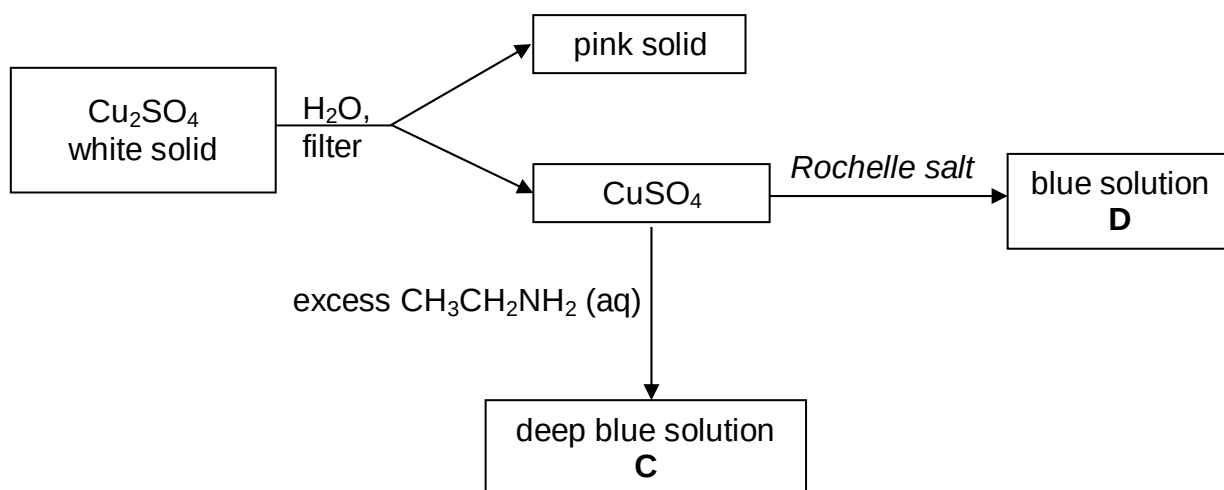
- (e)** Suggest a chemical test that can be used to distinguish between *fentanyl* and *morphine*.

[2]

[Total: 7]

- 6 Copper forms compounds with variable oxidation states and these compounds are used in numerous industries such as in wastewater treatment and as mineral supplements.

(a) The following scheme illustrates the reactions between different compounds of copper.



- (i) State the full electronic configuration of copper in the white solid.

[1]

- (ii) With reference to relevant E^θ data from the *Data Booklet*, describe and explain the type of reaction undergone when the white solid dissolves in water.

[2]

- (iii) Identify the species in solution **C** that is responsible for the deep blue colour and account for its formation from CuSO_4 . Include a relevant equation in your answer.

[2]

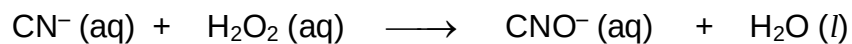
- (iv) Solution **D** is formed when *Rochelle salt* (an aqueous solution of potassium sodium tartrate $\text{KNaC}_4\text{H}_4\text{O}_6$) is mixed with a solution of CuSO_4 in basic medium.

Use the following data to determine the chemical formula of the copper tartrate anion complex.

- The composition by mass of the elements is
Cu: 17.76 % C: 26.85% H: 1.68% O: 53.71%
- The chemical formula takes the form of $[\text{ML}_2]^n-$.

[2]

- (b) Copper(II) ions are commonly used as *homogeneous catalysts* in the removal of harmful cyanide ions, CN^- from wastewater by hydrogen peroxide to form the less harmful cyanate CNO^- ions as illustrated in the following reaction.

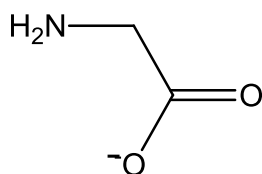


By considering relevant E^θ values from the *Data Booklet*, explain how copper(II) ions act as *homogeneous catalyst* in this reaction, writing balanced equations where appropriate.

[3]



- (c) When aqueous glycine solution is added to a heated ethanolic solution of copper(II) ethanoate, light blue needles of a planar, neutral copper–glycinate complex is obtained upon cooling.



glycinate ion

- (i) Draw the three-dimensional structure of the copper–glycinate complex ion.

[1]

- (ii) State the type of isomerism exhibited by the copper–glycinate complex ion.

[1]

[Total: 12]

END OF PAPER

Name: _____ Class: 15S _____ Reg Number: _____



MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9647/03

Paper 3 Free Response

14 September 2016

2 hours

Additional Materials: *Data Booklet*
 Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer 4 out of 5 questions in this paper.

Begin each question on a fresh sheet of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3, 4 & 5** respectively.

Hand in Questions **1 & 2** and **3, 4 & 5** separately.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

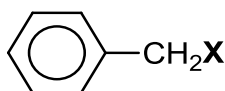
This document consists of **18** printed pages.

[Blank Page]

Answer any 4 out of 5 questions in this paper.

*Begin each question on a **fresh sheet** of writing paper.*

- 1 Benzyl halides are colourless liquids that have been used in chemical warfare due to their ability to cause severe eye, respiratory and skin irritation. Benzyl halides are also used in organic synthesis for the introduction of the benzyl protecting group for alcohols and carboxylic acids.



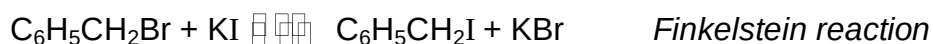
benzyl halide

- (a) Benzyl iodide, $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ can be synthesised from benzene in a **four** step pathway involving Friedel–Crafts alkylation. Friedel–Crafts alkylation involves the alkylation of a benzene ring in the presence of a suitable catalyst via electrophilic substitution.

Outline this synthesis route, suggesting relevant reagents, conditions and intermediate products.

[4]

- (b) Another method to synthesise benzyl iodide is via the *Finkelstein reaction*, which involves the conversion of benzyl bromide to benzyl iodide using stoichiometric amounts of potassium iodide under reflux conditions.



The rate equation is $\text{rate} = k [\text{C}_6\text{H}_5\text{CH}_2\text{Br}]$.

- (i) Draw diagrams to illustrate the mechanism for this reaction. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

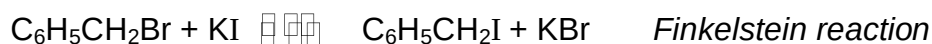
- (ii) Suggest a plausible chemical test that can be performed on a sample of the reaction mixture to test whether the reaction is effectively complete.

[2]

- (iii) Explain why benzyl bromide undergoes a unimolecular reaction with KI (aq) whereas (2-bromoethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$, undergoes a bimolecular reaction with KI (aq).

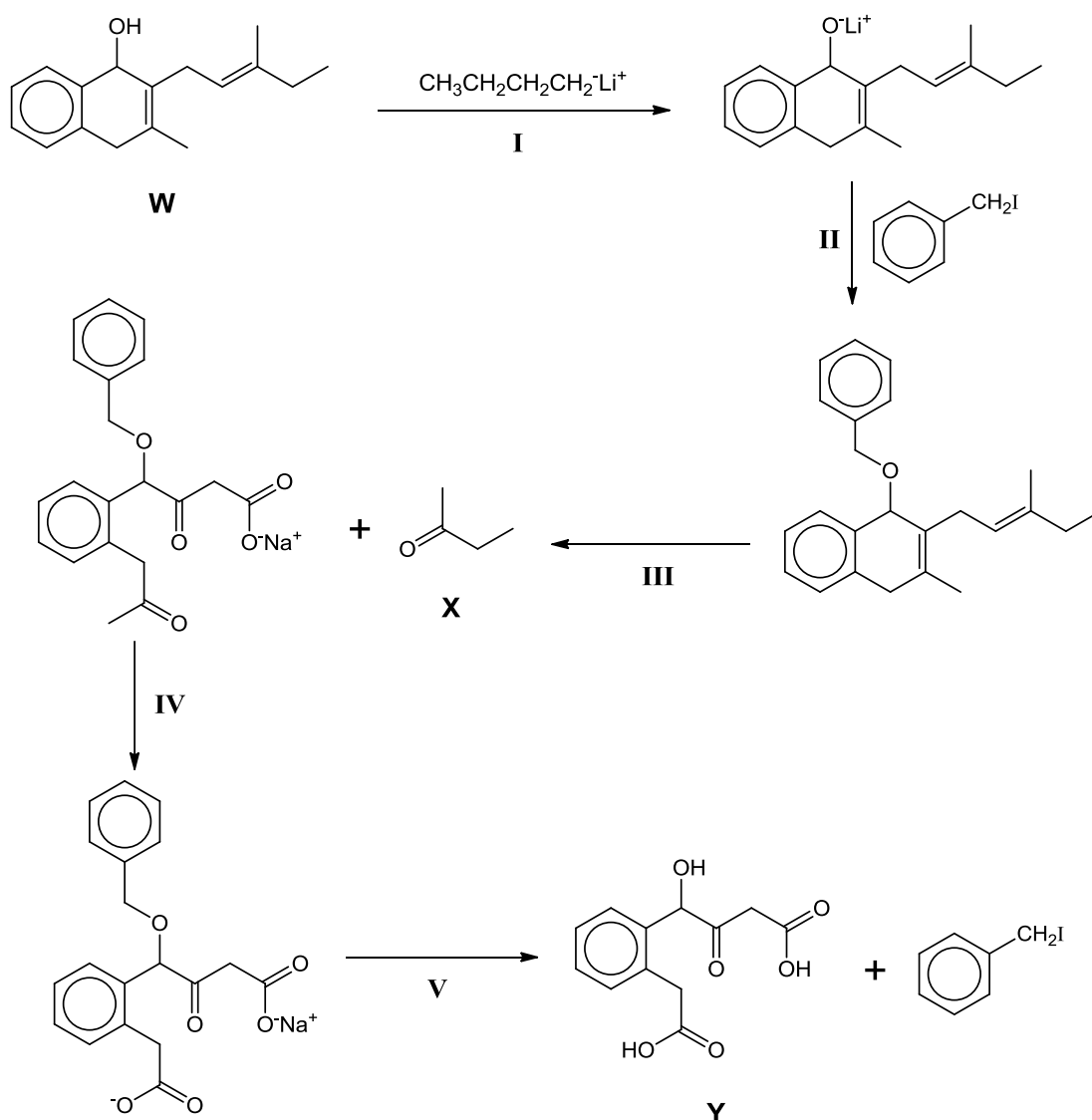
[1]

- (c) The *Finkelstein reaction* proceeds at a faster rate in the presence of polar solvents such as propanone, CH_3COCH_3 . The increase in rate lies in the difference in solubility between KI and KBr in propanone.



Potassium halides	Solubility in propanone
KI	Very soluble
KBr	Almost insoluble

- (i) Suggest why the *Finkelstein reaction* goes almost to completion. [1]
- (ii) In the solvation process, one potassium ion interacts with six propanone molecules. Draw a diagram to show how this interaction forms an octahedral unit. State clearly the type of interaction involved. [2]
- (iii) Suggest why potassium bromide is less soluble than potassium iodide in propanone by considering the lattice energy of the potassium halides and enthalpy change of solvation of the halides ions. [1]
- (d) Benzyl iodides are widely used in complex organic synthesis to form benzyl ethers ($\text{C}_6\text{H}_5\text{CH}_2\text{O-R}$), which are good blocking groups that protect alcohol functional groups from further reactions. These blocking groups are inert to hydrolysis under normal conditions, but they can be removed at the end of the reaction via the addition of an appropriate hydrogen halide molecule to obtain the original functional group and regenerate the benzyl iodide.
- The following illustrates a synthetic scheme from compound **W** in which a benzyl ether is acting as the protecting group.

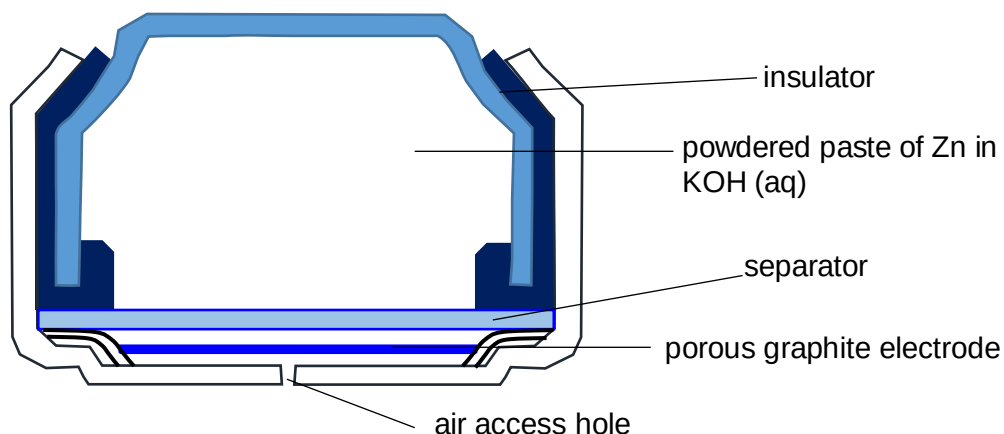


- (i) State the role of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^- \text{Li}^+$ in step I. [1]
- (ii) Predict with reasoning, the relative rate of the reaction in Step II when the reactant used is benzyl bromide, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ instead of benzyl iodide, $\text{C}_6\text{H}_5\text{CH}_2\text{I}$. Quote relevant values from the *Data Booklet* to substantiate your answer. [2]
- (iii) State the reagents and conditions needed for steps III, IV and V. [3]
- (iv) Write a balanced equation for the reaction between compound **X** and 2,4-dinitrophenylhydrazine. [1]

[Total: 20]

- 2 (a) Zinc–air batteries have received revived interest recently due to its higher energy density, larger storage capacity and lower production cost as compared to the commonly–used conventional lithium–ion batteries.

During discharge, oxygen from the air oxidises zinc to zinc oxide. The electrolyte used in the battery is KOH (aq). The zinc–air battery has a standard cell potential of +1.59 V.



- (i) Construct equations for the reactions which occur at the anode and cathode. Hence, construct the overall equation for the cell reaction. [2]
- (ii) Using suitable data from the *Data Booklet*, calculate the value for the $E^\ominus$ of the ZnO / Zn electrode reaction. [1]
- (iii) Suggest a reason why the air–access hole of these zinc–air batteries must be well–sealed during the packaging of these batteries for storage. [1]
- (iv) With reference to your answer in (a)(i), explain fully why the operating cell potential of the zinc–air batteries becomes less positive at high altitudes where the atmospheric pressure is lowered. [2]
- (v) Determine the current output (in amperes) of this zinc–air battery given that the air–access holes allow about 0.20 dm³ of air exchange in 1 hour at room temperature and pressure. You may assume that the percentage of O₂ present in air is 21.0%. [2]

- (b) Carbon dioxide, when present in sufficient concentration in air, may result in the formation of insoluble zinc carbonate that clogs the porous graphite electrode. This hinders the normal operation of the battery.

(i) Write an equation with state symbols for the thermal decomposition of zinc carbonate.

[1]

(ii) Zinc carbonate and barium carbonate decompose when heated to give similar products.

By quoting appropriate data from the *Data Booklet*, deduce whether zinc carbonate would decompose at a higher or lower temperature than barium carbonate. Explain your answer.

[2]

(iii) Using the following data and relevant data from the *Data Booklet*, construct a Born–Haber cycle to calculate the lattice energy of zinc carbonate.

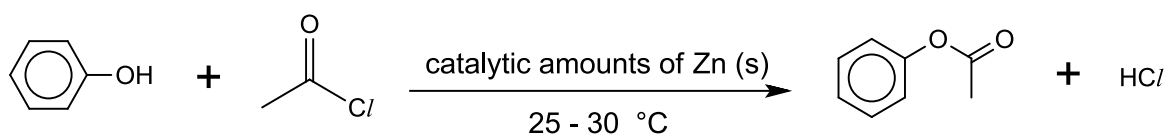
standard enthalpy change of atomisation of Zn (s) = + 131 kJ mol⁻¹

standard enthalpy change of formation of CO₃²⁻ (g) = - 321 kJ mol⁻¹

standard enthalpy change of formation of ZnCO₃ (s) = - 818 kJ mol⁻¹

[3]

- (c) Zinc exhibits some properties that are similar to those of a transition element. For example, zinc metal has demonstrated its potential as a *heterogeneous* catalyst for the acylation of a large variety of phenols with acyl chlorides.



Describe fully how zinc functions as a catalyst for this reaction.

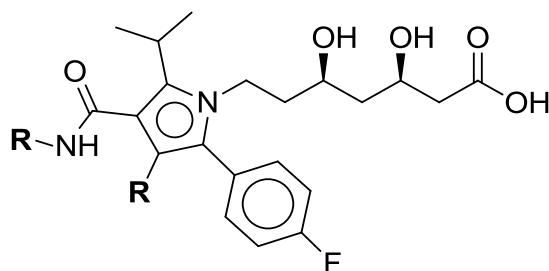
[3]

- (d) Similar to aluminium, zinc can be anodised to make it more resistant to corrosion. Draw a fully labelled diagram and with the aid of equation(s), explain how zinc can be anodised.

[3]

[Total: 20]

- 3 *Atorvastatin* has been a very popular drug since 1996. It is consumed to reduce blood cholesterol level and for prevention of heart diseases.



Atorvastatin

R is a hydrocarbon group

- (a) A sample of 1 g of *atorvastatin* was completely burnt in excess oxygen and 103.7 cm³ of NO₂ gas was produced. All volumes were measured at 80 °C and 1 atm.
- (i) Calculate the M_r of *atorvastatin*, to the nearest whole number, using the above information. [2]
- (ii) The actual M_r of *atorvastatin* is 558. Explain why there is a discrepancy between the calculated M_r in (a)(i) and the actual M_r . [2]
- (b) *Atorvastatin* is sold as the calcium salt in tablet form. Each tablet contains 40 mg of the calcium salt. The maximum dosage is 80 mg per day for an average 65 kg adult.



- (i) Use of information in the photograph above is relevant to this question.

Calculate the minimum number of bottles of tablets a patient needs to stock up for **a year**, assuming that he adheres strictly to the daily dosage limit and consumes it every day.

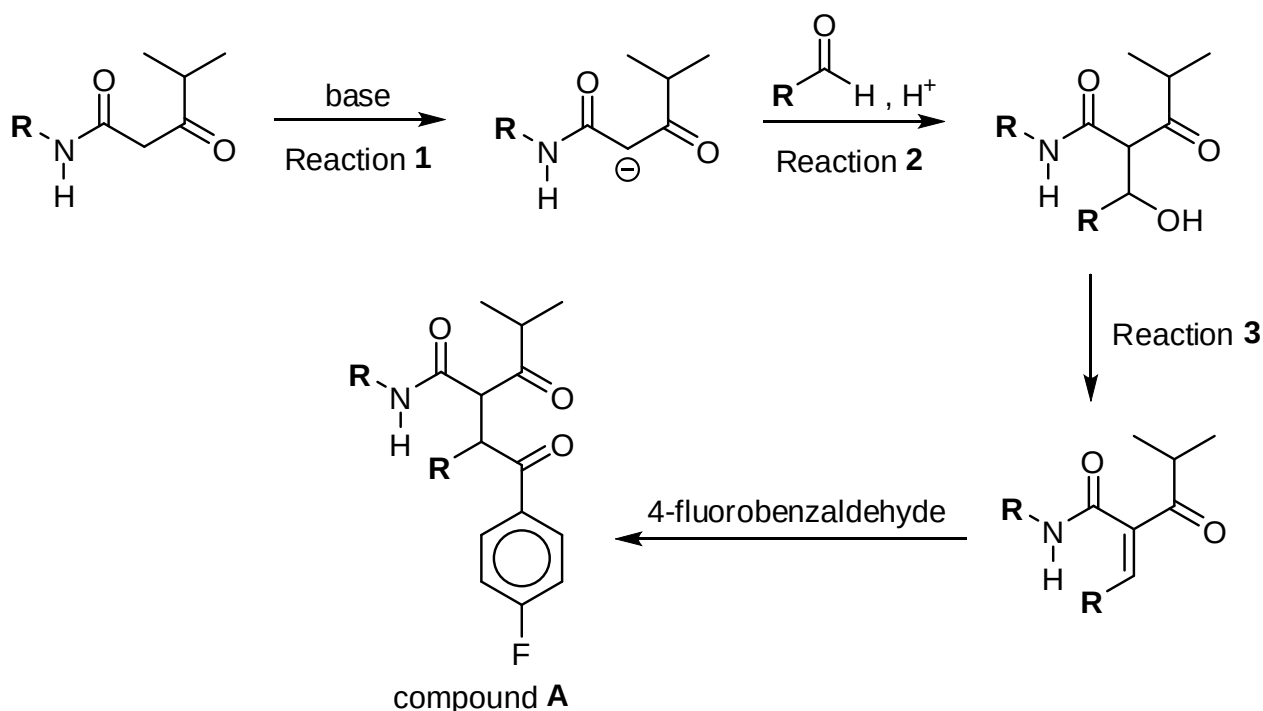
[1]

- (ii) Using structure and bonding, explain the differences in solubility of *atorvastatin* and *atorvastatin calcium* in CCl_4 .

[2]

In pharmaceutical companies, *atorvastatin* can be synthesised by reacting compound **A** with compound **C**.

- (c) Compound **A** is made from smaller molecules. The following reaction scheme shows the synthesis of compound **A**.



Reaction **1**, **2** and **3** are part of an aldol condensation reaction. A brief description of each reaction is given below.

Reaction **1**: The carbonyl α -carbon is deprotonated.

Reaction **2**: Nucleophilic addition takes place on the carbonyl compound.

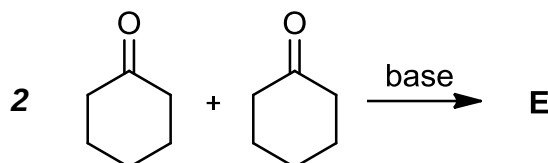
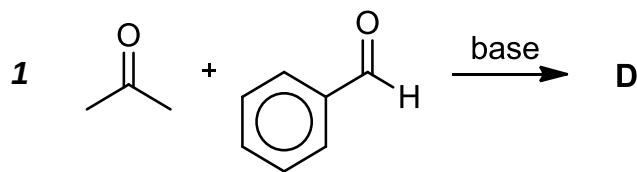
Reaction **3**: Elimination of the alcohol forms an alkene which is conjugated to the ketone.

- (i) Outline the mechanism for Reaction **2**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

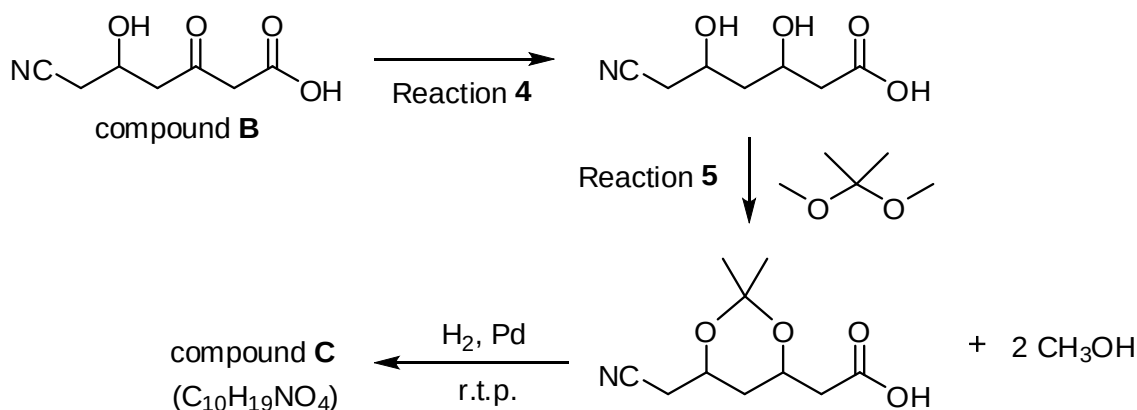
[2]

- (ii) Using the information in the reaction scheme given, suggest the products formed, **D** and **E**, when the following carbonyl compounds undergo aldol condensation reaction in the presence of a base.

[2]



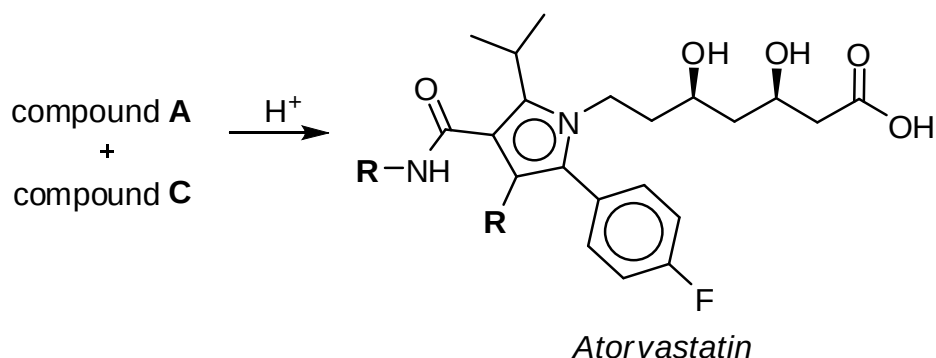
- (d) The following reaction scheme shows the synthesis of compound **C**.



- (i) State the reagent and condition for Reaction 4. [1]
- (ii) Suggest the type of reaction in Reaction 5. [1]
- (iii) Draw the structure of compound **C**. [1]
- (iv) Compound **B** forms a cyclic product, with the loss of one water molecule, when it is heated with concentrated sulfuric acid. Suggest the structure of the product formed. [1]

[1]

- (e) The following reaction scheme shows the final steps in the production of *atorvastatin*.

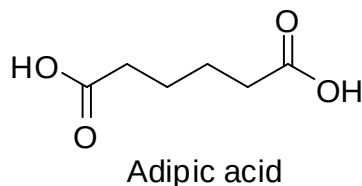


Atorvastatin contains several functional groups.

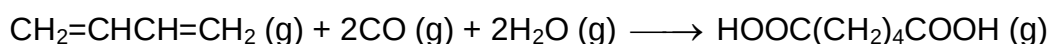
- (i) It has **two different** acidic functional groups. Name them and explain why one has a higher K_a value than the other. [3]
- (ii) The nitrogen atom in the five-membered ring is basic. Draw the structures of the products formed when *atorvastatin* is heated with acidified potassium dichromate(VI). [2]

[Total: 20]

- 4 Adipic acid is an organic compound with the formula $(\text{CH}_2)_4(\text{COOH})_2$. It is the most important of the dicarboxylic acids from the industrial perspective. Approximately 2.5 billion kilograms of this white crystalline powder are produced annually, predominantly as a precursor for the production of nylon 66.



- (a) One method to synthesis adipic acid is by the carbonylation of gaseous 1,3-butadiene with carbon monoxide and steam.

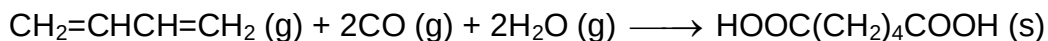


- (i) Use relevant bond energy data from the *Data Booklet* to calculate the enthalpy change for this reaction.

(Given that bond energy of $\text{C}\equiv\text{O}$ is 1079 kJ mol^{-1})

[2]

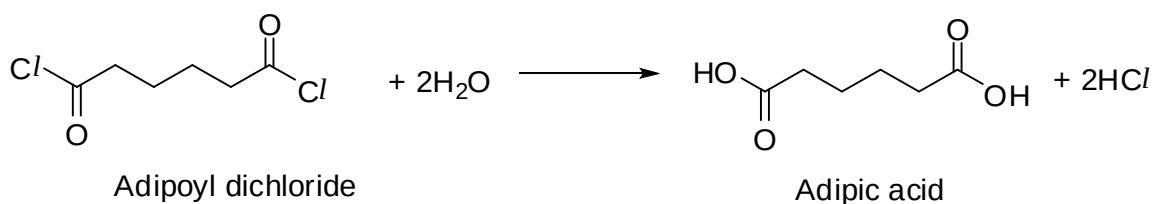
- (ii) The enthalpy change for the following reaction to form adipic acid in the solid form is -248 kJ mol^{-1} .



Account for the differences in the values for (a)(i) and (a)(ii).

[1]

- (iii) It is also possible to synthesise adipic acid by reacting adipoyl dichloride through a hydrolysis reaction with water.



Describe and explain the relative ease of hydrolysis of adipoyl dichloride and compound A shown below.



[2]

- (b) Adipic acid and its calcium salt are used as a buffer solution to remove sulfur dioxide from exhaust flue gases of fossil-fuel power plants. Calcium sulfate, CaSO_4 is formed at the end of the reaction.

(i) Draw the dot-and-cross diagram for the ion, SO_4^{2-} .

[1]

(ii) In principle, $\text{S}_2\text{O}_8^{2-}$ can be formed from the oxidation of SO_4^{2-} .

Draw the structure of $\text{S}_2\text{O}_8^{2-}$, given that there are four central atoms and that the ion is symmetrical with an O–O bond.

Account for its shape with respect to **each different** central atom using the VSEPR theory.

[3]

(iii) Adipic acid is a dibasic acid with $\text{p}K_a$ values of 4.4 and 5.4.

The optimal buffer pH for the adipic acid–calcium salt mixture is 4.6. Calculate the volume of 0.1 mol dm^{-3} of calcium hydroxide that needs to be added to 500 cm^3 of 0.01 mol dm^{-3} of adipic acid to yield the optimal buffer solution.

[3]

- (c) Compound **B** has the same molecular formula, $\text{C}_6\text{H}_{10}\text{O}_4$ as adipic acid. **B** is a neutral molecule but reacts with hot aqueous sulfuric acid to yield two organic compounds **C**, $\text{C}_4\text{H}_{10}\text{O}_2$ and **D** in a 1:1 ratio.

Compound **C** contains 2 chiral carbon atoms. Compound **C** forms no precipitate with 2,4–dinitrophenylhydrazine but reacts with hot aluminium oxide to form only three isomers **E**, **F** and **G** with the molecular formula of $\text{C}_4\text{H}_8\text{O}$. **Only** isomer **G** rotates the plane of polarised light.

Compound **D** reacts with hot alkaline Cu^{2+} solution to give a red precipitate. It also reacts with hot acidified KMnO_4 to form effervescence of carbon dioxide.

(i) Suggest structures for compounds **B**, **C**, **D**, **E**, **F** and **G**, showing your reasoning clearly.

[7]

(ii) Write a balanced chemical equation for the reaction between **D** and hot alkaline Cu^{2+} solution.

[1]

[Total: 20]

5 *Hemocyanin* and *chymotrypsin* are proteins used for various functions.

Hemocyanin is a copper-containing oxygen transport protein found in marine invertebrates such as squids. Its mode of transport of oxygen is similar to that of *haemoglobin*. In *hemocyanin*, oxygen is transported in the form of oxyhemocyanin.

(a) Describe what is meant by the *quaternary* structure of *hemocyanin*.

[1]

(b) In squids, one molecule of *hemocyanin* (Hc) binds to one molecule of oxygen via the oxygenation process, according to the following equation:



(i) In squid *hemocyanin*, when the partial pressure of oxygen gas is 0.13 atm at 25°C, the oxygen-binding sites are 33.0% saturated.

Calculate the equilibrium constant, K_c , at this temperature.

[2]

(ii) The Gibbs free energy change at 25°C when *hemocyanin* interacts with O_2 (g) is related to the equilibrium constant using the following equation.

$$\Delta G = -RT \ln K_c$$

Calculate the Gibbs free energy change.

[1]

(iii) It is claimed that “*global warming would harm aquatic organisms such as the squid population*”, through adversely affecting the oxygenation of squid *hemocyanin*.”

Verify this claim by considering the signs of the ΔH and ΔS of the oxygenation process.

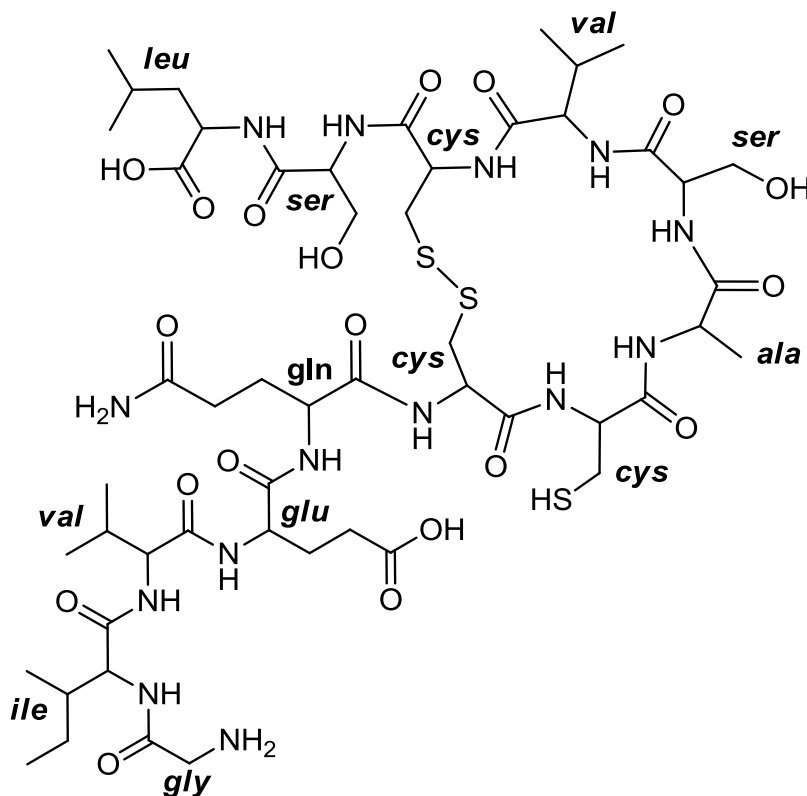
[2]

(iv) The blood of the squid is blue in colour as oxygenation causes a colour change between the colourless Cu(I) deoxygenated form of *hemocyanin* to the blue Cu(II) oxygenated form.

Explain why the oxygenated Cu(II) form of *hemocyanin* is blue in colour.

[3]

Chymotrypsin is an enzyme produced by the pancreas that is responsible for catalysing the hydrolysis of certain proteins in the small intestine during the digestive process. Part of the structure of *chymotrypsin* is given below along with the abbreviated names of its constituent amino acids: **gly**, **leu**, etc.



- (c) Use the abbreviated names of the amino acids to state the primary structure of the fragment of *chymotrypsin* given above. [2]
- (d) The biological function of *chymotrypsin* depends on its three-dimensional shape. Describe how the particular amino acids in *chymotrypsin* are likely to be involved in maintaining its three-dimensional shape. [2]
- (e) The activity of *chymotrypsin* is inhibited by prolonged heating with sodium hydroxide.

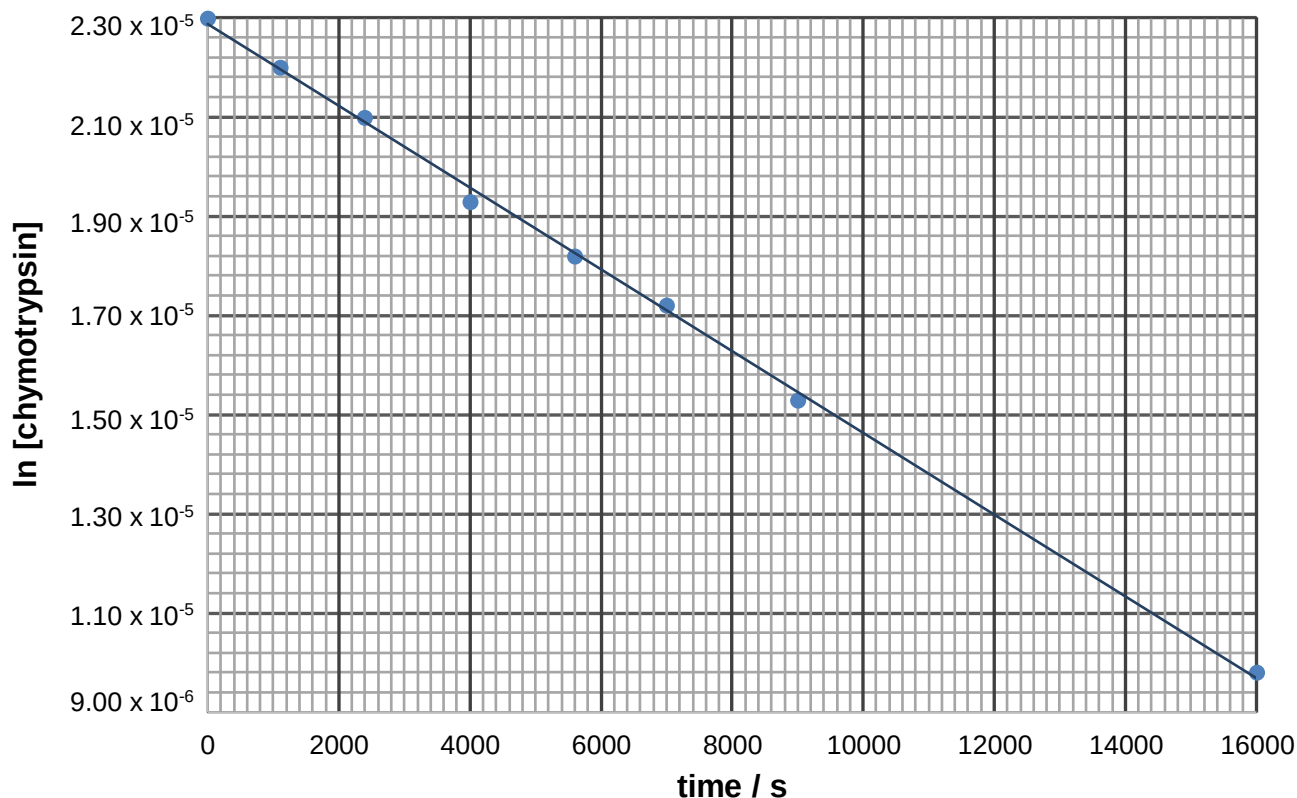
Draw the structure of the tripeptide obtained under these conditions from the part of *chymotrypsin* containing the amino acids: **ile-val-glu**.

[2]

- (f) *Chymotrypsin* undergoes denaturation by sodium hydroxide, with the mechanism dependent on pH. At high pH, the reaction is first order with respect to both the *chymotrypsin* and hydroxide ions.

In an experiment, the denaturation of the enzyme was monitored in the presence of excess alkali.

The plot of the time course of the reaction is shown below.



The rate law can be expressed in the form of:

$$\ln[A] = -kt + \ln[A]_0$$

where $[A]$ = concentration of a reactant at time, t

$[A]_0$ = initial concentration of that reactant

t = time since the reaction started

k = rate constant

- (i) Explain how the plot of the time course of the reaction confirms that the denaturation is first order with respect to *chymotrypsin* and how the conditions give rise to overall first order kinetics.

[1]

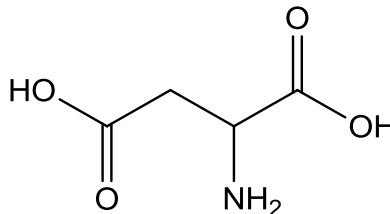
- (ii) Using the plot of the time course of the reaction, calculate the value of the experimentally-determined rate constant of this denaturation.

[1]

(iii) Hence, calculate the value of the true rate constant, given that concentration of NaOH used in the experiment was 1.5 mol dm^{-3} .

[1]

(g) One of the amino acids involved in the catalytic activity of *chymotrypsin* is aspartic acid.



Aspartic acid

There are three pK_a values associated with aspartic acid: 2.1, 3.9 and 9.8.

Suggest the predominant species present in solutions of aspartic acid with the following pH values of:

(i) 2.4

(ii) 7.0

[2]

[Total: 20]

END OF PAPER

2016 MJC H2 Chemistry Prelim Paper 1 (9647/01)

Suggested Answers

Qn	Ans
1	C
2	D
3	D
4	D
5	C

6	D
7	B
8	B
9	B
10	D

Qn	Ans
11	D
12	B
13	B
14	C
15	D

16	B
17	D
18	D
19	A
20	C

Qn	Ans
21	C
22	C
23	D
24	C
25	B

26	B
27	C
28	C
29	B
30	B

Qn	Ans
31	C
32	A
33	B
34	A
35	B

36	A
37	B
38	D
39	B
40	A

2016 MJC Prelim P2 Suggested Answers

1 Planning (P)

- (a) Ionic product = $(2.50 \times 10^{-3}) (2.00 \times 10^{-3})^2 = \underline{1.00 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}}$. *Show working to consider total volume is different.*

(b) Preparation of $0.01 \text{ mol dm}^{-3} \text{ Pb(NO}_3)_2$ standard solution (100 cm^3)

- 1) Weigh a clean, dry empty weighing bottle using a mass balance.
- 2) Weigh out approximately 0.331 g of solid $\text{Pb(NO}_3)_2$.
- 3) Transfer the solid into a clean 100 cm^3 beaker and reweigh the weighing bottle with the residue to determine the exact mass of $\text{Pb(NO}_3)_2$ used.
- 4) Dissolve the solid carefully with some deionised water and transfer it into a 100 cm^3 volumetric flask.
- 5) Top up the flask to the mark with deionised water, stopper and mix well to obtain a homogeneous solution.

Dilution of KI standard solution (100 cm^3)

- 1) Pipette 25.0 cm^3 of given $0.0400 \text{ mol dm}^{-3} \text{ PbI}_2$ solution into a 100 cm^3 volumetric flask.
- 2) Top of top the mark with deionised water, stopper and mix well.

Possible quantities and concentrations of solutions to be used (4 expt sets)

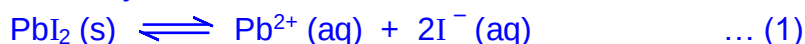
Expt	Vol. of Pb^{2+} / cm^3	Vol of I^- / cm^3	Vol of H_2O / cm^3	$[\text{Pb}^{2+}]_{(\text{mixture})}$ / mol dm^{-3}	$[\text{I}^-]_{(\text{mixture})}$ / mol dm^{-3}	Ionic product of PbI_2
5	2.50	2.00	5.50	0.00250	0.00200	$y_1: 1.00 \times 10^{-8}$
6	1.00	3.00	6.00	0.00100	0.00300	$y_2: 9.00 \times 10^{-9}$
7	2.00	2.00	6.00	0.00200	0.00200	8.00×10^{-9}
8	1.50	2.00	6.50	0.00150	0.00200	6.00×10^{-9}
9	1.00	1.00	8.00	0.00100	0.00100	1.00×10^{-9}

Experimental procedure

- 1) Fill three 50.00 cm^3 burettes with the prepared $0.0100 \text{ mol dm}^{-3} \text{ Pb(NO}_3)_2$ stock solution, $0.0100 \text{ mol dm}^{-3} \text{ KI}$ stock solution and deionised water respectively.
- 2) Run out 1.00 cm^3 of deionised water and 5.00 cm^3 of KI into a 100 cm^3 conical flask / beaker.
- 3) Run out 4.00 cm^3 of $\text{Pb(NO}_3)_2$ into the conical flask / beaker and swirl the flask well / stir with a glass rod.
- 4) Allow the flask / beaker to stand undisturbed for at least 30 min to attain equilibrium.

- 5) Note if any precipitate of yellow PbI_2 is present on standing.
- 6) Repeat the experiment using the various volumes shown in table (*Total volume = 10.00 cm³ / constant*).
- 7) Estimated $K_{\text{sp}} = \frac{y_1 + y_2}{2}$ where y_1 : *minimum ionic product with precipitation* and y_2 : *maximum ionic product without precipitation*.

(c) Solubility would decrease.



Due to presence of common ion (I^{-}), equilibrium position of (1) shifts left.

(d)

Salt	Solubility
PbCO_3	$s^2 = 7.4 \times 10^{-14}$ Solubility = $s = 2.72 \times 10^{-7} \text{ mol dm}^{-3}$
$\text{Pb}(\text{IO}_3)_2$	$4s^3 = 3.7 \times 10^{-13}$ Solubility = $s = 4.52 \times 10^{-5} \text{ mol dm}^{-3}$
$\text{Pb}_3(\text{PO}_4)_2$	$108s^5 = 7.9 \times 10^{-43}$ Solubility = $s = 1.49 \times 10^{-9} \text{ mol dm}^{-3}$

Most effective: PO_4^{3-}

2(ai) $[\text{OH}^{-}] = \sqrt{0.370 \times 5.6 \times 10^{-4}} = 0.01439 \text{ mol dm}^{-3}$
 $\text{pOH} = -\lg 0.01439 = 1.84$ hence $\text{pH} = \underline{12.2}$

(ii) No. of mole of ethylamine = $0.370 \times \frac{60}{1000} = 0.0222$

$$[\text{HC}] = \frac{0.0222}{\frac{20}{1000}} = 1.11 \text{ mol dm}^{-3}$$

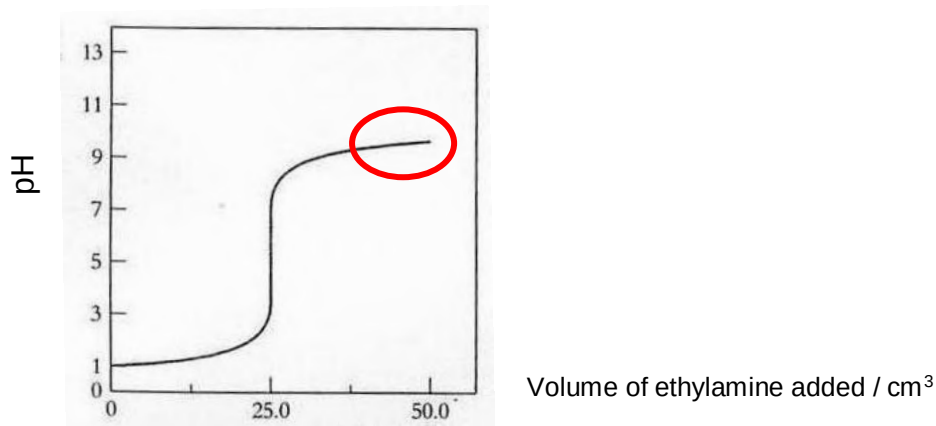
(iii) Heat absorbed by solution = $80 \times 4.18 \times 3.5 = 1170 \text{ J}$

$$\text{No. of moles of H}_2\text{O produced} = 0.370 \times \frac{60}{1000} = 0.0222$$

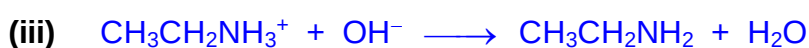
$$\text{Enthalpy change of neutralisation} = -\frac{1170}{0.0222} = \underline{-52.7 \text{ kJ mol}^{-1}}$$

(iv) Some energy evolved from the neutralisation process is used to further dissociate the weak base completely

(bii)



(bi) Methyl orange . Red to orange.

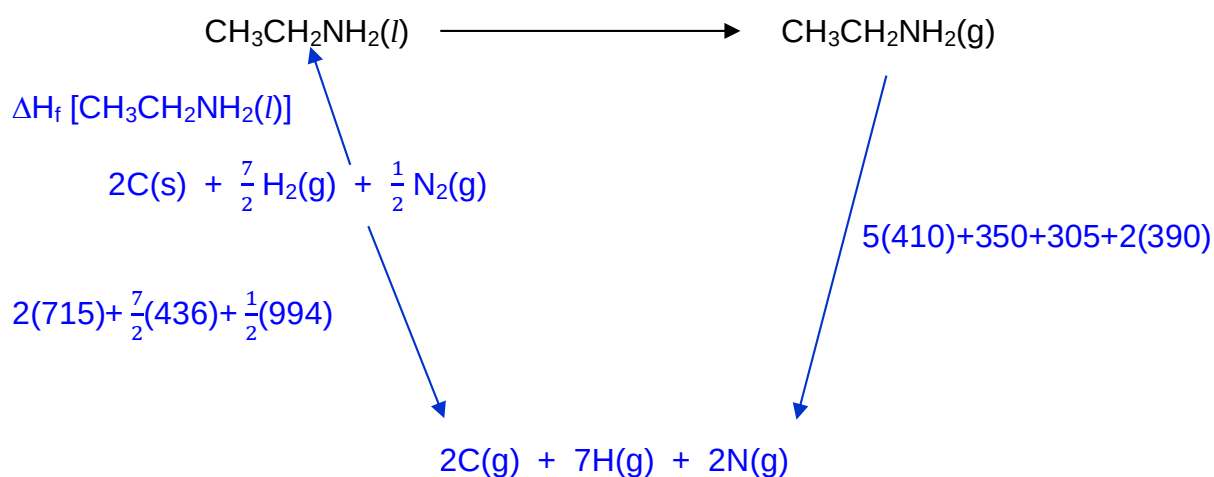


(ci)

Step	Type of reaction	Reagents and conditions
I	condensation	
II	reduction	LiAlH ₄ in dry ether

(ii) Add 2,4-DNPH to sample and heat. Synthesis is complete when no orange ppt is observed. *Accept other possible tests.*

(d)



$$\begin{aligned} \Delta H_f [\text{CH}_3\text{CH}_2\text{NH}_2(l)] + 29 + 3485 &= 3453 \\ \Delta H_f [\text{CH}_3\text{CH}_2\text{NH}_2(l)] &= \underline{-61.0 \text{ kJ mol}^{-1}} \end{aligned}$$

(ei) amide, amine

- (ii) Compound **Q** is more basic than Tamiflu. The electron-donating R group increases the electron density of the lone pair on N atom hence more available to accept a proton. Compound **R** is less basic. The lone pair of electron on N atom is delocalised into the benzene ring hence less available to accept a proton.



- (ii) $E^\ominus = +0.54 \text{ V}$ and $E^\ominus = +1.07 \text{ V}$. As $E^\ominus_{\text{Br}_2/\text{Br}^-}$ is more positive than $E^\ominus_{\text{I}_2/\text{I}^-}$, Br^- is a weaker reducing agent than I^- .

- (iii) Conc. H_3PO_4 is a weaker oxidising agent than conc. H_2SO_4
 $\text{KBr (s)} + \text{H}_3\text{PO}_4 \text{ (l)} \longrightarrow \text{HBr (g)} + \text{KH}_2\text{PO}_4 \text{ (s)}$

- (bi) KCl : ppt dissolves
 KBr : ppt dissolves
 KI : ppt does not dissolve

- (ii) NH_3 ligand combines with $\text{Ag}^+(\text{aq})$ to form diamminesilver(I) complex or $[\text{Ag}(\text{NH}_3)_2]^+$. Ionic product (of $[\text{Ag}^+][\text{I}^-]$ easily) exceed the low K_{sp} value hence thus AgI does not dissolve.

- (c) Number of mole of iodine in 25.0cm^3 aliquot = $\frac{1}{2} \times (0.0400 \times 0.010)$
 Number of mole of iodine in $250 \text{ cm}^3 = 2.00 \times 10^{-3}$

$$\frac{n_{\text{I}_2}}{n_{\text{BrO}_4^{n-}}} = \frac{2 \times 10^{-3}}{5 \times 10^{-4}} = 4$$



$$+7 + 4(-2) = n(-1)$$

$$\underline{n = 1}$$

- (di) $\text{MgCl}_2 \text{ (s)} + 6\text{H}_2\text{O (l)} \longrightarrow [\text{Mg}(\text{H}_2\text{O})_6]^{2+} \text{ (aq)} + 2\text{Cl}^- \text{ (aq)}$
 $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} \text{ (aq)} \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+ \text{ (aq)} + \text{H}^+ \text{ (aq)}$ pH = 6.5



- (ii) $\text{ZnO} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$
 $\text{ZnO} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{Zn}(\text{OH})_4$

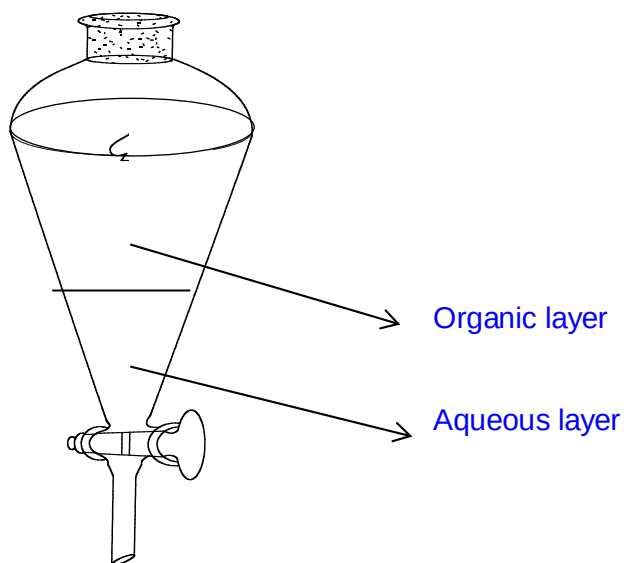
4(ai) Prevent the moisture from reacting with the sodium metal.

(ii) No. of moles of phenol = $(11.8 / 94) = 0.1255$ (same as phenoxide)

No. of moles of 1-bromo-3-methylbutane = $(20.0 \times 1.21) / 151$

Mass of (3-methylbutoxy)benzene = $0.1255 \times 164 = \underline{20.6 \text{ g}}$

(iii)

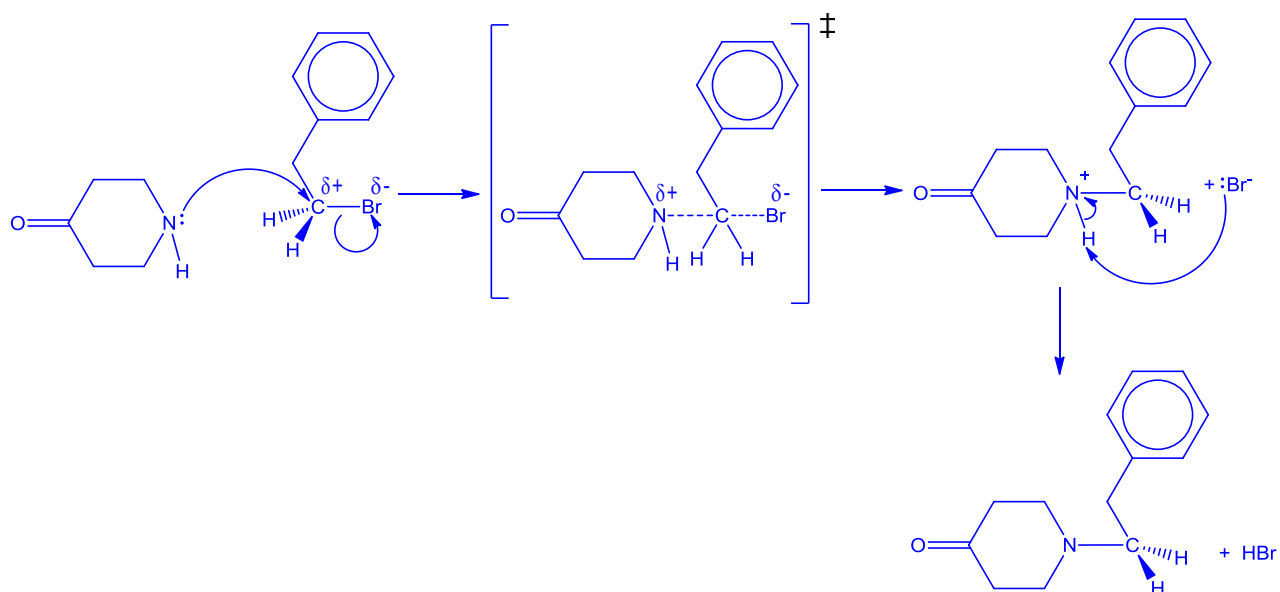


(bi) **1** (unreacted) phenol ; **2** water

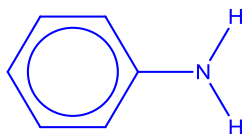
(ii) (3-methylbutoxy)benzene has a higher boiling point. The extensive van der Waals' forces of attraction between 3-methylbutoxy)benzene molecules is stronger than the hydrogen bonding in ethanol.

(iii) Boiling point of the (3-methylbutoxy)benzene is significantly higher than the other impurities. Temperature range is from 214°C - 218°C .

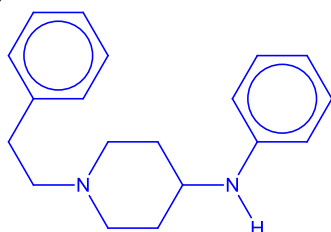
5(a) S_N2



(b)



(c)



(d) Carboxylic acid will undergo acid-base reaction with the amine groups instead.

(e) Add aqueous neutral iron (III) chloride. For morphine, a violet complex observed but not for fentanyl. *Accept other tests.*

6(ai) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(ii) $E^\ominus_{\text{cell}} = 0.52 - 0.15 = +0.37 > 0$. Hence, Cu^+ disproportionates into pink solid Cu and blue solution of Cu^{2+} .

(iii) The stronger $\text{CH}_3\text{CH}_2\text{NH}_2$ ligands replace H_2O ligands to form a deep blue complex $[\text{Cu}(\text{CH}_3\text{CH}_2\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$.



(iv)

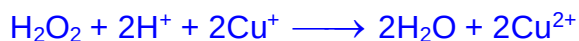
	Cu	C	H	O
% by mass	17.76	26.85	1.68	53.71
No. of moles	$\frac{17.76}{63.5}$	$\frac{26.85}{12.0}$	$\frac{1.68}{1.0}$	$\frac{53.71}{16.0}$
Simplest ratio	1	8	6	12

Chemical formula of anion is $[\text{Cu}(\text{C}_4\text{H}_3\text{O}_6)_2]^{4-}$

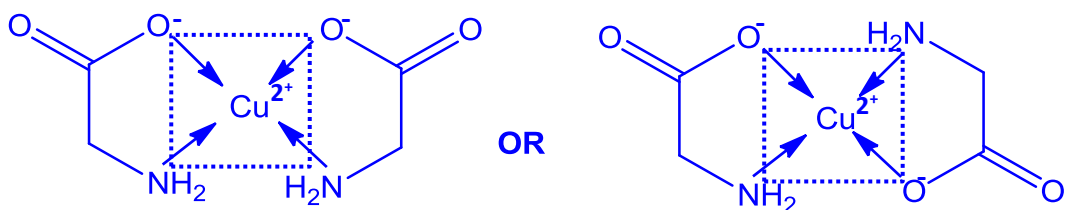
(b) $E^\ominus_{\text{cell}} = 0.15 - (-0.97) = +1.12 \text{ V} > 0$ hence reaction is feasible.



$E^\ominus_{\text{cell}} = 1.77 - 0.15 = +1.62 \text{ V} > 0$ hence reaction is feasible.



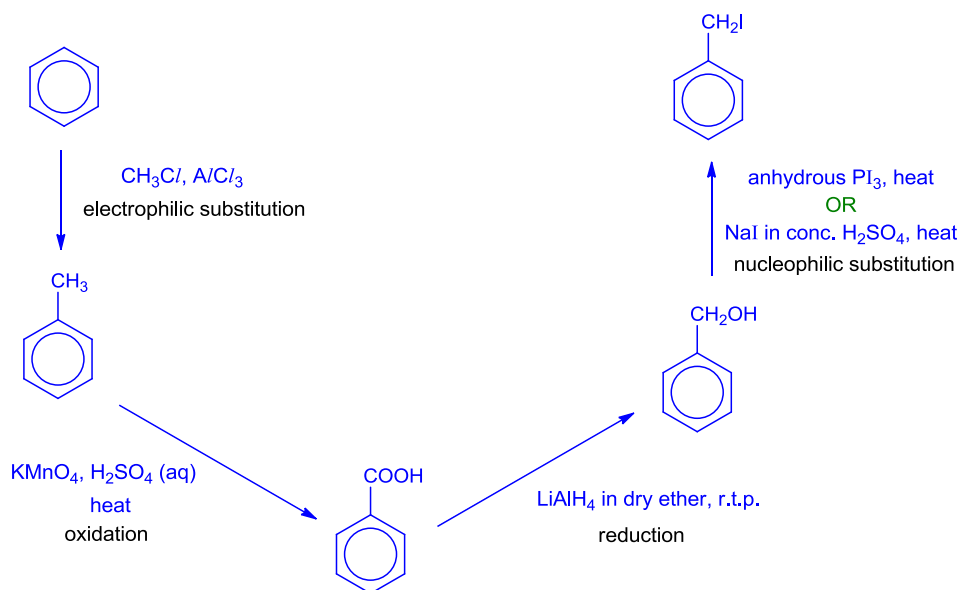
(ci)



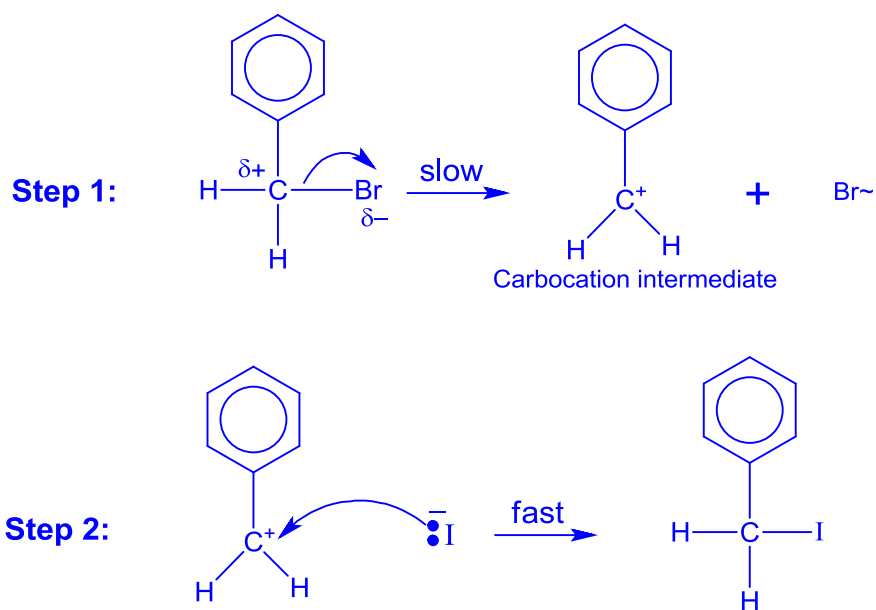
(ii) Cis-trans isomerism

2016 MJC Prelim Paper 3 Suggested Answers

1(a)

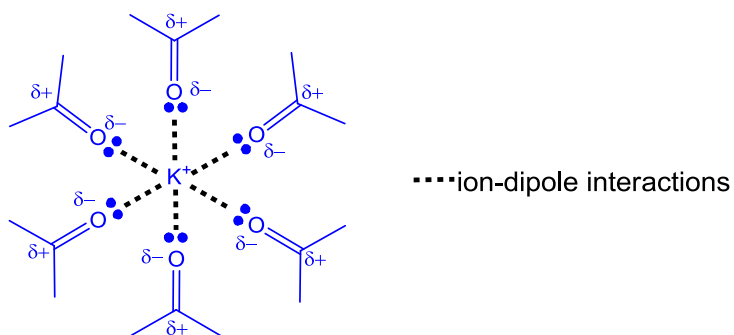


(b)



- (i) Add $\text{AgNO}_3(\text{aq})$. Observation: No yellow precipitate observed.
- (ii) The $\text{C}_6\text{H}_5\text{CH}_2^+$ carbocation is resonance stabilised
- (ci) KBr is precipitated out as a solid. Position of equilibrium shifts to the right.

(ii)



(iii) Enthalpy change of solution for KI in propanone is more exothermic.

(di) As a base.

(ii) $\text{BE (C-I)} = 240 \text{ kJ mol}^{-1}$; $\text{BE (C-Br)} = 280 \text{ kJ mol}^{-1}$

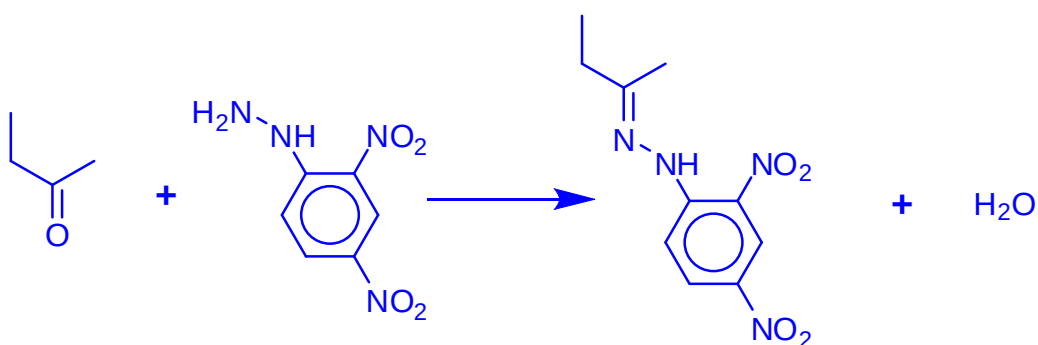
The C-Br bond is stronger than C-I bond hence rate is slower.

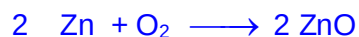
(iii) Step III: alkaline $\text{KMnO}_4(\text{aq})$, heat

Step IV: alkaline aq I_2 , heat

Step V: hydrogen iodide

(iv)





(ii) $+1.59 = 0.40 - E^\ominus (\text{ZnO} / \text{Zn})$
 $E^\ominus (\text{ZnO} / \text{Zn}) = -1.19 \text{ V}$

(iii) Prevent entry of O_2 so to minimise the battery's discharging process to prolong the shelf-life of the battery.

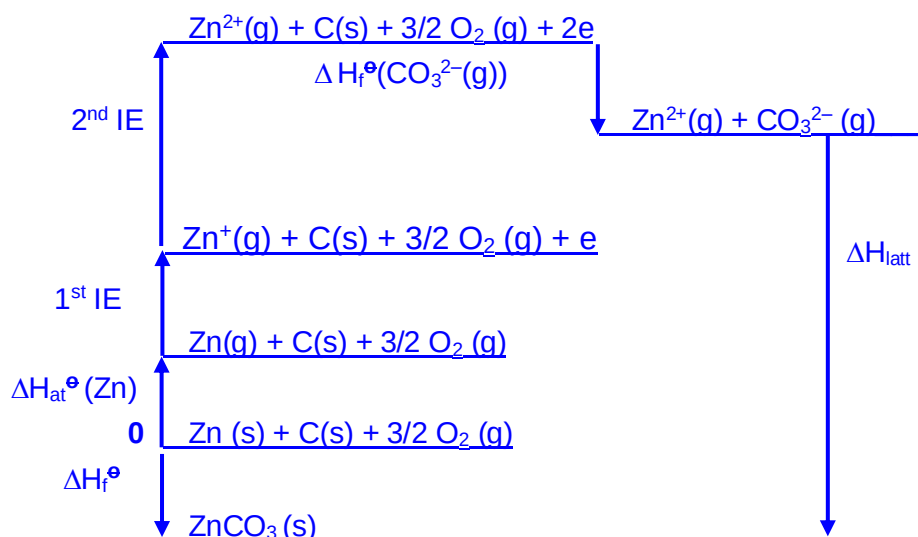
(iv) Partial pressure of O_2 hence the equilibrium position shifts left. $E^\ominus_{(\text{O}_2/\text{OH}^-)}$ will be less positive hence $E_{\text{cell}} < 1.59 \text{ V}$.

(v) No. of moles of $\text{O}_2 = \frac{I \times t}{n \times F} = \frac{I \times 60 \times 60}{4 \times 96500}$
 Current output of battery = 0.188 A



(ii) Zn^{2+} 0.074 nm; Ba^{2+} : 0.135 nm. Charge density: $\text{Zn}^{2+} > \text{Ba}^{2+}$. Zn^{2+} distorts the anion charge cloud to a greater extent, weakening and breaking the C–O bond in CO_3^{2-} . Hence, decomposition temperature of ZnCO_3 is lower than BaCO_3 .

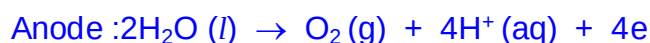
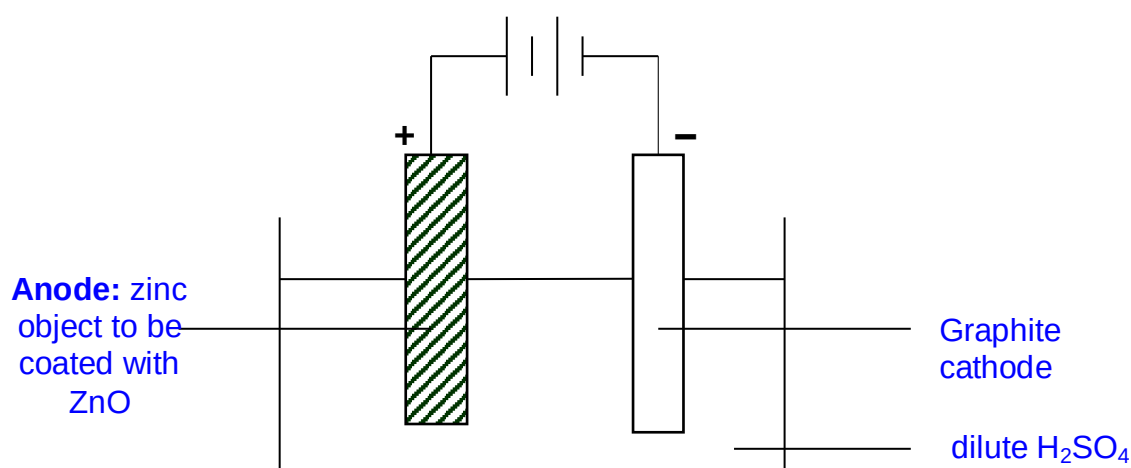
(iii)



By Hess' Law, $\Delta H_{\text{latt}}(\text{ZnCO}_3) = -3266 \text{ kJ mol}^{-1}$

- (c) Zn is a heterogeneous catalyst because of the availability of 3d & 4s electrons for temporary bond formation with reactants. Reactant molecules are adsorbed onto the Zn catalyst surface. This adsorption increases the surface concentration of the reactants and weakens the covalent bonds lowering the activation energy such that molecules are brought close for reaction to take place easily. Products formed diffuse away from the surface of the catalyst.

(d)



3(ai) No of moles of NO_2 gas produced = $\frac{PV}{RT} = \frac{1.01 \times 10^5 \times 103.7 \times 10^{-6}}{8.31 \times 353}$

$$M_r \text{ of atorvastatin} = \frac{1}{1.785 \times 10^{-3}} = 560$$

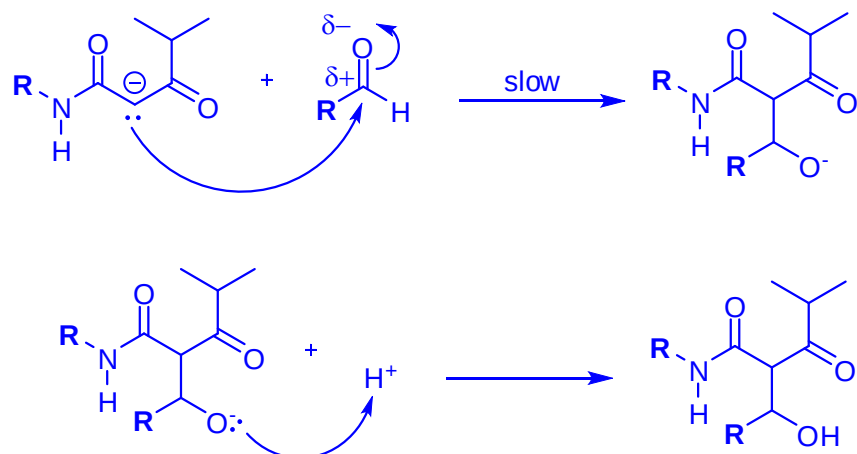
- (ii) NO_2 is a real gas with significant intermolecular forces of attraction.

- (bi) No of tablets required in year = 2×365 .

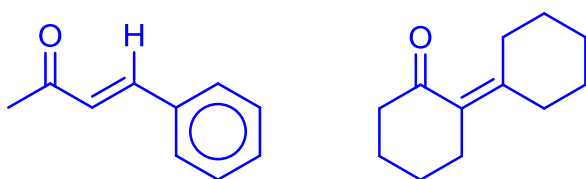
$$\text{No of bottles needed} = \frac{730}{90} = 8.11 \approx 9$$

- (ii) The weak van der Waal's forces between the *atorvastatin* molecules is compatible with that between CCl_4 molecules. The *atorvastatin* calcium cannot form ion-dipole interaction with the CCl_4 molecules, hence it will not dissolve.

(i)



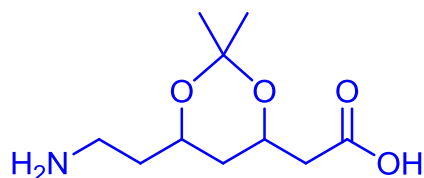
(ii)



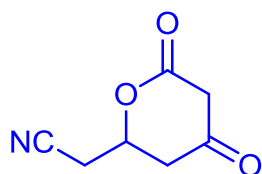
(di) NaBH₄ in ethanol

(ii) Nucleophilic substitution

(iii)

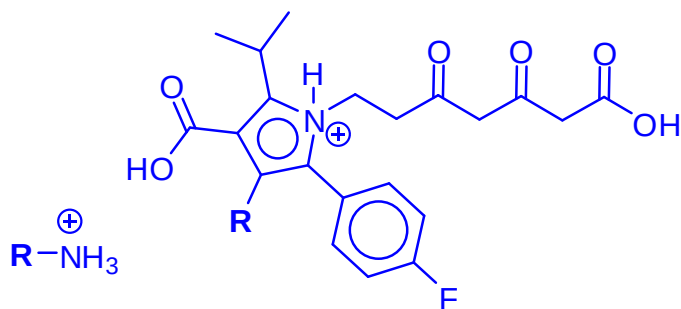


(iv)



(ei) The carboxylic acid group has higher K_a . The carboxylate anion is resonance stabilised. The alcohol has lower K_a . The electron donating alkyl group increases the intensity of the negative charge on the oxygen atom of the alkoxide anion hence destabilising it.

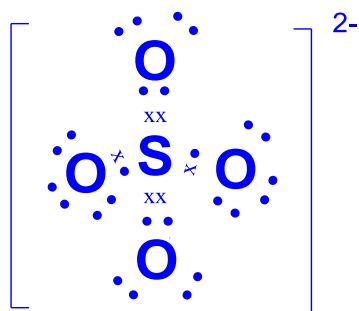
(ii)



4(ai) $\Delta H_{\text{rxn}} = 2(1079) + 4(460) + 1(350) + 2(610) + 6(410) - [5(350) + 2(740) + 2(360) + 2(460) + 8(410)] = -122 \text{ kJ mol}^{-1}$

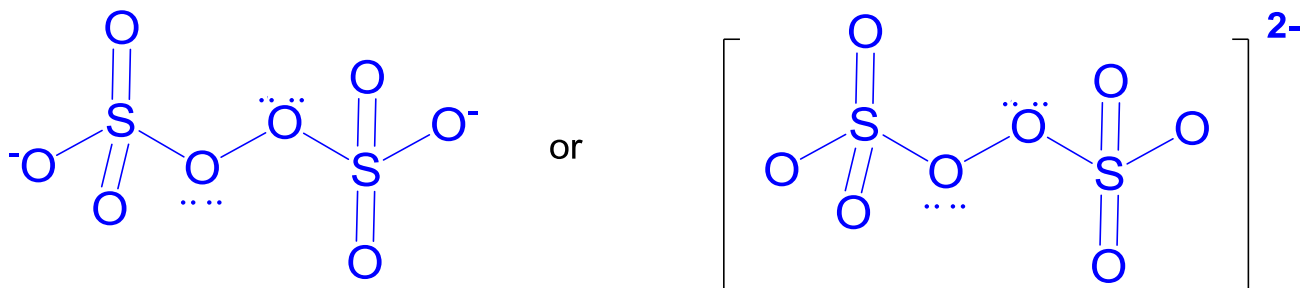
(ii) The difference is due to ΔH_{fusion} plus vaporisation of adipic acid. *Accept other answers.*

(iii) For adipoyl dichloride, the carbonyl C atom is bonded to electronegative atoms hence the electron deficient carbonyl C atom is very susceptible to hydrolysis. For compound A, the lone electron pair of the chlorine atom is delocalised with the adjacent C=C double bond hence rendering partial double bond character.



(bi)

(ii)



The shape with respect to S is tetrahedral.
The shape with respect to O is bent

(iii) Let $y \text{ dm}^3$ = vol of base added.

No. of mole of $\text{HA}^- = 0.2y$

Final no. of mole of $\text{H}_2\text{A} = 5 \times 10^{-3} - 0.2y$

$$4.6 = 4.4 + \lg \frac{0.2y/(0.5+y)}{(5 \times 10^{-3} - 0.2y)/(0.5+y)}$$

$$y = 0.0153 \text{ dm}^3$$

(ci) **B** undergoes acidic hydrolysis $\rightarrow$ **B** is an ester.

C does not undergo condensation with 2,4-dinitrophenylhydrazine.

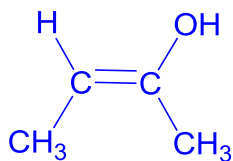
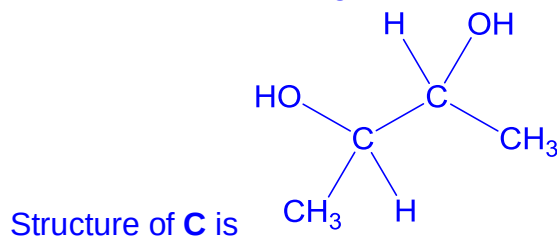
$\rightarrow$ **C** does not contain aldehyde or ketone

C undergoes elimination with hot Al_2O_3 . $\rightarrow$ **E** to **G** contains alkene

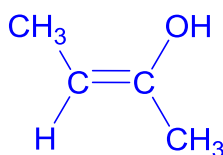
E and **F** are cis-trans isomers and **G** contains chiral carbon and is a structural isomer of **E** & **F**.

D undergoes oxidation with Fehling's $\rightarrow$ **D** contains aliphatic aldehyde.

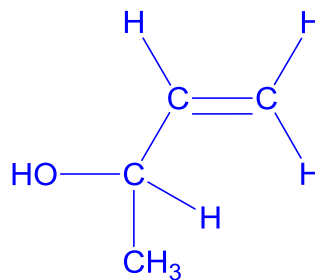
D is ethanedioic acid and it undergoes further oxidation to form carbon dioxide.



E

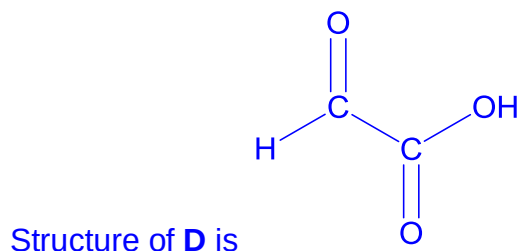


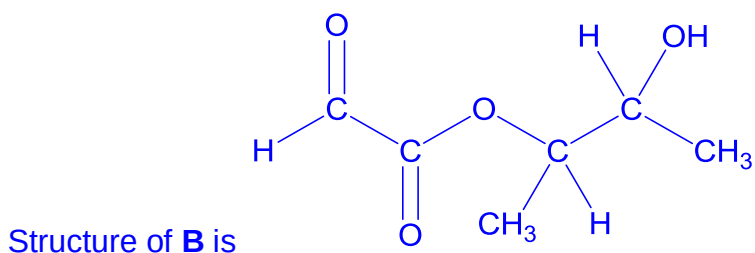
F



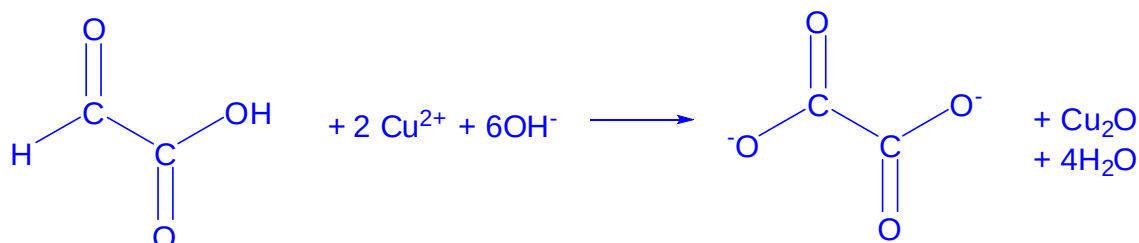
G

E and F (can interchange)





(i)



5(a) Quaternary structure is the combination of two or more polypeptide chains interacting to form a more complex structure. The sub-units in the structure interact via van der Waals' forces, ionic bonds and hydrogen bonds.

(bi) $[\text{O}_2] = \frac{(0.13 \times 1.01 \times 10^5)}{(8.31)(298)} = 5.30 \times 10^{-3} \text{ mol dm}^{-3}$. Accept answer in mol m^{-3}

$$K_c = 0.33 \times \frac{1}{5.30 \times 10^{-3}} = 62.3$$

(ii) $\Delta G = - (8.31) (298) \ln (62.3) = - 10.2 \text{ kJ mol}^{-1}$

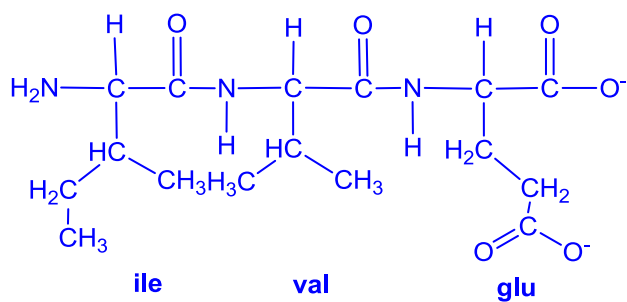
(iii) ΔS is negative since there is a decrease in disorder as there is a decrease in number of moles of gas. ΔH is negative. When temperature is high, $|\Delta H| < |T\Delta S|$, hence ΔG is positive hence oxygenation of squid is not supported leading to death.

(iv) Cu(II) has partially-filled d orbitals. The d orbitals are split into two groups by ligands. The d electron is promoted to the *higher* d orbital. During the transition, the d electron absorbs red/ orange/yellow wavelength light from the visible region of the electromagnetic spectrum and the remaining wavelengths (blue) not absorbed will appear as the colour observed.

(c) *gly – ile – val – glu – gln – cys – cys – ala – ser – val – cys – ser – leu*

(d) van der Waals' attraction between *val* and *leu*; hydrogen bond between *gln* and *ser*; disulfide bond between side chains of *cys*.

(e)



(fi) The plot is a straight line graph. $[\text{NaOH}]$ is kept constant hence the rate is independent of $[\text{NaOH}]$

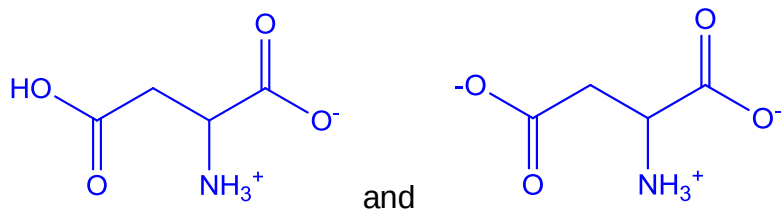
(ii) $-k' = -8.21 \times 10^{-10}$ Allow range of $8.0 - 8.4 \times 10^{-10}$

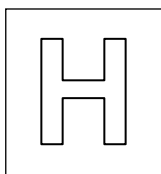
(iii) $\frac{8.21 \times 10^{-10}}{k} = k [1.5]$
 $ \phantom{\frac{8.21 \times 10^{-10}}{k}} = 5.47 \times 10^{-10}$

(g)

pH 2.4

pH 7.0





NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

Paper 1 Multiple Choice

9647/01

27 September 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, class and tutor's name on the Answer Sheet in the spaces provided unless this has been done for you.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 In an experiment, lanthanum, ^{57}La , was reacted with hydrogen to produce the non-stoichiometric ionic compound $\text{LaH}_{2.9}$. Assuming that the compound contains H^- , La^{2+} and La^{3+} , what is the percentage of La^{3+} present in $\text{LaH}_{2.9}$?

A 10%
B 20%
C 80%
D 90%

- 2 The two most common isotopes of titanium are $^{56}_{22}\text{Ti}$ and $^{58}_{22}\text{Ti}$.

Which statement about the isotopes of titanium is correct?

A Both isotopes have more electrons than neutrons.
B One of the isotopes has more protons than the other.
C The electronic configuration of Ti^{2+} ion for both isotopes is the same.
D In the same electric field strength, $^{56}_{22}\text{Ti}$ will be deflected more than $^{58}_{22}\text{Ti}$.

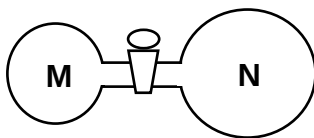
- 3 Which compound does **not** have a co-ordinate bond?

A CO **B** CS_2 **C** NO_3^- **D** NH_4^+

- 4 In which of the following pairs do the species have the same bond angle?

A H_2O_2 and N_2F_2 **B** PH_3 and SF_3^+
C POCl_3 and SO_3^{2-} **D** HCHO and BrF_3

- 5 Two glass vessels **M** and **N** are connected by a closed valve.



M contains helium at 20 °C at a pressure of 1×10^5 Pa. **N** has been evacuated, and has three times the volume of **M**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to 100 °C.

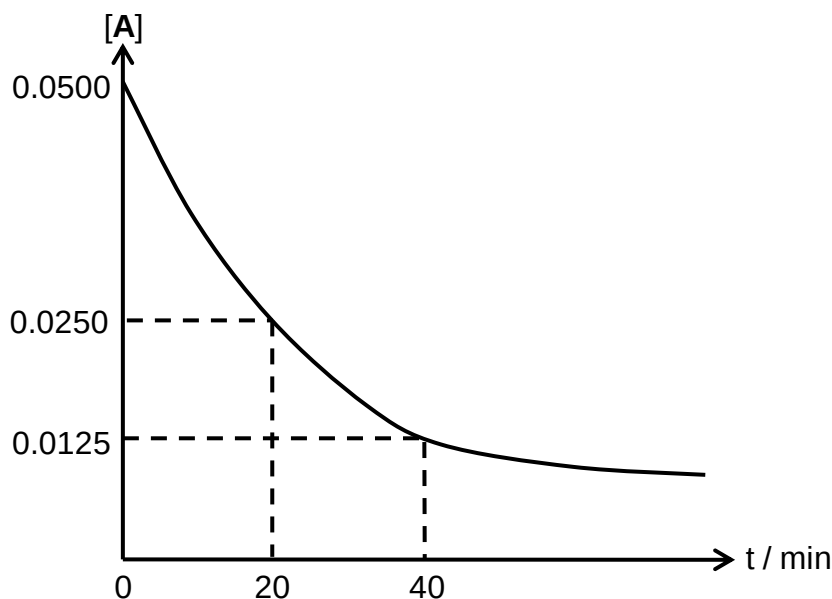
What is the final pressure in the system?

- A 3.18×10^4 Pa
 - B 4.24×10^4 Pa
 - C 1.25×10^5 Pa
 - D 5.09×10^5 Pa
- 6 Which value would be required to estimate the lattice energy for the hypothetical ionic compound MgH?
- A the electronic affinity of hydrogen
 - B the first ionisation energy of hydrogen
 - C the magnesium–hydrogen bond energy
 - D the standard enthalpy change of formation of MgH_2

- 7 A student performed an experiment to investigate a hypothetical reaction.



The graph of $[\text{A}]$ against time(t) for the experiment is shown below.



Given that the initial $[\text{B}]$ is 2.0 mol dm^{-3} and units for the rate constant is $\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$, which of the following statements is true?

- A The reaction is elementary.
 - B The half-life of the reaction remains constant when a catalyst is added.
 - C The gradient of tangent at $t = 0 \text{ min}$ increases by four times when the initial $[\text{B}]$ doubles.
 - D The half-life of the reaction remains constant when $[\text{A}]$ doubles but halved when $[\text{B}]$ doubles.
- 8 Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, was used by J. R. Glauber in the 17th century as a medicinal agent. At 25°C , the numerical value of the equilibrium constant, K_p for the loss of water of hydration from Glauber's salt is 4.08×10^{-25} .



Which of the following statements can be correctly deduced about this equilibrium reaction?

- A The reaction reaches dynamic equilibrium when the forward and reverse rate constants are equal.
- B The numerical value of the vapour pressure of water at 25°C in a closed container holding a sample of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s})$ is 3.64×10^{-3} .
- C The ratio of the hydrated form to anhydrous form of the Glauber's salt remains the same when nitrogen gas is added while keeping the total pressure of the system constant.
- D The numerical value of K_p will increase when temperature is increased.

- 9 Highly toxic disulfur decafluoride decomposes by a free-radical process.



In a study of the decomposition, S_2F_{10} was placed in a 2.0 dm^3 flask and heated to 100°C . The equilibrium $[\text{S}_2\text{F}_{10}]$ was found to be 0.5 mol dm^{-3} . More S_2F_{10} was then added and the new equilibrium $[\text{S}_2\text{F}_{10}]$ was 2.5 mol dm^{-3} .

What is the amount of S_2F_{10} reacted in terms of the equilibrium constant, K_c of the decomposition reaction when more S_2F_{10} was added?

- A $(0.5K_c)^{0.5} - (2.5K_c)^{0.5}$
- B $(2.5K_c)^{0.5} - (0.5K_c)^{0.5}$
- C $(2K_c)^{0.5} - (10K_c)^{0.5}$
- D $(10K_c)^{0.5} - (2K_c)^{0.5}$

- 10 Phosphorus acid, H_3PO_3 , has two acid dissociation values:

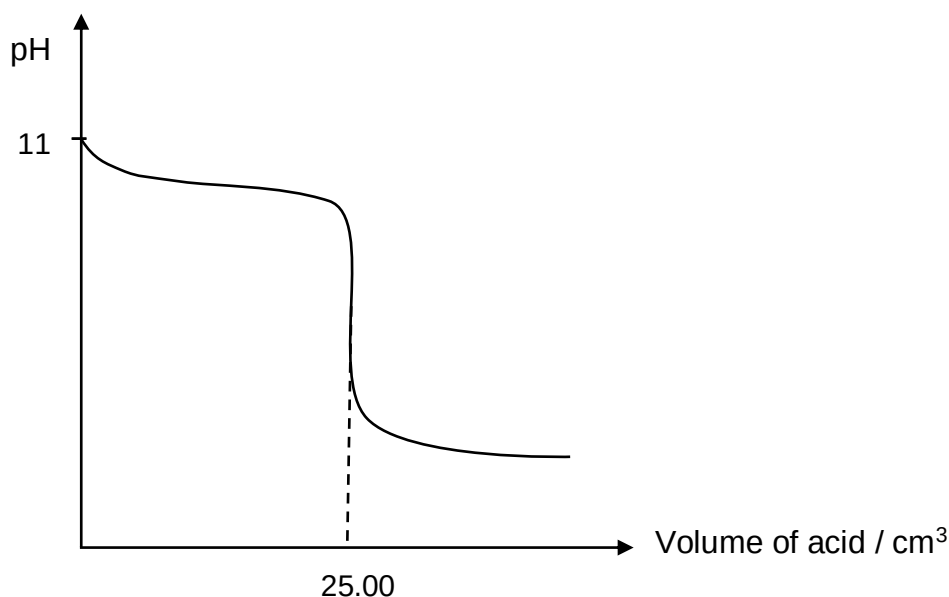
$$K_{a1} = 1.0 \times 10^{-2} \text{ mol dm}^{-3} \quad K_{a2} = 2.5 \times 10^{-7} \text{ mol dm}^{-3}$$

Which of the following statements is correct about H_3PO_3 ?

- I: H_3PO_3 is a dibasic acid as one of the H atom is bonded to P atom.
- II: The K_b values of H_2PO_3^- and HPO_3^{2-} are 4.0×10^{-12} and 1.0×10^{-12} respectively.
- III: K_{a2} is smaller than K_{a1} because it gets increasingly difficult to remove a H^+ from a negatively charged ion.

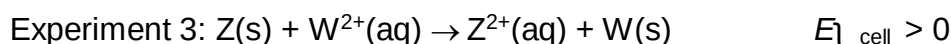
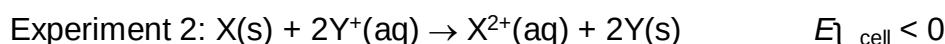
- A I only
- B I & III
- C II & III
- D All statements are correct

- 11 The diagram below shows the change of pH produced when 20.0 cm³ of trimethylamine was titrated with 0.01 mol dm⁻³ of HCl(aq) at 25 °C.



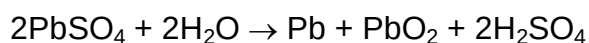
Which of the following statements is **incorrect**?

- A The K_b value of trimethylamine is 8.00×10^{-5} .
 - B When 35.00 cm³ of acid is added, pH of the solution is 2.7.
 - C Phenolphthalein is not a suitable indicator for the above titration.
 - D When concentration of HCl is doubled, the end point volume of the titration would be halved while the pH at equivalence point would remain the same.
- 12 The e.m.f of three different experiments was measured under standard conditions and the results are shown below:



Which of the following statements is correct?

- A Z^{2+} is the strongest oxidising agent.
 - B If concentration of $Y^+(aq)$ is lowered in experiment 2, the E_{cell} would be more positive.
 - C The reaction of $Z(s) + W^{2+}(aq) \rightarrow Z^{2+}(aq) + W(s)$ is spontaneous.
 - D The reducing power decreases in the order $Z > W > Y > X$.
- 13 In a lead-acid battery reaction, the charging process is achieved by passing an electric current through the cell. The overall reaction equation for the charging process is given below.

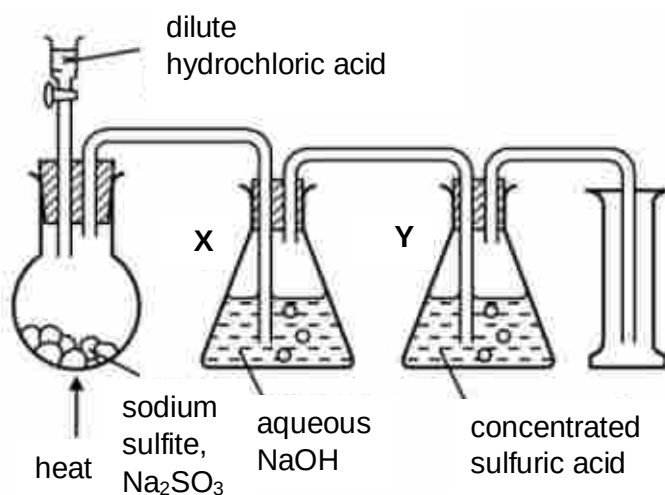


After charging, PbSO_4 on one plate is converted to PbO_2 . The other plate is converted to Pb . When the two plates are connected, a current will flow, enabling the discharging process to take place.

Which species is oxidised when the battery is discharged?

- A Pb
- B H_2O
- C PbO_2
- D SO_4^{2-}

- 14 The diagram represents an **unsuccessful** attempt to prepare and collect sulfur dioxide.



Which modification would make the experiment successful?

- A omitting flask X entirely
- B omitting flask Y entirely
- C using dilute sulfuric acid instead of dilute hydrochloric acid
- D collecting by upward delivery

- 15 Which of the following statements for strontium or its compounds is **incorrect**?
- A Strontium sulfate is sparingly soluble in water.
 - B Strontium hydroxide is dehydrated to the oxide on strong heating.
 - C Strontium reacts with cold water to form strontium oxide and hydrogen.
 - D Strontium carbonate decomposes at a higher temperature than calcium carbonate.
- 16 Letters written on paper using aqueous ammonium thiocyanate are invisible until turned blood red by brushing the paper with aqueous iron(III) chloride. If the ammonium thiocyanate is first made alkaline, the letters are orange and less clear.
- Which of the following statements is correct?
- A The colour changes are due to ligand exchange reactions only.
 - B Aqueous iron(III) chloride can exist as $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ in solution.
 - C With aqueous ammonium thiocyanate, $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{3+}$ complex is formed.
 - D With alkaline ammonium thiocyanate, the letters are less clear because a less stable complex is formed.
- 17 For the sequence hydrogen chloride, hydrogen bromide and hydrogen iodide, there is a decrease in
- I volatility
 - II $\text{p}K_{\text{a}}$ value
 - III thermal stability
 - IV reducing power
- A I & IV
 - B II & III
 - C I, II & III
 - D All of the above
- 18 A mixture of 1 mol of chlorine and 1 mol of bromine was reacted completely with iron(II) solution. The resulting mixture was subsequently treated with excess $\text{AgNO}_3(\text{aq})$. After standing for 5 minutes, excess dilute $\text{NH}_3(\text{aq})$ was added to the mixture and filtered to obtain filtrate **F** and residue **G**.
- Which of the following statements is correct?
- A If excess $\text{HNO}_3(\text{aq})$ is added to filtrate **F**, a white precipitate of mass 143.5 g will be obtained.
 - B Mass of residue **G** is 376 g.
 - C Filtrate **F** contains $[\text{Ag}(\text{NH}_3)_2]^+$, Cl^- and Fe^{3+} ions.
 - D Residue **G** is made up of more than one precipitate.

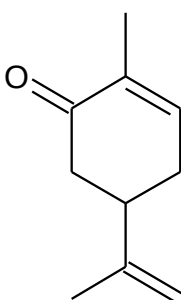
- 19** Cracking is a thermal decomposition process by which large hydrocarbon molecules are broken down by passing them over a heated catalyst at high pressure. The products are smaller alkanes and alkenes.

The cracking of a single hydrocarbon molecule, C_nH_{2n+2} , produces two hydrocarbon molecules only. Each hydrocarbon product contains the same number of carbon atoms in one molecule. Each hydrocarbon product has non-cyclic structural isomers.

What is the value of n ?

- A** 4 **B** 6 **C** 8 **D** 9

- 20** Carvone is found in spearmint.



Carvone

How many σ and π bonds are present in this molecule?

	σ	π
A	11	6
B	13	6
C	25	3
D	25	6

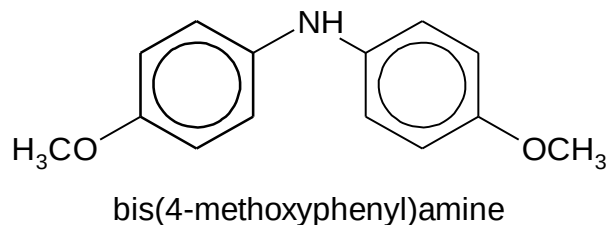
- 21** Many different compounds have been used in aerosol sprays, refrigerators and in making foamed plastics.

Which compound will cause the most ozone depletion?

- A** CCl_3F
B $CH_2FCHClF$
C $CH_3CH_2CH_2CH_3$
D N_2O

22 The reactivity of methoxybenzene, $\text{C}_6\text{H}_5\text{OCH}_3$ is similar to that of phenol.

How many moles of aqueous nitric acid are required to react with one mole of bis(4-methoxyphenyl)amine?

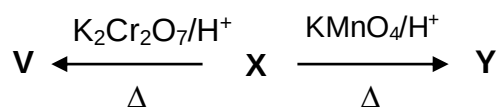


- A 2
- B 3
- C 4
- D 5

23 Which of the following will **not** yield a final organic product containing deuterium? ($\text{D} = {}^2\text{H}$)

	compound	reagents and conditions
A		DCI , D_2O , heat under reflux
B	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$	D_2O , room conditions
C	$\text{CH}_3\text{CH}_2\text{CHO}$	DCN , trace NaCN , 15°C
D		CH_3OD , conc D_2SO_4 , heat under reflux

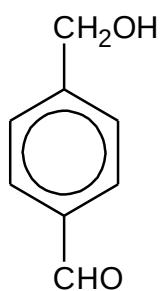
- 24 Compound **X** is used to synthesize DEET, a common active ingredient in mosquito repellent. A brick-red precipitate is observed when it reacts with Fehling's reagent. 1 mol of **X** undergoes the following reactions.



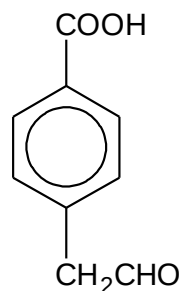
Y reacts with HNO_3 under suitable conditions to produce only 1 possible organic product. **V** reacts with Na_2CO_3 to produce only 1 mol of $\text{CO}_2(\text{g})$.

What could **X** be?

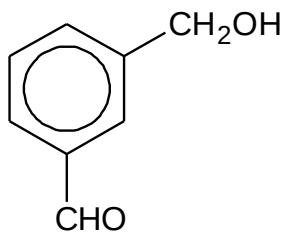
A



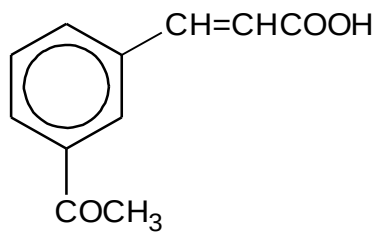
B



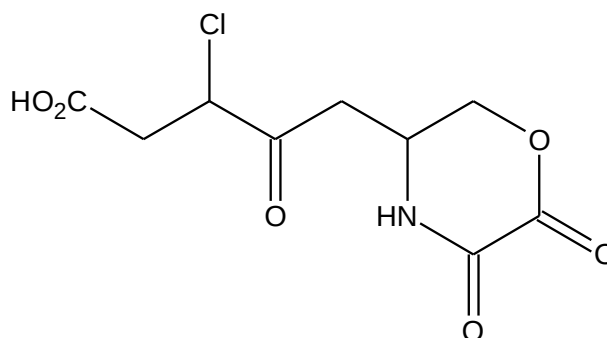
C



D



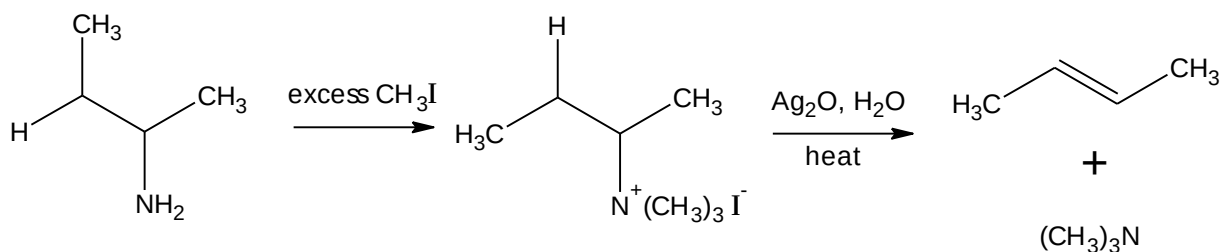
25 Which of the following statements about compound **W** is correct?



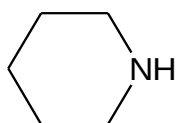
compound **W**

- A** An aqueous solution of **W** is approximately neutral as there is 1 carboxylic acid group and 1 amine group present in the structure.
- B** The product formed when **W** is reduced by LiAlH_4 will react with Na to produce 2 moles of $\text{H}_2(\text{g})$.
- C** The reduction of **W** by LiAlH_4 will cause the oxidation state of any carbon involved in the reduction to decrease from +3 to -1.
- D** **W** will require 3 moles of $\text{NaOH}(\text{aq})$ for complete reaction if the reaction is to take place with heating.

- 26 The Hofmann elimination is a process where an amine undergoes treatment with excess methyl iodide to form a tertiary amine intermediate followed by treatment with silver oxide, water and heat to form an alkene.

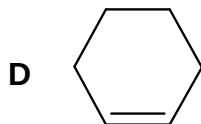
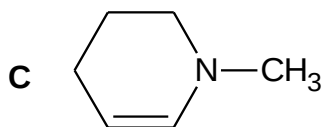


What is the structure of the alkene formed when a cyclic amine, piperidine, undergoes the Hofmann elimination?

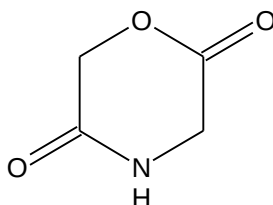


Piperidine

- A $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
 B $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$



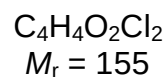
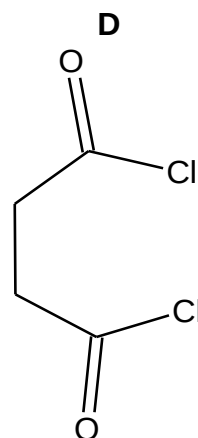
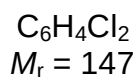
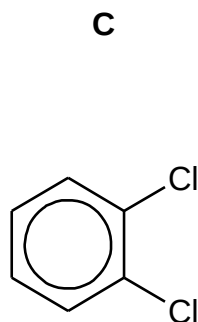
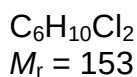
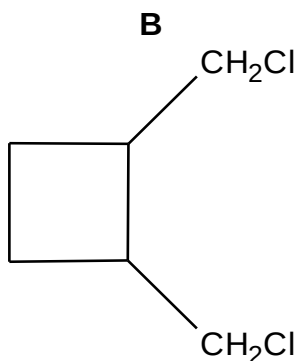
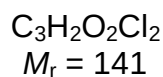
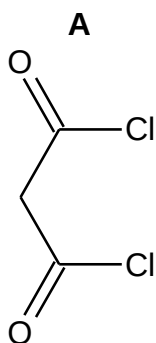
- 27 Which of the following compounds can be used, in a 1-step conversion, to produce the following cyclic structure?



- A $\text{HO}_2\text{CCH}_2\text{NH}_2$ and $\text{HO}_2\text{CCH}_2\text{OH}$
 B $\text{HO}_2\text{CCH}_2\text{CONHCH}_2\text{OH}$
 C $\text{ClOCCH}_2\text{COCl}$ and $\text{H}_2\text{NCH}_2\text{OH}$
 D ClOCCH_2OH and $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$

- 28 One gram of each of the following compounds was heated with NaOH(aq), and then dilute HNO₃(aq) and AgNO₃(aq) were added.

Which compound will produce the largest mass of AgCl(s) in 30 seconds?



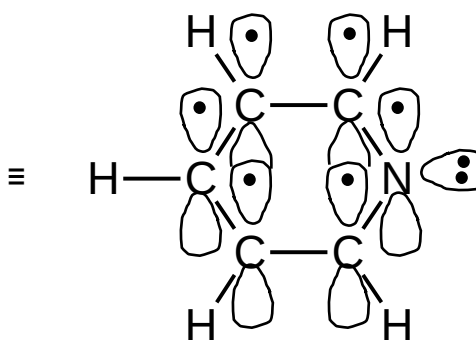
- 29 Consider the following four compounds.

1 ethanamide, CH_3CONH_2

2 phenylamine,

3 piperidine,

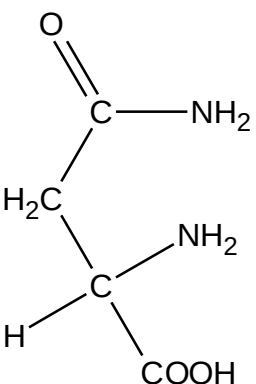
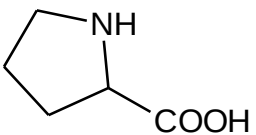
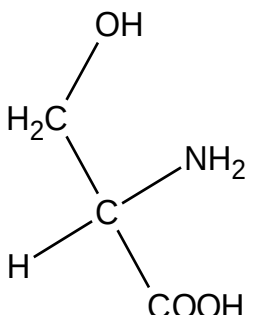
4 pyridine,



What is the relative order of decreasing basicity of these compounds?

A	3	2	1	4
B	3	2	4	1
C	3	4	2	1
D	3	4	1	2

30 Upon complete hydrolysis, 1 mol of polypeptide **X** gives the following amino acids.

amino acid	structure	M_r	mass of amino acid / g
asparagine		132	16.8
proline		115	7.3
serine		105	13.3

What is the M_r of **X**?

- A 352
- B 499
- C 517
- D 589

Section B

For each of the questions in this section one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31** The hexagonal form of boron nitride, h-BN, is analogous to graphite where it has a planar hexagonal layered structure of alternating boron and nitrogen atoms.

Which properties are shown by h-BN?

- 1** Its N atoms are sp^2 hybridised.
- 2** It can be used as a dry lubricant.
- 3** It is soluble in organic solvents but not soluble in water.

- 32** Which of the following has the same value as the standard enthalpy change of formation of carbon monoxide?

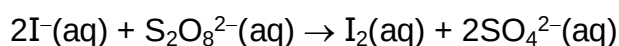
- 1** $\Delta H_f(\text{CO}_2) - \Delta H_f(\text{CO})$
- 2** $\Delta H_f(\text{CO}) - \Delta H_f(\text{graphite})$
- 3** $\frac{1}{2} \Delta H_f(\text{CO}_2)$

The responses **A** to **D** should be selected on the basis of

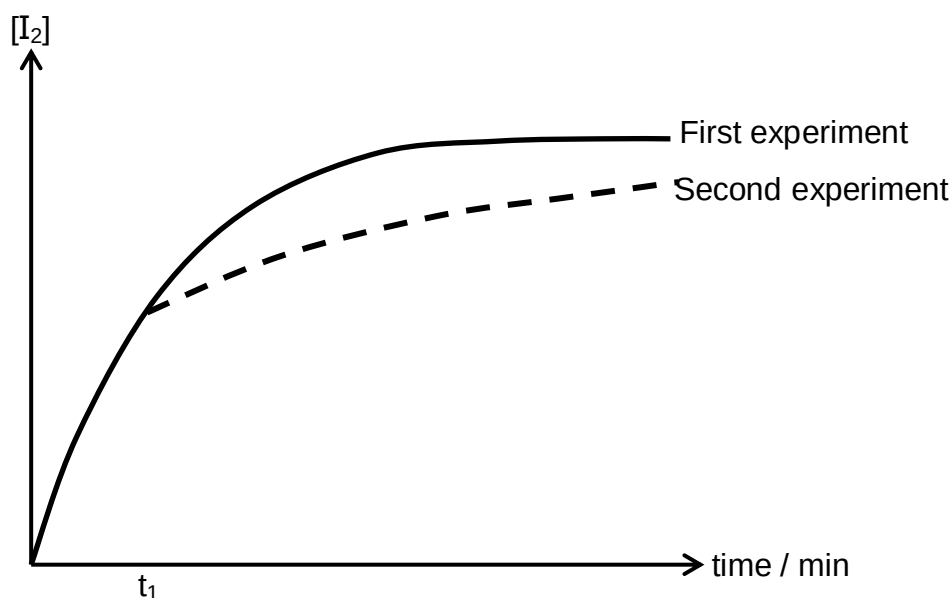
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

33 A student investigated the reaction between iodide and peroxodisulfate.

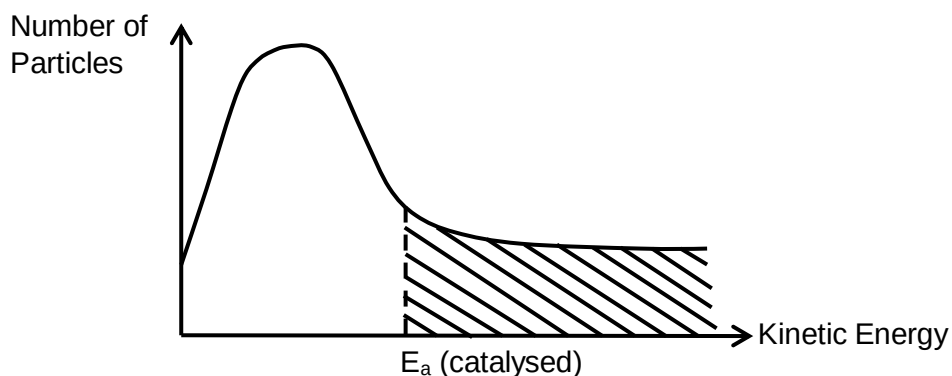


He first performed the experiment by adding $\text{Fe}^{3+}(\text{aq})$ as catalyst. He then performed a second experiment under the same condition but did a change at t_1 . The graphs of $[\text{I}_2]$ against time for both experiments are shown below.



Which of the following statements are correct?

- 1** acidified $\text{VO}_2\text{Cl}(\text{aq})$ can also be used as a catalyst.
- 2** Sodium cyanide could have been added at t_1 .
- 3** The Boltzmann distribution graph for the first experiment is as follow



The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

34 Phosphorus is an element in the third period, Na to Ar, of the Periodic Table.

What is true for phosphorus and none of the other elements in this period?

- 1** Phosphorus is the only element in this period with exactly four atoms in its molecules.
- 2** Phosphorus is the only element in this period which forms two acidic oxides.
- 3** Phosphorus is the only element in this period whose chlorides react with water to form acidic solutions.

35 Which of the statements of the Group II elements (magnesium to barium) or their compounds is correct?

- 1** Reactivity of Group II elements with oxygen increases down the group.
- 2** The volume of acidic gas evolved from the decomposition of 1 mol of Group II nitrate is four times that of the neutral gas evolved.
- 3** Solubility of the Group II sulfates decreases down the group.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

36 The use of the *Data Booklet* is relevant to this question.

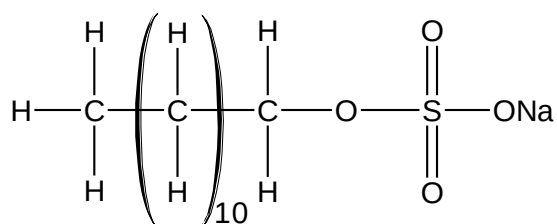
Which of the following species would convert manganese(II) sulfate to manganese(IV) oxide in acidic solution?

- 1 $\text{Pb}(\text{NO}_3)_4$
- 2 $\text{Na}_2\text{S}_2\text{O}_8$
- 3 CoCl_2

37 Which of these **always** applies to a nucleophile?

- 1 It has a lone pair of electrons.
- 2 It is negatively charged.
- 3 It attacks a double bond.

38 Long-chain alkanes are converted on an industrial scale into alkylsulfates for use as detergents, e.g. sodium lauryl sulfate.



sodium lauryl sulfate

What deductions about the properties of this substance can be made from this structure?

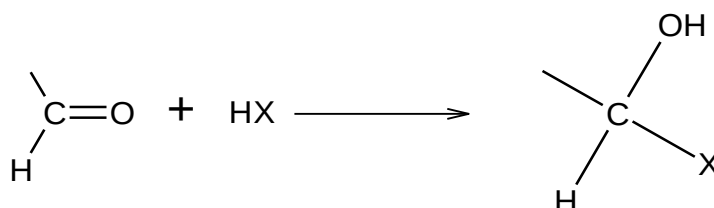
- 1 Part of the structure is polar and is hydrophilic.
- 2 The alkyl chain is soluble in oil droplets.
- 3 All the C–C–C bond angles are 109° .

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

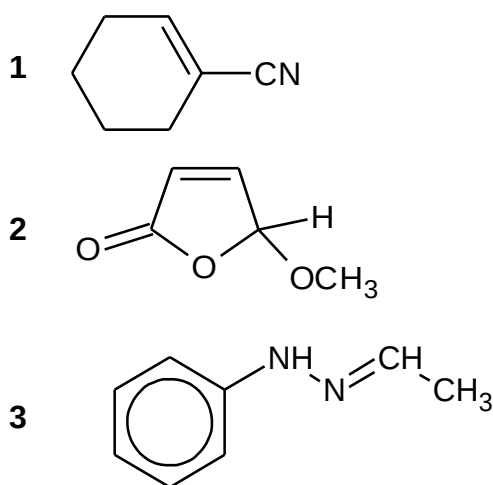
No other combination of statements is used as a correct response.

39 There is a range of reactions of the aldehyde group which have the pattern



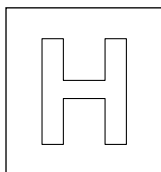
of which the formation of a cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?



40 Which of the following reactions produce a carbocation as an intermediate product and an organic molecule containing a chiral centre that is optically inactive as the final product?

- 1** $\text{C}_6\text{H}_{10} + \text{HBr} \rightarrow \text{C}_6\text{H}_{11}\text{Br}$
- 2** $\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 + \text{NaNO}_3 \rightarrow \text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{Br} + \text{NaBr}$
- 3** $\text{CH}_3\text{C}(\text{CH}=\text{CH}_2)(\text{CH}_2\text{CH}_3)\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{C}(\text{CH}=\text{CH}_2)(\text{CH}_2\text{CH}_3)\text{OH} + \text{NaBr}$



NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

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NAME

CLASS

1	5		

INDEX
NO.

TUTOR

CHEMISTRY

9647/02

Paper 2 Structured

14 September 2016

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

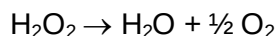
For Examiner's Use		
1	P	/12
2	/ 15	/60
3	/ 6	
4	/ 13	
5	/ 6	
6	/ 20	

This document consists of **17** printed pages and **1** blank page.

Answer **all** questions in the spaces provided.

1 Planning (P)

Baker's yeast is a useful enzyme which can be used to catalyse the decomposition of hydrogen peroxide.



You are provided with

Set-up apparatus:

- 1 x retort stand with clamp
- 1 x 100 cm³ conical flask
- 1 x L-shape glass tube connector fitted with a rubber bung
- 1 x rubber tubing connection
- 1 x gas syringe (possible capacities of 10, 20 or 100 cm³)

Reagents and apparatus

- 100 cm³ of yeast suspension
- 100 cm³ of 3% (by weight) hydrogen peroxide
- Distilled water
- Stopwatch
- All other common laboratory equipment

When 8.0 cm³ of the yeast suspension, 4.0 cm³ of H₂O₂ and 18.0 cm³ of distilled water is mixed, 10 cm³ of oxygen gas was produced in 90 s.

Use the above information and the reagents provided to design an experiment to

- prove first order reaction with respect to yeast by a graphical method
- prove first order reaction with respect to hydrogen peroxide by a graphical method

In your experiment, you should perform 4 other experimental runs (including the above run) to measure the volume of oxygen gas produced at regular intervals. The volume of yeast suspension used should be varied in all the runs while keeping volume of H₂O₂ constant at 4.0 cm³.

In your experiment, illustrate / describe the following:

- A labelled set-up for your experiment using the set-up apparatus provided
- Table of volumes that you will be using in your experiment
- Calculations to determine the maximum volume of oxygen gas produced in each experimental run. In your calculations, assume that the density of H₂O₂ is 1.00 g cm⁻³ and conditions are at r.t.p.
- Procedure for measuring the volume of oxygen gas produced at regular intervals and use the results to find the initial rate for each run graphically
- Graphical analysis involving initial rates to deduce order with respect to yeast
- Graphical analysis involving half-lives to deduce order with respect to H₂O₂ based on one selected run

Experimental setup:

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[Total: 12]

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*For
Examiner's
Use*

- 2 A solder is an alloy of metals which is used to join other metal pieces together. A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

An experimental procedure can confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

- (i) copper metal,
- (ii) aluminium as aluminium hydroxide,
- (iii) zinc as zinc hydroxide.

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm^{-3} sulfuric acid,
- 1.00 mol dm^{-3} ammonia.

No other reagents should be used. Standard laboratory equipment is available.

- (a) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, aluminium hydroxide and zinc hydroxide in **Step 1**, **Step 2** and **Step 3** respectively.

Step 1		Step 2		Step 3
reagent(s) added		reagent(s) added		reagent(s) added
substance(s) present in solution	→	substance(s) present in solution	→	substance(s) present in solution
substance(s) removed by filtration (if any)		substance(s) removed by filtration (if any)		substance(s) removed by filtration (if any)

[3]

- (b) (i) For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure, explain why particular quantities of reagent should be chosen.

Step 1

.....

.....

Step 2

.....

.....

Step 3

.....

..... [4]

- (ii) Write the ionic equations for the reactions taking place in **Step 2**.

.....

..... [2]

- (iii) State the observations for the reactions taking place in **Step 1** and **Step 3**.

Step 1

Step 3 [2]

- (c) Aluminium hydroxide and zinc hydroxide that have been extracted are difficult to dry so it is better to convert them to their oxides.
Describe how this could be done and how you would ensure that each hydroxide has been completely converted into its oxide.

.....

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..... [2]

- (d) If the mass of aluminium oxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder. [1]

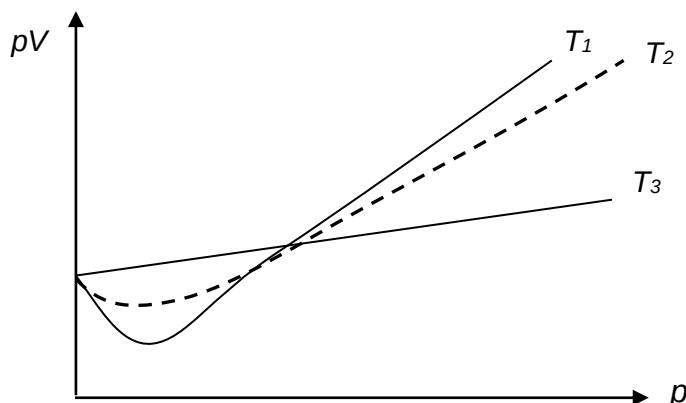
- (e) Even if the experimental difficulties of extracting all of the copper from the mixture were overcome, it would be difficult to obtain an accurate mass of copper from this experiment. Suggest why this is so.

.....
.....
..... [1]

[Total: 15]

- 3 The relationship $pV=nRT$ can be derived from the laws of mechanics by assuming ideal behaviour for gases.

- (a) The graph below represents the relationship between pV and p for a real gas at three different temperatures, T_1 , T_2 and T_3 .



- (i) Draw **one** line on the graph to show what the relationship should be for the same amount of an **ideal** gas. [1]

- (ii) With reference to the graph, state and explain which temperature, T_1 , T_2 or T_3 is the lowest temperature.

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..... [2]

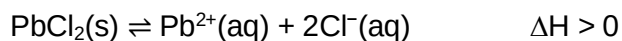
- (b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas **Y**, filling the flask. The results, measured at 26°C and $1.00 \times 10^5 \text{ Pa}$ are shown.

Mass of flask containing air	= 47.930 g
Mass of flask containing Y	= 47.989 g
Density of air	= $0.00118 \text{ g cm}^{-3}$

Calculate the relative molecular mass, M_r , of **Y**. [3]

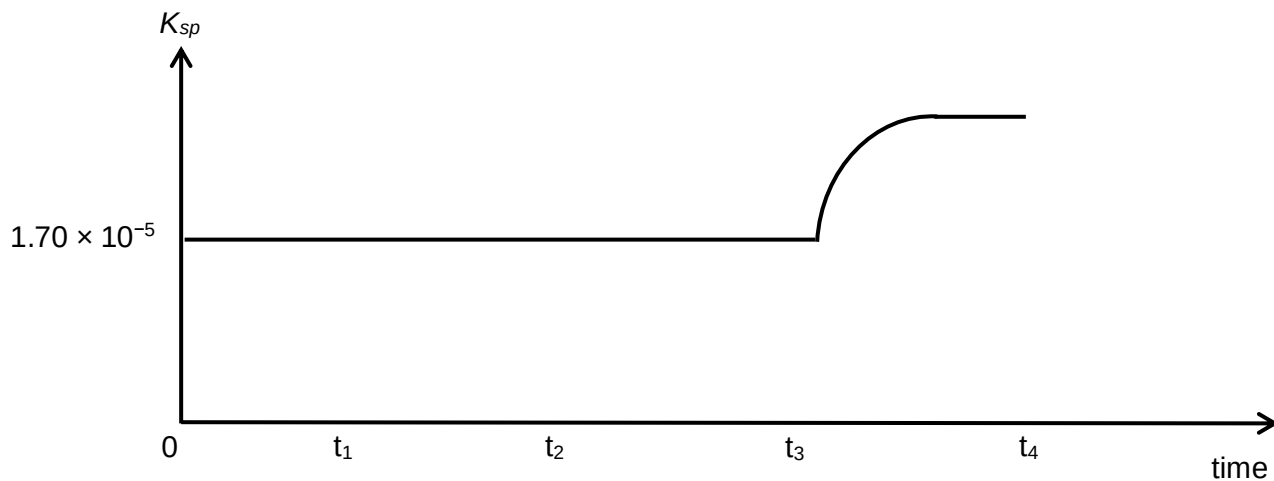
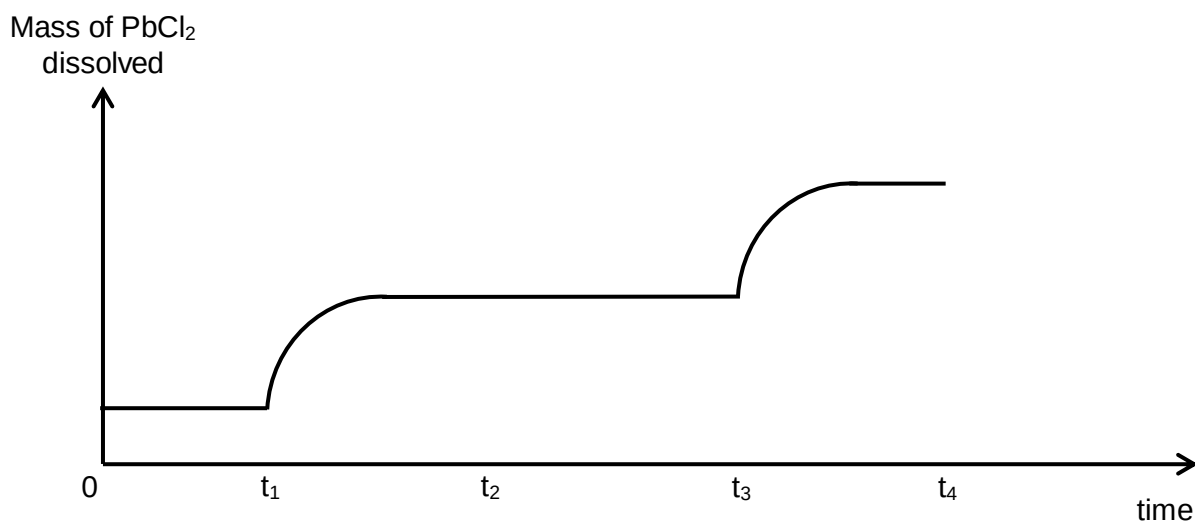
[Total: 6]

- 4 PbCl_2 is a sparingly soluble salt.



A student investigated the solubility product and solubility of PbCl_2 under different conditions. He first added 0.0100 g of solid PbCl_2 into 120 cm^3 of an unknown concentration of $\text{HCl}(\text{aq})$ at 25 $^{\circ}\text{C}$ and subsequently made four changes at t_1 , t_2 , t_3 and t_4 .

The graphs below show the mass of PbCl_2 dissolved and solubility product of PbCl_2 against time.



- (a) Given that 0.00465 g of PbCl_2 remained undissolved after addition of 0.0100 g of PbCl_2 into HCl, deduce the unknown concentration of the HCl. [3]

- (b) Determine the mass of PbCl_2 that can dissolve in 500 cm^3 of water at 25°C . [2]

- (c) Some possible changes listed below were made by the student at t_1 , t_2 and t_3 .
1. Cool reaction mixture to 10 °C in water bath
 2. Heat reaction mixture to 50 °C in water bath
 3. Addition of $\text{AgNO}_3(\text{aq})$
 4. Addition of $\text{PbCl}_2(\text{s})$
 5. Addition of water

With reference to both graphs, suggest and explain the changes made at t_1 , t_2 and t_3 .

change made at t_1

explanation

.....

.....

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.....

change made at t_2

explanation

.....

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.....

change made at t_3

explanation

.....

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.....

..... [6]

- (d) The student added concentrated HCl at t_4 . On both the graphs on **Page 10**, draw how the two graphs would look like after t_4 . [2]

[Total: 13]

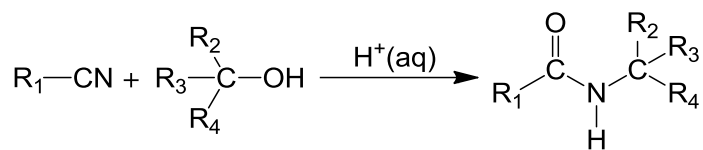
- 6 Compound **A** ($C_{12}H_{16}O_2$) exhibits optical isomerism. It does not react with hot acidified $K_2Cr_2O_7$. 1 mole of **A** reacts with 1 mole of PCl_5 to form **B**. **A** reacts with cold dilute $KMnO_4$ to form **C** ($C_{12}H_{18}O_4$). Upon heating with acidified $KMnO_4$, **A** gives **D** ($C_9H_{10}O_4$) and **E**. **D** produces effervescence when aqueous Na_2CO_3 is added. 1 mole of **D** reacts with 3 moles of aqueous bromine. **E** gives **F**, a yellow precipitate with warm alkaline aqueous iodine.

Draw the structures of **A**, **B**, **C**, **D**, **E** and **F**.

A	B
C	D
E	F

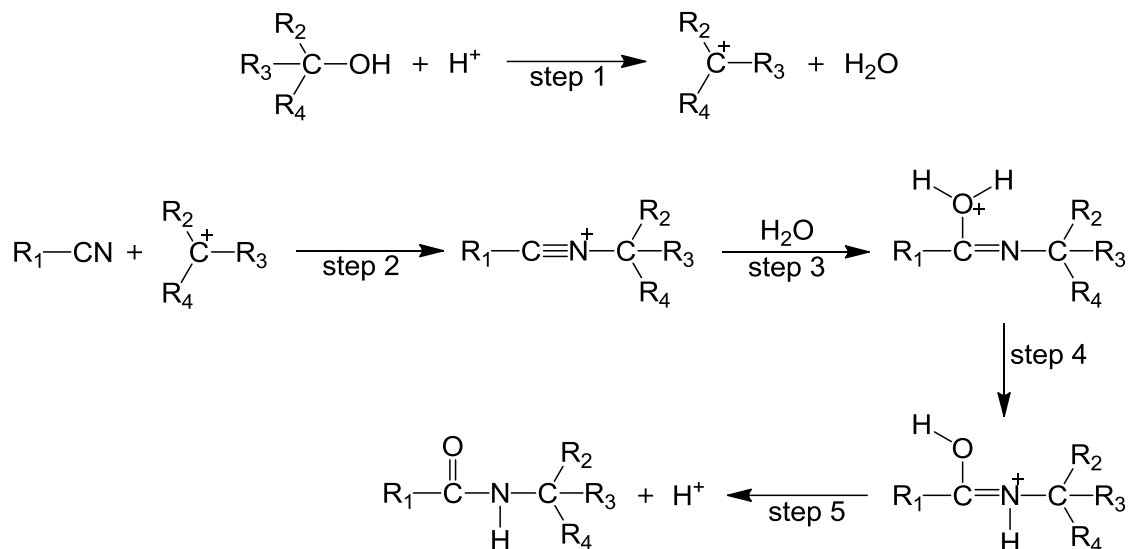
[Total: 6]

- 5 The Ritter reaction is an organic reaction used to convert a nitrile and a tertiary alcohol, in a second order reaction, to form an amide using strong aqueous acid as the catalyst.

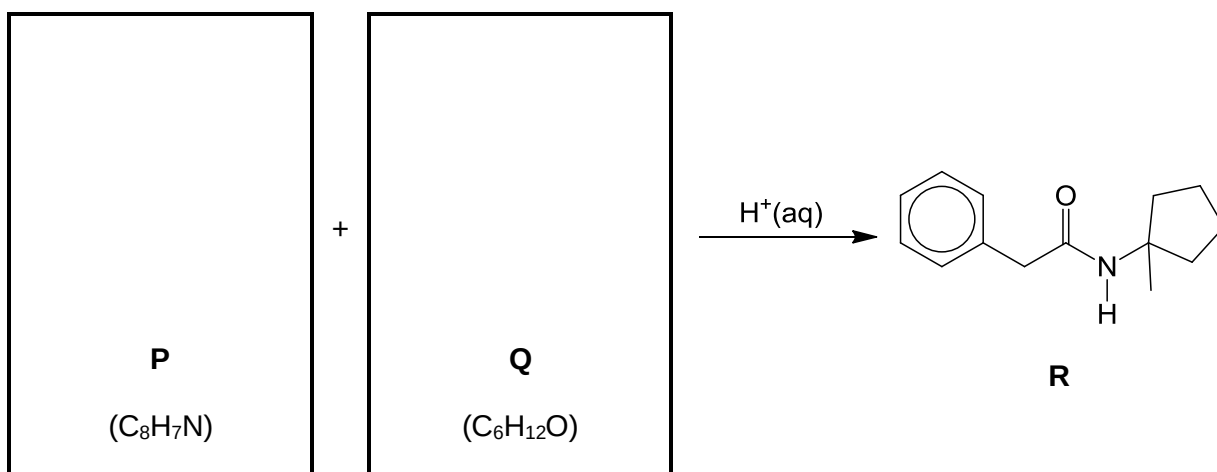


R_1, R_2, R_3 and R_4 are alkyl groups

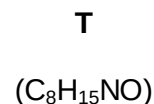
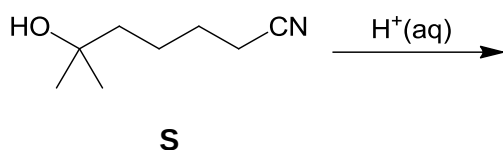
The proposed mechanism is as follows:



- (a) Predict the structures of **P**, **Q** and **T** for each of the following Ritter reactions. [3]



15



- (b) Describe a simple chemical test to distinguish compound **R** and **S**, stating clearly the observations.

Test.....

Observation.....

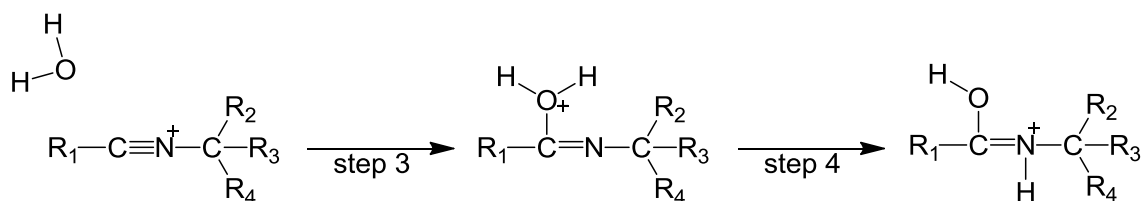
..... [2]

- (c) Suggest the types of reaction occurring in steps 3 and 4.

Step 3.....

Step 4..... [2]

- (d) Complete the mechanism of step 3 and 4 below with arrows, showing the lone pairs and dipole charges. [3]



- (e) Suggest which step of the proposed mechanism on **Page 14** is the slowest step. Explain your reasoning.

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..... [1]

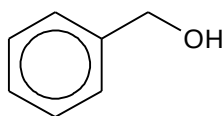
(f) Primary alcohols such as ethanol are not suitable reagents for the Ritter reaction.

(i) Draw a diagram to show the orbitals of the carbon in the carbocation in step 1 and state the type of hybridisation involved. [1]

(ii) Suggest why tertiary alcohols are used in the Ritter reaction but not primary alcohols.

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..... [2]

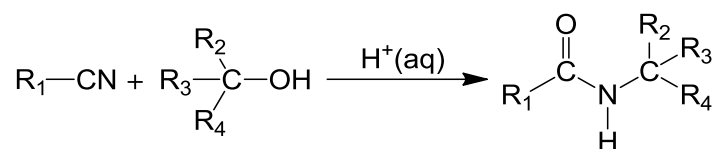
(iii) Suggest why phenylmethanol is a suitable reagent for the Ritter reaction even though it is a primary alcohol.



phenylmethanol

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..... [1]

- (g) This equation for the Ritter reaction is repeated from page 14.



R_1 , R_2 , R_3 and R_4 are alkyl groups

- (i) Using suitable data from the *Data Booklet*, calculate the enthalpy change of reaction. [2]

- (ii) Suggest and explain if the Ritter reaction is spontaneous at high or low temperature.

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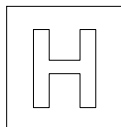
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..... [3]

[Total: 20]



NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

Paper 3 Free Response

9647/03

21 September 2016

2 hours

Additional Materials: Writing Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **13** printed pages and **1** blank page.

[Turn over

Answer any **four** questions.

- 1(a)** Copper(I) sulfate, Cu_2SO_4 , can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.

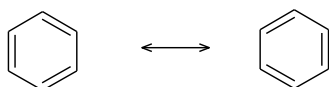
(i) Suggest, with a reason, the colour of copper(I) sulfate. [2]

(ii) Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]

- (b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $\text{PdN}_2\text{H}_6\text{Cl}_2$. Two of these, **A** and **B**, are non-ionic, with $M_r = 211$. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having $M_r = 422$, and contains palladium in both its cation and anion.

For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]

- (c)** Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.

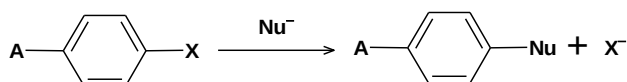


Benzene (two resonance forms)

The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.

Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.

An example of a reaction is as follows:



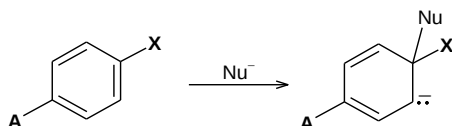
where **A** is an electron withdrawing group and **X** is a halogen

The mechanism of this reaction has two steps:

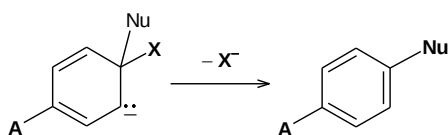
- addition of the nucleophile
- elimination of the halogen leaving group

3

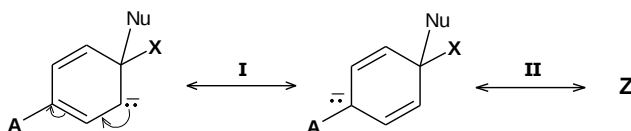
Step 1 involves the addition of the nucleophile (Nu^-). The Nu^- attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.



Step 2 involves the loss of the halogen X, reforming the aromatic ring.

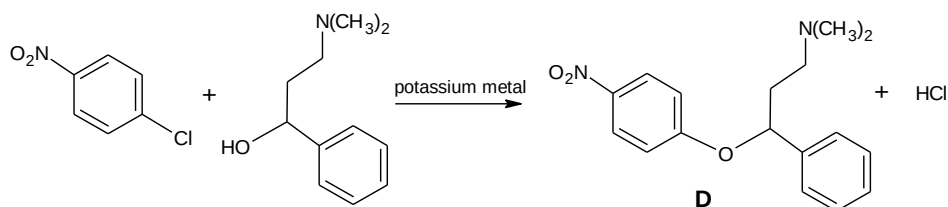


Two other resonance structures of the intermediate in **Step 1** are shown below:

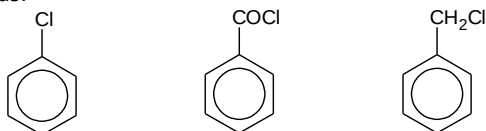


- (i) Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**. [2]

The reaction below shows the synthesis of compound, **D**.



- (ii) Suggest the role of potassium metal in the reaction. [1]
- (iii) Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons. [3]
- (d) Describe and explain the relative ease of hydrolysis of the following three chloro-compounds. [3]

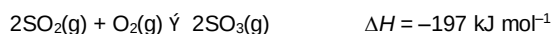


[Total: 20]

2 Sulfuric acid, H_2SO_4 , can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.

(a) Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom. [2]

(b) The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:



Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400 °C. When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.

(i) Write an expression for the equilibrium constant, K_p , of the reaction. [1]

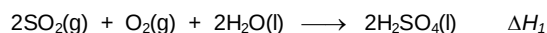
(ii) Calculate the value of K_p at 400 °C, stating its units. [3]

(iii) How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain. [2]

(c) Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO , BaO and SiO_2 .

State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid. [4]

(d) Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO_2 emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:



Using the data below and data from (b), construct an energy cycle to calculate

(i) the enthalpy change of formation of $\text{SO}_2(\text{g})$, and hence

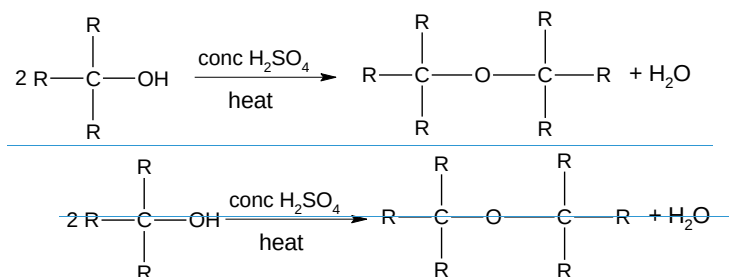
(ii) the enthalpy change of reaction, ΔH_1 for the above reaction.

Enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$	$= -286 \text{ kJ mol}^{-1}$
Enthalpy change of formation of $\text{H}_2\text{SO}_4(\text{l})$	$= -811 \text{ kJ mol}^{-1}$
Enthalpy change of formation of $\text{SO}_3(\text{g})$	$= -493 \text{ kJ mol}^{-1}$

[4]

5

- (e) Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.



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The mechanism occurs via 3 steps:

Step 1:

An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.

Step 2:

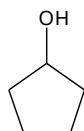
A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates

an oxonium ion $\begin{array}{c} \text{R} \\ | \\ \text{R}'-\text{O}^+-\text{H} \end{array}$ intermediate.

Step 3:

Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.

- (i) Draw the ether formed when cyclopentanol undergoes the above reaction.



cyclopentanol

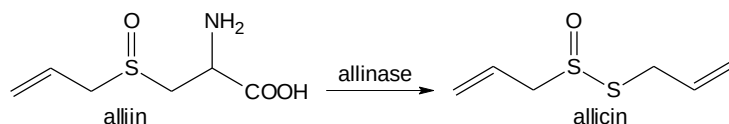
[1]

- (ii) Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]

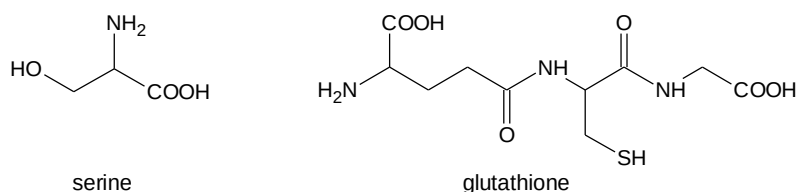
[Total: 20]

- 3 Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.

(a) When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.



Allicin can also be biosynthesised by using serine and glutathione.

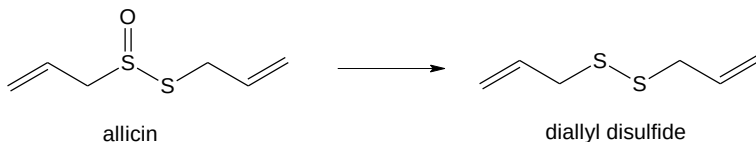


- (i) Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]
- (ii) When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae. Draw the structural formula of **each** of these esters. [2]
- (iii) Draw the structural formulae of the products when glutathione is hydrolysed. [3]

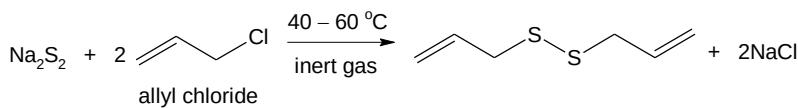
Alliin has pK_a values of 1.84 and 8.45.

- (iv) Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]
- pH 1
 - pH 7
 - pH 11
- (v) Calculate the pH of 0.10 mol dm^{-3} solution of alliin. [1]
- (vi) With reference to the pK_a values, identify the major species formed when 10 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]
- (vii) Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Briefly describe how you have calculated the various key points on the curve. [4]

- (b) Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of alliin.



Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 °C in an inert atmosphere.



- (i) Give the *IUPAC* name of allyl chloride. [1]
- (ii) Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water. [2]
- (iii) State the type of reaction when diallyl disulfide is converted back to allixin. [1]

[Total: 20]

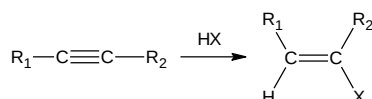
- 4 Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of C_nH_{2n-2} i.e.



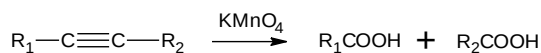
where R_1 and R_2 = H or alkyl or aryl groups

Alkynes exhibit similar chemical properties to alkenes.

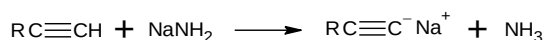
e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes



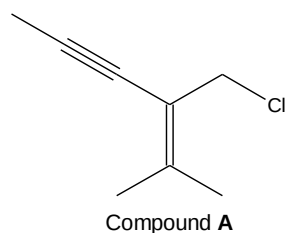
e.g. oxidation by hot concentrated $KMnO_4$ to form mixture of carboxylic acids



However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.



- (a) Ethyne, C_2H_2 , is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.
- (i) Write an equation for the first stage. [1]
- (ii) Suggest a structure for the dihalide formed. [1]
- (iii) When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products. Write an equation to explain the formation of these inorganic by-products. [1]
- (b) Compound **A**, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).



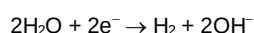
One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]

10

- (c) Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, NaNH_2 followed by heating under reflux to form compound **C**, C_8H_{10} . Compound **C** reacts with hot concentrated KMnO_4 to produce butane-1,4-dioic acid only.

- (i) Explain the reaction with NaNH_2 . [1]
- (ii) Hence, explain the formation of compound **C**. [1]
- (iii) Suggest skeletal structures for compounds **B** and **C**. [2]

When a current of 1.0 A was passed through aqueous potassium maleate ($\text{KO}_2\text{CCH}=\text{CHCO}_2\text{K}$) for 15 minutes, it was found that 110 cm^3 H_2 , measured at r.t.p, was collected at the cathode. The following reaction took place.



- (d) State the relationship between the Faraday constant, F and the Avogadro's constant, L . [1]
- (e) Using the data above and the *Data Booklet*, calculate a value for Avogadro's constant. [3]
- (f) Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:

- mass of bottle containing NaOH before experiment = 10.501 g
- mass of bottle containing NaOH after experiment = 10.904 g
- initial reading on syringe _____ = 10.0 cm^3
- final reading on syringe _____ = 120.0 cm^3

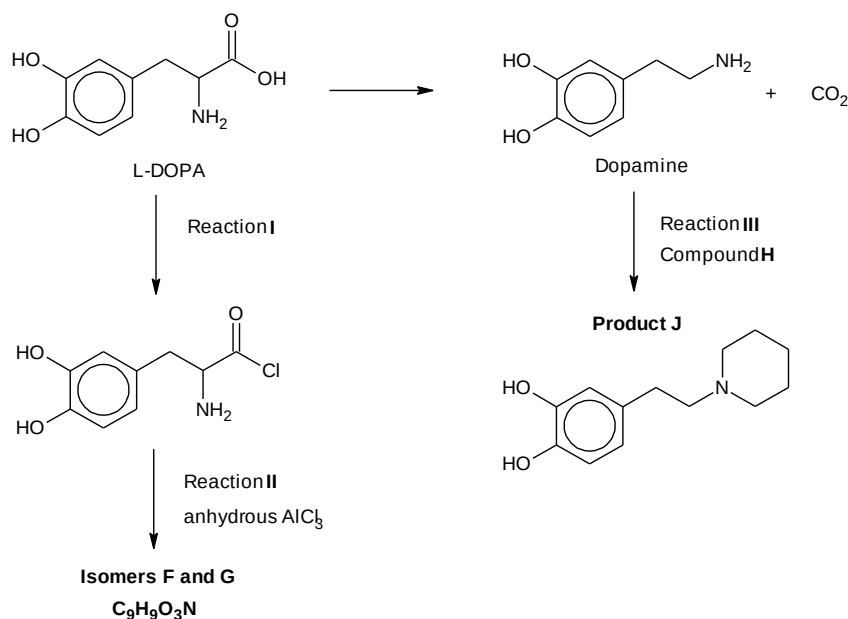
- (i) State the oxidation state of carbon in ethyne. [1]
- (ii) With the help of an equation, explain the purpose of passing the anode gas through NaOH . [1]
- (iii) Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]
- (iv) Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]
- (g) When aqueous potassium maleate was acidified, maleic acid, $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ ($\text{pK}_{\text{a}1} = 1.90$ and $\text{pK}_{\text{a}2} = 6.07$) was liberated. Fumaric acid ($\text{pK}_{\text{a}1} = 3.03$ and $\text{pK}_{\text{a}2} = 4.44$) is a stereoisomer of maleic acid. With a suitable illustration, suggest a reason why maleic acid has a lower $\text{pK}_{\text{a}1}$ but higher $\text{pK}_{\text{a}2}$ than fumaric acid. [2]

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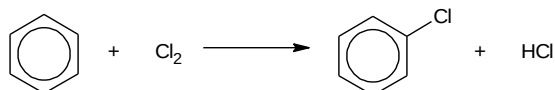
[Total: 20]

- 5(a) Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.

Below is a synthetic route involving L-DOPA and dopamine:



- (i) State the reagents and conditions and any observations in Reaction I. [1]
- (ii) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.



The reaction occurs in several steps.

- The first step is the reaction between Cl_2 and AlCl_3 .



- The benzene is then attacked by the Cl^+ cation in the second step.

- The first step is the reaction between Cl_2 and AlCl_3 .



- The benzene ring is then attacked by the Cl^+ cation in the second step.

AlCl_3 reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.

Predict the structures of isomers **F** and **G** in Reaction II. [2]

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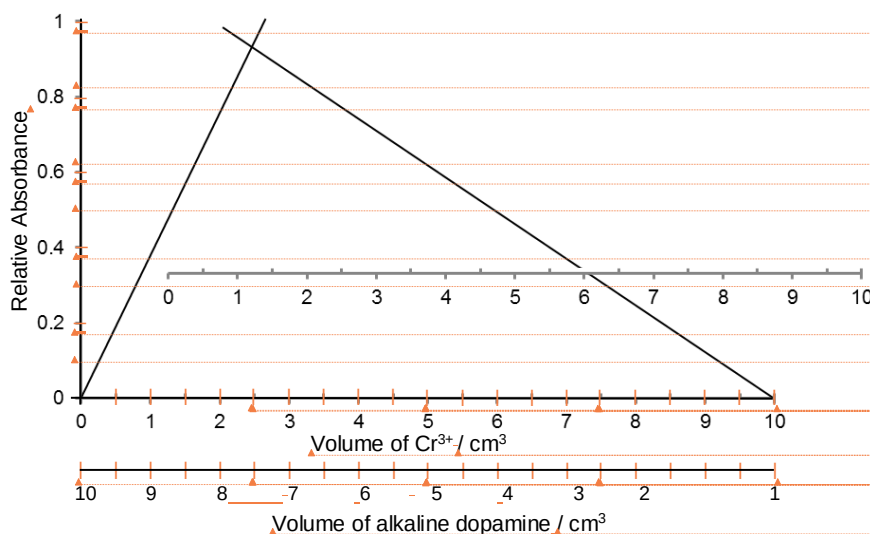
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- (iii) In Reaction III, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]

- (b) Dopamine is a bidentate ligand. When different volumes of $0.0030 \text{ mol dm}^{-3}$ of aqueous Cr(III) and $0.0020 \text{ mol dm}^{-3}$ of alkaline dopamine solution were mixed, a complex **R** is formed. Analysis of **R** shows that its formula is $[\text{Cr}(\text{C}_8\text{H}_9\text{NO}_2)_x(\text{H}_2\text{O})_y]^z$, where x , y and z are integers.

To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.



- (i) Use the graph and the information given to determine the formula of complex **R**. Show your workings clearly. [3]
- (ii) The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d-orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o . The relationship between Δ_o and colours of complexes can be described in the equation below:

$$\Delta_o = \frac{hc}{\lambda}$$

where h is Planck's constant, c is the speed of light and λ is the wavelength of light absorbed

colour	absorbed λ / nm
violet	410
indigo	430
blue	480
blue-green	500
green	530
yellow	580
orange	610
red	680

Given that Δ_o for complex **R** is $4.125 \times 10^{-22} \text{ kJ}$ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**. [2]

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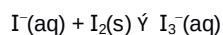
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- (c) Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:



- (i) Draw a fully labelled experimental set-up for a voltaic cell made up of a $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ half-cell and a I_2/I^- half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons. [3]
- (ii) By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to a solution of $\text{I}_2(\text{aq})$, the I_2/I^- half-cell. [3]
- (d) Explain the following statements.

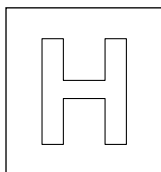
- (i) BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity. [2]
- (ii) SiCl_4 reacts violently in water but CCl_4 has no reaction with water. [1]
- (iii) Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist. [1]

[Total: 20]

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NYJC 2016 Prelim H2 Chemistry Paper 1 Answers

1	D	6	A	11	D	16	B	21	A	26	A	31	B	36	B
2	C	7	D	12	C	17	C	22	B	27	D	32	B	37	D
3	B	8	B	13	A	18	D	23	D	28	A	33	B	38	A
4	B	9	D	14	A	19	C	24	B	29	C	34	D	39	C
5	A	10	B	15	C	20	C	25	B	30	C	35	A	40	C



NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

Teachers' Mark Scheme

CLASS

1	5		

INDEX
NO.

TUTOR

CHEMISTRY

9647/02

Paper 2 Structured

14 September 2016

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

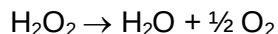
For Examiner's Use		
1	P	/12
2	/ 15	/60
3	/ 6	
4	/ 13	
5	/ 6	
6	/ 20	

This document consists of **17** printed pages and **1** blank page.

Answer **all** questions in the spaces provided.

1 Planning (P)

Baker's yeast is a useful enzyme which can be used to catalyse the decomposition of hydrogen peroxide.



You are provided with

Set-up apparatus:

- 1 x retort stand with clamp
- 1 x 100 cm³ conical flask
- 1 x L-shape glass tube connector fitted with a rubber bung
- 1 x rubber tubing connection
- 1 x gas syringe (possible capacities of 10, 20 or 100 cm³)

Reagents and apparatus

- 100 cm³ of yeast suspension
- 100 cm³ of 3% (by weight) hydrogen peroxide
- Distilled water
- Stopwatch
- All other common laboratory equipment

When 8.0 cm³ of the yeast suspension, 4.0 cm³ of H₂O₂ and 18.0 cm³ of distilled water is mixed, 10 cm³ of oxygen gas was produced in 90 s.

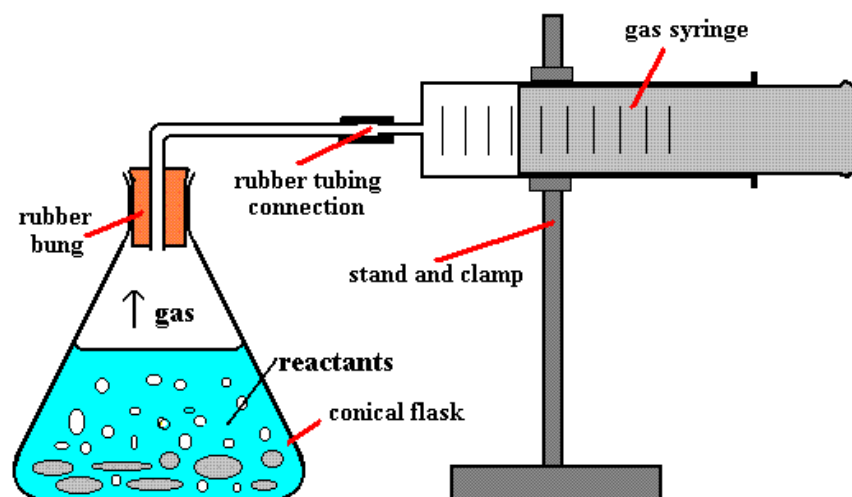
Use the above information and the reagents provided to design an experiment to

- prove first order reaction with respect to yeast by a graphical method
- prove first order reaction with respect to hydrogen peroxide by a graphical method

In your experiment, you should perform 4 other experimental runs to measure the volume of oxygen gas produced at regular intervals. The volume of yeast suspension used should be varied in all the runs while keeping volume of H₂O₂ constant at 4.0 cm³.

In your experiment, illustrate / describe the following:

- A labelled set-up for your experiment using the set-up apparatus provided
- Table of volumes that you will be using in your experiment
- Calculations to determine the maximum volume of oxygen gas produced in each experimental run. In your calculations, assume that the density of H₂O₂ is 1.00 g cm⁻³ and conditions are at r.t.p.
- Procedure for measuring the volume of oxygen gas produced at regular intervals and use the results to find the initial rate for each run graphically
- Graphical analysis involving initial rates to deduce order with respect to yeast
- Graphical analysis involving half-lives to deduce order with respect to H₂O₂ based on one selected run

Experimental setup:

1 mark – 3 apparatus drawn and labelled correctly

1 mark – all apparatus drawn, labelled and connected correctly

Table of volumes

Run	Vol of yeast /cm ³	Vol of H ₂ O ₂ /cm ³	Vol of water /cm ³	Total volume /cm ³
1	4.0	4.00	22.0	30.0
2	6.0	4.00	20.0	30.0
3	8.0	4.00	18.0	30.0
4	10.0	4.00	16.0	30.0
5	12.0	4.00	14.0	30.0

1 mark – volume of yeast is between 2 – 20 cm³, volume of H₂O₂ is constant

1 mark – volume of water added accordingly to keep total volume constant

Calculations to determine the maximum volume of oxygen gas produced in each experimental run

Mass of 4.00 cm³ of H₂O₂ = 1.00 x 4.00 = 4.00 g

Moles of H₂O₂ = (4.00 x 0.03) / 34.0 = 0.00353 mol **[1]**

Moles of O₂ gas = ½ (0.00353) = 0.00176 mol

Volume of O₂ gas = 0.00176 x 24000 = 42.4 cm³ **[1]**

Hence minimum size of syringe to be used is the 100 cm³ size if the reaction is allowed to go to completion

Procedure for measuring the volume of oxygen gas produced at fixed intervals

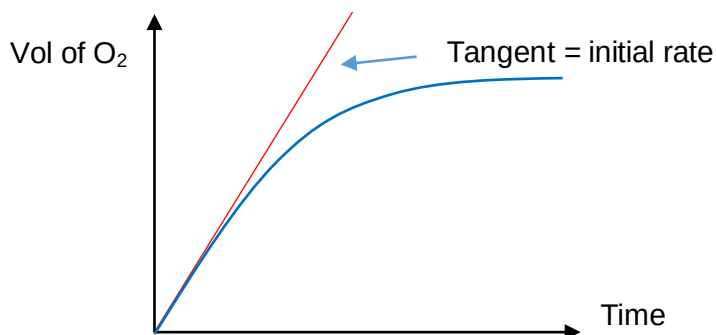
1. Record the initial reading on the syringe
2. Using a burette, measure 2.0 cm^3 of the yeast suspension and add into the conical flask
3. Using a measuring cylinder, measure 24.0 cm^3 of the distilled water and add into the conical flask.
4. Using a burette, measure 4.00 cm^3 of the H_2O_2 into a small beaker.
5. Pour the H_2O_2 into the conical flask, stopper the conical flask with the conical flask and start the stop watch immediately. Swirl the conical flask a few times
6. Record the reading on the syringe every 10 seconds (or other regular time intervals, until 5 readings are collected i.e. 10 cm^3 is produced.
7. Repeat steps 1 – 9 for the next 4 experimental runs, changing the volumes according to the table given. For run 5 (or any other run), make sure to use the 100 cm^3 syringe and allow the reaction to go to completion.

1 mark – 3/7 steps correctly written with appropriate apparatus used

1 mark – all steps correctly written with appropriate apparatus used

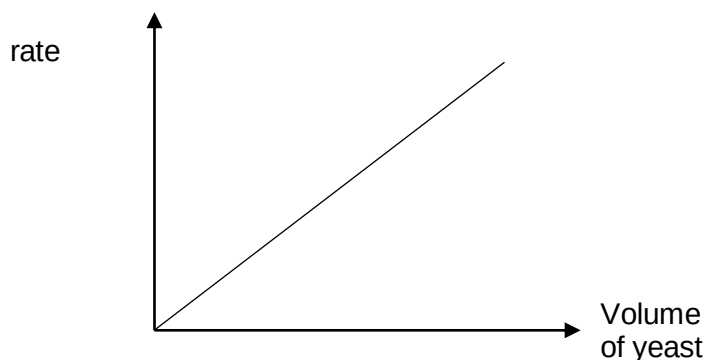
Graphical analysis using the initial rates to deduce order with respect to yeast

For the five set of readings, plot the volume of O_2 produced against time. The tangent at time = 0 is the initial rate (see graph below)



1 mark

Using the initial rates obtained, plot a graph of initial rates against volume of yeast used. If order is 1, a straight line through the origin should be obtained.

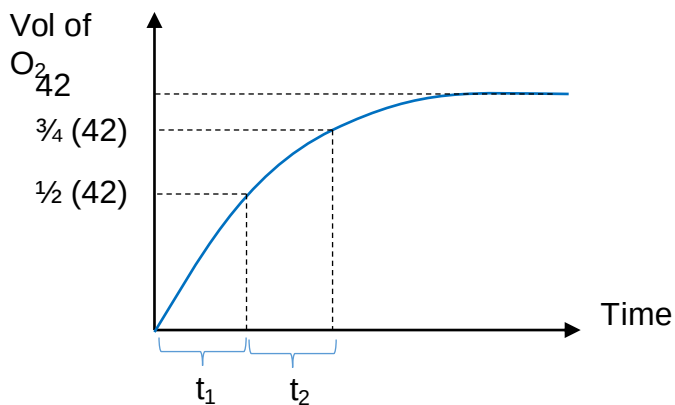


1 mark

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Graphical analysis using a half-life method to deduce order with respect to H_2O_2 using the selected run

Using the graph for run 5, find 2 consecutive half-lives. If order is one, the half-lives should be constant i.e. $t_1 = t_2$. [1]



1 mark – correct graph. X accepted instead of 42 but the graph must plateau.

[Total: 12]

- 2 A solder is an alloy of metals which is used to join other metal pieces together. A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

An experimental procedure can confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

- (i) copper metal,
- (ii) aluminium as aluminium hydroxide,
- (iii) zinc as zinc hydroxide.

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm⁻³ sulfuric acid,
- 1.00 mol dm⁻³ ammonia.

No other reagents should be used. Standard laboratory equipment is available.

- (a) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, aluminium hydroxide and zinc hydroxide in **Step 1**, **Step 2** and **Step 3** respectively.

Step 1	Step 2	Step 3
reagent(s) added H_2SO_4	reagent(s) added NH_3	reagent(s) added H_2SO_4
substance(s) present in solution ZnSO_4 $\text{Al}_2(\text{SO}_4)_3$	substance(s) present in solution $\text{Zn}(\text{NH}_3)_4^{2+}$ $(\text{NH}_4)_2\text{SO}_4 - \text{blank ok}$	substance(s) present in solution $(\text{NH}_4)_2\text{SO}_4 - \text{blank ok}$
substance(s) removed by filtration (if any) Cu	substance(s) removed by filtration (if any) $\text{Al}(\text{OH})_3$	substance(s) removed by filtration (if any) $\text{Zn}(\text{OH})_2$

[3]

6 points – 3 mks.

- (b) (i) For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure, explain why particular quantities of reagent should be chosen.

Step 1 excess H_2SO_4 – to completely dissolve Zn and Al [1]

.....

.....

Step 2 excess NH_3 – to ppt $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ and subsequently form $\text{Zn}(\text{NH}_3)_4^{2+}$
/dissolve $\text{Zn}(\text{OH})_2$ [1]

.....

Step 3 sufficient/enough H_2SO_4 [1] – neutralise/react with NH_3 [1] so that $\text{Zn}(\text{OH})_2$ is.
re-ppt but not excess as that $\text{Zn}(\text{OH})_2$ reacts/dissolves

..... [4]

- (ii) Write the ionic equations for the reactions taking place in **Step 2**.

$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3$ [1]

$[\text{Zn}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightarrow \text{Zn}(\text{NH}_3)_4^{2+}$ [1] [2]

- (iii) State the observations for the reactions taking place in **Step 1** and **Step 3**.

Step 1 Pink solid in colourless solution. Effervescence produced. Gas evolved
extinguished lighted splint with a 'pop' sound.....

Step 3 White ppt re-ppt/re-forms [2]

- (c) Aluminium hydroxide and zinc hydroxide that have been extracted are difficult to dry so it is better to convert them to their oxides.
Describe how this could be done and how you would ensure that each hydroxide has been completely converted into its oxide.

- Weigh the hydroxides and heat [1]
- Cool and re-weigh
- Repeat heating and cooling until constant mass is achieved [1]

.....

.....

.....

.....

..... [2]

- (d) If the mass of aluminium oxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder. [1]



$$n(\text{Al}_2\text{O}_3) = 1.50/102.0 = 0.0147 \text{ mol}$$

$$n(\text{Al}) = 2(0.0147) = 0.0294 \text{ mol}$$

$$m(\text{Al}) = 0.0294 \times 27.0 = 0.794 \text{ g} \quad [1]$$

- (e) Even if the experimental difficulties of extracting all of the copper from the mixture were overcome, it would be difficult to obtain an accurate mass of copper from this experiment. Suggest why this is so.

Mass/amount/percentage of copper is small.....

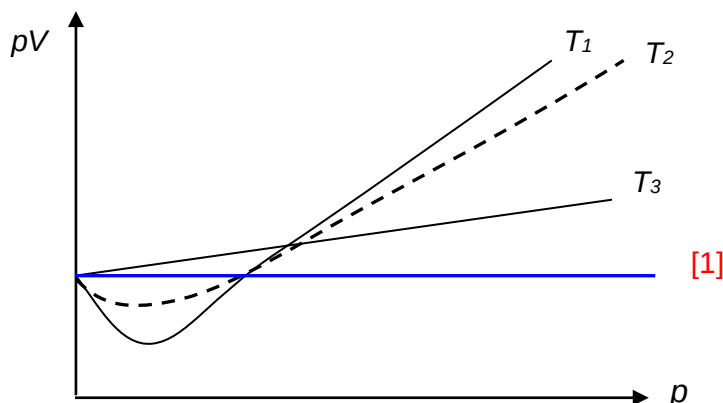
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..... [1]

[Total: 15]

- 3 The relationship $pV=nRT$ can be derived from the laws of mechanics by assuming ideal behaviour for gases.

- (a) The graph below represents the relationship between pV and p for a real gas at three different temperatures, T_1 , T_2 and T_3 .



- (i) Draw **one** line on the graph to show what the relationship should be for the same amount of an **ideal** gas. [1]
- (ii) With reference to the graph, state and explain which temperature, T_1 , T_2 or T_3 is the lowest temperature.

T_1 (because it shows greatest deviation) [1]

With decrease in temperature, KE of particles is reduced, and intermolecular

forces of attraction become more significant, and the gas behaves less ideally [1]

.....

..... [2]

- (b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas Y, filling the flask. The results, measured at 26°C and $1.00 \times 10^5 \text{ Pa}$ are shown.

Mass of flask containing air	= 47.930 g
Mass of flask containing Y	= 47.989 g
Density of air	= $0.00118 \text{ g cm}^{-3}$

Calculate the relative molecular mass, M_r , of Y. [3]

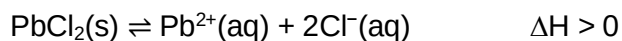
$$\begin{aligned}
 \text{Mass of air} &= 100 \times 0.00118 &= 0.118 \text{ g} \\
 \text{Mass of flask} &= 47.930 - 0.118 &= 47.812 \text{ g} \\
 \text{Mass of Y} &= 47.989 - 47.812 &= 0.177 \text{ g} \quad [1]
 \end{aligned}$$

$$pV = nRT = \frac{m}{M_r}RT$$

$$\begin{aligned}
 M_r &= \frac{m}{pV}RT = \frac{0.177 \times 8.31 \times 299}{1 \times 10^5 \times 100 \times 10^{-6}} \quad [1] \text{ correct working} \\
 &= 44.0 \quad [1] \text{ correct answer}
 \end{aligned}$$

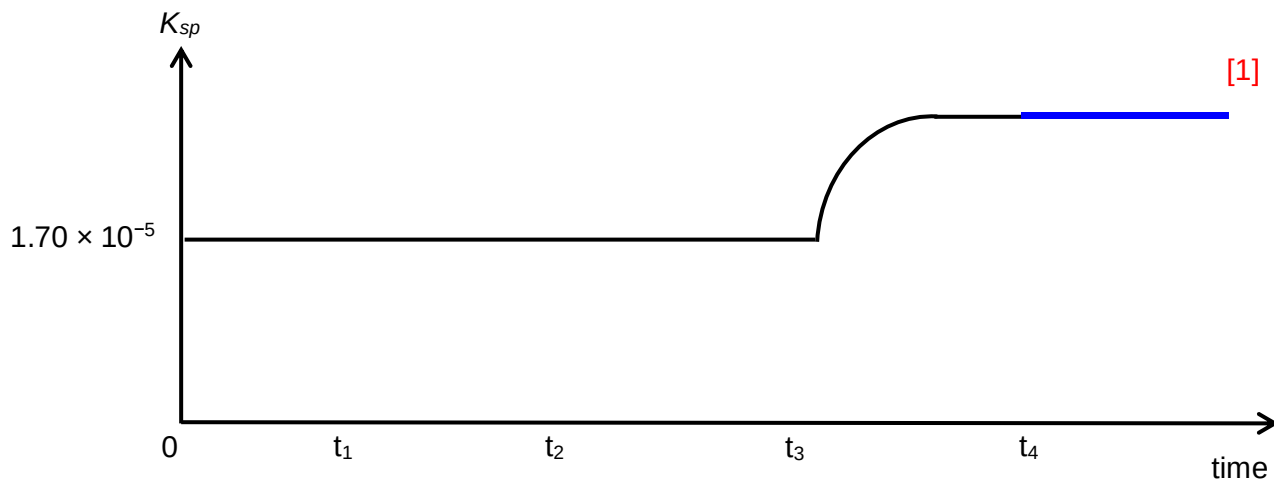
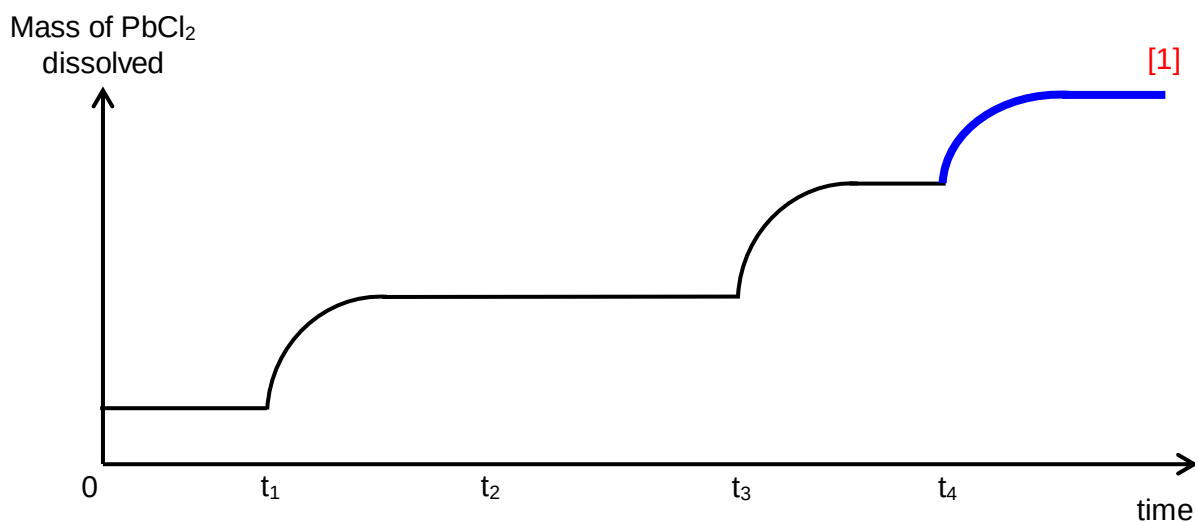
[Total: 6]

- 4 PbCl_2 is a sparingly soluble salt.



A student investigated the solubility product and solubility of PbCl_2 under different conditions. He first added 0.0100 g of solid PbCl_2 into 120 cm^3 of an unknown concentration of $\text{HCl}(\text{aq})$ at 25 $^{\circ}\text{C}$ and subsequently made four changes at t_1 , t_2 , t_3 and t_4 .

The graphs below show the mass of PbCl_2 dissolved and solubility product of PbCl_2 against time.

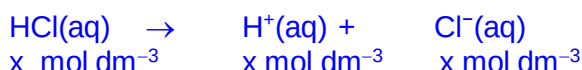
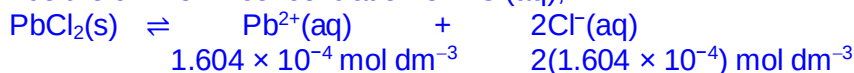


- (a) Given that 0.00465 g of PbCl_2 remained undissolved after addition of 0.0100 g of PbCl_2 into HCl, deduce the unknown concentration of the HCl. [3]

$$\text{Mass of PbCl}_2 \text{ dissolved} = 0.0100 - 0.00465 = 0.00535 \text{ g [1]}$$

$$\text{Solubility of PbCl}_2 \text{ in HCl(aq), } x = \frac{0.00535 / 278.0}{120 / 1000} = 1.604 \times 10^{-4} \text{ mol dm}^{-3} \text{ [1]}$$

Let x be the unknown concentration of HCl(aq) ,



At saturation, ionic product = K_{sp}

$$\begin{aligned} K_{\text{sp}} &= [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ 1.70 \times 10^{-5} &= (1.604 \times 10^{-4})(2 \times 1.604 \times 10^{-4} + x)^2 \\ x &= 0.3252 \\ &= \underline{0.325 \text{ mol dm}^{-3}} \text{ [1]} \end{aligned}$$

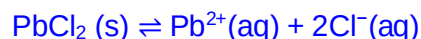
Alternative:

Assuming $2(1.604 \times 10^{-4})$ is small,

$$\begin{aligned} K_{\text{sp}} &= [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ 1.70 \times 10^{-5} &= (1.604 \times 10^{-4})(x)^2 \\ x &= 0.3256 \\ &= \underline{0.326 \text{ mol dm}^{-3}} \end{aligned}$$

- (b) Determine the mass of PbCl_2 that can dissolve in 500 cm^3 of water at 25°C . [2]

Let m be the mass of PbCl_2 dissolve in 500 cm^3 of water.



$$\text{Solubility of PbCl}_2 \text{ in water} = \frac{m / 278.0}{500 / 1000} \text{ [1]}$$

K_{sp} remain unchanged at 25°C .

$$\begin{aligned} K_{\text{sp}} &= [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ 4 \left(\frac{m / 278.0}{500 / 1000} \right)^3 &= 1.70 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \\ m &= 2.252 \text{ g} = \underline{2.25 \text{ g}} \text{ [1]} \end{aligned}$$

(c) Some possible changes listed below were made by the student at t_1 , t_2 and t_3 .

1. Cool reaction mixture to 10 °C in water bath
2. Heat reaction mixture to 50 °C in water bath
3. Addition of $\text{AgNO}_3(\text{aq})$
4. Addition of $\text{PbCl}_2(\text{s})$
5. Addition of water

With reference to both graphs, suggest and explain the changes made at t_1 , t_2 and t_3 .

change made at t_1 **Addition of water or Addition of $\text{AgNO}_3(\text{aq})$ [1]**

explanation

The total volume increase when water is added to reaction mixture, hence $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ decrease. According to Le Chatelier's Principle, position of equilibrium shifts right to increase the $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$. Thus, more PbCl_2 dissolve. K_{sp} remain constant as K_{sp} is temperature dependent [1]

or Addition of $\text{AgNO}_3(\text{aq})$, presence of Ag^+ caused precipitation of $\text{AgCl}(\text{s})$, hence $[\text{Cl}^-]$ decrease. According to Le Chatelier's Principle, position of equilibrium shifts right to increase $[\text{Cl}^-]$. Thus, more PbCl_2 dissolve and K_{sp} remain constant as K_{sp} is temperature dependent.

change made at t_2 **Addition of $\text{PbCl}_2(\text{s})$ [1]**

explanation The solution is already saturated. Hence, as more $\text{PbCl}_2(\text{s})$ is added, the mass of PbCl_2 dissolve will not increase. K_{sp} remain constant as K_{sp} is temperature dependent. [1]

change made at t_3 **Heat reaction mixture to 50 °C in water bath [1]**

explanation According to Le Chatelier's Principle, as temperature increase, the position of equilibrium shifts right to favour the forward endothermic reaction, to absorb heat.

Hence, $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ increase. The mass of CaSO_4 dissolved and K_{sp} increase. [1]

[6]

(d) The student added concentrated HCl at t_4 . On both the graphs on **Page 10**, draw how the two graphs would look like after t_4 . [2]

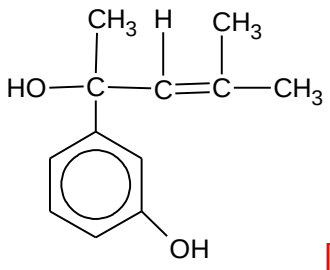
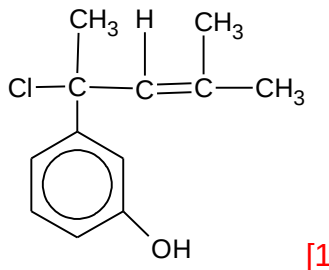
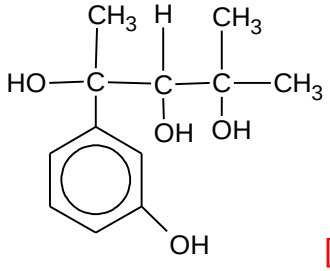
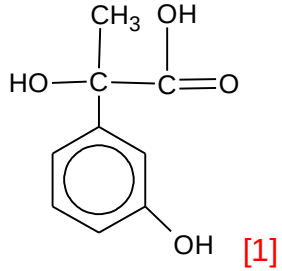
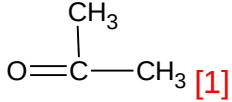


Formation of complex, PbCl_4^{2-} , increases the solubility of PbCl_2 . Hence, mass of PbCl_2 dissolve increase. K_{sp} remain constant as K_{sp} is temperature dependent.

[Total: 13]

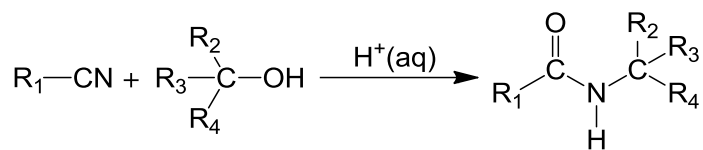
- 5 Compound **A** ($C_{12}H_{16}O_2$) exhibits optical isomerism. It does not react with hot acidified $K_2Cr_2O_7$. 1 mole of **A** reacts with 1 mole of PCl_5 to form **B**. **A** reacts with cold dilute $KMnO_4$ to form **C** ($C_{12}H_{18}O_4$). Upon heating with acidified $KMnO_4$, **A** gives **D** ($C_9H_{10}O_4$) and **E**. **D** produces effervescence when aqueous Na_2CO_3 is added. 1 mole of **D** reacts with 3 moles of aqueous bromine. **E** gives **F**, a yellow precipitate with warm alkaline aqueous iodine.

Draw the structures of **A**, **B**, **C**, **D**, **E** and **F**.

 A	 B
 C	 D
 E	CHI_3 F

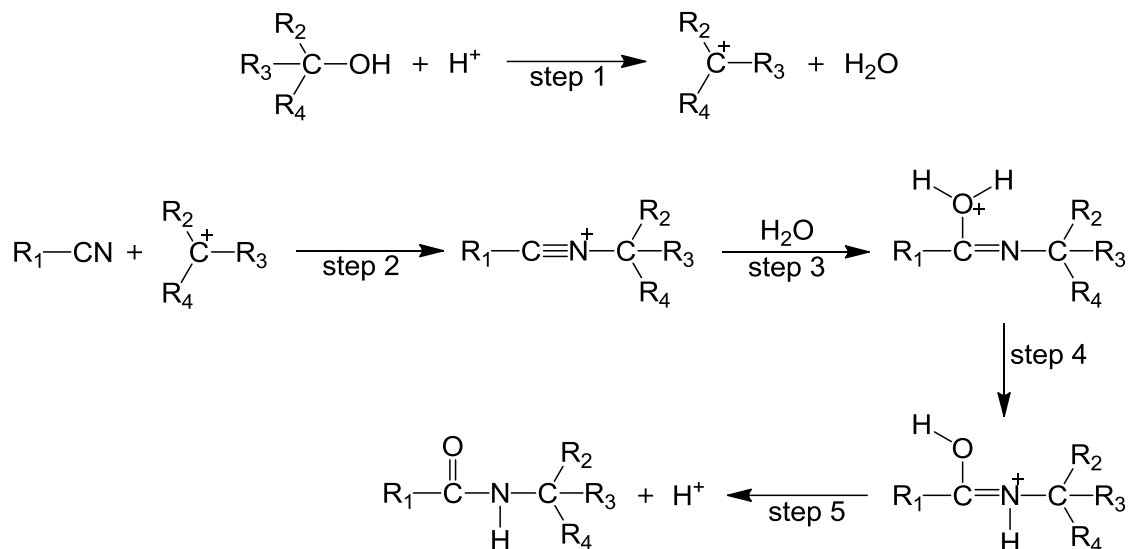
[Total: 6]

- 6 The Ritter reaction is an organic reaction used to convert a nitrile and a tertiary alcohol, in a second order reaction, to form an amide using strong aqueous acid as the catalyst.

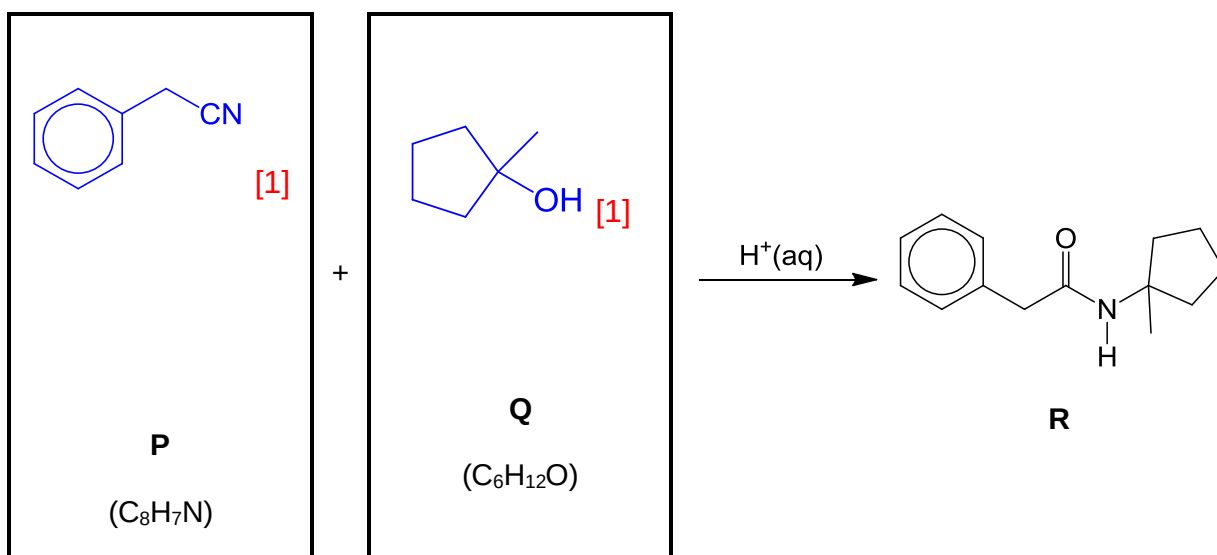


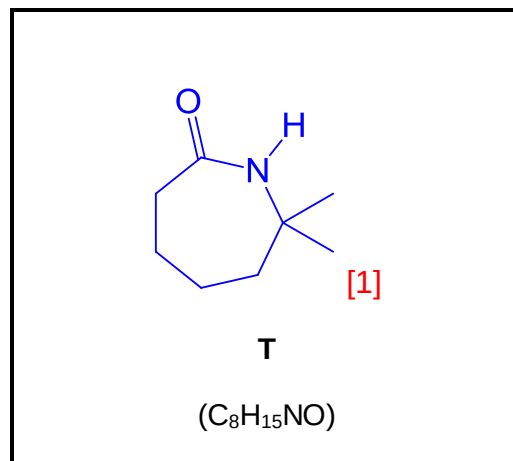
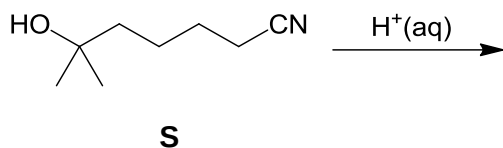
R_1, R_2, R_3 and R_4 are alkyl groups

The proposed mechanism is as follows:



- (a) Predict the structures of **P**, **Q** and **T** for each of the following Ritter reactions. [3]





- (b) Describe a simple chemical test to distinguish compound **R** and **S**, stating clearly the observations.

Test..... (1) Na, room temp or (2) PCl₅/SOCl₂, room temp or (3) KMnO₄, H₂SO₄(aq), heat [1]

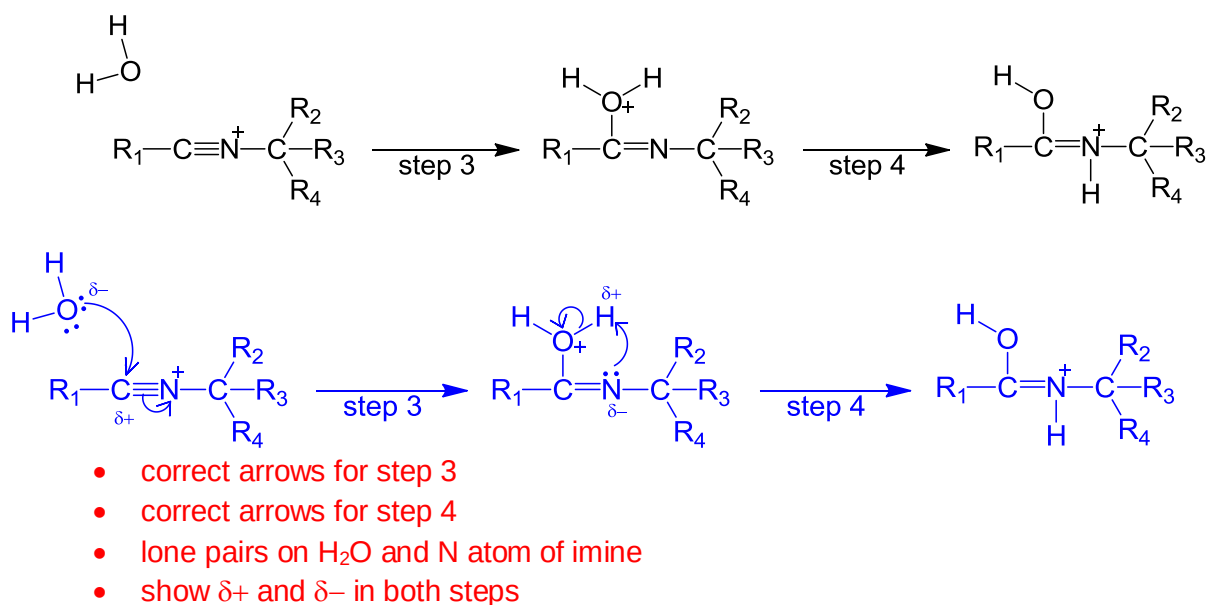
Observation..... (1) Compound **S**: effervescence of H₂ gas evolved which extinguishes lighted splint with a pop sound. Compound **R**: no effervescence of H₂ observed.
 (2) Compound **S**: white fumes of HCl evolved Compound **R**: no white fumes.
 (3) Compound **R**: Purple KMnO₄ decolourise, white ppt of Benzoic acid formed.
 Compound **S**: purple KMnO₄ remained. [1] [2]

- (c) Suggest the types of reaction occurring in steps 3 and 4.

Step 3..... Nucleophilic Addition [1]

Step 4..... Acid-base [1] [2]

- (d) Complete the mechanism of step 3 and 4 below with arrows, showing the lone pairs and dipole charges. [3]



4 • = 3 marks

3 • = 2 marks 2 • = 1 mark

1 • = 0 marks

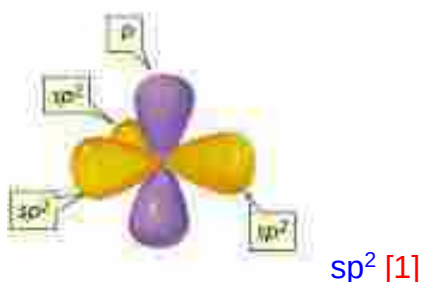
- (e) Suggest which step of the proposed mechanism on **Page 14** is the slowest step. Explain your reasoning.

Step 1 is the slowest step as Ritter reaction is a second order reaction (as stated in the question), involving one molecule of tertiary alcohol and a H^+ ion. [1]

..... [1]

- (f) Primary alcohols such as ethanol are not suitable reagents for the Ritter reaction.

- (i) Draw a diagram to show the orbitals of the carbon in the carbocation in step 1 and state the type of hybridisation involved. [1]



- (ii) Suggest why tertiary alcohols are used in the Ritter reaction but not primary alcohols.

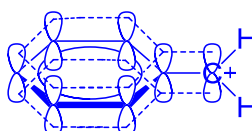
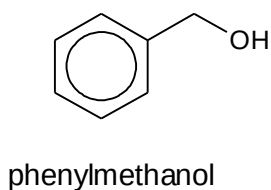


Tertiary alcohol forms a tertiary carbocation in step 1, which is more stable than a primary carbocation from a primary alcohol. [1]

The three electron donating alkyl groups donate electrons to the carbocation to disperse the positive charge (decrease the positive charge intensity) and stabilise the tertiary carbocation. [1]

..... [2]

- (iii) Suggest why phenylmethanol is a suitable reagent for the Ritter reaction even though it is a primary alcohol.



Note:

The primary carbocation formed from phenylmethanol in step 1 has an unhybridised p-orbital which forms an overlap with the π -orbital of the carbons in benzene.

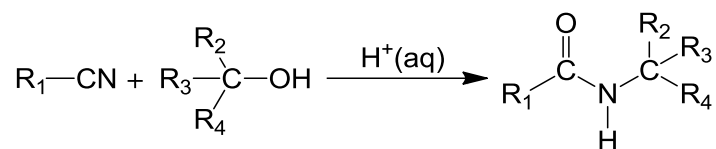
The positive charge on the carbocation delocalised into the benzene ring, therefore stabilising the primary carbocation. [1]

or

Electron from the benzene ring delocalised to the carbocation, stabilising the positive charge.

..... [1]

- (g) This equation for the Ritter reaction is repeated from page 14.



R₁, R₂, R₃ and R₄ are alkyl groups

- (i) Using suitable data from the *Data Booklet*, calculate the enthalpy change of reaction. [2]

From the *Data Booklet*,

BE (C≡N) = 890

BE (C–N) = 305

BE (C–O) = 360

BE (C=O) = 740

BE (O–H) = 460

BE (N–H) = 390

$\Delta H_r = \sum \text{BE}(\text{bonds broken}) - \sum \text{BE}(\text{bonds formed})$

= 890 + 360 + 460 – (2×305 + 740 + 390) [1] for correct substitution of values

= –30 kJ mol^{–1} [1] for final answer and allow ecf

- (ii) Suggest and explain if the Ritter reaction is spontaneous at high or low temperature.

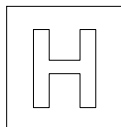
$\Delta G = \Delta H - T\Delta S$

- Low temperature
- ΔS is negative
- as there is a decrease in entropy, whereby two reactant molecules undergo Ritter reaction to form one product molecule.
- $-T\Delta S$ is positive, ΔG is negative only at low temperature

1• = 0 mark 2• = 1 mark 3• = 2 marks 4• = 3 marks

..... [3]

[Total: 20]



NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

Teachers' Mark Scheme

CHEMISTRY

Paper 3 Free Response

9647/03

21 September 2016

2 hours

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **13** printed pages and **1** blank page.

[Turn over

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Complex Script Font: 18 pt, English (Singapore)

Answer any **four** questions.

- 1(a)** Copper(I) sulfate, Cu_2SO_4 , can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.

- (i) Suggest, with a reason, the colour of copper(I) sulfate. [2]

Colourless. [1] Cu^+ has an electronic configuration of $[\text{Ar}] 3d^{10}$ or fully filled d orbitals, hence d-d transition cannot take place. [1]

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- (ii) Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]

$E_{(\text{Cu}^{2+}/\text{Cu}^+)} = +0.15 \text{ V}$
 $E_{(\text{Cu}^+/\text{Cu})} = +0.52 \text{ V}$
 [1] for quoting E values

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$E_{\text{cell}} = E_{(\text{Cu}^+/\text{Cu})} - E_{(\text{Cu}^{2+}/\text{Cu}^+)} = +0.52 - (+0.15) = +0.37 \text{ V} > 0$
 Since $E_{\text{cell}} > 0$, reaction is feasible. [1]

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$2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$ [1]

- (b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $\text{PdN}_2\text{H}_6\text{Cl}_2$. Two of these, **A** and **B**, are non-ionic, with $M_r = 211$. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having $M_r = 422$, and contains palladium in both its cation and anion.

For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]

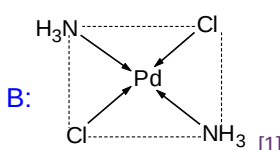
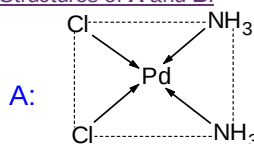
$M_r(\text{PdN}_2\text{H}_6\text{Cl}_2) = 106 + 2(14.0) + 6 + 2(35.5) = 211$

A and **B** have the molecular formula $\text{PdN}_2\text{H}_6\text{Cl}_2$. (•)

C has the molecular formula $(\text{PdN}_2\text{H}_6\text{Cl}_2)_2 \rightarrow \text{Pd}_2\text{N}_4\text{H}_{12}\text{Cl}_4$. (•)

Since palladium (II) salts form square planar complexes, it has a coordination number of 4. (•)

Structures of **A** and **B**:



Since **A** has a dipole moment and **B** has no dipole moment, **A** is a polar molecule and **B** is a non-polar molecule. (•)

$4(\bullet) - [2], 3(\bullet), 2(\bullet) - [1]$

C: $[\text{Pd}(\text{NH}_3)_3\text{Cl}]^+ ; [\text{Pd}(\text{NH}_3)\text{Cl}_3]^-$ OR

$[\text{Pd}(\text{NH}_3)_4]^{2+}; [\text{PdCl}_4]^{2-}$

[1] each for correct cation and anion $M_r(\text{PdN}_2\text{H}_6\text{Cl}_2) = 106 + 2(14.0) + 6 + 2(35.5) = 211$

A and **B** have the molecular formula $\text{PdN}_2\text{H}_6\text{Cl}_2$. [1]

C has the molecular formula $(\text{PdN}_2\text{H}_6\text{Cl}_2)_2 \rightarrow \text{Pd}_2\text{N}_4\text{H}_{12}\text{Cl}_4$. [1]

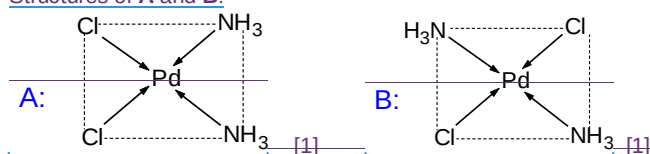
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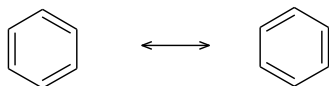
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Structures of A and B:



C: $[\text{Pd}(\text{NH}_3)_3\text{Cl}]^+ : [\text{Pd}(\text{NH}_3)\text{Cl}_3]^-$ OR
 $[\text{Pd}(\text{NH}_3)_4]^{2+} : [\text{PdCl}_4]^{2-}$
 [1] each for correct cation and anion

- (c) Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.

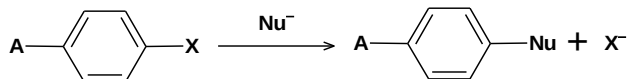


Benzene (two resonance forms)

The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.

Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.

An example of a reaction is as follows:

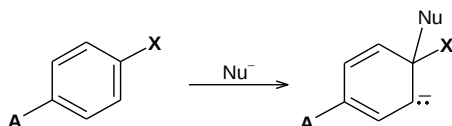


where A is an electron withdrawing group and X is a halogen

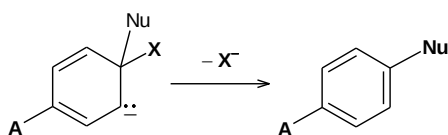
The mechanism of this reaction has two steps:

- addition of the nucleophile
- elimination of the halogen leaving group

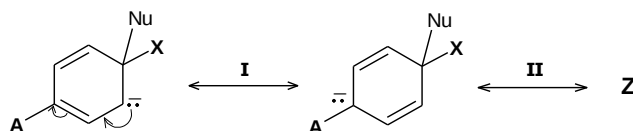
Step 1 involves the addition of the nucleophile (Nu^-). The Nu^- attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.



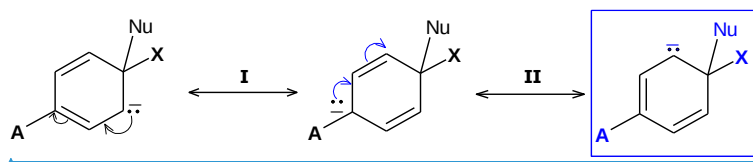
Step 2 involves the loss of the halogen X , reforming the aromatic ring.



Two other resonance structures of the intermediate in **Step 1** are shown below:



- (i) Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**. [2]



[1] for correct structure of **Z**
[1] for correct arrow pushing

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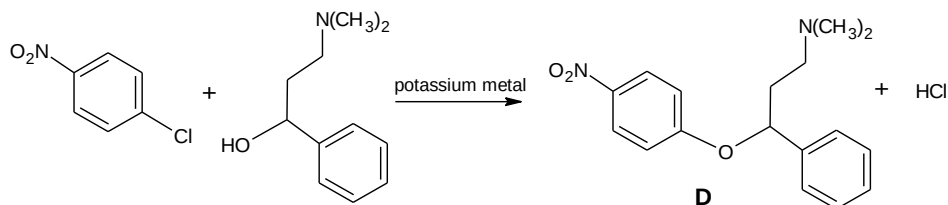
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The reaction below shows the synthesis of compound, **D**.



- (ii) Suggest the role of potassium metal in the reaction. [1]

It is used to generate a stronger nucleophile, $\text{C}_6\text{H}_5\text{CH}(\text{O}^-)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$. [1]

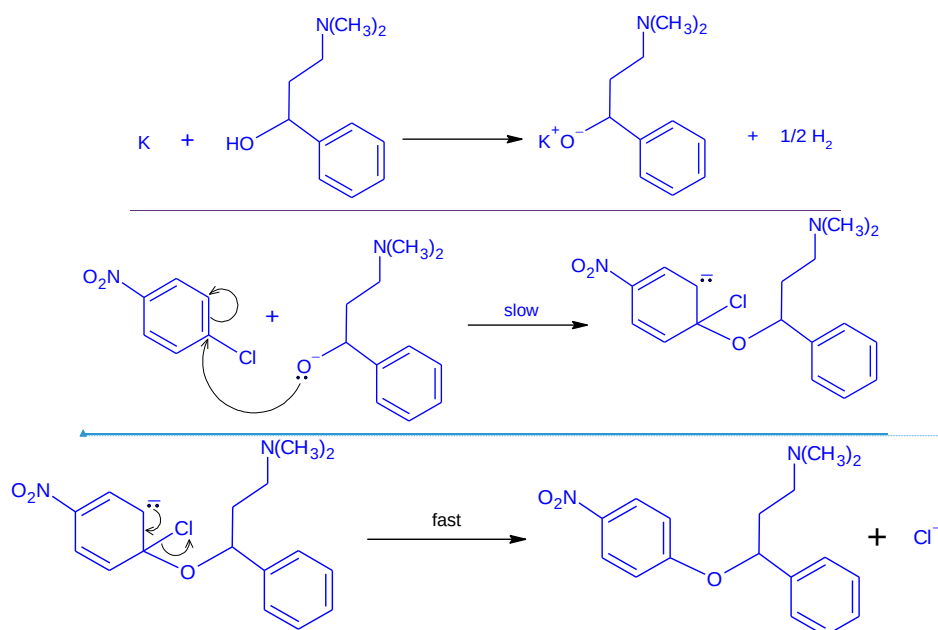
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- (iii) Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons. [3]

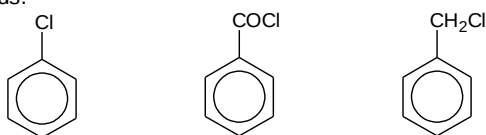


[1] for step 1 (accept -OH as the nucleophile)

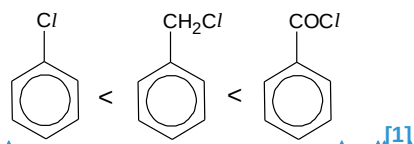
[1] for step 2

[1] for labelling slow and fast steps correctly

- (d) Describe and explain the relative ease of hydrolysis of the following three chloro-compounds. [3]



The relative ease of hydrolysis of the three chloro-compounds in increasing order is as follows:



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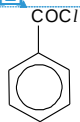
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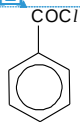
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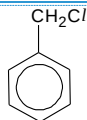
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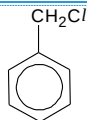
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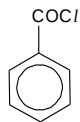
Chlorobenzene is resistant to hydrolysis. The p orbital of chlorine overlaps with π electron cloud of benzene ring hence strengthening the C-Cl bond and hence the bond does not break easily. [1]

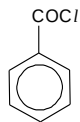


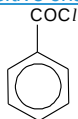
Hydrolysis of  is the fastest. The acyl/C=O carbon atom is attached to 2 highly

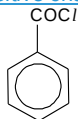


electronegative atoms, O and Cl while that in  is only attached to one electronegative atom (Cl).



Hence acyl/C=O carbon atom in  is more electron deficient (i.e. carries a larger partial positive charge δ^+) than the carbon atom in $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.



Therefore  is most susceptible to nucleophilic attacks. [1]

[Total: 20]

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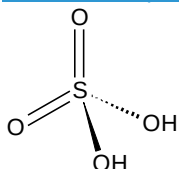
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- 2 Sulfuric acid, H_2SO_4 , can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.

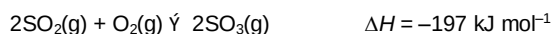
- (a) Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom. [2]

tetrahedral shape + Diagram [1]



bond angle about S = 109.5° [1]

- (b) The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:



Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400°C . When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.

- (i) Write an expression for the equilibrium constant, K_p , of the reaction. [1]

$$K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 P_{\text{O}_2}} \quad [1]$$

- (ii) Calculate the value of K_p at 400°C , stating its units. [3]

	$2\text{SO}_2(\text{g})$	$+\text{O}_2(\text{g})$	$\rightleftharpoons 2\text{SO}_3(\text{g})$
Initial Partial Press /atm	2	1	0
Change in Press /atm	-2x	-x	+2x
Final Partial Press /atm	$2 - 2x$	$1 - x$	2x

Total Pressure, $P_T = 2 - 2x + (1 - x) + 2x = 3 - x$ [1]

$$\% \text{SO}_3 = \frac{2x}{3 - x} = 0.30$$

$$\therefore x = 0.391 \quad [1]$$

$$K_p = \frac{(0.782)^2}{(1.218)^2 (0.609)} = 0.679 \text{ atm}^{-1} \quad \text{correct answer and units [1]}$$

- (iii) How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain. [2]

% conversion to SO_3 will increase.

With increased pressure, by Le Chatelier's Principle, position of equilibrium will shift to the right so as to favour the side which produces the less number of moles of gas.

- (c) Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO, BaO and SiO₂.

State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid. [4]

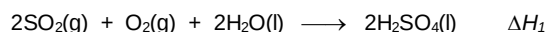
Solid MgO is insoluble in water / sparingly soluble in water.
It is a basic oxide and dissolves in H₂SO₄(aq) to form a colorless solution.

Solid BaO dissolves in water to form colorless solution, upon adding H₂SO₄(aq) a white ppt BaSO₄ is formed
SiO₂ does not dissolve in water or acid.

[2] for observations with water

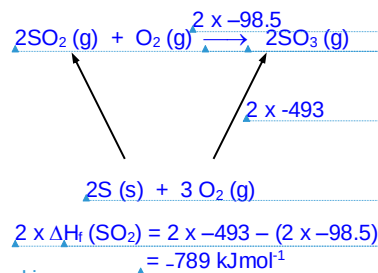
[2] for observations with dil H₂SO₄

- (d) Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO₂ emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:



Using the data below and data from (b), construct an energy cycle to calculate

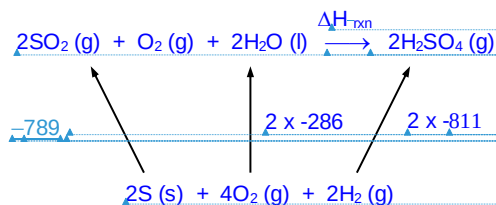
- (i) the enthalpy change of formation of SO₂(g), and hence



[1] for ans, [1] for working

- (ii) the enthalpy change of reaction, ΔH_1 for the above reaction.

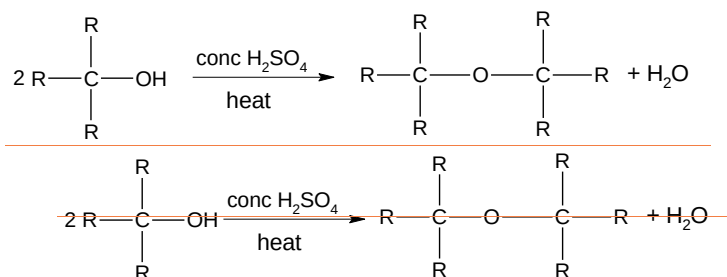
Enthalpy change of formation of H₂O(l) = -286 kJ mol⁻¹
 Enthalpy change of formation of H₂SO₄(l) = -811 kJ mol⁻¹
 Enthalpy change of formation of SO₃(g) = -493 kJ mol⁻¹



$$\begin{aligned}
 \therefore \Delta H_{\text{rxn}} &= (2 \times -811) - (-789) - (2 \times -286) \\
 &= -261 \text{ kJ mol}^{-1}
 \end{aligned}$$

[1] for ans, [1] for working

- (e) Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.



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The mechanism occurs via 3 steps:

Step 1:

An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.

Step 2:

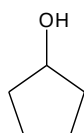
A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates

an oxonium ion $\begin{array}{c} \text{R} \\ | \\ \text{O}^+ \\ | \\ \text{R}'-\text{H} \end{array}$ intermediate.

Step 3:

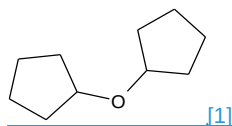
Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.

- (i) Draw the ether formed when cyclopentanol undergoes the above reaction.



cyclopentanol

[1]



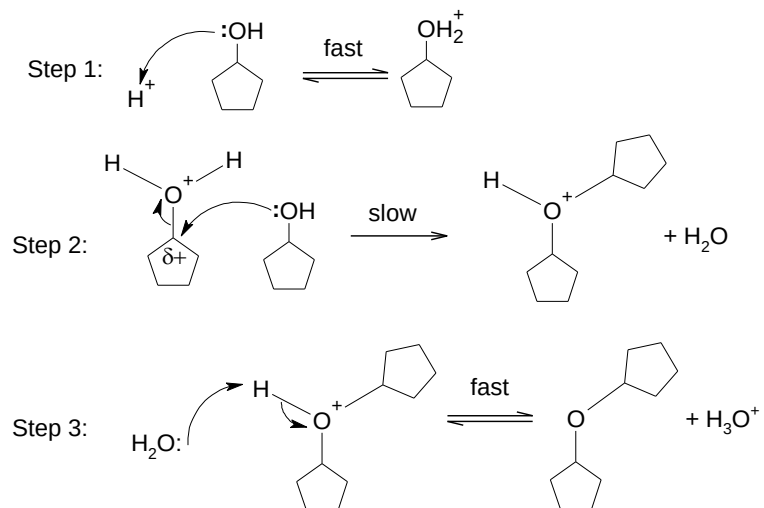
[1]

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- (ii) Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]

11

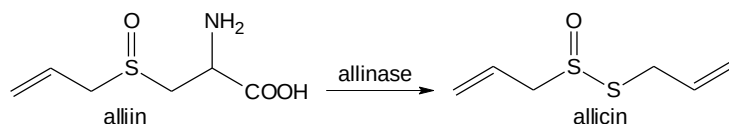


1 mk for each step (with arrows, lone pairs) total 3 mks

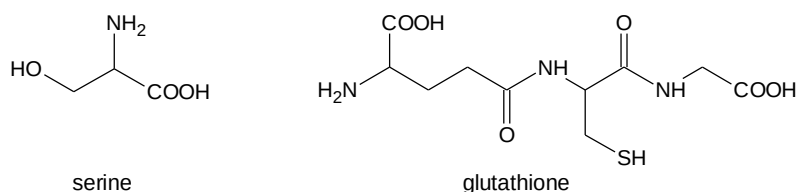
[Total: 20]

- 3 Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.

(a) When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.



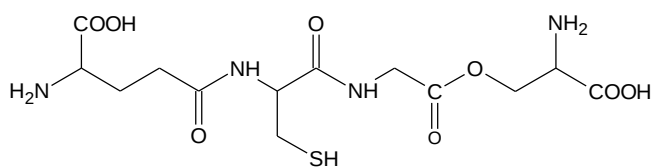
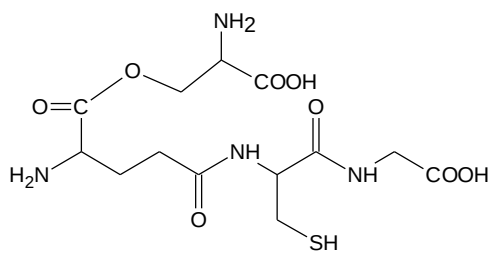
Allicin can also be biosynthesised by using serine and glutathione.



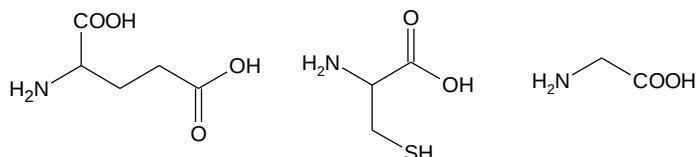
- (i) Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]

Enzyme allinase is denatured by heat. [1]

- (ii) When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae. Draw the structural formula of **each** of these esters. [2]



- (iii) Draw the structural formulae of the products when glutathione is hydrolysed. [3]



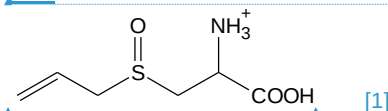
[1] x 3

Alliin has pK_a values of 1.84 and 8.45.

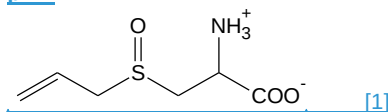
- (iv) Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]

- pH 1
- pH 7
- pH 11

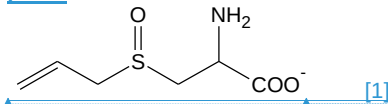
pH 1



pH 7



pH 11

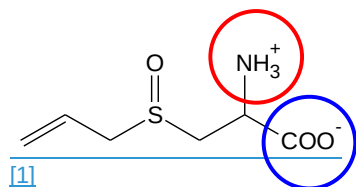


- (v) Calculate the pH of 0.10 mol dm⁻³ solution of alliin. [1]

$$[H^+] = \sqrt{10^{-1.84} \times 0.10} = 0.03801 \text{ mol dm}^{-3}$$

$$pH = -\lg 0.01188 = 1.42 \quad [1]$$

- (vi) With reference to the pK_a values, identify the major species formed when 10 cm³ of 0.10 mol dm⁻³ NaOH is added to 10 cm³ of 0.10 mol dm⁻³ protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]



$$pK_a = 8.45$$

$$K_a = 10^{-8.45} = 3.54 \times 10^{-9}$$

$$pK_b = 14 - 1.84 = 12.16$$

$$K_b = 10^{-12.16} = 6.918 \times 10^{-13}$$

[1]

Since $K_a(-\text{NH}_3^+) > K_b(-\text{COO}^-)$, the solution will be acidic. [1]

- (vii) Sketch the pH-volume added curve you would expect to obtain when 30 cm³ of 0.10 mol dm⁻³ NaOH is added to 10 cm³ of 0.10 mol dm⁻³ protonated alliin. Briefly describe how you have calculated the various key points on the curve. - [4]

At 5 cm³, 1st maximum buffering capacity point

$$\text{pH} = \text{p}K_1 = 1.84$$

At 10 cm³, 1st equivalence point, solution contains $\text{RCH}(\text{NH}_3^+)\text{COO}^-$ which is an acidic salt with $K_a = K_2 = 10^{-8.45}$



$$[\text{RCH}(\text{NH}_3^+)\text{COO}^-] = \frac{\frac{10}{1000} \times 0.10}{\frac{20}{1000}} = 0.05 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg \sqrt{0.05 \times 10^{-8.45}} = 4.875 \approx 4.88$$

$$\text{OR } \text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} = \frac{1.84 + 8.45}{2} = 5.145 = 5.15$$

At 15 cm³, 2nd maximum buffering capacity point

$$\text{pH} = \text{p}K_2 = 8.45$$

At 20 cm³, 2nd equivalence point, solution contains $\text{RCH}(\text{NH}_2)\text{COO}^-$ which is a basic salt with $K_b = 10^{-(14 - K_2)} = 10^{-(14 - 8.45)} = 10^{-5.55}$

$$[\text{RCH}(\text{NH}_2)\text{COO}^-] = \frac{\frac{10}{1000} \times 0.10}{\frac{30}{1000}} = 0.03333 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg \sqrt{0.03333 \times 10^{-5.55}} = 3.513$$

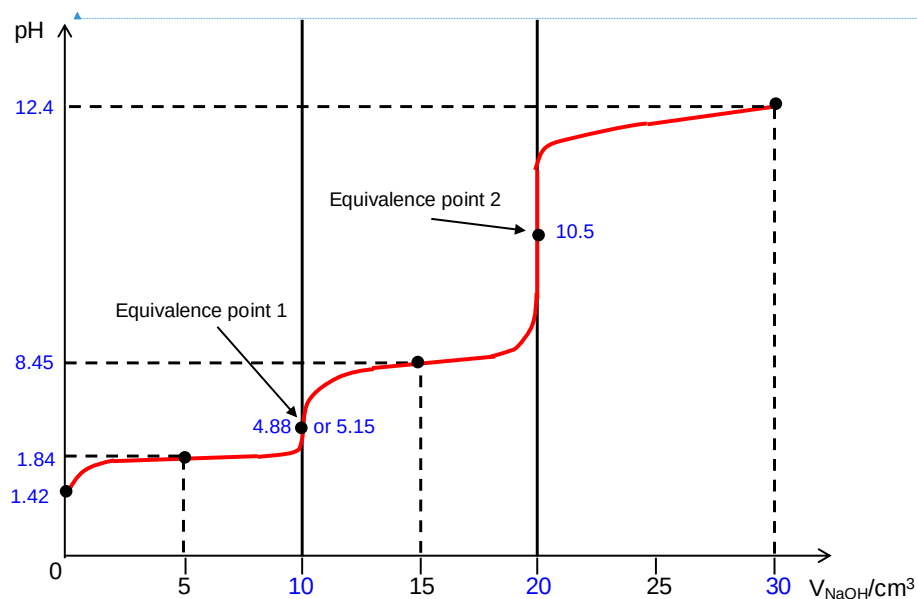
$$\text{pH} = 14 - 3.513 = 10.48 \approx 10.5$$

At 30 cm³, solution contains 10 cm³ excess NaOH

$[\text{OH}^-]$ = concentration of the 10 cm³ of excess NaOH in a total solution

$$= \frac{\frac{10}{1000} \times 0.10}{\frac{40}{1000}} = 0.025 \text{ mol dm}^{-3}$$

$$\text{pH} = 14 - \text{pOH} = 14 - (-\lg 0.025) = 12.4$$



Key points to look out for

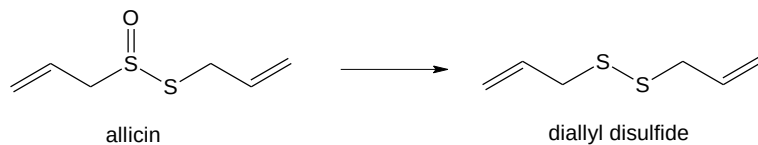
- Label the x and y-axis clearly
- Curve start at pH = 1.42 with a sharp increase before flattening off due to formation of buffer
- Two neutralisation points at 10 cm³ and 20 cm³, labelling of pH values at equivalence points is not needed
- Two buffer regions centred at pH values 1.84 and 8.45 (clearly labelled) respectively
- When $V_{\text{NaOH}} = 30 \text{ cm}^3$, pH = 12.4, showed calculations on how this pH value is obtained

Total of 4 marks

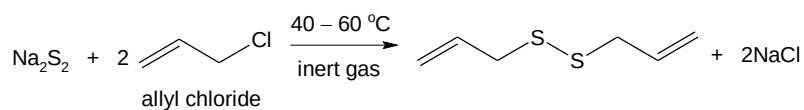
Deduct 1 mark for each missing bullet point

- (b) Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of alliin.

16



Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 °C in an inert atmosphere.



- (i) Give the *IUPAC* name of allyl chloride. [1]

3-chloroprop-1-ene [1]

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- (ii) Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water. [2]

Diallyl disulfide is a non-polar molecule. The energy evolved in the formation of dispersion forces between diallyl disulfide and water molecules is insufficient [1] to overcome the energy required to break the dispersion forces between diallyl disulfide molecules and hydrogen bonding between water molecules. [1]

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- (iii) State the type of reaction when diallyl disulfide is converted back to allicin. [1]

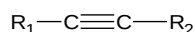
Oxidation [1]

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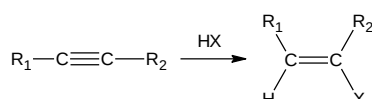
- 4 Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of C_nH_{2n-2} i.e.



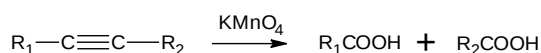
where R_1 and R_2 = H or alkyl or aryl groups

Alkynes exhibit similar chemical properties to alkenes.

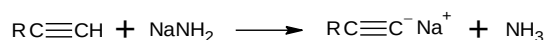
e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes



e.g. oxidation by hot concentrated $KMnO_4$ to form mixture of carboxylic acids



However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.



- (a) Ethyne, C_2H_2 , is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.

- (i) Write an equation for the first stage.

[1]



[1]

- (ii) Suggest a structure for the dihalide formed.

[1]

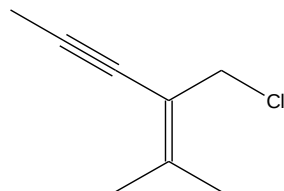


- (iii) When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products. Write an equation to explain the formation of these inorganic by-products.

[1]



- (b) Compound A, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).



H2 Chemistry 9647/03 NYJC J2/16 PX

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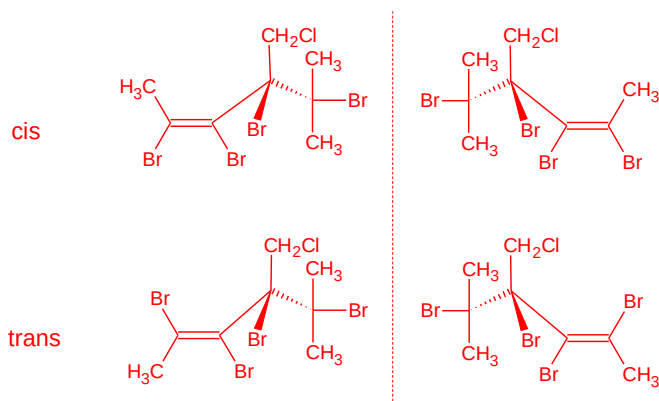
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Compound A

One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]



- (c) Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, NaNH_2 followed by heating under reflux to form compound **C**, C_8H_{10} . Compound **C** reacts with hot concentrated KMnO_4 to produce butane-1,4-dioic acid only.

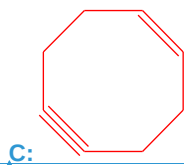
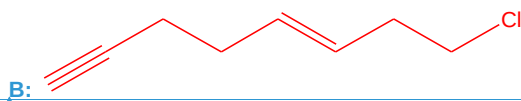
- (i) Explain the reaction with NaNH_2 . [1]

To deprotonate the terminal alkyne group
Or acid-base reaction with terminal alkyne. [1]

- (ii) Hence, explain the formation of compound **C**. [1]

The deprotonated alkyne acts as a nucleophile which undergoes intramolecular nucleophilic substitution to form Compound **C** [1]

- (iii) Suggest skeletal structures for compounds **B** and **C**. [2]



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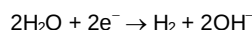
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When a current of 1.0 A was passed through aqueous potassium maleate ($\text{KO}_2\text{CCH}=\text{CHCO}_2\text{K}$) for 15 minutes, it was found that $110\text{ cm}^3\text{ H}_2$, measured at r.t.p., was collected at the cathode. The following reaction took place.



- (d) State the relationship between the Faraday constant, F and the Avogadro's constant, L . [1]

$F = Le$ where e = charge on 1 electron [1]

- (e) Using the data above and the *Data Booklet*, calculate a value for Avogadro's constant. [3]

$Q = 1.0 \times 15 \times 60 = 900\text{ C}$ [1]
 $n(\text{H}_2) = 110 / 24000 = 0.00458\text{ mol}$
 $n(\text{e}^-) = 2 n(\text{H}_2) = 0.00917\text{ mol}$ [1]
 $F = Q / n(\text{e}^-) = 98182 = 98200\text{ C}$
 $L = 98182 / 1.60 \times 10^{-19} = 6.14 \times 10^{23}$ [1]

- (f) Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:

- mass of bottle containing NaOH before experiment = 10.501 g
- mass of bottle containing NaOH after experiment = 10.904 g
- initial reading on syringe = 10.0 cm^3
- final reading on syringe = 120.0 cm^3

- (i) State the oxidation state of carbon in ethyne. [1]

-1 [1]

- (ii) With the help of an equation, explain the purpose of passing the anode gas through NaOH . [1]

$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
 Purpose of NaOH is to absorb CO_2 [1]

- (iv)(iii) Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]

Change in mass of NaOH = mass of CO_2 produced = 0.403 g
 $n(\text{CO}_2) = 0.403 / 44.0 = 0.009159\text{ mol}$
 $V(\text{CO}_2) = 24000 \times n(\text{CO}_2) = 220\text{ cm}^3$ [1]

- (v)(iv) Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]

Volume of ethyne gas = 110 cm^3
 $\text{O}_2\text{CCH}=\text{CHCO}_2^- \rightarrow \text{C}_2\text{H}_2 + 2\text{CO}_2 + 2\text{e}^-$

- (g) When aqueous potassium maleate was acidified, maleic acid, $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ ($\text{p}K_{\text{a}1} = 1.90$ and $\text{p}K_{\text{a}2} = 6.07$) was liberated. Fumaric acid ($\text{p}K_{\text{a}1} = 3.03$ and $\text{p}K_{\text{a}2} = 4.44$) is a stereoisomer of maleic acid. With a suitable illustration, suggest a reason why maleic acid has a lower $\text{p}K_{\text{a}1}$ but higher $\text{p}K_{\text{a}2}$ than fumaric acid. [2]

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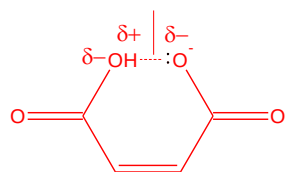
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20

hydrogen bonding



[1]

Maleic acid is the cis-isomer while fumaric acid is the trans isomer. Hence the negative carboxylate ion is stabilised by intramolecular hydrogen bonding. Hence maleic acid is stronger acid than fumaric acid. [1]

[Total: 20]

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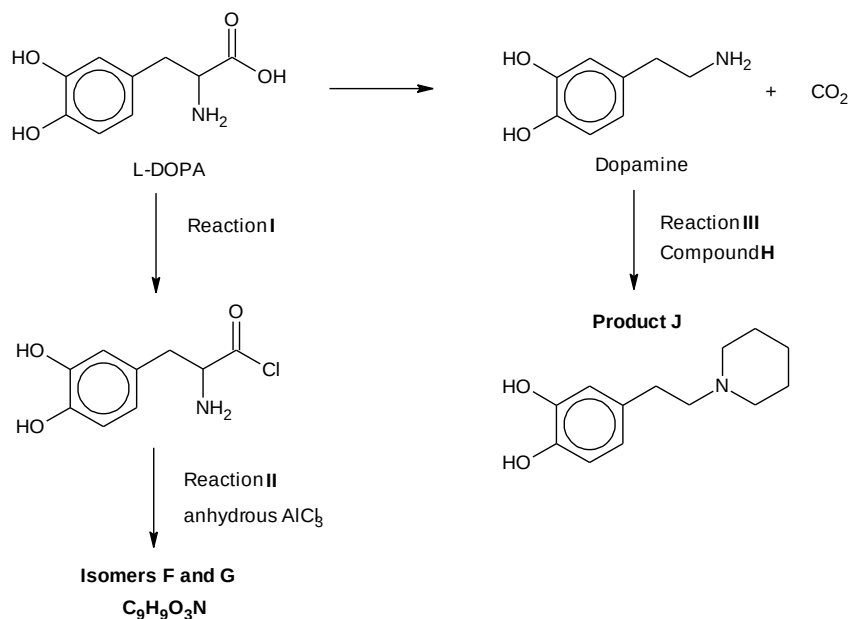
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- 5(a) Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.

Below is a synthetic route involving L-DOPA and dopamine:



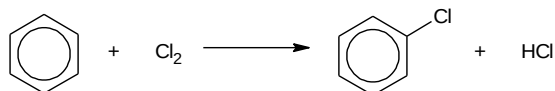
- (i) State the reagents and conditions and any observations in Reaction I. [1]

Reagents & conditions: PCl_5 or SOCl_2

Observation: White fumes of HCl

1 mark for both

- (ii) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.



The reaction occurs in several steps.

- The first step is the reaction between Cl_2 and AlCl_3 .



- The benzene is then attacked by the Cl^+ cation in the second step.

- The first step is the reaction between Cl_2 and AlCl_3 .



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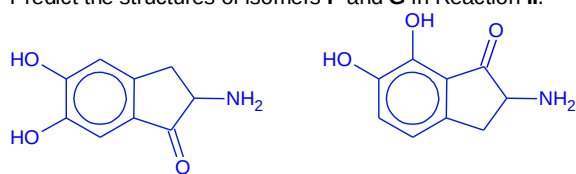
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- The benzene ring is then attacked by the Cl^+ cation in the second step.

AlCl_3 reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.

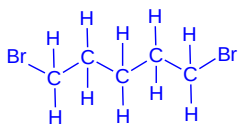
Predict the structures of isomers **F** and **G** in Reaction II.

[2]



1 mark each

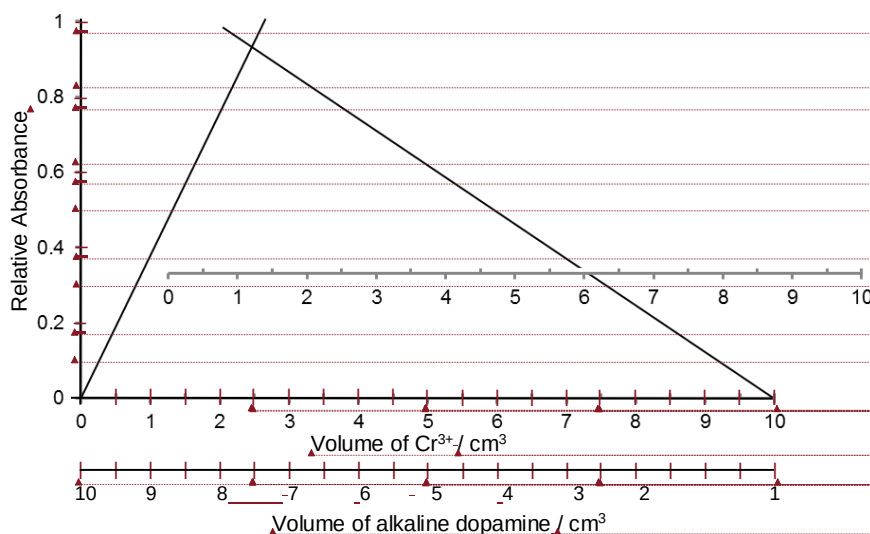
- (iii) In Reaction III, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]



[12] – correct RX & displayed formula

- (b) Dopamine is a bidentate ligand. When different volumes of $0.0030 \text{ mol dm}^{-3}$ of aqueous Cr(III) and $0.0020 \text{ mol dm}^{-3}$ of alkaline dopamine solution were mixed, a complex **R** is formed. Analysis of **R** shows that its formula is $[\text{Cr}(\text{C}_8\text{H}_9\text{NO}_2)_x(\text{H}_2\text{O})_y]^z$, where x , y and z are integers.

To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.



- (i) Use the graph and the information given to determine the formula of complex **R**. Show your workings clearly. [3]

$$\begin{aligned}
 & \frac{n(\text{Cr}^{3+}) : n(\text{dopamine})}{= 0.0030 \times \frac{2.5}{1000} : 0.0020 \times \frac{7.5}{1000}} \\
 & = 7.50 \times 10^{-6} : 1.50 \times 10^{-5} \\
 & = 1:2 \quad [1] \\
 & \therefore x = 2
 \end{aligned}$$

Since 1 dopamine ligand in alkaline condition has a 2- charge, 2 dopamine ligands in alkaline condition has a 4- charge As H_2O ligands are neutral and Cr has 3+ charge, $z = -1$. [1]

Since most transition metal complexes have a coordination number 6, and there are 2 bidentate ligands (e.g. binds to metal centre x4), y would likely be 2. [1]
Hence formula of complex **R**: $[\text{Cr}(\text{C}_8\text{H}_9\text{NO}_2)_2(\text{H}_2\text{O})_2]^-$ $\therefore x = 2$

- (ii) The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d-orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o . The relationship between Δ_o and colours of complexes can be described in the equation below:

$$\Delta_o = \frac{hc}{\lambda}$$

where h is Planck's constant, c is the speed of light and λ is the wavelength of light absorbed

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colour	absorbed λ / nm
violet	410
indigo	430
blue	480
blue-green	500
green	530
yellow	580
orange	610
red	680

Given that Δ_o for complex **R** is 4.125×10^{-22} kJ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**. [2]

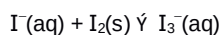
$$\Delta_o = \frac{hc}{\lambda}$$

$$\lambda = \frac{6.63 \times 10^{-34} (3 \times 10^8)}{4.125 \times 10^{-22} \times 1000} \quad [1]$$

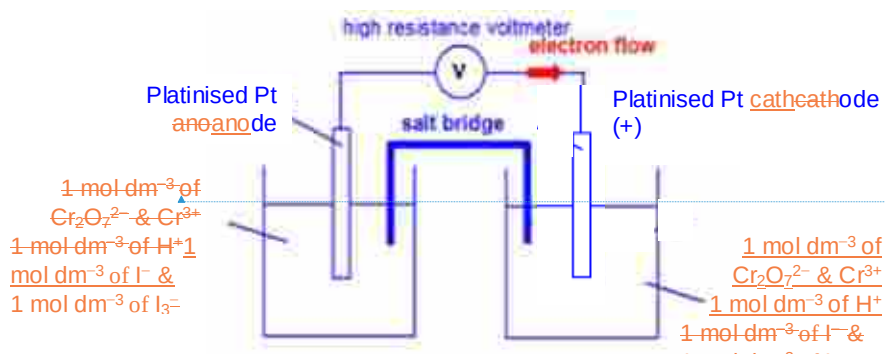
$$= 4.82 \times 10^{-7} \text{ m or } 482 \text{ nm}$$

Since colour absorbed is blue (482 nm – blue), the colour of complex **R** should be the orange (complementary colour). [1]

- (c) Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:



- (i) Draw a fully labelled experimental set-up for a voltaic cell made up of a $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ half-cell and a I_2/I^- half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons. [3]



All 5 points – 3 marks, 3-4 points – 2 marks, 2 points – 1 mark

- $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ half cell (with acidified medium)
- I_2/I^- half cell (with Pt electrode)
- Complete circuit (salt bridge), standard condition (1 mol dm^{-3})
- Direction of electron flow
- Clear indication of anode, cathode

- (ii) By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to a solution of the $\text{I}_2(\text{aq})$. ~~1/2~~ half-cell. [3]

$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	(+0.54)
$\text{V}^{3+} + 2\text{e}^- \rightarrow \text{V}^{2+}$	(-0.26)
$\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$	(+0.34)
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	(+1.00)

$\text{I}_2(\text{aq}) + \text{V}^{2+}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{V}^{3+}(\text{aq})$
 $E_{\text{cell}} = (+0.54) - (-0.26) = +0.80 \text{ V} > 0 \therefore \text{reaction is feasible.} \bullet$

$\text{I}_2(\text{aq}) + 2\text{V}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{I}^-(\text{aq}) + 2\text{VO}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq})$
 $E_{\text{cell}} = (+0.54) - (+0.34) = +0.20 \text{ V} > 0 \therefore \text{reaction is feasible.} \bullet$

$\text{I}_2(\text{aq}) + 2\text{VO}_2^+(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{I}^-(\text{aq}) + 2\text{VO}_2^+(\text{aq}) + 4\text{H}^+(\text{aq})$
 $E_{\text{cell}} = (+0.54) - (+1.00) = -0.46 \text{ V} < 0 \therefore \text{reaction is not feasible.} \bullet$

V^{2+} will be oxidised to V^{3+} and finally VO_2^+ while I_2 will be reduced to I^- . $\bullet$

All 4 points – 3 marks, 2-3 points – 2 marks, 1 point – 1 mark
 A must to show calculation of E_{cell} for all 3 equations.

- (d) Explain the following statements.

- (i) BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity. [2]

BrF_3 autoionises/ ionises in the liquid state to give BrF_2^+ and BrF_4^- ions which are mobile, thus accounting for its electrical conductivity. [1]
 $2\text{BrF}_3 \rightarrow \text{BrF}_2^+ + \text{BrF}_4^-$ [1]

- (ii) SiCl_4 reacts violently in water but CCl_4 has no reaction with water. [1]

Water molecules could not form co-ordinate bonds with the central carbon atom of CCl_4 because carbon is in period 2 and cannot accommodate lone pair of electrons from H_2O . [1]

- (iii) Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist. [1]

Xenon has larger radii; therefore the electron attraction to the nucleus is weaker in comparison to the smaller noble gases. OR
 Energy levels of the 5p orbital, 6s and 4f orbitals are very close and hence energetically accessible. Only a small amount of energy is needed to excite the paired electrons from the 5p orbitals to the 6s and 4f electrons where they can then form covalent bonds with other atoms. [1]

[Total: 20]

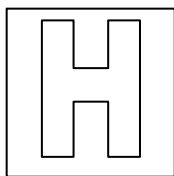
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PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

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INDEX
NUMBER

CHEMISTRY

9647/01

Paper 1 Multiple Choice

23 September 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, Centre number and index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

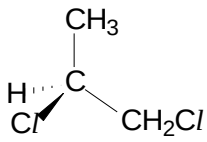
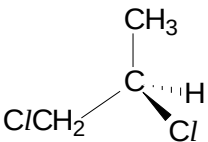
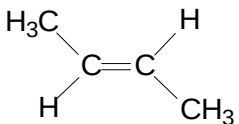
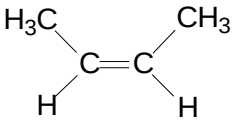
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

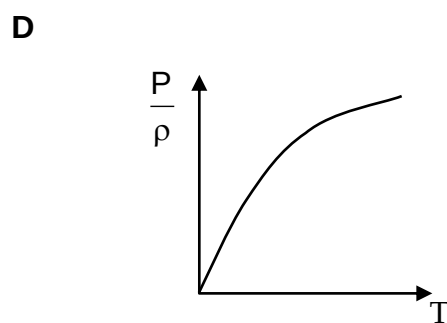
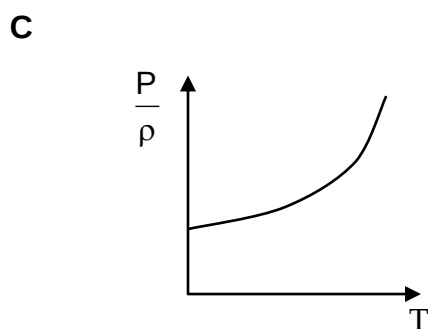
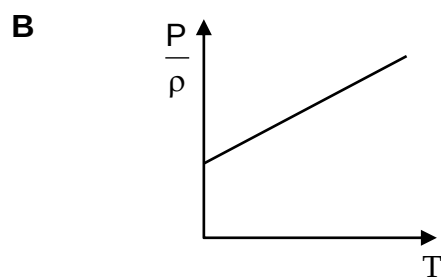
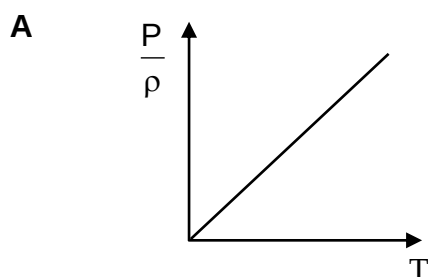
Section A

For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 Which of the following quantities is equal to the Avogadro constant?
- A** the number of atoms in 24 dm³ of nitrogen gas at r.t.p. condition
B the number of molecules in 1 dm³ of oxygen at 273 K and 1 atm
C the number of electrons removed to form Ne⁺ ions from 6.02 x 10⁻²³ mol of Ne atoms
D the number of ions in 83.5 g of [Co(NH₃)₅Cl]Cl₂
- 2 Which of the following species has no unpaired electrons?
- A** Fe **B** Ge²⁺ **C** Si **D** Ti³⁺
- 3 Why is the molecule of BCl₃ planar, whereas the molecule of PH₃ is pyramidal?
- A** The repulsion between chlorine atoms is greater than that between hydrogen atoms.
B The covalent radius of chlorine is greater than that of hydrogen.
C The boron atom in BCl₃ has six electrons in its valence shell, whereas the phosphorus atom in PH₃ has eight.
D The boron atom has no d-orbitals available for bonding.
- 4 In which pair do the isomers have identical boiling points?
- A**  and 
- B**  and 
- C** CH₃CH₂CH₂CH₂OH and (CH₃)₂CHCH₂OH
- D** CH₃(CH₂)₄CH₃ and (CH₃)₂CHCH(CH₃)₂

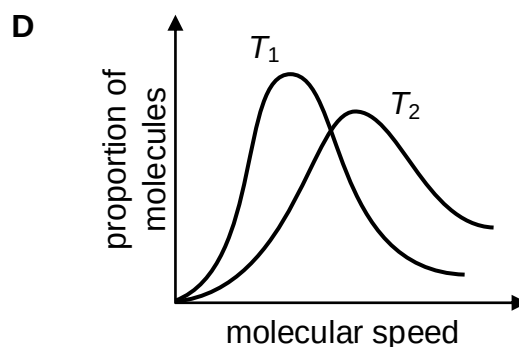
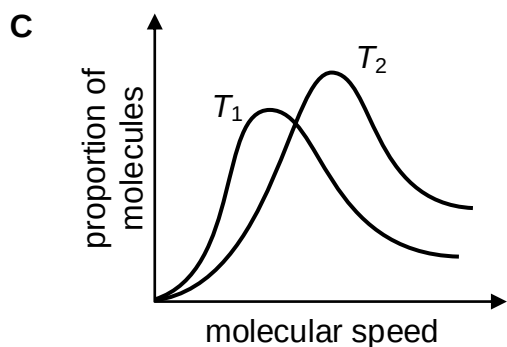
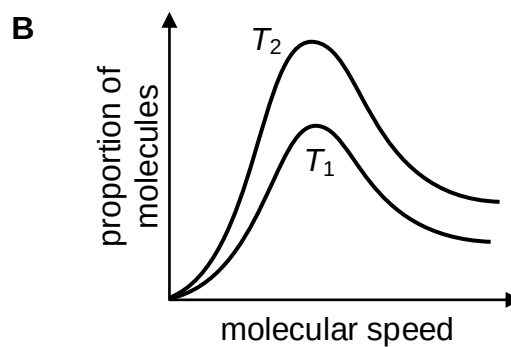
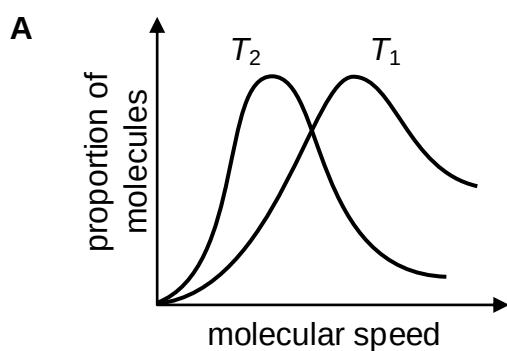
- 5 Which of the following shows a graph of $\frac{P}{\rho}$ against T for an ideal gas?

(P = pressure; ρ = density; T = temperature in $^{\circ}\text{C}$).



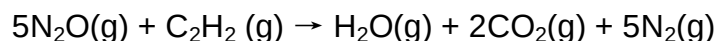
- 6 One mol of neon gas at temperature T_1 was added to another one mol of neon and the temperature was increased to T_2 .

Which of the following diagrams correctly represents the Boltzmann distribution of molecular speeds before and after the changes were made?



- 7 *Use of Data Booklet is relevant to this question.*

Dinitrogen oxide burns in ethyne to produce water vapour, carbon dioxide and nitrogen gas as the only products.



Given that the N=N and N=O bond energies in dinitrogen oxide are +418 kJ mol⁻¹ and +686 kJ mol⁻¹ respectively, what is the enthalpy change of the reaction?

- A +1670 kJ mol⁻¹
- B +1710 kJ mol⁻¹
- C -1670 kJ mol⁻¹
- D -1710 kJ mol⁻¹

- 8 Quarter-life, $t_{1/4}$, of a radioactive isotope is defined as the time taken for the sample to decay to $\frac{1}{4}$ its original amount.

Potassium-argon dating is used to determine the age of a rock. ⁴⁰K is a radioactive isotope of potassium and it decays to ⁴⁰Ar with a constant $t_{1/4}$ of 2.50×10^9 years. A sample of moon rock was found to contain 6.25% of the original amount of ⁴⁰K.

How old is the rock?

A 2.50×10^9 years	B 5.00×10^9 years
C 7.50×10^9 years	D 1.00×10^{10} years

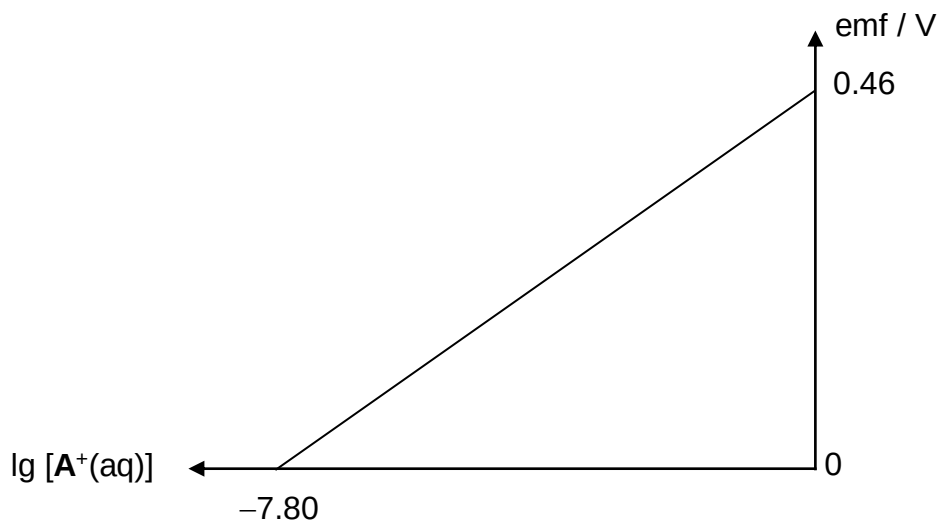
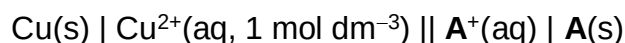
- 9 During electrolysis, 0.785 g of chromium is deposited on the cathode when 8690 C of electricity is passed into a chromium-containing electrolyte.

Which of the following could have been the electrolyte?

A CrCl ₂	B CrCl ₃	C K ₂ CrO ₃	D K ₂ Cr ₂ O ₇

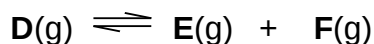
- 10 Use of the Data Booklet is relevant to this question.

The graph below shows the variation in electromotive force (emf) of the following electrochemical cell with $\lg [\text{A}^+(\text{aq})]$ at 298 K.



Which of the following statements is incorrect?

- A Cu(s) is the negative electrode.
 - B The direction of electron flow in the external circuit will be reversed when the concentration of $\text{A}^+(\text{aq})$ is $1.00 \times 10^{-7} \text{ mol dm}^{-3}$.
 - C The standard electrode potential of the $\text{A}^+(\text{aq}) \mid \text{A(s)}$ half-cell is +0.80 V.
 - D The emf of the given cell under standard conditions will be +0.46 V.
- 11 Gas **D** dissociates on heating to set up the equilibrium below:

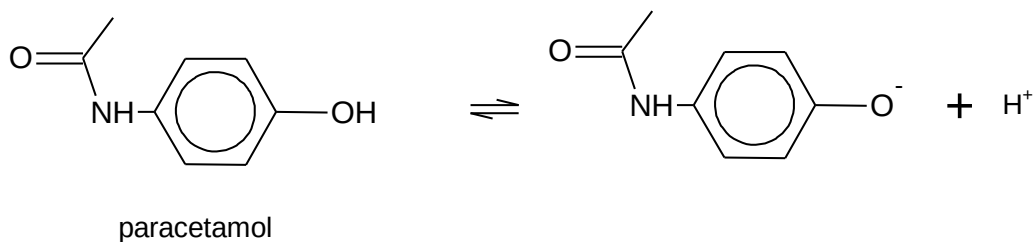


A quantity of **D** was heated at a constant pressure, p , at a certain temperature. The equilibrium partial pressure of **D** was found to be $\frac{1}{7}p$.

What is the equilibrium constant, K_p , at this temperature?

- A $\frac{6p}{7}$
- B $\frac{9p}{7}$
- C $\frac{36p}{7}$
- D $6p$

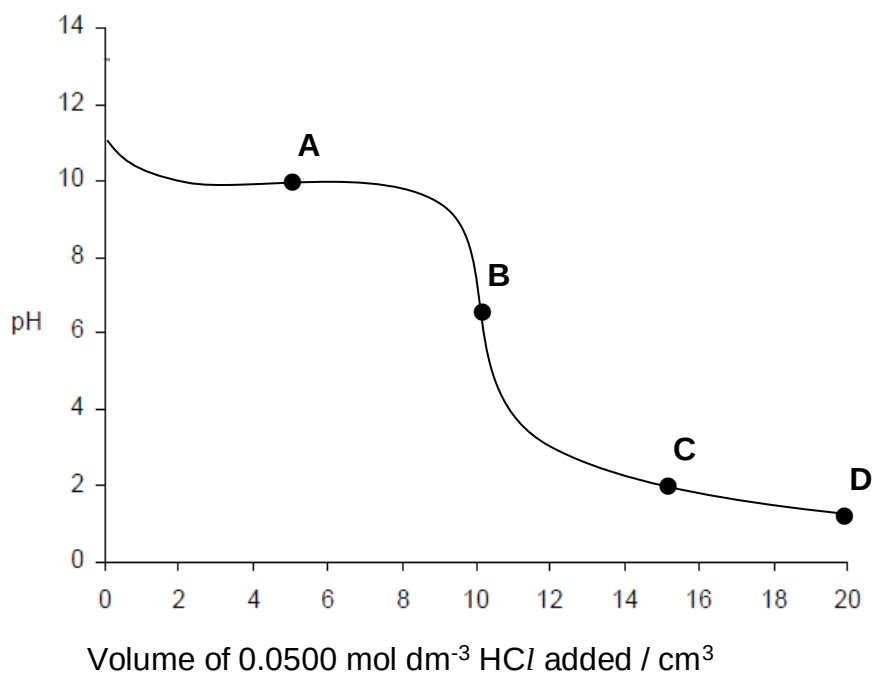
- 12** Paracetamol ($pK_a = 9.5$) is a widely used over-the-counter pain reliever and fever reducer. Its solubility in water is 12.78 mg cm^{-3} at 25°C . (M_r of Paracetamol = 151.0)



What is its pH in water at 25°C ?

- A** 1.07
B 5.29
C 6.79
D 8.71
- 13** The pH change when $0.0500 \text{ mol dm}^{-3} \text{ HCl}$ is added dropwise to 5.00 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ CH}_3\text{NH}_2 (\text{aq})$ is shown in the graph below.

At which point on the graph is $\text{pH} = 14 - pK_b$, where K_b is the base dissociation constant of the weak base?



- 14 Which of the following statements explains the observations that magnesium hydroxide dissolves in ammonium chloride, but not in aqueous sodium chloride?
- A The ammonium ion changes the solubility product of $\text{Mg}(\text{OH})_2$.
 - B NH_4^+ ion is first formed, and then acts through a common ion effect.
 - C NH_4Cl dissociates less fully than NaCl .
 - D The NH_4^+ ion acts as an acid.

- 15 A saturated solution of $\text{Ca}(\text{OH})_2$ is found to have a pH of 12.3 at 25 °C.

Which of the following statements is incorrect?

- A The K_{sp} of $\text{Ca}(\text{OH})_2$ is $4 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$.
 - B The solubility of $\text{Ca}(\text{OH})_2$ would increase when temperature is raised to 35 °C.
 - C The solubility of $\text{Ca}(\text{OH})_2$ will decrease when solid Na_2O is added.
 - D The pH of the solution would increase when $\text{Ca}(\text{NO}_3)_2$ is added
- 16 *Use of the Data Booklet is relevant to this question.*

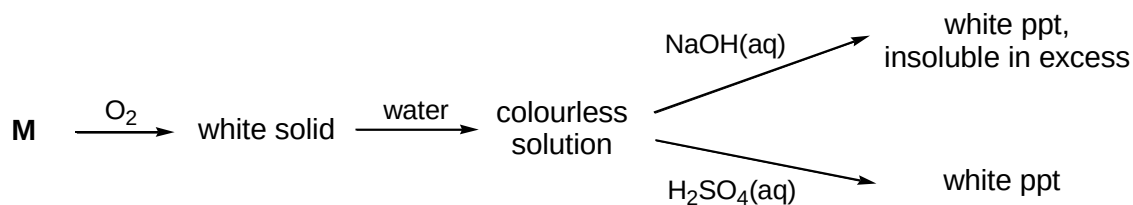
Natural water in reservoirs often contains very finely divided solid particles of between 1 and 100 nm in diameter which have negative charges on their surface.

One stage in the water purification process consists of adding salt solutions containing high charge-density cations which will neutralise the negative charges and cause the solid particles to join together and be precipitated out.

Which compound, in aqueous solution, would be the most effective in precipitating the finely divided solid particles?

- A AlCl_3
- B MgCl_2
- C SiCl_4
- D PCl_3

17



Based on the information above, what could element **M** be?

- A aluminium
- B calcium
- C potassium
- D silicon

18 HCl is stable to heat, but HI decomposes into its elements when heated.

What is the reason for this difference?

- A HI is a stronger reducing agent than HCl .
- B $Cl-Cl$ bond is stronger than $I-I$ bond.
- C $H-Cl$ bond is stronger than $H-I$ bond.
- D HI is more volatile than HCl .

19 *Use of the Data Booklet is relevant to this question.*

Which of the following solutions would result in a colour change when left to stand in the atmosphere?

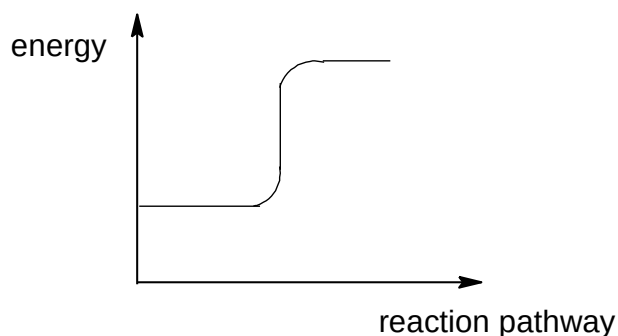
- A an acidified solution of cobalt(II) nitrate
- B a solution of potassium hexacyanoferrate(III)
- C an acidified solution of tin(II) chloride
- D an acidified solution of vanadium(II) sulfate

- 20 Adding concentrated HCl(aq) to $\text{CuSO}_4\text{(aq)}$ causes the colour of the solution to change from blue to green.

Which of the following row correctly shows the number of d-electrons and the energy gap between the d-orbitals, before and after the reaction?

	number of d-electrons	energy gap between the d-orbitals
A	changes	changes
B	changes	remains the same
C	remains the same	changes
D	remains the same	remains the same

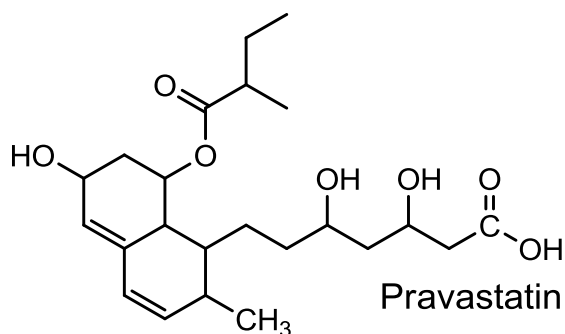
- 21 In the reaction of methane with chlorine in the presence of light, the following energy level diagram (for single reaction step) is obtained.



To which of the following steps does this diagram apply?

- A $\cdot\text{CH}_3 + \cdot\text{CH}_3 \longrightarrow \text{C}_2\text{H}_6$
- B $\text{CH}_4 + \cdot\text{Cl} \longrightarrow \text{CH}_3\text{Cl} + \cdot\text{H}$
- C $\cdot\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \cdot\text{Cl}$
- D $\text{Cl}_2 \longrightarrow \cdot\text{Cl} + \cdot\text{Cl}$

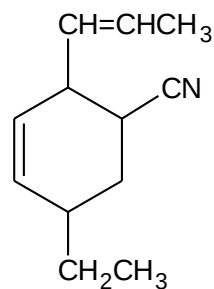
- 22 The cholesterol-lowering agents called statins, such as pravastatin, are among the most widely prescribed drugs in the world.



How many chiral centres are present in the product when pravastatin was treated with H_2 , Ni catalyst at 200°C ?

- A 6 B 7 C 8 D 9

23

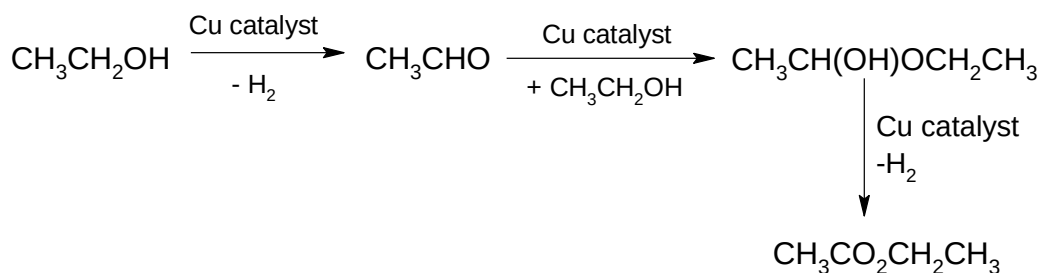


compound **P**

Which of the following statements about compound **P** is incorrect?

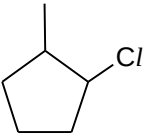
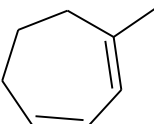
- A There is only one sp hybridised carbon atom in a molecule of **P**.
 B A molecule of **P** contains four π bonds.
 C After **P** reacts with HCl(g) , all but one carbon atom in the product formed are sp^3 hybridised.
 D After **P** reacts with LiAlH_4 , all the carbon atoms in the product formed are sp^3 hybridised.

- 24 Industrially, ethyl ethanoate may be prepared from cheap, low-grade ethanol as follows:



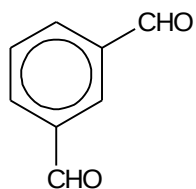
Which process is included in the above reaction sequence?

- A disproportionation
 B electrophilic addition
 C nucleophilic addition
 D reduction
- 25 Which process will **not** give a good yield of $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CO}_2\text{H}$?

- A  $\xrightarrow[\text{heat}]{\text{KOH in ethanol}}$ $\xrightarrow{\text{hot KMnO}_4 (\text{aq}), \text{H}_3\text{O}^+}$
- B $\text{H}_2\text{NCO}(\text{CH}_2)_3\text{CHClCH}_3 \xrightarrow[\text{heat}]{\text{KOH(aq)}} \xrightarrow{\text{hot KMnO}_4 (\text{aq}), \text{H}_3\text{O}^+}$
- C $\text{CH}_3\text{CH}(\text{OH})(\text{CH}_2)_3\text{CH}_2\text{Cl} \xrightarrow[\text{heat}]{\text{NaOH in ethanol}} \xrightarrow{\text{hot KMnO}_4 (\text{aq}), \text{H}_3\text{O}^+}$
- D  $\xrightarrow{\text{hot KMnO}_4 (\text{aq}), \text{H}_3\text{O}^+}$

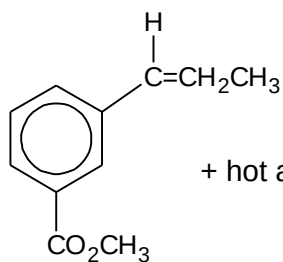
26 Which of the following reactions would **not** produce 1,3-dicarboxylic acid?

A



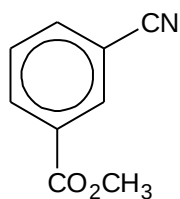
+ Fehling's solution followed by acidification

B



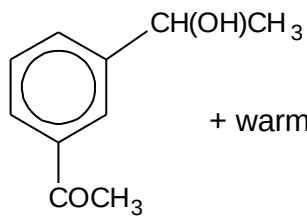
+ hot acidified potassium manganate(VII)

C



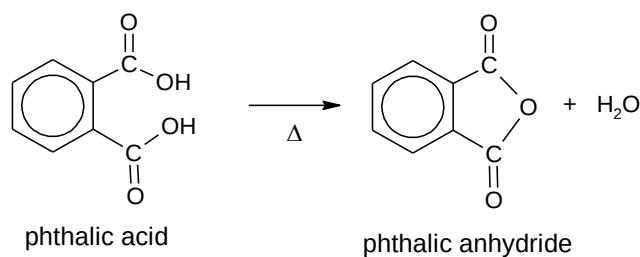
+ aq H_2SO_4 , heat

D

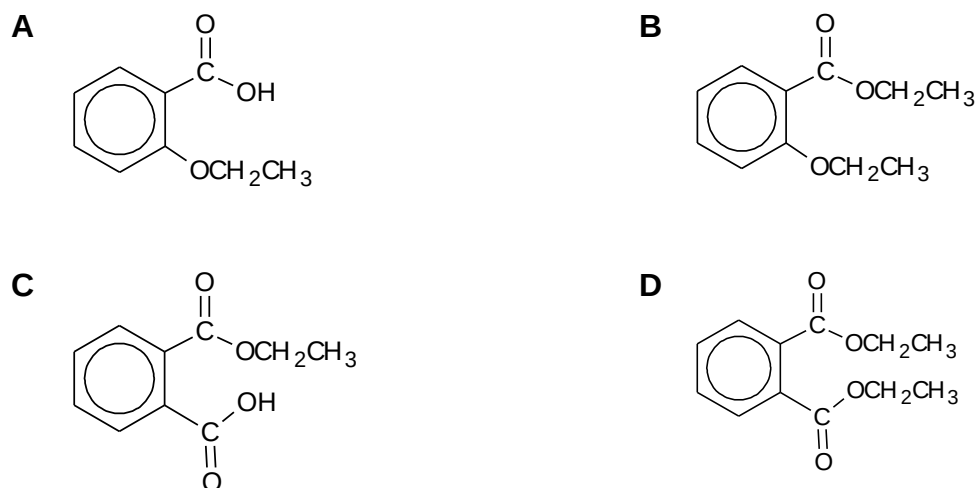


+ warm, alkaline aqueous iodine followed by acidification

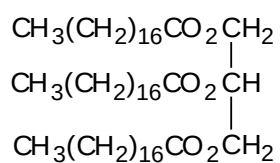
- 27 When heated strongly, phthalic acid undergoes condensation reaction to form phthalic anhydride.



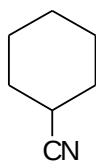
On reaction with water, the anhydride gives phthalic acid. What would be formed when phthalic anhydride reacts with ethanol instead of water?



- 28 Experiments are carried out on three compounds **Q**, **R**, and **S**.



Q



R



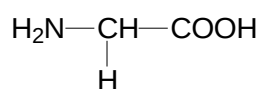
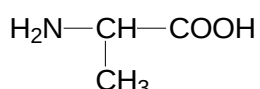
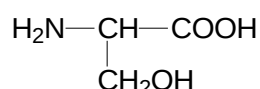
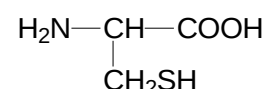
S

A sample of 0.01 mol of each compound is heated under reflux with 50 cm³ of 1 mol dm⁻³ aqueous NaOH (in excess) until hydrolysis is completed and any ammonia gas produced was expelled from the solution. The excess NaOH was then titrated in each case and was found to require 20 cm³, 30 cm³ and 40 cm³ of 1 mol dm⁻³ HCl for neutralisation.

Which sequence of compounds matches these results?

	20 cm ³	30 cm ³	40 cm ³
A	Q	R	S
B	Q	S	R
C	R	S	Q
D	S	R	Q

- 29** Why are amides, RCONH_2 , less basic than amines, RNH_2 ?
- A** Amides form zwitterion in which the nitrogen atom carries a positive charge.
 - B** Amides have a resonance structure involving the movement of a pair of electrons from the nitrogen atom to the oxygen atom.
 - C** Electrons on the nitrogen atom move on the C-N bond giving it some double bond character so that it is more difficult to break.
 - D** The amide carbonyl group withdraws electrons from the NH_2 group to make the hydrogen atoms more acidic.
- 30** Silk fibroin is a type of fibrous protein made up almost entirely of β -pleated sheets. The main amino acids found in silk fibroin are alanine, glycine, serine and cysteine. The structures of these amino acids are given below.

*glycine**alanine**serine**cysteine*

Which of the following statements about the type of interactions present in silk fibroin is incorrect?

- A** The β -pleated sheets are held together by hydrogen bonding.
- B** There are van der Waals' forces between glycine and alanine in the protein.
- C** There are disulfide linkages present in silk fibroin.
- D** Serine forms ionic bonds with another serine amino acid in the protein.

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31** A 0.0200 mol sample of an oxochloride of **T**, TOCl_y required 10.00 cm³ of 0.400 mol dm⁻³ acidified potassium manganate(VII) for oxidation to TO_3^- ions.

Which of the following statements are correct?

- 1** 5 mol TOCl_y react with 1 mol MnO_4^- .
- 2** The change in oxidation state of **T** in the reaction is +1.
- 3** The value of *y* in TOCl_y is 2.

- 32** The ion U^{5+} has 38 electrons and 46 neutrons.

Which of the following statements are correct?

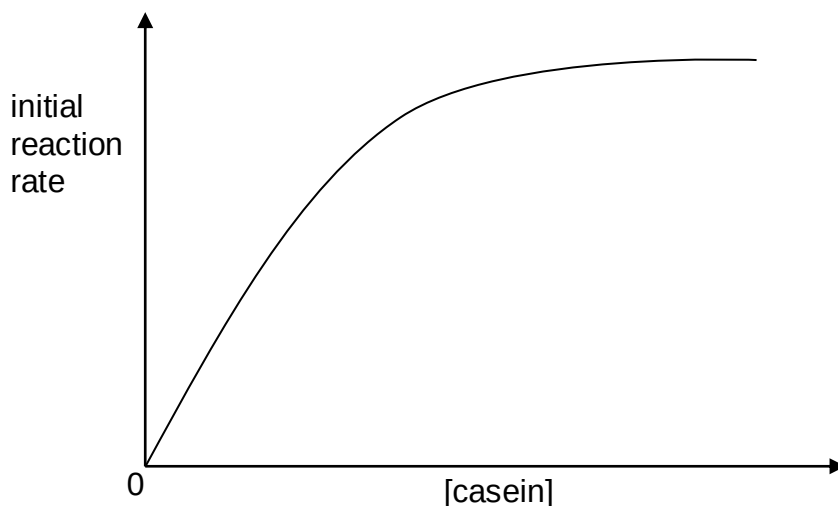
- 1** In an electric field, the ion U^{5+} will be deflected to the same extent as the yttrium ion, $^{89}\text{Y}^{5+}$.
- 2** The electronic configuration of U^{5+} is $[\text{Kr}] 4d^2$.
- 3** The third ionisation energy of element **U** is significantly higher than its second ionisation energy.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 33** The graph shows the results of an investigation of the initial rate of hydrolysis of casein by the enzyme trypsin. In the experiments, the initial concentration of casein was varied but that of trypsin was kept constant.



Which conclusions can be deduced from these results?

- 1** When [casein] is low, the rate is first order with respect to [casein].
 - 2** When [casein] is high, the rate is dependent of [trypsin].
 - 3** When [casein] is high, the rate is dependent of [casein].
- 34** Button cells are tiny cells used to power small electronic devices such as wrist watches and calculators. One such cell consists of lithium electrode and a paste of manganese(IV) oxide electrode dipped in an organic electrolyte. The e.m.f. produced by the cell is 3.00 V. In discharging the cell, LiMnO_2 will be formed.

Which of the following statements about the Li- MnO_2 cell are correct?

- 1** Electrons flow from the lithium electrode to the manganese(IV) oxide electrode.
- 2** The equation for the reaction at the cathode is $\text{MnO}_2 + \text{e}^- \rightarrow \text{MnO}_2^-$.
- 3** Water is added to manganese(IV) oxide to form the paste.

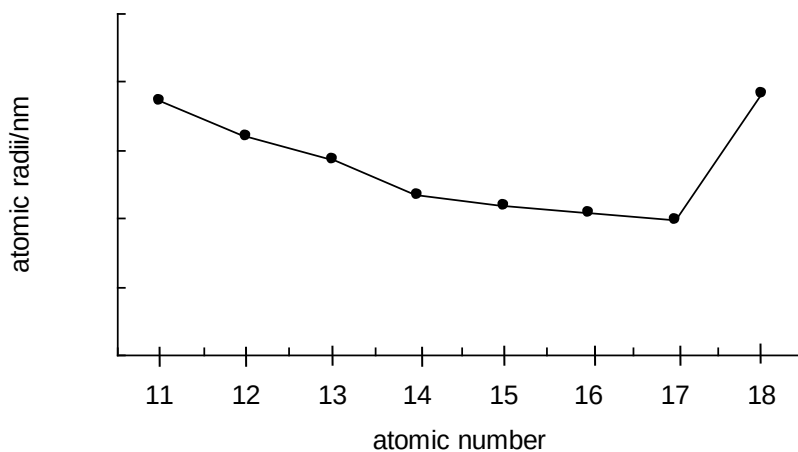
The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

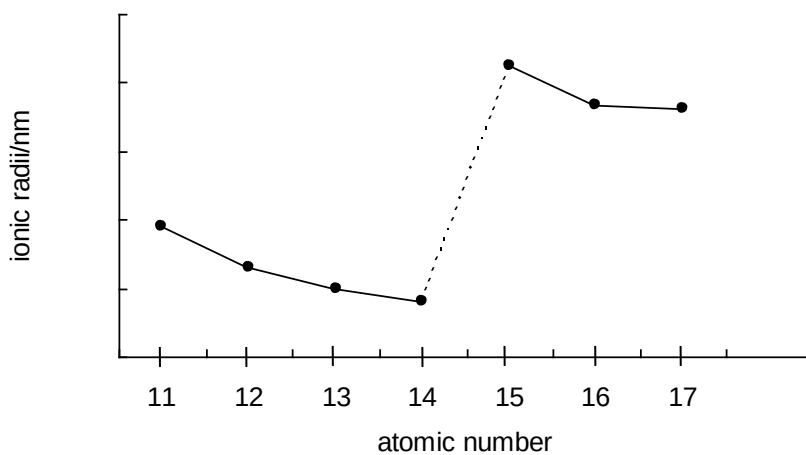
No other combination of statements is used as a correct response.

35 Which of the following graphs correctly represents the variation in the specified property of the elements in Period 3?

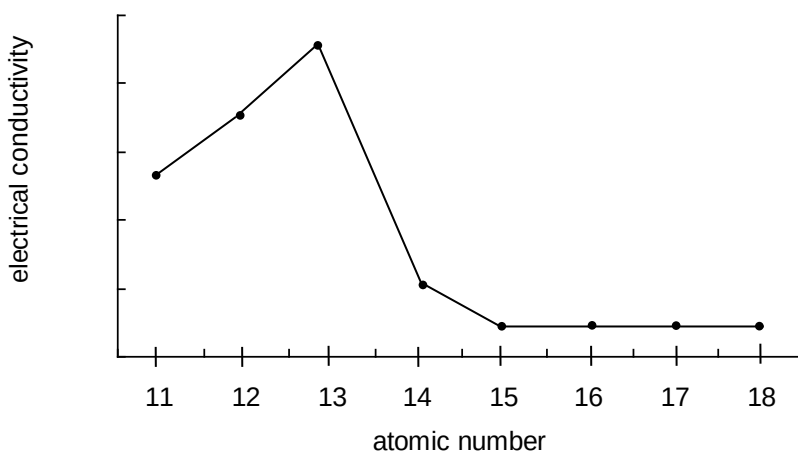
1



2



3



The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

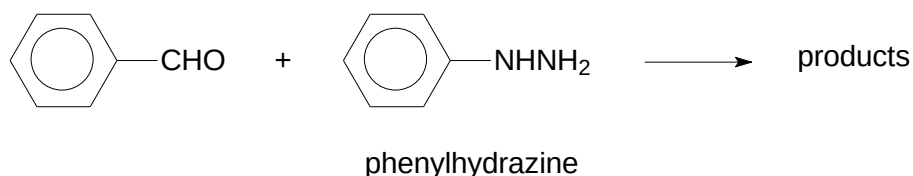
36 For the reaction,



which of the following statements are likely to be correct?

- 1** The reaction involves an electrophilic attack by $\text{CH}_3\text{CH}_2\text{O}^-$.
- 2** The rate determining step involves the formation of a carbocation.
- 3** The reaction will take place more rapidly when X is I than when X is Cl.

37 The reaction of phenylhydrazine is similar to that of 2,4-dinitrophenylhydrazine.



Which changes in bonding occur in the reactants and products during the reaction above?

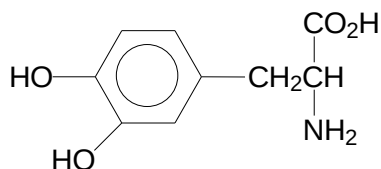
	Bond broken	Bond formed
1	C–H	C–C
2	N–H	O–H
3	C=O	C=N

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 38** *Dopamine* is a neurotransmitter found in many animals, including vertebrates and invertebrates.



Dopamine

Which of the following statements are **correct**?

- 1** 1 mole of *dopamine* reacts with 3 moles of acyl chloride
- 2** 1 mole of *dopamine* reacts with 1.5 moles of $\text{Br}_2(\text{aq})$.
- 3** 1 mole of *dopamine* reacts with 3 moles of Na_2CO_3 .

- 39** Compound **V**, with molecular formula C_6H_{12} , was reacted with acidified potassium manganate(VII) and the resultant mixture obtained was colourless. The mixture was thereafter distilled to form distillate **W** and residual solution **X**.

Distillate **W** is able to form a yellow precipitate with alkaline aqueous iodine. Residual solution **X** reacts with sodium carbonate to form a colourless gas.

Which of the following statements are **true**?

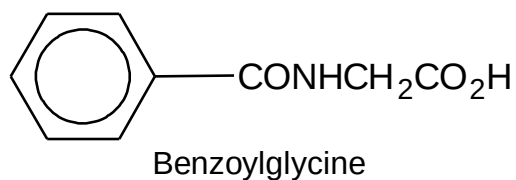
- 1** Compound **V** will decolourise aqueous bromine.
- 2** Distillate **W** can form an orange precipitate with 2,4-dinitrophenylhydrazine.
- 3** Residual solution **X** can form white fumes with PCl_5 .

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

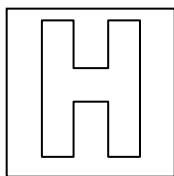
40 Benzoylglycine (hippuric acid) was first isolated from stallions' urine.



Which properties does this compound possess?

- 1** It can be hydrolysed to produce an amino acid.
- 2** It can be made by reacting benzoyl chloride with aminoethanoic acid.
- 3** It can be neutralised by reaction with cold aqueous sodium hydroxide.

End of Paper



PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE
NAME

CT
GROUP

1	5	S		

INDEX
NUMBER

CHEMISTRY

9647/02

Paper 2 Structured

13 September 2016

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

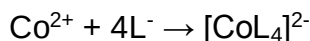
FOR EXAMINER'S USE	
Paper 2	
1	/12
2	/12
3	/14
4	/8
5	/9
6	/17
Penalty	sf units
Total	/72

This document consists of **17** printed pages.

Answer **all** questions in the spaces provided.

1 Planning (P)

The formation of a cobalt(II) complex ion, from Co^{2+} and an unknown ligand(L^-), is accompanied by the appearance of a blue colouration.



A machine, known as a spectrometer, is able to measure the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the solution. The amount of light absorbed is then expressed as an absorbance value, and the absorbance value is proportional to the concentration of the cobalt(II) complex ion.

This technique can be used to confirm the formula of the cobalt(II) complex ion. A series of solutions containing varying volume ratios of L^- to Co^{2+} , both of the same concentration, while keeping the total volume of the Co^{2+} and L^- constant, is prepared. A spectrometer is used to measure the absorbance of the solutions. A graph of absorbance value against volume of L^- is then plotted.

Using the graph of absorbance value against volume of L^- , the ratio of L^- to Co^{2+} equal to that in the cobalt(II) complex ion can be then determined from the maximum point. This is known as the “Job’s Method”.

- (a) The spectrometer is set to use the wavelength of the light that is absorbed most strongly by the complex ion.

Colour	Wavelengths (nm)
Red	620-750
Orange	590-620
Yellow	570-590
Green	495-590
Cyan	475-495
Blue	450-475
Violet	380-450

Suggest a wavelength in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

.....

.....

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.....

[2]

- (b) Using the information given above, you are required to write a plan to confirm the formula of the cobalt(II) complex ion as $[\text{CoL}_4]^{2-}$.

You may assume that you are provided with:

- solid cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$;
- solution of L^- , of concentration $0.100 \text{ mol dm}^{-3}$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 250 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous cobalt(II) nitrate;
- the preparation of five 50 cm^3 complex ion solutions containing varying volume ratios of L^- to Co^{2+} ;
- how the absorbance values would be obtained;
- a sketch of the graph of absorbance value against volume of L^- that you would expect to obtain;
- how the calculation can be performed to determine the formula of $[\text{CoL}_4]^{2-}$.

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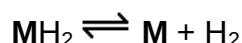
.....

[10]
[Total: 12]

- 2 The mission of the Hydrogen and Fuel Cells Programme by the U.S. Department of Energy (DoE) is to reduce petroleum use, greenhouse gas emissions, and air pollution and to contribute to a more diverse and efficient energy infrastructure by enabling the widespread commercialisation of hydrogen and fuel cell technologies.

One such technology involves creating an energy system concept that stores hydrogen in the form of metal hydrides. Magnesium hydride (MgH_2) is one of the compounds currently being researched on its viability on hydrogen storage. One way to release hydrogen from metal hydrides is to react them with water, where a hydroxide is formed as a side product.

The other way to obtain hydrogen is through the thermal decomposition of the metal hydride MH_2 . When hydrogen is needed, these metal hydrides can be heated to release molecular hydrogen.



This adsorption and desorption of hydrogen in metals serves like a 'hydrogen bank'. The rate of desorption of hydrogen is proportional on the strength of ionic bonds formed between the metal and hydride ions.

Apart from MgH_2 , other Group II hydrides are also being studied and researched on the same purpose. The table below shows some properties of the Group II hydrides.

	MgH₂	CaH₂	SrH₂	BaH₂
Percentage of H / % by mass of H	7.7	4.8	2.2	1.4
Density / g cm⁻³	1.74	1.54	2.64	3.62
Melting point / °C	650	842	777	727
ΔH_f / kJ mol⁻¹	-114	-144	-119	-118

- (a) (i) Write an equation for the reaction between solid MgH_2 and water.

..... [1]

- (ii) Draw the dot-and-cross diagram for MgH_2 .

[1]

- (b) (i) Explain, with reasoning, the trend on the rate of desorption of hydrogen for the Group II metal hydrides from CaH_2 to BaH_2 .

.....
.....
.....
..... [2]

- (ii) Which metal hydride, CaH_2 or BaH_2 , would you expect to decompose more readily? Explain your answer by using relevant data from the above table.

.....
.....
.....
..... [2]

- (iii) Using relevant information from the *Data Booklet* and the information given below, construct a Born-Haber cycle to calculate the lattice energy for CaH_2 .
(The first electron affinity for hydrogen is $-72.8 \text{ kJ mol}^{-1}$ and the enthalpy change of atomisation of calcium is $+178 \text{ kJ mol}^{-1}$)

.....
..... [3]

- (c) A car company is planning to develop cars that run on hydrogen fuel produced by MgH_2 .

The following information is for a typical petrol-fuelled car.

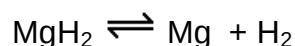
Weight of vehicle / kg	1088
Fuel tank / L	42
Fuel consumption / km L^{-1}	17
Energy consumption of petrol / kJ kg^{-1}	46.4
Density of petrol / g cm^{-3}	0.8 g

- (i) Calculate the energy produced by a petrol-fuelled car running at full tank.

[1]

- (ii) It was found that 1 kg of hydrogen produce 3 times more energy than petrol with the same mass.

Assuming 100% efficiency, calculate the amount of magnesium metal needed to store the hydrogen as the hydride to provide the same amount of energy in the hydrogen-fuelled car. (1 L = 1000 cm^3)



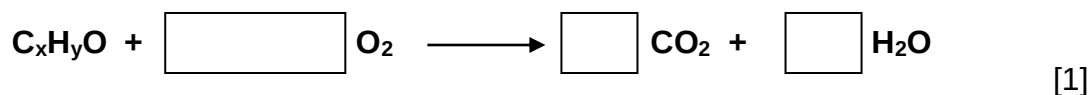
[2]

[Total: 12]

- 3 (a) In the presence of excess oxygen, a liquid alcohol, compound **A**, C_xH_yO , undergoes complete combustion to produce 3.19 dm^3 of hot gases at a temperature of 250°C at a pressure of 1 atm,

Upon cooling to room temperature, the volume contracted to 836 cm^3 . The gases were then passed through aqueous sodium hydroxide and the final volume remaining was 100 cm^3 .

- (i) Fill in the following blanks for the equation for the complete combustion of **A**.



- (ii) Using the *ideal gas equation*, find the amount of CO_2 and amount of H_2O that was produced respectively from the complete combustion of compound **A**.

[3]

- (iii) Using your answer to (a)(i) and (a)(ii), calculate the value of x and y and hence, write down the empirical formula for **A**.

[1]

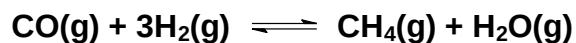
- (ii) The actual number of moles of gases obtained from the combustion is found to be higher than that calculated when using the *ideal gas equation*.

Account for the difference between the two results.

.....

[1]

- (b) Methane can be obtained when carbon monoxide is heated to 900 °C with hydrogen gas as shown in the following equation.



- (ii) Write an expression for the K_c of the reaction, stating its units.

- (iii) 1 mol of carbon monoxide was heated with 4 mol of hydrogen gas in a 10 dm³ vessel. At equilibrium, the vessel contained 0.387 mol of methane. [1]

Calculate the K_c for the reaction of carbon monoxide.

[2]

- (iv) Suggest, with an explanation, how the position of equilibrium might alter when 1 mol of helium was added into the vessel.

.....
.....

[1]

(c) Anhydrous aluminium sulfate is commonly used in organic reactions to remove water. It decomposes at 600 °C to produce an insoluble white solid and misty fumes. The white solid dissolves in both aqueous sodium hydroxide and aqueous hydrochloric acid while the misty fumes turn moist blue litmus red.

(i) Suggest the identities of the white solid and the misty fumes. Hence, write a balanced equation for the decomposition of aluminium sulfate.

.....

[2]

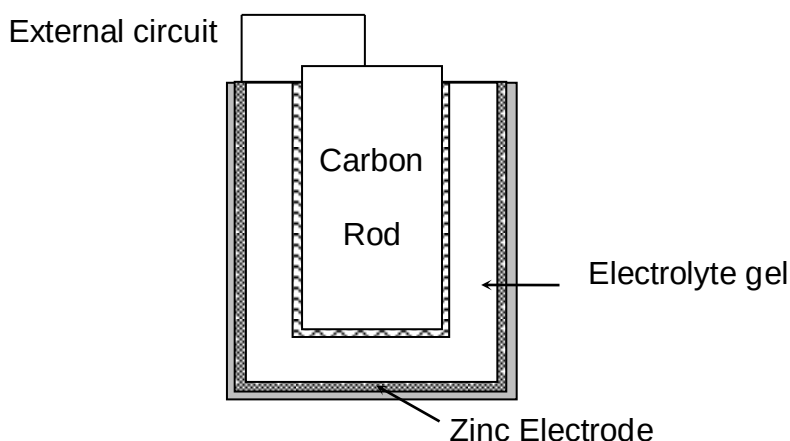
(ii) Write equations for the reactions of the white solid with aqueous sodium hydroxide and hydrochloric acid.

.....

[2]

[Total: 14]

4 Batteries for hearing aids comprise of zinc and carbon electrodes. These electrodes in an electrolyte, maintained at a pH of 11, forms a galvanic cell in which zinc is oxidised and oxygen from the air is reduced.



(a) Write a balanced equation for the overall chemical reaction and calculate the E^θ_{cell} of this cell.

[2]

- (b) Indicate, on the diagram on page 10, the polarity of both electrodes and the direction of electron flow in the external circuit.

[2]

- (c) Explain how the e.m.f. of the cell would change if the pH of the electrolyte decreases.

.....

.....

.....

.....

[2]

- (d) If a current of 4×10^{-5} A was drawn from the cell, calculate how long a zinc electrode weighing 2 g will last before it needs to be replaced. Give your answer correct to the nearest day.

[2]

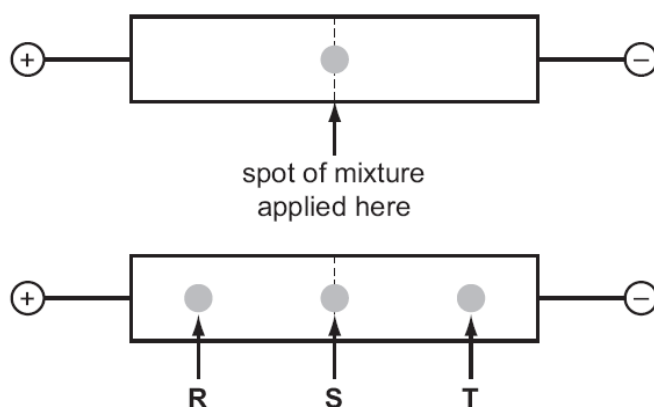
[Total: 8]

The diagram illustrates the primary structure of insulin, consisting of two polypeptide chains, Chain A and Chain B, connected by disulfide bonds. Chain A is 21 amino acids long, and Chain B is 30 amino acids long. The amino acids are represented by colored spheres (blue for basic, purple for acidic, green for polar, and yellow for non-polar). The N-terminus (H₂N) and C-terminus (CO₂H) are indicated. A callout labeled 'Section X' points to a specific region of Chain B, which is highlighted by a dashed blue circle. This region contains the amino acids Arg, Gly, and Glu.

amino acid	Abbreviated name	Formula of side chain (R in RCH(NH₂)CO₂H)	pI
arginine	arg	-(CH ₂) ₃ NHC(NH ₂)=NH	10.76
cysteine	cys	-CH ₂ SH	5.07
glutamic acid	glu	-CH ₂ CH ₂ COOH	3.22
glycine	gly	-H	5.97

- [1]

- (b) The diagram shows the results of electrophoresis on a mixture of the amino acids obtained from hydrolysis of section X at pH 6.0.



Draw the structure of the species responsible for the spots labelled **R**, **S** and **T**.

R	S	T

[3]

- (c) The polypeptide chains of insulin coil to form short sections of α -helix which stabilises the secondary structure.

Describe with the aid of a sketch, how a polypeptide chain is held in the shape of an α -helix.

[3]

- (d) The three-dimensional structure of insulin is further stabilised by disulfide linkages. Write an equation for the formation of such linkage and state the type of reaction involved.
-
-

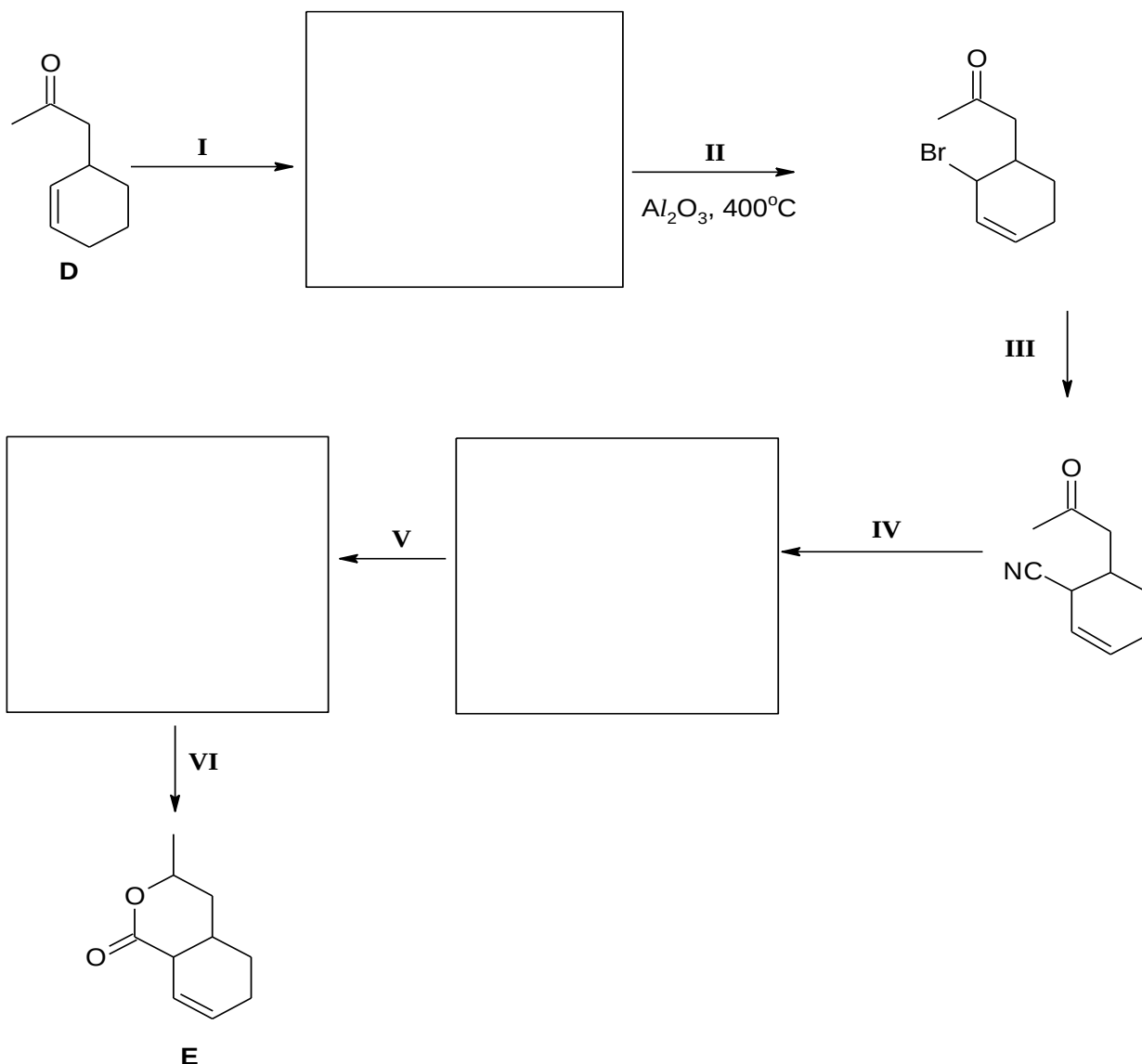
[2]

[Total: 9]

- 6 Lactones are cyclic esters. They are formed by intramolecular esterification of the corresponding hydroxycarboxylic acids.

- (a) (i) The reaction scheme below shows how lactone **E** is synthesised from compound **D**.

Complete the reaction scheme by giving the structural formulae of the intermediate organic products in the spaces provided and stating the reagents and conditions for steps I, III, IV, V and VI.



Step	Reagents and conditions
I	
III	
IV	
V	
VI	

[8]

- (ii) Suggest a simple chemical test to distinguish compound **D** from **E**.

.....

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.....

[2]

- (iii) Name and outline the mechanism when compound **D** is treated with HCN in the presence of aqueous NaOH at 10 °C.

[3]

- (b) Lactones with three- or four-membered rings are very reactive compared to five- or six-membered rings, making their isolation difficult.

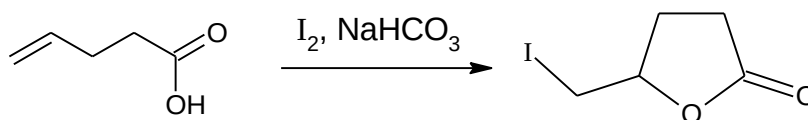
Suggest why lactones with three- or four-membered rings are very reactive.

.....

..... [1]

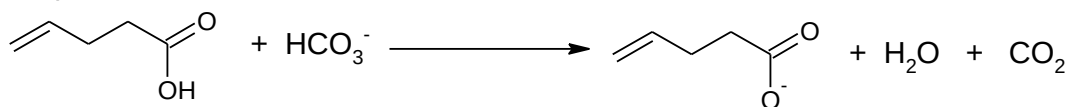
- (c) Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown below.



Two simplified steps in the iodolactonisation mechanism are given below.

Step 1



Step 2



- (i) Suggest the role of HCO_3^- in step 1 of the mechanism.

.....

[1]

- (ii) The type of reaction in Step 2 of the mechanism is electrophilic addition.

Draw the structure of intermediate **F**.

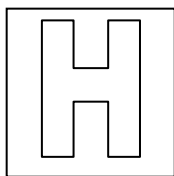
[1]

- (iii) Suggest the structural formulae of the final organic product formed when $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{COOH}$ undergoes iodolactonisation in a similar process as above.

[1]

[Total: 17]

End of Paper



PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE
NAME

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GROUP

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INDEX
NUMBER

CHEMISTRY

9647/03

Paper 3 Free Response

15 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Graph Paper
 Data Booklet
 Cover Page

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work that you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough workings.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

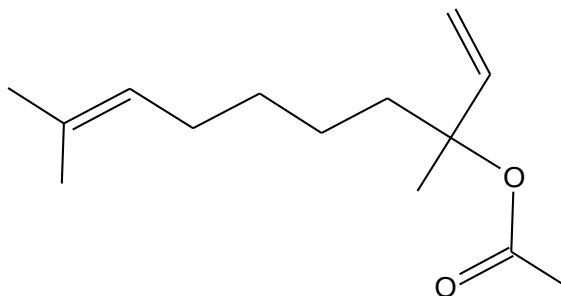
The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

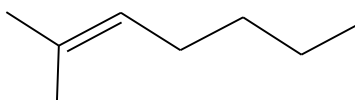
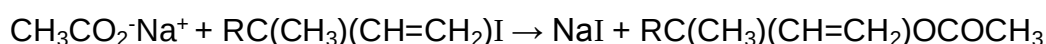
Answer any **four** questions.

Begin **each** question on a fresh piece of writing paper.

- 1 (a) Linalyl acetate is a naturally occurring phytochemical found in many flowers. It is one of the principal components of the essential oils of bergamot and lavender. It has the following structure.



Linalyl acetate can be synthesised by the reaction of carboxylate anion with an alkyl halide as shown below:



where R =

The kinetics of this reaction was determined by measuring the concentration of the remaining $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ with time.

The initial concentrations of $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ and $\text{CH}_3\text{CO}_2^-\text{Na}^+$ were $0.0050 \text{ mol dm}^{-3}$ and $0.100 \text{ mol dm}^{-3}$ respectively. The following data was obtained.

Time/ min	$[\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}] / \text{mol dm}^{-3}$
0	0.0050
15	0.0040
30	0.0032
45	0.0026
60	0.0021
75	0.0017

- (i) Plot a suitable graph to show that the order of reaction with respect to $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ is one. [3]
- (ii) A new set of experiment was carried out and the initial concentrations of $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ and $\text{CH}_3\text{CO}_2^-\text{Na}^+$ was increased to $0.0100 \text{ mol dm}^{-3}$, and $0.200 \text{ mol dm}^{-3}$ respectively. When a similar graph was plotted, it was found that the gradient at each point doubled.

Deduce the order of reaction with respect to $\text{CH}_3\text{CO}_2^-\text{Na}^+$, and explain your answer. [2]

(iii) Construct a rate equation for the reaction between $\text{CH}_3\text{CO}_2^-\text{Na}^+$ and $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$, stating the units for the rate constant. [1]

(iv) Using your answer in (a)(iii), suggest the mechanism for the reaction between $\text{CH}_3\text{CO}_2^-\text{Na}^+$ and $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ that leads to the formation of the ester, $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{OCOCH}_3$. [3]

(b) An example of a homogeneous catalyst is $\text{Fe}^{2+}(\text{aq})$, which is used in the oxidation of sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$, with acidified potassium manganate(VII), KMnO_4 . Ethanedioate is oxidised to carbon dioxide.

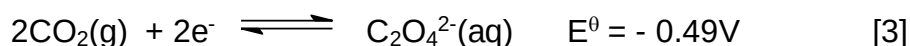
(i) What do you understand by the term *homogeneous* catalyst? [1]

(ii) Write an overall equation for the reaction of sodium ethanedioate with acidified potassium manganate(VII). [1]

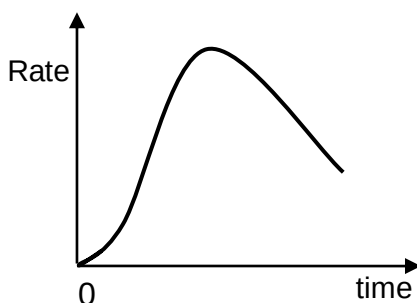
(iii) The E°_{cell} of the reaction between sodium ethanedioate with acidified potassium manganate(VII) is +2.01 V. However, the reaction is found to proceed at a very slow rate.

Explain why the reaction between sodium ethanedioate and acidified potassium manganate(VII) is slow. [1]

(iv) By considering suitable E° values from the *Data Booklet* and the data given below, explain how Fe^{2+} functions as a catalyst for the reaction between sodium ethanedioate with acidified potassium manganate(VII), writing equations where appropriate.



(v) In the absence of a Fe^{2+} catalyst, the rate of reaction between potassium manganate(VII), and sodium ethanedioate is shown in the graph below.



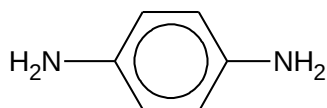
Explain the shape of the graph. [2]

(c) The rate of a chemical reaction is usually increased at elevated temperatures.

Explain, with the aid of a Boltzmann Distribution graph, why an increase in temperature increases the rate of reaction. [3]

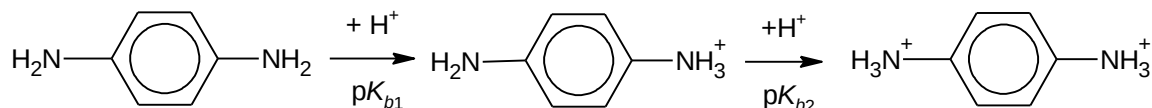
[Total: 20]

- 2 (a) Ammonia and *para*-phenylenediamine, $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$, are *Bronsted-Lowry bases* that are used widely in permanent hair dyes. *Para*-phenylenediamine has the structure shown below:



para-phenylenediamine

Para-phenylenediamine, $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$, can ionise in stages.



The two $\text{p}K_b$ values associated with *para*-phenylenediamine are shown in the table below.

Base	formula	$\text{p}K_{b1}$	$\text{p}K_{b2}$
ammonia	NH_3	4.7	-
<i>para</i> -phenylenediamine	$\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$	7.7	11.0

- (i) Explain what is meant by the term *Bronsted-Lowry base*. [1]
- (ii) Suggest a reason why the $\text{p}K_{b1}$ value of *para*-phenylenediamine is higher than the $\text{p}K_{b1}$ of ammonia. [1]
- (iii) Suggest a reason why the $\text{p}K_{b1}$ value of *para*-phenylenediamine is lower than $\text{p}K_{b2}$. [1]
- (iv) Explain what is meant by a *buffer solution*. [1]
- (v) Assuming that a solution at pH 6.5 contains only $[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2]$ and $[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+]$, calculate the ratio of $\frac{[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+]}{[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2]}$ in the solution.
(ignore the effect of $\text{p}K_{b2}$ of *para*-phenylenediamine on the pH) [2]
- (vi) Calculate the pH of solution containing equimolar amount of $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+$ and $^+\text{H}_3\text{NC}_6\text{H}_4\text{NH}_3^+$ [2]

- (b)** Ammonia is commonly used in qualitative analysis of halides in aqueous solutions, such as detecting the presence of chloride and bromide ions in natural water sources such as rivers, lakes and streams.

- (i)** 5 cm³ of 0.0100 mol dm⁻³ of silver nitrate is added to a 30 cm³ sample of river water containing chloride ions.

What is the minimum concentration, in mol dm⁻³, of chloride ions present in the river water when the first trace of precipitate appears?

Given solubility product of the silver chloride is $2.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

[2]

- (ii)** To a test tube containing another river sample containing bromide ions, describe what you would see when aqueous silver nitrate is added to the sample, followed by excess aqueous ammonia to the resulting mixture. [1]

- (iii)** Explain, with aid of appropriate equation(s), the observations in **(b)(ii)**.

You should use the concepts of Le Chatelier's Principle and solubility product, K_{sp} , to explain your answer. [4]

- (c) (i)** When iodine reacts with sodium hydroxide, iodide and iodate(V) are formed.

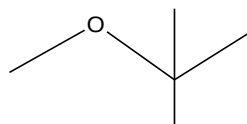
Write a balanced ionic equation, with state symbols, for the formation of IO_3^- when iodine reacts with sodium hydroxide. Name the type of reaction taking place. [2]

- (ii)** When Group II iodates(V), $\text{M}(\text{IO}_3)_2$, are heated at high temperature, it form the metal oxide, iodine vapour and a colourless gas that relights glowing splinter.

It was observed that Group II iodates(V) down the group have to be heated more strongly before the iodine vapour appears. Explain why thermal stability increases down the group for Group II iodate(V). [3]

[Total: 20]

- 3 (a) Liquid methyl t-butyl ether, **MTBE**, is a fuel additive that is used as an oxygenate to raise the octane number in fuel. This will help the fuel to burn completely and reduce air pollution.



MTBE

- (i) What is meant by the term *standard enthalpy change of formation* of **MTBE**? [1]

- (ii) Use the following data and relevant data from *Data Booklet* to construct an appropriate energy cycle, find the standard enthalpy change of formation of **MTBE**.

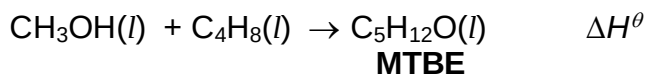
Standard enthalpy change of atomisation of C(s)	+715 kJ mol ⁻¹
Standard enthalpy change of atomisation of MTBE (l)	+6822 kJ mol ⁻¹

[4]

- (iii) Given that the standard enthalpy change of vaporisation of **MTBE** is +30.4 kJ mol⁻¹ and using relevant data from the *Data Booklet* and (a)(ii), calculate the bond energy of C-O in **MTBE**. [2]

- (iv) Suggest a reason for the difference in the C-O bond energy in (a)(iii) from the value given in the *Data Booklet*. [1]

- (b) **MTBE** can be produced from methanol and but-1-ene by the following equation. The reaction has a standard entropy change of reaction of -281 J mol⁻¹ K⁻¹.



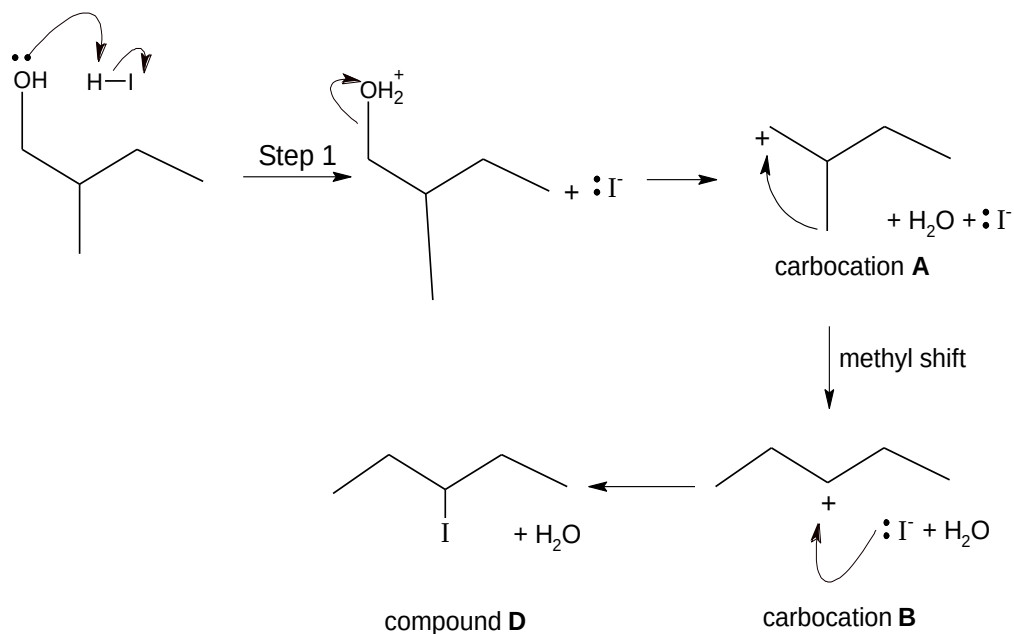
The table below lists the ΔH_f^θ (standard enthalpy change of formation) values for some compounds.

compound	$\Delta H_f^\theta / \text{kJ mol}^{-1}$
CH ₃ OH(l)	-239
C ₄ H ₈ (l)	-0.4

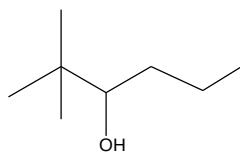
- (i) Calculate the ΔH_f^θ for the reaction in (b) using the values from the table above and your answer to (a)(ii). [1]
- (ii) Determine the feasibility of the production of **MTBE** from methanol and but-1-ene at 298 K. [2]

- (c) Methyl shift can occur in organic chemistry reactions in reactions involving carbocation intermediates.

An example of a methyl shift in a reaction between an alcohol and HI is shown below. In this reaction compound **D** is produced as the major product.



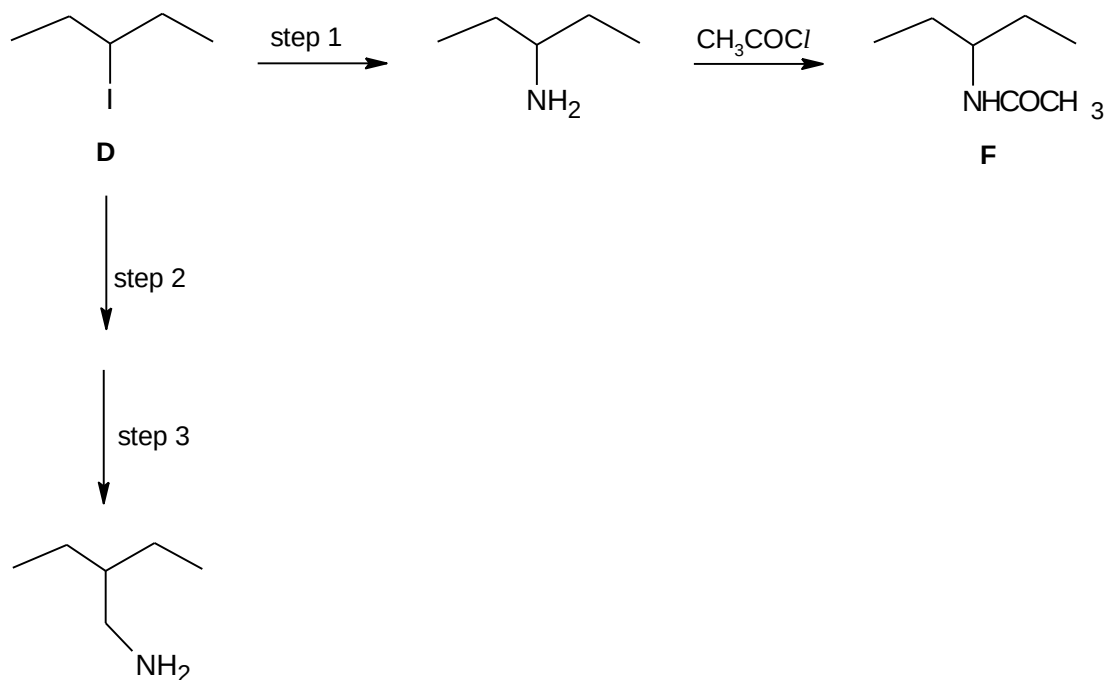
- (i) What is the role of HI in step 1? [1]
- (ii) Suggest a reason why there is a methyl shift to produce carbocation **B** from carbocation **A**. [1]
- (iii)



The structure of compound **E** is .

Predict the major final product formed when compound **E** reacts with HBr based on the methyl shift reaction given in (c). [1]

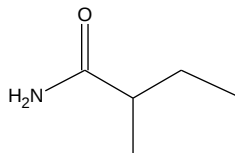
(iv) Compound **D** undergoes the following reactions.



Suggest suitable reagents for steps 1, 2 and 3.

[3]

(v) Suggest one simple chemical test which would enable you to distinguish



between compound **F** and

You should state the reagents and conditions for the test and describe the observations.

[3]

[Total: 20]

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- 4 (a) Compound **G**, $C_{10}H_{15}NO_3$, is a natural stimulant made in the adrenal gland of the kidney and is carried in the bloodstream and affects the autonomous nervous system, which controls functions such as heart rate and dilation of the pupils.

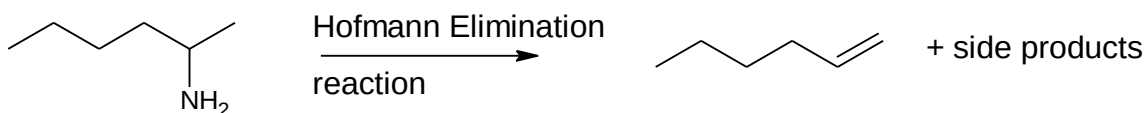
G is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate.

G undergoes reaction with hot acidified potassium dichromate(VI) to form **J**. **J** gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give a silver mirror with Tollens' reagent. Upon heating with concentrated H_2SO_4 , **G** forms **K**, $C_{10}H_{13}NO_2$. **K** does not react with PCl_5 . On heating with acidified potassium manganate(VII), **K** forms three compounds, **L**, $C_7H_6O_4$, **M**, $C_2H_4O_2$, and an ammonium salt, $CH_3NH_3^+$.

Deduce the structures for each compound, **G** to **M**, and give an account of the chemistry involved. [10]

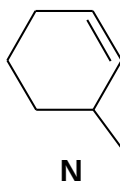
- (b) Like alcohols and halogenoalkanes, amines can be converted into alkenes by an elimination reaction known as Hofmann elimination.

For example, 1-methyl-pentylamine is converted into hex-1-ene as shown.



An interesting feature of the Hofmann elimination is that it gives a **less substituted alkene** compared to other elimination reactions.

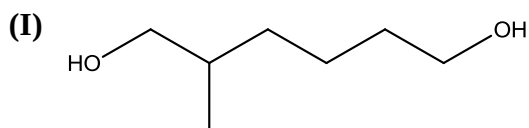
- (i) Draw the likely structure of the starting amine if the following alkene **N** is the main product formed when the amine undergoes a Hofmann elimination reaction.



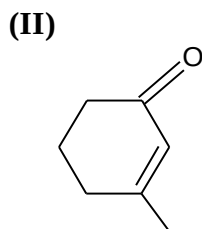
[1]

- (ii) Suggest, in no more than 3 steps, a suitable synthetic pathway to convert **N** into the following compounds.

For each step, state clearly the reagents and conditions, indicating the structural formula of all intermediate compounds formed.



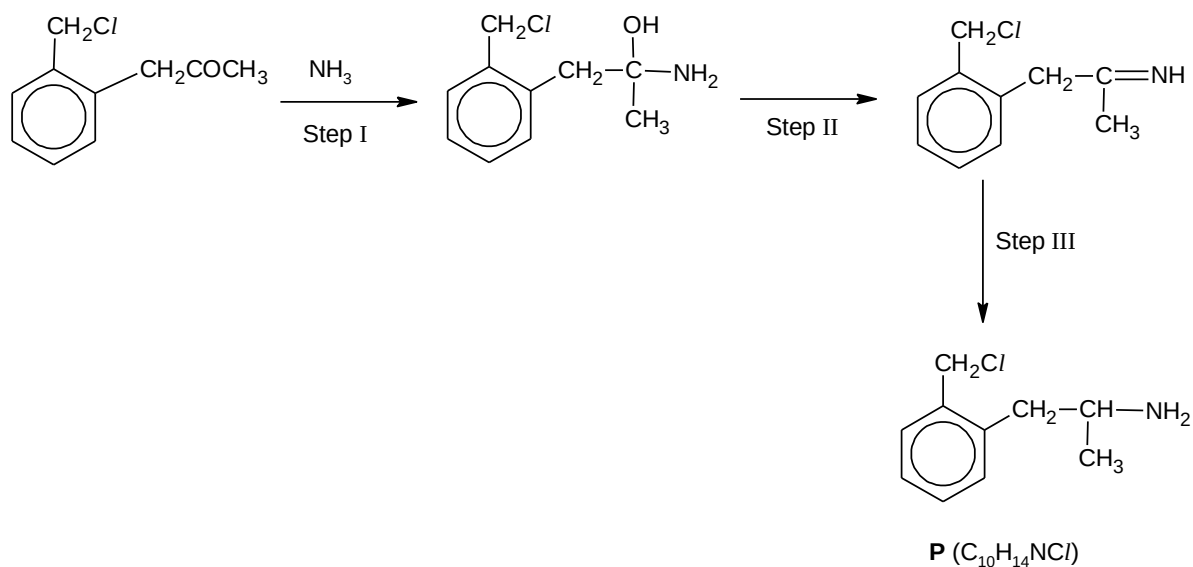
[2]



[3]

- (c) Amines can be formed by reductive amination of an aldehyde or ketone with ammonia or amine in the presence of reducing agent.

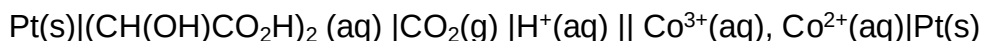
A reductive amination to produce an amine **P** takes place in the pathway shown.



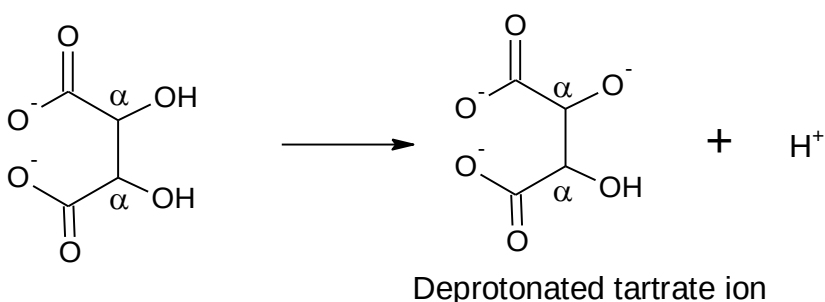
- (i) Suggest the type of reaction that occurs in steps I and II. [2]
- (ii) Suggest the reagents and conditions for step III. [1]
- (iii) On heating, **P** forms **Q**, $\text{C}_{10}\text{H}_{13}\text{N}$. Suggest a structure for **Q**. [1]

[Total: 20]

- 5 (a) An electrochemical cell involving tartaric acid, $(\text{CH}(\text{OH})\text{CO}_2\text{H})_2$, has the following cell diagram notation.



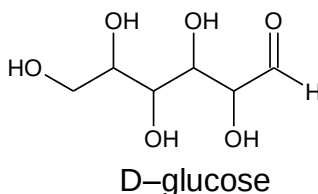
- (i) Given that the e.m.f of the cell is +0.80 V and using relevant data from the *Data Booklet*, determine the standard electrode potential of the $\text{CO}_2(\text{g}) | (\text{CH}(\text{OH})\text{CO}_2\text{H})_2(\text{aq})$ half-cell. [2]
- (ii) Draw a labelled diagram of the above electrochemical cell. [3]
- (b) Fehling's solution is made by adding equal volumes of a blue solution **A** containing aqueous copper(II) sulfate and a colourless solution **B** containing potassium sodium tartrate and sodium hydroxide. In a strong base, an alpha-hydroxy group in the tartrate ion, $(\text{CH}(\text{OH})\text{CO}_2^-)_2$, deprotonates as shown in the diagram below.



The deprotonated tartrate ion acts as a bidentate ligand and binds to the $\text{Cu}^{2+}(\text{aq})$ using both oxygen atoms from the **alpha-hydroxy groups**. A square planar bistartratocuprate(II) complex, $[\text{Cu}(\text{tart})_2]^{4-}$, forms, and a deep blue solution is seen.

[tart = deprotonated tartrate ion]

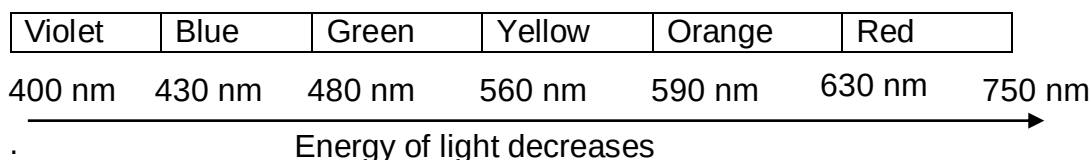
- (i) Draw the shape of $[\text{Cu}(\text{tart})_2]^{4-}$ complex, indicating clearly the type of bonds formed between the Cu^{2+} and the ligands. [2]
- (ii) The open straight chain form of D-glucose, a reducing sugar, is shown.



State what would be observed when D-glucose solution is warmed with a few drops of Fehling's solution. Hence, or otherwise, write the balanced equation for the reaction described above. [2]

- (iii) Explain why there is a need to form the $[\text{Cu}(\text{tart})_2]^{4-}$ complex in the Fehling's solution test. [1]
- (iv) Explain why the Fehling's solution is deep blue while potassium sodium tartrate solution is colourless. [4]

- (v) Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

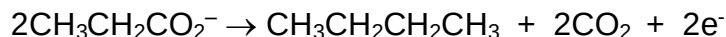


To test for proteins, Biuret reagent which also contains the $[\text{Cu}(\text{tart})_2]^{4-}$ complex is used. In the presence of peptides, it undergoes ligand exchange to form $[\text{Cu}(\text{peptide})_2]^{2+}$. The deep blue solution turns violet.

Using the above electromagnetic spectrum of visible light, state the relative field strength of peptides and deprotonated tartrate ions. Explain your answer. [3]

- (c) Adolf Kolbe first published a method describing the preparation of an alkane from the electrolysis of an aqueous solution of sodium salt of a monoprotic acid, using inert electrodes.

In the Kolbe electrolysis of sodium propanoate, butane was formed at the anode in the following reaction.



- (i) Write the half equation for the reaction at the cathode during the electrolysis of sodium propanoate. Hence write an equation for the **overall** reaction. [2]
- (ii) A student tried to synthesise another hydrocarbon using an aqueous solution of a sodium salt of a diprotic acid, succinic acid, $(\text{CH}_2\text{CO}_2\text{H})_2$. The succinate ion, $(\text{CH}_2\text{CO}_2^-)_2$, undergoes a similar reaction as propanoate ion at the anode.



Suggest an identity of the hydrocarbon **R**.

[1]

[Total : 20]

End of Paper

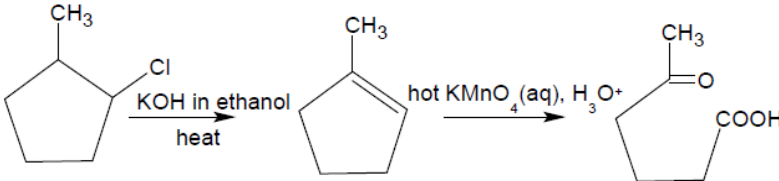
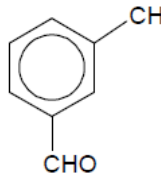
H2 Chemistry Preliminary Examination Paper 1 Worked solution

1	D	Option A is wrong: the number of atoms in 24 dm³ of nitrogen gas at r.t.p. condition $24 \text{ dm}^3 \text{ N}_2 \equiv 1 \text{ mol N}_2 \equiv 2 \text{ mol N} \equiv 2 \times L$ Option B is wrong: the number of molecules in 1 dm³ of oxygen at 273 K and 1 atm $1 \text{ dm}^3 \text{ O}_2 \equiv 1/22.4 \text{ mol O}_2 \equiv 1/22.4 \times L$ Option C is wrong: the number of electrons removed to form Ne⁺ ions from $6.02 \times 10^{-23} \text{ mol}$ of Ne atoms No of electrons removed = $(6.02 \times 10^{23}) \times (6.02 \times 10^{-23}) = 6.02^2 \text{ electrons}$ Option D is correct: the number of ions in 83.5 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ Amount = $83.5/250.4 = 1/3 \text{ mol}$ $1 \text{ mol } [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \equiv 3 \text{ mol ions}$ $1/3 \text{ mol } [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \equiv 1 \text{ mol ions} = L$
2	B	Option A is wrong: ${}_{26}\text{Fe} : [\text{Ar}] 3d^6 4s^2$ (one unpaired d-orbital) Option B is correct: ${}_{32}\text{Ge}^{2+} : [\text{Ar}] 3d^{10} 4s^2$ (no unpaired, all paired) Option C is wrong: ${}_{14}\text{Si} : [\text{Ne}] 3s^2 3p^2$ (two unpaired p-orbitals) Option D is wrong: ${}_{22}\text{Ti}^{3+} : [\text{Ar}] 3d^1$ (one unpaired d-orbital)
3	C	By VSEPR theory, BCl_3 has 3 bond pairs, and no lone pairs. This give rise to trigonal planar structure. PH_3 has 3 bond pairs and 1 lone pair, therefore it is trigonal pyramidal structure.
4	A	The molecules in option A are a pair of enantiomers. Enantiomers are known to have identical chemical and physical properties, with the exception of its ability to rotate plane polarised light. Therefore the enantiomers will have identical boiling point.
5	B	Option A is wrong : $P = \frac{\rho RT}{M_r}$ $\frac{P}{\rho} = kT = k(t \text{ } ^\circ\text{C} + 273) \text{ (similar to } y = mx + c\text{)}$ Plot wrong as y-intercept is zero. Note temp axis is in $^\circ\text{C}$ and y-intercept = $273k$. Option B is correct: $\frac{P}{\rho} = kT = k(t + 273) \text{ (similar to } y = mx + c\text{)}$ Option C is wrong: Not a linear plot of $y = mx + c$ Option D is wrong: Not a linear plot of $y = mx + c$

6	C	One mol of neon gas at temperature T_1 was added to another one mol of neon and the temperature was increased to T_2. As such, the area under the curve should increase since there is an increase in the number of moles of gases. When temperature increases to T_2, the curve should tend to the right as the molecular speed should increase at a higher temperature. Option C is correct								
7	C	$\Delta H = (5(\text{BE}(\text{N}=\text{N}) + \text{BE}(\text{N}=\text{O}) + 2\text{BE}(\text{C}-\text{H}) + \text{BE}(\text{C}\equiv\text{C})) - (2\text{BE}(\text{O}-\text{H}) + 4\text{BE}(\text{C}=\text{O}) + 5(\text{N}\equiv\text{N})))$ $= (5(418 + 686) + 2(410) + (840)) - (2(460) + 4(740) + 5(994))$ $= -1670 \text{ kJ mol}^{-1}$								
8	B	<table border="1"><thead><tr><th>No. of quarter life</th><th>Amount of ^{40}K left</th></tr></thead><tbody><tr><td>0</td><td>100%</td></tr><tr><td>1</td><td>25%</td></tr><tr><td>2</td><td>6.25%</td></tr></tbody></table> Since two quarter life have passed, the time required would be $2.5 \times 10^9 \times 2 = 5.0 \times 10^9$ years	No. of quarter life	Amount of ^{40}K left	0	100%	1	25%	2	6.25%
No. of quarter life	Amount of ^{40}K left									
0	100%									
1	25%									
2	6.25%									
9	D	0.785 g Cr $\equiv$ 0.0151 mol Cr 8690 C $\equiv$ 0.09005 mol e 0.0151 mol Cr $\equiv$ 0.09005 mol e 1 mol Cr $\equiv$ 5.96 mol e $\equiv$ 6 mol e $\text{Cr}^{n+} + ne \rightarrow \text{Cr}$ $n = 6$ Option A is wrong : OS of Cr = +2 Option B is wrong : OS of Cr = +3 Option C is wrong : OS of Cr = +4 Option D is correct : OS of Cr = +6								
10	B	$\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}, 1 \text{ mol dm}^{-3}) \parallel \text{A}^+(\text{aq}) \mid \text{A(s)}$ Option A is wrong as statement is correct : The Cu^{2+}/Cu half-cell is the anode and Cu is the negative electrode Option B is correct as statement is incorrect : $[\text{A}^+(\text{aq})] = 1.00 \times 10^{-7}$ and $\log [\text{A}^+(\text{aq})] = -7$. From the graph, emf > 0 and the direction of electron flow will not be reversed. Option C is wrong as statement is correct : $E_{\text{cell}}^{\ominus} = E_{\text{red}}^{\ominus} + E_{\text{ox}}^{\ominus} + 0.46 = E_{\text{red}}^{\ominus} + (-0.34) E_{\text{red}}^{\ominus} = +0.80\text{V}$ Option D is wrong as statement is correct : At std conditions, $[\text{A}^+(\text{aq})] = 1.00 \text{ mol dm}^{-3}$ $\log [\text{A}^+(\text{aq})] = 0$ emf = +0.46 V (from graph)								

11	B	$\text{D(g)} \rightleftharpoons \text{E(g)} + \text{F(g)}$<table><tr><td>Initial pressure/atm</td><td>p</td><td>0</td><td>0</td></tr><tr><td>Eqm pressure/atm</td><td>$\frac{1p}{7}$</td><td>$\frac{3p}{7}$</td><td>$\frac{3p}{7}$</td></tr></table> Note : Total pressure = p (constant) $K_p = \frac{\left(\frac{3}{7} \text{ atm}\right)^2}{\left(\frac{1}{7} \text{ atm}\right)} = 9p/7 \text{ atm}$	Initial pressure/atm	p	0	0	Eqm pressure/atm	$\frac{1p}{7}$	$\frac{3p}{7}$	$\frac{3p}{7}$
Initial pressure/atm	p	0	0							
Eqm pressure/atm	$\frac{1p}{7}$	$\frac{3p}{7}$	$\frac{3p}{7}$							
12	B	Method 1: Calculation –confirmation method $\text{pK}_a = 9.5$ $K_a = 10^{-9.5}$ $[\text{paracetamol}] = [(12.78 \times 10^{-3})/151] / (1 \times 10^{-3}) = 0.084 \text{ mol dm}^{-3}$ $K_a = \frac{[\text{anion}][\text{H}^+]}{[\text{paracetamol}]}$$10^{-9.5} = \frac{[\text{anion}][\text{H}^+]}{[0.0846]}$$[\text{H}^+] = 5.17 \times 10^{-6}$$\text{pH} = -\lg[\text{H}^+] = 5.29$ Method 2: Elimination method – smart guess • Paracetamol behaves as weak acid, which undergoes partial dissociation • hence pH must be near to 7 • Most probable pH is 5.29								
13	A	$\text{pH} = 14 - \text{pK}_b$ $\text{pK}_b = 14 - \text{pH}$ $\text{pK}_b = \text{pOH}$ i.e. max buffer capacity Option A is correct								
14	D	NH_4^+ is the conjugate acid of a weak base, NH_3. NH_4^+ dissociates partially in water to produce H_3O^+ as follows: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ $\text{Mg(OH)}_2(\text{s})$ then undergoes an acid–base reaction (neutralisation) with the H_3O^+ ions produced. $\text{Mg(OH)}_2(\text{s}) + 2\text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$								

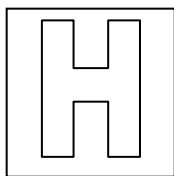
15	D	A saturated solution of Ca(OH)_2 is found to have a pH of 12.3 at 25 °C. $\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \dots \text{eqm (1)}$ Option A is correct: K_{sp} of $\text{Ca(OH)}_2 = [\text{Ca}^{2+}][\text{OH}^-]^2 = (1/2 \times 10^{-1.7}) (10^{-1.7})^2 = 4 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$. Option B is correct: The solubility of Ca(OH)_2 would increase when temperature is raised to 35 °C. Option C is correct: When solid Na_2O is added, NaOH is formed, hence $[\text{OH}^-]$ increases. As such, POE of eqm (1) above will shift to the left, hence $[\text{OH}^-]$ decrease. The solubility of Ca(OH)_2 will decrease. Option D is incorrect: When $\text{Ca(NO}_3)_2$ is added, $[\text{Ca}^{2+}]$ increases. As such, POE of eqm (1) above will shift to the left, hence $[\text{OH}^-]$ decrease. The pH of the solution would decrease.
16	A	• Important information in question : high charge-density cations • Only AlCl_3 and MgCl_2 will dissolve in water to give cations, Al^{3+} and Mg^{2+} • Hence, most effective high charge-density cation is Al^{3+}
17	B	• All of the elements burns in presence of oxygen to give respective oxides. All the metal oxides formed will be soluble in water but SiO_2 is insoluble in water. • Al_2O_3 is amphoteric oxide which reacts with NaOH, ie soluble in excess NaOH through formation of the following complex $\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}[\text{Al}(\text{OH})_4](\text{aq})$ • Both K_2O and CaO are basic oxide which do not react with NaOH, thus remains as white ppt. • However, only CaO will react with H_2SO_4 to give a sparingly soluble white ppt. $\text{CaO}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CaSO}_4(\text{s}) + \text{H}_2\text{O}(\text{l})$
18	C	• Thermal decomposition of hydrogen halides, HX, involves the breaking of the covalent H-X bond. • General trend of Group VII halides: Going down Group VII, the valence np orbital of the halogen atom is larger and more diffused. Thus, the overlap of orbitals between the 1s orbital of H and the np orbital of halogen atom becomes less effective. Consequently, the H-X bond is longer and weaker as indicated by the bond energies. Less energy is required to break the H-X bond going down the group, i.e. thermal stability decreases. • Conclusion : H-C/ bond is stronger than H-I bond.
19	D	Option A : $E_{\text{cell}} = -0.59\text{V}$, reaction is not feasible. Option B: hexacyanoferrate(III) cannot be further oxidised. Option C: Sn is not a transition element, therefore while it can be oxidised from Sn^{2+} to Sn^{4+}, there is no color change. Option D is correct: $E_{\text{cell}} = 0.97\text{V}$, therefore reaction is feasible. V^{2+} is green, and it changes to V^{3+} which is violet.

25	C	Option A:  Option B: $\text{H}_2\text{NCO}(\text{CH}_3)_3\text{CHC/CH}_3 \xrightarrow[\text{heat}]{\text{KOH(aq)}} \text{-OOC}(\text{CH}_3)_3\text{CH(OH)CH}_3 \xrightarrow[\text{H}_3\text{O}^+]{\text{hot KMnO}_4(\text{aq})} \text{CH}_3\text{CO}(\text{CH}_2)_3\text{COOH}$ Option C: $\text{CH}_3\text{CH(OH)(CH}_2)_3\text{CH}_2\text{Cl} \xrightarrow[\text{heat}]{\text{NaOH in ethanol}} \text{CH}_3\text{CH(OH)(CH}_2)_2\text{CH=CH}_2 \xrightarrow[\text{H}_3\text{O}^+]{\text{hot KMnO}_4(\text{aq})} \text{CH}_3\text{CH(OH)(CH}_2)_2\text{COOH (major product)}$ Option D: The compound oxidises to $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{COOH}$.
26	A	The rest of the options will produce 1,3-dicarboxylic acid. Option A:  Will not be able to oxidise the compound. Only Tollens' reagent can oxidise this compound to 1,2-dicarboxylic acid.
27	C	Using the example of phthalic anhydride producing phthalic acid with water, ethanol should follow the same reaction as water. The general formula of the reaction is shown in the equation below. $\text{C}_6\text{H}_4(\text{CO})_2\text{O (anhydride)} + \text{ROH} \rightarrow \text{C}_6\text{H}_4(\text{COOH})\text{COOR} \quad [\text{R} - \text{CH}_3\text{CH}_2-]$
28	B	Q 1 mol of Q requires 3 mol of NaOH for the hydrolysis process. Amount of NaOH left after hydrolysis = $(50/100 \times 1) - 0.03 = 0.02$ mol 1 mol NaOH requires 1 mol of HCl for neutralisation Vol of HCl required to neutralise the remaining NaOH = $0.02 / 1 = 0.02\text{dm}^3 = 20\text{cm}^3$ R 1 mol of R requires 1 mol of NaOH for the hydrolysis process. Amount of NaOH left after hydrolysis = $(50/100 \times 1) - 0.01 = 0.04$ mol 1 mol NaOH requires 1 mol of HCl for neutralisation Vol of HCl required to neutralise the remaining NaOH = $0.04 / 1 = 0.04\text{dm}^3 = 40\text{cm}^3$ S 1 mol of S requires 2 mol of NaOH for substitution of 2 Br. Amount of NaOH left after hydrolysis = $(50/100 \times 1) - 0.02 = 0.03$ mol 1 mol NaOH requires 1 mol of HCl for neutralisation Vol of HCl required to neutralise the remaining NaOH = $0.03 / 1 = 0.03\text{dm}^3 = 30\text{cm}^3$

29	B	Option A: Amino acids form zwitterions not amides. Option B: Basicity depends on the availability of lone pairs of electron on nitrogen for coordination with proton. The lone pair of electrons on the N atom can be <u>delocalised</u> with the π electrons of the C=O double bond. This creates the resonance structure. This makes the amides less basic than amines. Option C: Need to concentrate on the availability of lone pairs of electrons on nitrogen, not on how it is more difficult to break the C-N bond. Option D: The powerful <u>electron-withdrawing effect of the carbonyl group C=O</u> reduces the electron density on the N atom, making it less effective as a proton acceptor. Not make the hydrogen atoms more acidic.
30	D	Option A: True Option B: Both glycine and alanine have non polar R groups, hence would have van der Waals' forces between them. Option C: Cystein is a sulfur containing amino acid which is capable of forming disulfide linkages between the cysteine molecules. Option D: Serine forms hydrogen bonds with another serine amino acid in the protein as the side group is an alcohol group.
31	A	Option 1 is correct : $0.0200 \text{ mol T} \equiv 0.00400 \text{ mol MnO}_4^-$ $5 \text{ mol T} \equiv 1 \text{ mol MnO}_4^-$ Option 2 is correct : $5 \text{ mol T} \equiv 1 \text{ mol MnO}_4^- \equiv 5 \text{ mol e}$ $1 \text{ mol T} \equiv 1 \text{ mol e}$ $1 \text{ mol T} \text{ lost } 1 \text{ mol e}$ Change in OS of T = +1 Option 3 is correct : $\text{TOCl}_y \rightarrow \text{TO}_3^-$ $+4 \quad \quad +5$ OS of T in $\text{TOCl}_y = +4$ In TOCl_y, $+4 + (-2) + (y(-1)) = 0$ $y = 2$

32	A	Option 1 is correct: The ion U^{5+} has the symbol ${}^{89}_{43}\text{U}^{5+}$ and thus the same charge by mass ratio as yttrium ion, ${}^{89}\text{Y}^{5+}$. Both deflected to same extent. Option 2 is correct: U is the technetium, Tc. Electronic configuration of Tc is $[\text{Kr}] 4d^5 5s^2$ and that of U^{5+} is $[\text{Kr}] 4d^2$. Option 3 is correct : $\text{U}^{2+}(\text{g}) \rightarrow \text{U}^{3+}(\text{g}) + \text{e}^-$ (3rd IE) $[\text{Kr}] 4d^5 \quad [\text{Kr}] 4d^4$ The energy required to remove the a mol of e from $\text{U}^{2+}(\text{g})$ will be significantly higher than 2nd IE as it involves the removal of electron from an inner quantum shell.
33	B	Trypsin is an enzyme that catalyses the reaction. When the [substrate] (casein) is low, increasing the concentration of casein will increase the rate of reaction as there are plenty of active sites available on the catalyst, therefore its first order with respect to casein. However, as the concentration of casein rise, the active sites in the enzyme will be saturated, and therefore, increasing the concentration of casein will have no effect on the rate of reaction, thus it's a zero order reaction.
34	B	Option 1 is correct: In discharging the cell, $\text{Li}^+ \text{MnO}_2^-$ will be formed. Li is oxidised to Li^+ and electrons released will flow to the MnO_2 electrode. Option 2 is correct: At the MnO_2 electrode (cathode), MnO_2 gains electron and is reduced to MnO_2^-. Option 3 is wrong: Water cannot be used as it will react with Li, a Group I metal.
35	A	Graph 1 is correct: (Explanation can be found in Pg 4 Periodicity notes) - The atomic radii of the elements <u>decrease</u> across period 3 gradually. Across a period, there is an increase in the <u>effective nuclear charge</u>, due to increasing <u>number of protons</u> in the nucleus and approximately constant shielding effect. - The radius of Ar is, in fact, the van der Waals' radius between two atoms. Hence, largest radius. Graph 2 is correct: explanation will use actual element and its ion to minimise confusion (Pg 4 Periodicity notes) - The cationic radius decreases from atomic number 11 to 14 (which is actually Na^+ to Si^{4+}) (Electronic configuration: <u>$1s^2 2s^2 2p^6$</u>). - Nuclear charge increases from Na^+ to Si^{4+} due to an increase in protons. - Shielding effect remains approximately constant as these cations are isoelectronic. - Due to the increase in nuclear charge, the valence electrons in these ions are held more tightly to the nucleus, accounting for a smaller cationic radius. - The anionic radius decreases from Si^{4-} to Cl^- (Electronic configuration: <u>$1s^2 2s^2 2p^6 3s^2 3p^6$</u>) - Similarly for the anions (Si^{4-}, P^{3-}, S^{2-} and Cl^-) are isoelectronic (constant shielding). The decrease in anionic radii is also due to the increase in nuclear charge. - Radii of anions > Radii of cations because of an <u>extra shell</u> of electrons in the anions.

		Graph 3 is correct: Explanation can be found in Pg 5 Periodicity notes - Na, Mg and Al are metals. Conductivity increases from Na to Al due to an <u>increase</u> in the number of valence electrons donated to the delocalised electron cloud by the metal atoms. - Si is a metalloid (having both properties of metals and non-metals). It has low conductivity. It is a <u>semi-conductor</u>. - P, S and Cl are non-metals. The electrons are localised in covalent pairs and are unable to move to conduct electricity. They have very low conductivities. They are <u>non-conductors</u> (insulators). $\begin{array}{ccccccc} \text{Na} & \text{Mg} & \text{Al} & \text{Si} & \text{P}_4 & \text{S}_8 & \text{Cl}_2 \\ \leftarrow & \text{Metals} & \rightarrow & \text{Metalloid} & \leftarrow & \text{Non-Metals} & \rightarrow \end{array}$
36	C	Option 1: The reaction involves nucleophilic attack not electrophilic attack. Option 2: The RX compound is a tertiary RX hence it will be undergoing SN₁ mechanism which involves the formation of a carbocation in the slow step. Option 3: The reaction involves the cleaving of C-X bond so if the X is I, the reaction will take place rapidly as the C-I bond is weaker than C-Cl bond.
37	C	During the reaction, C=O bond from benzaldehyde and 2 N-H bonds from phenylhydrazine will be broken. The products will have C=N bond and O-H (from water) being formed.
38	D	Option 1: One mole of dopamine has 1 –NH₂ group and 2 –OH groups. Hence, one mole of dopamine will react with 3 moles of RCOCl. (the –NH₂ group will form amide with RCOCl and the –OH group will form ester with RCOCl). Option 2: Dopamine will undergo electrophilic substitution with 3 moles of Br₂(aq) wrt to the two phenol groups. Option 2: Option 3: One mole of dopamine will react with one mole of Na₂CO₃ as only the –COOH group in the compound will react.
39	A	Distillate W forms a yellow ppt with alkaline aq iodine – W has –C=O group. X reacts with Na₂CO₃ – X has –COOH group. Option 1: Given the formula of V, V should have unsaturated bonds in it so it should be able to decolourise aq bromine. Option 2: W is a carbonyl compound so it should be able to form orange ppt with 2,4-DNPH. Option 3: X has –COOH group so it should be able to react with PCl₅.
40	A	Option 1: It can be hydrolysed to form Benzoic acid and aminoethanoic acid. Option 2: Benzoyl chloride and aminoethanoic acid can undergo nucleophilic substitution/condensation to form benzoylglycine and HCl as the products. Option 3: Cold NaOH(aq) can react with –COOH group through acid-base reaction.



PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE
NAME

CT
GROUP

1	5			

INDEX
NUMBER

CHEMISTRY

9647/02

Paper 2 Structured

13 September 2016

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

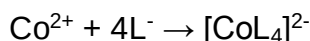
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 2			
1	/ 12	5	/ 9
2	/ 12	6	/ 17
3	/ 14	Penalty	sf units
4	/ 8	Total	/ 72

Answer **all** questions in the spaces provided.

1 Planning (P)

The formation of a cobalt(II) complex ion, from Co^{2+} and an unknown ligand (L^-), is accompanied by the appearance of a blue colouration.



A machine, known as a spectrometer, is able to measure the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the solution. The amount of light absorbed is then expressed as an absorbance value, and the absorbance value is proportional to the concentration of the cobalt(II) complex ion.

This technique can be used to confirm the formula of the cobalt(II) complex ion. A series of solutions containing varying volume ratios of L^- to Co^{2+} , both of the same concentration, while keeping the total volume of the Co^{2+} and L^- constant, is prepared. A spectrometer is used to measure the absorbances of the solutions. A graph of absorbance against volume of L^- is then plotted.

Using the graph of absorbance against volume of L^- , the ratio of L^- to Co^{2+} equal to that in the cobalt(II) complex ion can be then determined from the maximum point. This is known as the “Job’s Method”.

- (a) The spectrometer is set to use the wavelength of the light that is absorbed most strongly by the complex ion.

Colour	Wavelengths (nm)
Red	620-750
Orange	590-620
Yellow	570-590
Green	495-590
Cyan	475-495
Blue	450-475
Violet	380-450

Suggest a wavelength in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

[2]

Any value from 591 to 619 nm.

The observed colour of the cobalt complex ion is blue thus the colour complementary to blue, orange, will be absorbed.

- (b) Using the information given above, you are required to write a plan to confirm the formula of the cobalt(II) complex ion as $[\text{CoL}_4]^{2-}$.

You may assume that you are provided with:

- solid cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$;
- solution of L^- , of concentration $0.100 \text{ mol dm}^{-3}$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 250 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous cobalt(II) nitrate;
- the preparation of five 50 cm^3 complex ion solutions containing varying volume ratios of L^- to Co^{2+} ;
- how the absorbance values would be obtained;
- a sketch of the graph of absorbance against volume of L^- that you would expect to obtain;
- how the calculation can be performed to determine the formula of $[\text{CoL}_4]^{2-}$.

[10]

Preparation of aqueous Co^{2+}

M_r of cobalt nitrate = 290.9

Amount of cobalt nitrate in $250 \text{ cm}^3 = (0.1 / 1000) \times 250 = 0.0250 \text{ mol}$

Mass of cobalt nitrate required = $0.0250 \times 290.9 = 7.27 \text{ g}$

Using a clean and dry weighing boat / bottle, weigh accurately 7.27 g of solid cobalt nitrate with an electronic balance.

Transfer the solid into a 100 cm^3 beaker.

Rinse the weighing boat with deionised water and transfer the washings into the beaker.

Dissolve the solid with deionised water.

Transfer the solution into a 250 cm^3 graduated flask with the aid of a filter funnel and a glass rod.

Rinse the beaker with deionised water and transfer the washings into the graduated flask.

Top the graduated flask to the mark with deionised water.

Cap the graduated flask and shake well to ensure the solution is well mixed.

Preparation of 4 solutions

Flask	Vol of L^- / cm^3	Vol of Co^{2+} / cm^3
1	25.00	25.00
2	35.00	15.00
3	40.00	10.00
4	42.00	8.00
5 (max 6:1 ratio)	45.00	5.00

- 5 solutions
- Total volume = 50 cm^3
- At least 2 volume smaller or greater than 40 cm^3 of L^-
- No volume of L^- or Co^{2+} should be 0 cm^3 .

Procedure

- Fill a burette with the prepared Co^{2+} solution and another with the L^- solution.
- Transfer 25 cm^3 of Co^{2+} solution into a 100 cm^3 conical flask, followed by 25 cm^3 of L^- solution.
- Swirl the solution to ensure it is homogeneous
- Repeat steps 1 to 3 for with the stated volumes of solutions for Flask 2 to 4.
- Set up the spectrometer to absorb yellow light.
- Measure and record the absorbance of each of the 4 solutions.
- Plot a graph of absorbance against volume of L^- solution.

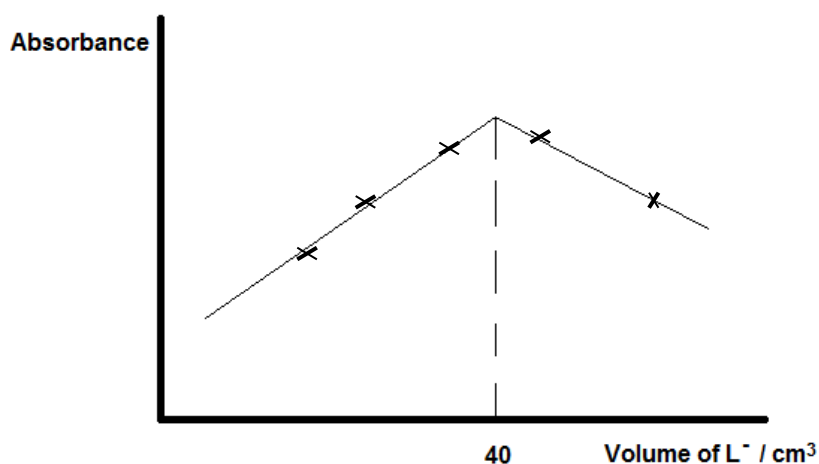
Calculations

Maximum of point = 40 cm^3 of L^-

Amount of $\text{L}^- = (40 / 1000) \times 0.1 = 0.00400 \text{ mol}$

Amount of $\text{Co}^{2+} = (10 / 1000) \times 0.1 = 0.00100 \text{ mol}$

Ratio of L^- to $\text{Co}^{2+} = 4:1$

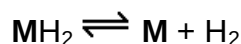
Graph

[10]
[Total: 12]

- 2 The mission of the Hydrogen and Fuel Cells Programme by the U.S. Department of Energy (DoE) is to reduce petroleum use, greenhouse gas emissions, and air pollution and to contribute to a more diverse and efficient energy infrastructure by enabling the widespread commercialisation of hydrogen and fuel cell technologies.

One such technology involves creating an energy system concept that stores hydrogen in the form of metal hydrides. Magnesium hydride (MgH_2) is one of the compounds currently being researched on its viability on hydrogen storage. One way to release hydrogen from metal hydrides is to react them with water, where a hydroxide is formed as a side product.

The other way to obtain hydrogen is through the thermal decomposition of the metal hydride MH_2 . When hydrogen is needed, these metal hydrides can be heated to release molecular hydrogen.

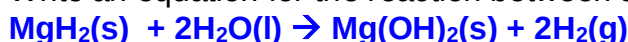


This adsorption and desorption of hydrogen in metals serves like a 'hydrogen bank'. The rate of desorption of hydrogen is proportional on the strength of ionic bonds formed between the metal and hydride ions.

Apart from MgH_2 , other Group II hydrides are also being studied and researched on the same purpose. The table below shows some properties of the Group II hydrides.

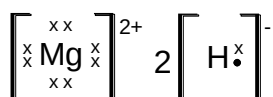
	MgH_2	CaH_2	SrH_2	BaH_2
Percentage of H / % by mass of H	7.7	4.8	2.2	1.4
Density / g cm⁻³	1.74	1.54	2.64	3.62
Melting point / °C	650	842	777	727
ΔH_f / kJ mol⁻¹	-114	-144	-119	-118

- (a) (i) Write an equation for the reaction between solid MgH_2 and water.



[1]

- (ii) Draw the dot-and-cross diagram for MgH_2 .



[1]

- (b) (i) Explain, with reasoning, the trend on the rate of desorption of hydrogen for the Group II metal hydrides from CaH_2 to BaH_2 .

$$\text{Strength of ionic bond} \propto \frac{q_+ q_-}{r_+ + r_-}$$

Radius of cation, r_+ : $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$

Strength of ionic bond : $\text{BaH}_2 < \text{SrH}_2 < \text{CaH}_2$

Rate of desorption of hydrogen from $\text{CaH}_2 < \text{SrH}_2 < \text{BaH}_2$ (fastest)

[2]

- (ii) Which metal hydride, CaH_2 or BaH_2 , would you expect to decompose more readily? Explain your answer by using relevant data from the above table.

ΔH_f becomes less exothermic from CaH_2 to BaH_2

$-\Delta H_f$ becomes less endothermic from CaH_2 to BaH_2

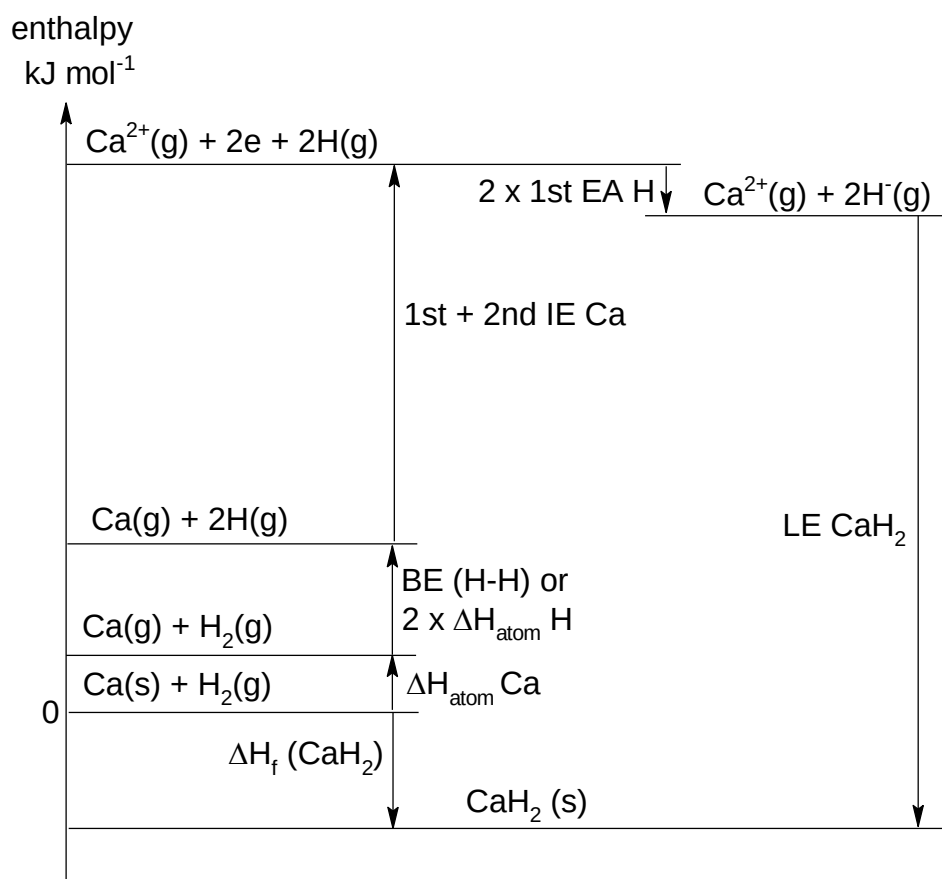
Hence,

Ease of decomposition: $\text{CaH}_2 < \text{BaH}_2$

[2]

- (iii) Using relevant information from the *Data Booklet* and the information given below, construct a Born-Haber cycle to calculate the lattice energy for CaH_2 .

(The first electron affinity for hydrogen is $-72.8 \text{ kJ mol}^{-1}$ and the enthalpy change of atomisation of calcium is $+178 \text{ kJ mol}^{-1}$)



$$\Delta H_f^\ominus (\text{CaH}_2) = \Delta H_{\text{at}}^\ominus (\text{Ca}) + 2\Delta H_{\text{at}}^\ominus (\text{H}) + 1^{\text{st}} \text{IE}(\text{Ca}) + 2^{\text{nd}} \text{IE}(\text{Ca}) + 2 \times 1^{\text{st}} \text{EA}(\text{H}) + \Delta H_{\text{latt}}^\ominus (\text{CaH}_2)$$

$$-144 = 178 + 436 + 590 + 1150 + 2(-72.8) + \Delta H_{\text{latt}}^\ominus (\text{CaH}_2)$$

$$\text{LE} = -2.35 \times 10^3 \text{ kJ mol}^{-1}$$

[3]

- (c) A car company is planning to develop cars that run on hydrogen fuel produced by MgH_2 .

The following information is for a typical petrol-fuelled car.

Weight of vehicle / kg	1088
Fuel tank / L	42
Fuel consumption / km L⁻¹	17
Energy consumption of petrol / kJ kg⁻¹	46.4
Density of petrol / g cm⁻³	0.8 g

- (i) Calculate the energy produced by a petrol-fuelled car which is running at full tank.

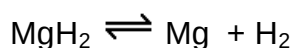
$$\text{Mass of fuel at full tank} = 42 \times 1000 \times 0.8 = 33600 \text{ g}$$

$$\begin{aligned} \text{Energy produced by the petrol at full tank} &= 33600/1000 \times 46.4 \\ &= 1559.04 \text{ kJ} \end{aligned}$$

[1]

- (ii) It was found that 1 kg of hydrogen produce 3 times more energy than petrol with the same mass.

Assuming 100% efficiency, calculate the amount of magnesium metal needed to store the hydrogen as the hydride to provide the same amount of energy in the hydrogen-fuelled car. (1 L = 1000 cm³)



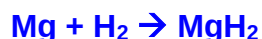
1 kg petrol produces 46.4 kJ of energy

1 kg H₂ produces (46.4 × 3) = 138.9 kJ of energy

Hence to produce 1559.04 kJ of energy,
mass of hydrogen required = 1559.04/138.9 = 11.15 kg

or

$$\text{Mass of H}_2 = 33600 / 3 = 11.2 \text{ kg}$$



$$\text{Number of mole of H}_2 \text{ needed} = 11.15 \times 1000/2 = 5575 \text{ or } 5600$$



$$\text{Number of mole of Mg needed} = 5575$$

$$\begin{aligned} \text{Mass of Mg metal needed} &= 5575 \times 0.0243 \\ &= 135 \text{ kg or } 136 \text{ kg} \end{aligned}$$

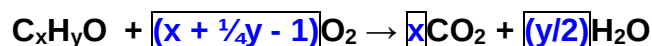
[2]

[Total: 12]

- 3 (a) In the presence of excess oxygen, a liquid alcohol, compound **A**, C_xH_yO , undergoes complete combustion to produce 3.19 dm^3 of hot gases at a temperature of 250°C at a pressure of 1 atm ,

Upon cooling to room temperature, the volume contracted to 836 cm^3 . The gases were then passed through aqueous sodium hydroxide and the final volume remaining was 100 cm^3 .

- (i) Fill in the following blanks for the equation for the complete combustion of **A**.



[1]

- (ii) Using the *ideal gas equation*, find the amount of CO_2 and amount of H_2O that was produced respectively from the complete combustion of compound **A**.

$$\text{Amount of gases in hot gases} = (101000 \times 3.19 \times 10^{-3}) / (8.31 \times 523) = 0.0741 \text{ mol}$$

$$\text{Volume of } CO_2 = 836 - 100 = 736 \text{ cm}^3$$

$$\text{Amount of } CO_2 = (101000 \times 736 \times 10^{-6}) / (8.31 \times 298) = 0.0300 \text{ mol}$$

$$\text{Volume of } O_2 = 100 \text{ cm}^3$$

$$\text{Amount of } O_2 = (101000 \times 100 \times 10^{-6}) / (8.31 \times 298) = 0.00408 \text{ mol}$$

$$\text{Amount of } H_2O = 0.0741 - 0.0300 - 0.00408 = 0.0401 \text{ mol}$$

[3]

- (iii) Using your answer to (a)(i) and (a)(ii), solve for x and y in C_xH_yO and hence determine the empirical formula of **A**.

$$\text{Amount of C} = 0.0300 \text{ mol}$$

$$\text{Amount of H} = 0.0401 \times 2 = 0.0802 \text{ mol}$$

$$\text{Empirical ratio (C:H)} = 0.0300 : 0.0802$$

$$x = 3; y = 8$$

$$\text{Empirical formula} = C_3H_8O$$

[1]

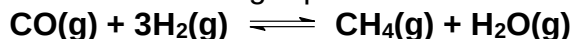
- (ii) The actual number of moles of gases obtained from the combustion is found to be **higher** than that calculated when using the *ideal gas equation*.

Account for the difference between the two results.

Significant intermolecular forces exists between the gas molecules, hence the gases deviates from ideality.

[1]

- (b) Methane can be obtained when carbon monoxide is heated to 900 °C with hydrogen gas as shown in the following equation.



- (ii) Write an expression for the K_c of the reaction, stating its units.

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \text{ mol}^{-2} \text{ dm}^6$$

[1]

- (iii) 1 mol of carbon monoxide was heated with 4 mol of hydrogen gas in a 10 dm³ vessel. At equilibrium, the vessel contained 0.387 mol of methane.

Calculate the K_c for the reaction of carbon monoxide.

	CO	3H ₂	⇌	CH ₄	H ₂ O
Initial mol	1	4		0	0
Δ mol	-0.387	-1.161		+0.387	+0.387
Eq mol	0.613	2.839		0.387	0.387
[] mol dm ⁻³	<u>0.0613</u>	<u>0.284</u>		<u>0.0387</u>	<u>0.0387</u>

$$K_c = \frac{(0.0387)(0.0387)}{(0.0613)(0.284)^3} = 1.07 \text{ mol}^{-2} \text{ dm}^6$$

[2]

- (iv) Suggest, with an explanation, how the position of equilibrium might alter when 1 mol of helium was added into the vessel.

When an inert gas is added, the total pressure increase but the partial pressure of the reactants and products do not change. There would not be any change to the position of equilibrium.

OR

When an inert gas is added, since the volume of the vessel remains the same, the concentration of the reactants and products do not change. There would not be any change to the position of equilibrium.

[1]

- (c) Anhydrous aluminium sulfate is commonly used in organic reactions to remove water. It decomposes at 600 °C to produce only an insoluble white solid and misty fumes. The white solid dissolves in both aqueous sodium hydroxide and aqueous hydrochloric acid while the misty fumes turn moist blue litmus red.

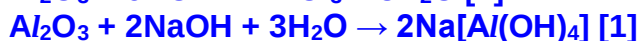
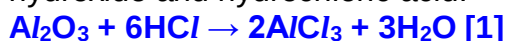
- (i) Suggest the identities of the white solid and the misty fumes. Hence, write a balanced equation for the decomposition of aluminium sulfate.

White solid: Al₂O₃ Misty fumes: SO₃



[2]

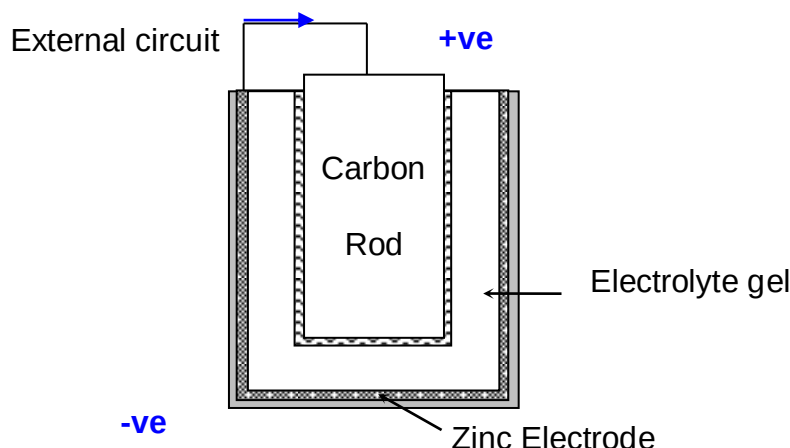
- (ii) Write equations for the reactions of the white solid with aqueous sodium hydroxide and hydrochloric acid.



[2]

[Total: 14]

- 4 Batteries for hearing aids comprise of zinc and carbon electrodes. These electrodes in an electrolyte, maintained at a pH of 11, forms a galvanic cell in which zinc is oxidised and oxygen from the air is reduced.



- (a) Write a balanced equation for the overall chemical reaction and calculate the E^θ_{cell} of this cell.



$$E^\theta_{\text{cell}} = +0.40 + (+0.76) = +1.16 \text{ V}$$

[2]

- (b) Indicate, on the diagram above, the polarity of both electrodes and the direction of electron flow in the external circuit.

[2]

- (c) Explain how the e.m.f. of the cell would change if the pH of the electrolyte decreases.

When pH decreases, $[\text{OH}^-]$ falls and so, position of equilibrium of the reduction half-cell shifts to the right. Hence, $E_{\text{reduction}}$ becomes more positive, making e.m.f. more positive.

[2]

- (d) If a current of $4 \times 10^{-5} \text{ A}$ was drawn from the cell, calculate how long a zinc electrode weighing 2 g will last before it needs to be replaced. Give your answer correct to the nearest day.

$$\text{Amount of Zn} = \frac{2}{65.4} = 0.03058 \text{ mol}$$



$$\text{Amount of electrons} = 2 \times 0.03058 = 0.06116 \text{ mol}$$

$$\therefore Q = 0.06116 \times 96500 = 5902 \text{ C}$$

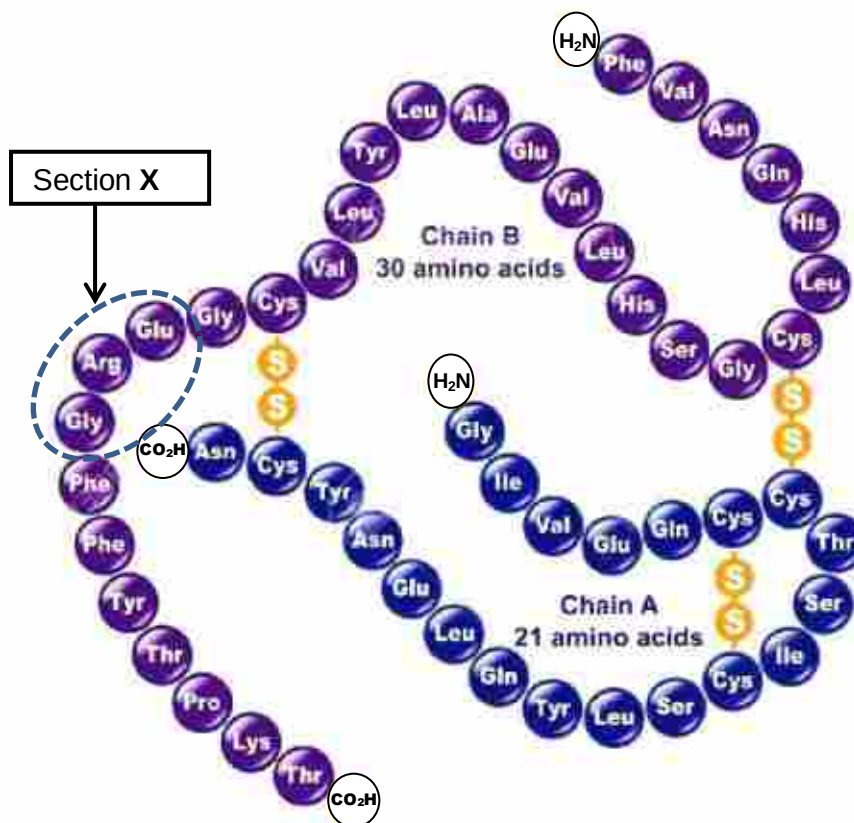
$$t = \frac{Q}{I} = \frac{5902}{4 \times 10^{-5}} = 1.476 \times 10^8 \text{ s} = \underline{1708 \text{ days}}$$

[2]

[Total: 8]

- 5 Insulin is a hormone made by the pancreas that allows your body to use glucose from carbohydrates in the food that you eat for energy. Insulin helps keeps your blood sugar level from getting too high or too low.

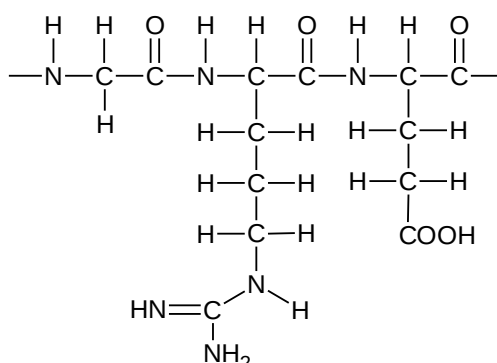
The insulin molecule consists of 51 amino acid residues, in two polypeptide chains.



Some information on the amino acids of insulin is given below.

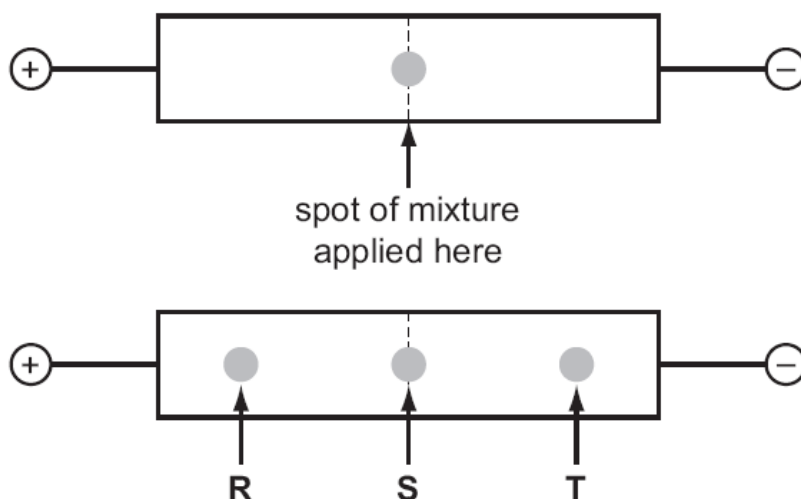
amino acid	Abbreviated name	Formula of side chain (R in $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$)	pI
arginine	arg	$-(\text{CH}_2)_3\text{NHC}(\text{NH}_2)=\text{NH}$	10.76
cysteine	cys	$-\text{CH}_2\text{SH}$	5.07
glutamic acid	glu	$-\text{CH}_2\text{CH}_2\text{COOH}$	3.22
glycine	gly	$-\text{H}$	5.97

- (a) Draw the structural formula of section X in insulin.
Formula must start with N terminus, showing R groups, ending with C terminus:



[1]

- (b) The diagram shows the results of electrophoresis on a mixture of the amino acids obtained from hydrolysis of section X at pH 6.0.



Draw the structure of the species responsible for the spots labelled **R**, **S** and **T**.

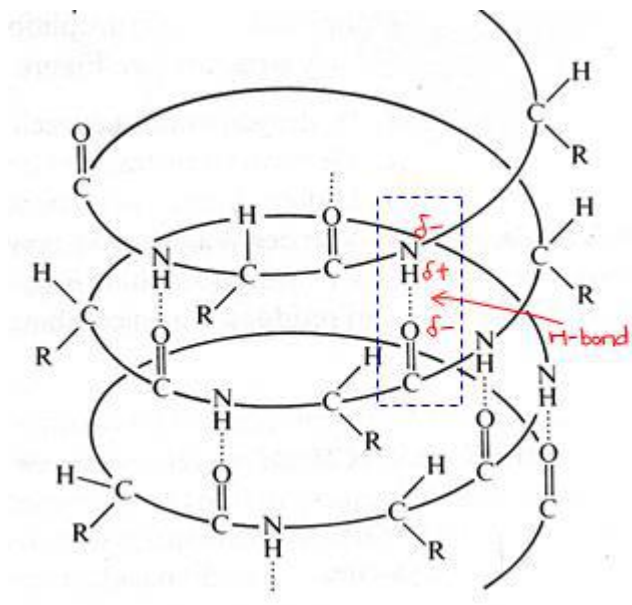
R	S	T
$\begin{array}{c} \text{H}_3\text{N}^+-\text{CH}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CO}_2^- \end{array}$	$\begin{array}{c} \text{H}_3\text{N}^+-\text{CH}-\text{CO}_2^- \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H}_3\text{N}^+-\text{CH}-\text{CO}_2^- \\ \\ (\text{CH}_2)_3\text{NHC}(\text{NH}_3)^+=\text{NH} \end{array}$ Accept protonation on any basic amine group of side chain. (more than 1 protonation also allowed)

k

[3]

- (c) The polypeptide chains of insulin coil to form short sections of α -helix which stabilises the secondary structure.

Describe with the aid of a sketch, how a polypeptide chain is held in the shape of an α -helix.



[3]

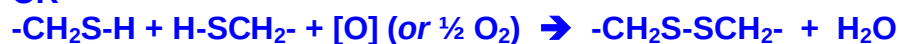
- (d) The three-dimensional structure of insulin is further stabilised by disulfide linkages.

Write an equation for the formation of such linkage and state the type of reaction involved.

Type of reaction: oxidation



OR

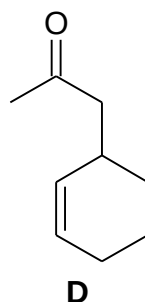


[2]

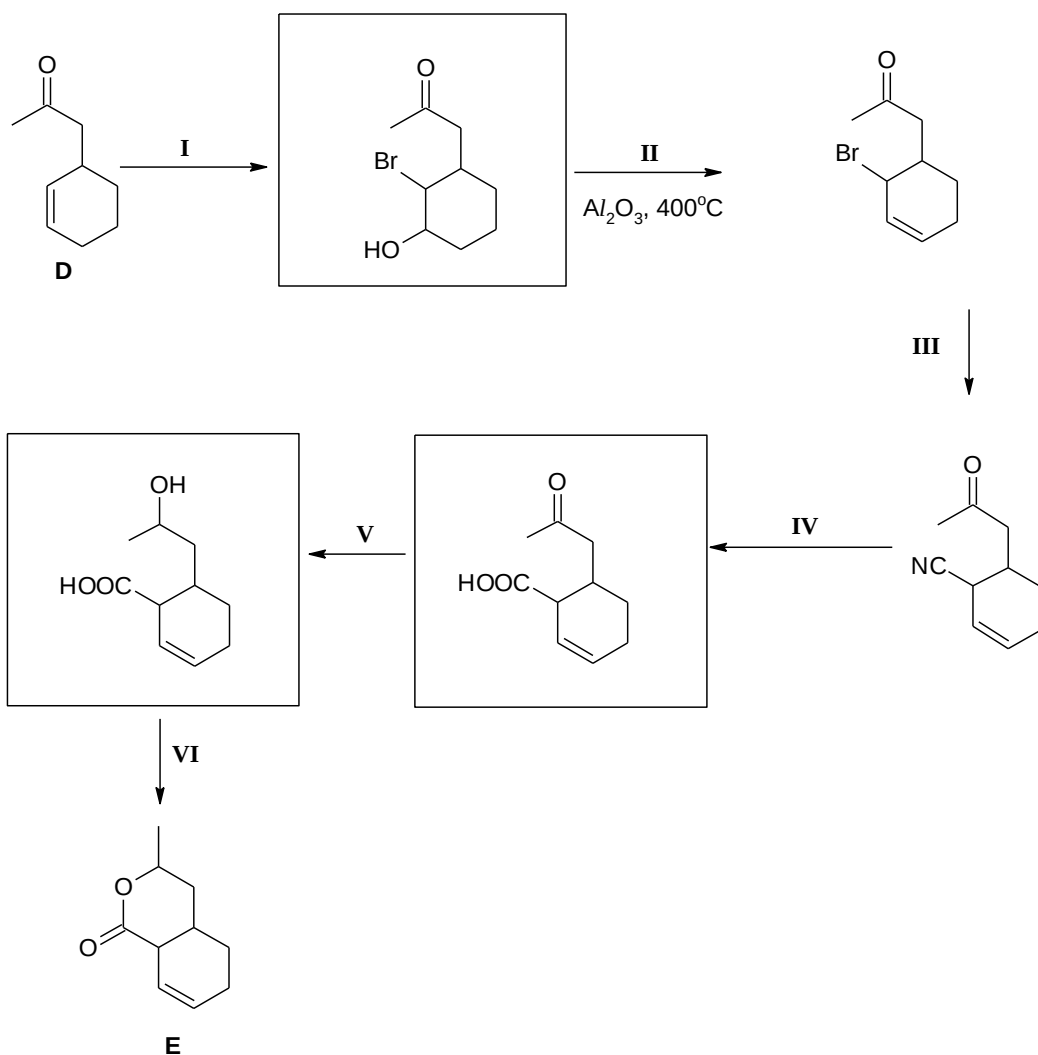
[Total: 9]

- 6 Lactones are cyclic esters. They are formed by intramolecular esterification of the corresponding hydroxycarboxylic acids.

(a) (i) The reaction scheme below shows how lactone **E** is synthesised from compound **D**.



Complete the reaction scheme by giving the structural formulae of the intermediate organic products in the spaces provided and stating the reagents and conditions for steps I, III, IV, V and VI.



Step	Reagents and conditions
I	$\text{Br}_2(\text{aq})$
III	NaCN/KCN in ethanol, heat
IV	$\text{H}_2\text{SO}_4(\text{aq})$, heat
V	NaBH_4 in methanol
VI	concentrated H_2SO_4 , heat

[8]

- (ii) Suggest a simple chemical test to distinguish compound **D** from **E**.

Reagents and conditions: 2,4-dinitrophenylhydrazine

Observations:

For compound **D**, orange ppt is formed.

For compound **E**, no orange ppt is formed (or no observable change)

Or

Reagents and conditions: $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4(\text{aq})$, heat

Observations:

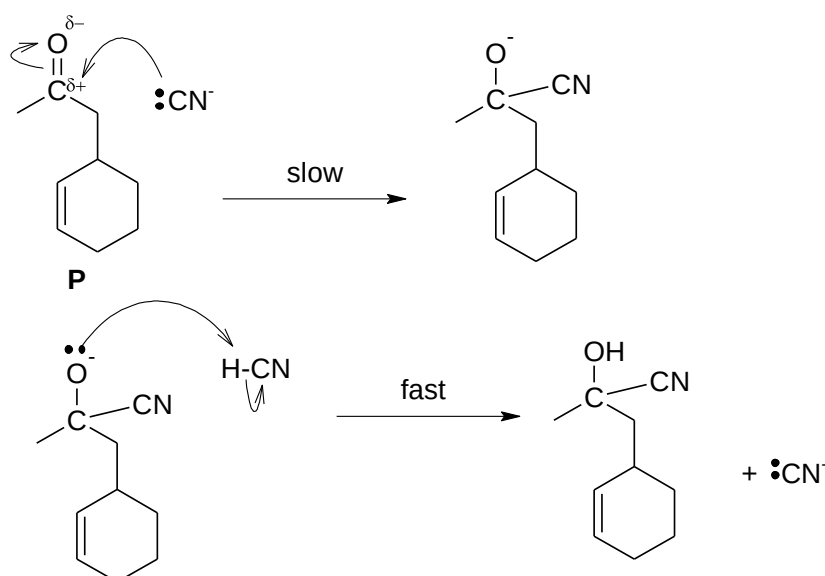
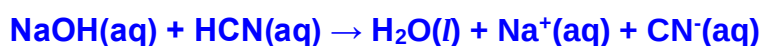
For compound **D**, orange solution remains (or no observable change)

For compound **E**, orange solution turned green.

[2]

- (iii) Name and outline the mechanism when compound **D** is treated with HCN in the presence of aqueous NaOH at 10°C .

Name of mechanism: Nucleophilic Addition



[3]

- (b) Lactones with three- or four-membered rings are very reactive compared to five- or six-membered rings, making their isolation difficult.

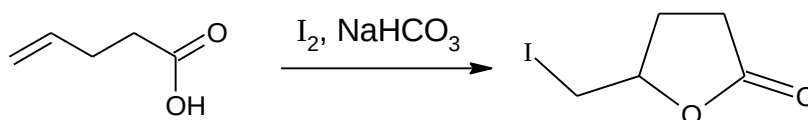
Suggest why lactones with three- or four-membered rings are very reactive.

Three- or four-membered rings have significant ring/angle strain.

[1]

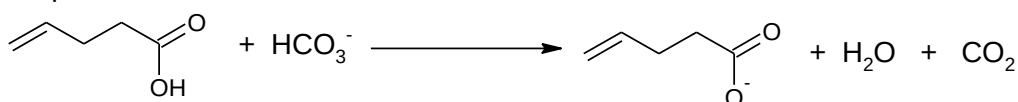
- (c) Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown below.

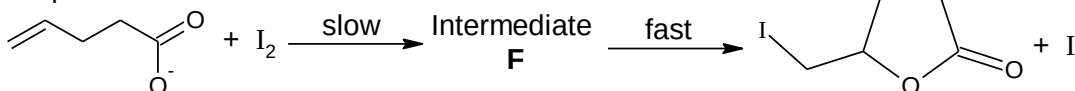


Two simplified steps in the iodolactonisation mechanism are given below.

Step 1



Step 2



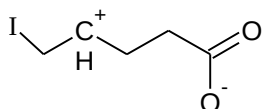
- (i) Suggest the role of HCO_3^- in step 1 of the mechanism.

It acts as a base to abstract H^+ from the carboxylic acid.

[1]

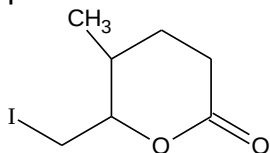
- (ii) The type of reaction in Step 2 of the mechanism is electrophilic addition.

Draw the structure of intermediate F.



[1]

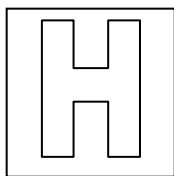
- (iii) Suggest the structural formulae of the final organic product formed when $CH_2=CHCH(CH_3)CH_2CH_2COOH$ undergoes iodolactonisation in a similar process as above.



[1]

[Total: 17]

End of Paper



PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE
NAME

ANSWER SCHEME

CT
GROUP

1	5			

INDEX
NUMBER

CHEMISTRY

9647/03

Paper 3 Free Response

15 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet
 Cover Page

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work that you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough workings.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

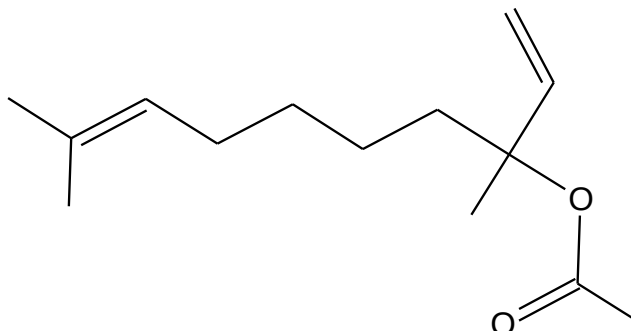
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

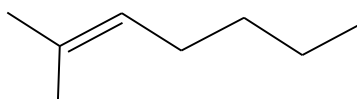
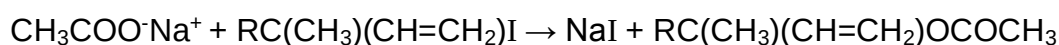
At the end of the examination, fasten all your work securely together.

Answer any **four** questions.
Begin **each** question on a fresh piece of writing paper.

- 1 (a) Linalyl acetate is a naturally occurring phytochemical found in many flowers. It is one of the principal components of the essential oils of bergamot and lavender. It has the following structure.



Linalyl acetate can be synthesised by the reaction of carboxylate anion with an alkyl halide as shown below:



where R =

The kinetics of this reaction was determined by measuring the concentration of the remaining $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ with time. The initial concentrations of $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ and $\text{CH}_3\text{COO}^-\text{Na}^+$ were $0.0050 \text{ mol dm}^{-3}$ and $0.100 \text{ mol dm}^{-3}$ respectively. The following data was obtained.

Time/ min	$[\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}] / \text{mol dm}^{-3}$
0	0.0050
15	0.0040
30	0.0032
45	0.0026
60	0.0021
75	0.0017

- (i) Plot a suitable graph to show that the order of reaction with respect to $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ is one. [3]
constant $t_{1/2}$ (at about 48.25 minutes) first order

- (ii) A new set of experiment was carried out and the initial concentrations of $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ and $\text{CH}_3\text{CO}_2^-\text{Na}^+$ was increased to $0.0100 \text{ mol dm}^{-3}$, and $0.200 \text{ mol dm}^{-3}$ respectively. When a similar graph was plotted, it was found that the gradient at each point doubled.

Deduce the order of reaction with respect to $\text{CH}_3\text{CO}_2^-\text{Na}^+$, and explain your answer. [2]

The reaction was zero order with respect to $\text{CH}_3\text{COO}^-\text{Na}^+$.

Gradient of a concentration-time graph gives the rate of reaction.

The reaction is first order with respect to $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$, and doubling the concentration will double the rate. This implies that changing the concentration of $\text{CH}_3\text{CO}_2^-\text{Na}^+$ has no effect on the rate of reaction.

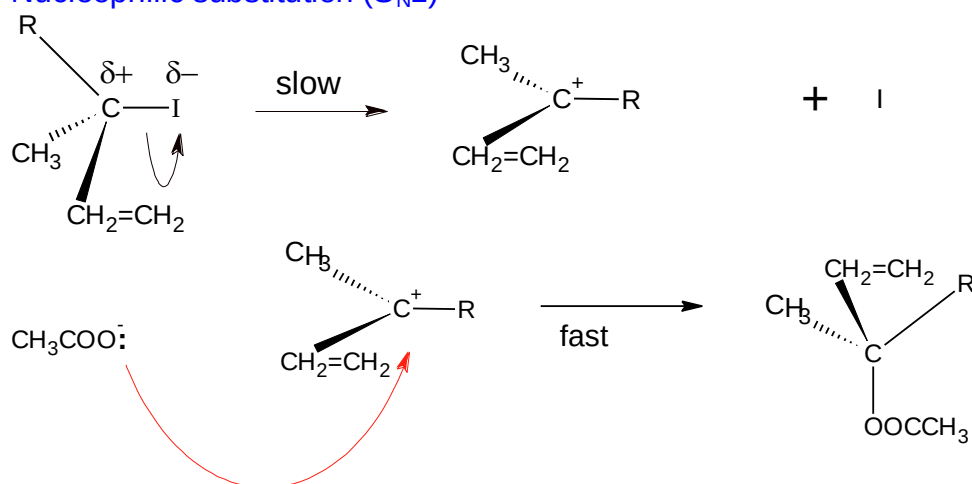
- (iii) Construct a rate equation for the reaction between $\text{CH}_3\text{COO}^-\text{Na}^+$ and $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$, stating the units for the rate constant. [1]

Rate = $k[\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}]$

Units of $k = \text{min}^{-1}$

- (iv) Using your answer in (iii), suggest the mechanism for the reaction between $\text{CH}_3\text{CO}_2^-\text{Na}^+$ and $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ that leads to the formation of the ester, $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{OCOCH}_3$. [3]

Nucleophilic substitution ($\text{S}_{\text{N}}1$)



- (b) An example of a homogeneous catalyst is $\text{Fe}^{2+}(\text{aq})$, which is used in the oxidation of sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$, with acidified potassium manganate(VII), KMnO_4 . Ethanedioate is oxidised to carbon dioxide.

- (i) What do you understand by the term *homogeneous* catalyst. [1]

A homogeneous catalyst is a catalyst that exists in the same phase as the reactants.

- (ii) Write an overall equation for the reaction of sodium ethanedioate with acidified potassium manganate(VII). [1]

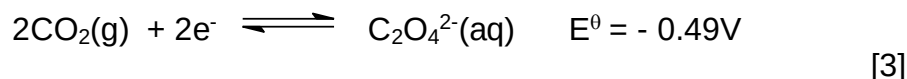


- (iii) The E°_{cell} of the reaction between sodium ethanedioate with acidified potassium manganate(VII) is +2.01 V. However, the reaction is slow.

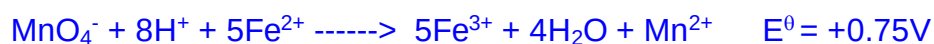
Explain why the reaction is slow. [1]

High activation energy due to the repulsion between two negatively charged ions MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ to react, the rate of reaction is very slow.

- (iv) By considering suitable E° values from the *Data Booklet* and the data given below, explain how Fe^{2+} functions as a catalyst for the reaction between sodium ethanedioate with acidified potassium manganate(VII), writing equations where appropriate.

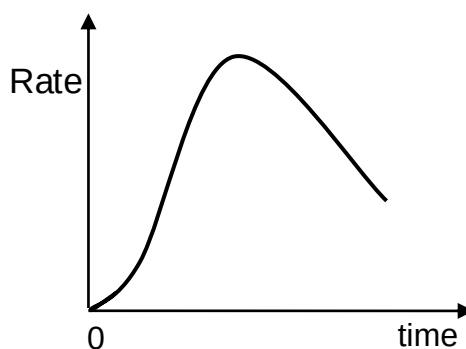


Fe^{2+} can speed up the rate of reaction as it is able to attract the oppositely charged ions in the following equations:



Since the E° is positive for both reactions, they are energetically feasible.

- (iv) In the absence of a Fe^{2+} catalyst, the rate of reaction between potassium manganate(VII), and sodium ethanedioate is shown in the graph below.



Explain the shape of the graph.

[2]

The rate of reaction is slow at the beginning of the reaction.

As the reaction proceeds, $[\text{Mn}^{2+}]$ increases, which catalyses the reaction. The rate of reaction increases.

The rate of reaction will eventually decrease as [reactants] decreases to very low levels despite the increasing concentration of the Mn^{2+} catalyst.

- (c) The rate of a chemical reaction is usually increased at elevated temperatures.

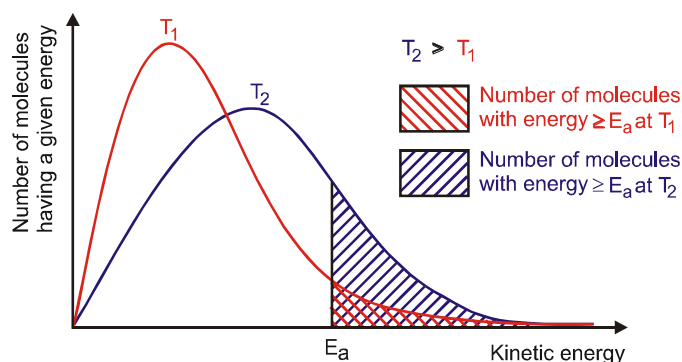
Explain, with the aid of a Boltzmann Distribution graph, why an increase in temperature increases the rate of reaction.

[3]

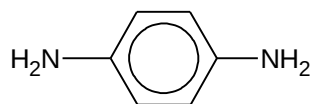
[Total: 20]

At a higher temperature, the average kinetic energy of the particles is higher. The particles move faster and collide with each other more frequently.

In addition, the number of particles with energy $\geq E_a$ increases exponentially, resulting in a greater number of effective collisions per unit time. This gives rise to a large increase in the rate of reaction.

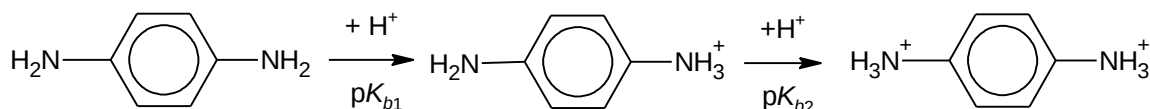


- 2 (a) Ammonia and *para*-phenylenediamine, $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$, are *Bronsted-Lowry bases* that are used widely in permanent hair dyes. *Para*-phenylenediamine has the structure shown below:



para-phenylenediamine

Para-phenylenediamine, $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$, can ionise in stages.



The two $\text{p}K_b$ values associated with *para*-phenylenediamine are shown in the table below.

Base	formula	$\text{p}K_{b1}$	$\text{p}K_{b2}$
ammonia	NH_3	4.7	-
<i>para</i> -phenylenediamine	$\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$	7.7	11.0

- (i) Using ammonia, NH_3 , explain what is meant by the term *Bronsted-Lowry base*. [1]

Ammonia, NH_3 , has a lone pair of electrons which acts as a base to accept a proton.

- (ii) Suggest a reason why the $\text{p}K_{b1}$ value of *para*-phenylenediamine is higher than the $\text{p}K_{b1}$ of ammonia. [1]

The lone pair of electrons on N of $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$ can be delocalized into the benzene ring, making it less available to accept a proton, compared to NH_3 . Hence $\text{p}K_{b1}$ value of *para*-phenylenediamine is larger than the $\text{p}K_{b1}$ of ammonia.

- (iii) Suggest a reason why the $\text{p}K_{b1}$ value of *para*-phenylenediamine is lower than $\text{p}K_{b2}$. [1]

More energy is required to accept another H^+ by $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+$, from H_2O to form $\text{H}_3\text{NC}_6\text{H}_4\text{NH}_3^{2+}$, which is electrostatically unfavourable. Hence $\text{p}K_{b1}$ value of *para*-phenylenediamine is lower than $\text{p}K_{b2}$.

OR

The lone pair of electrons on NH_2 of $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+$ can be delocalized into the benzene ring to a greater extent, making it less available to accept a proton. Hence $\text{p}K_{b1}$ value of *para*-phenylenediamine is lower than the $\text{p}K_{b2}$.

- (iv) Explain what is meant by a *buffer solution*. [1]

A buffer solution is one which is able to **resist** a change in pH (i.e. maintain an almost constant pH) upon the addition of a **small** amount of acid or alkali, or on dilution.

- (v) Assuming that a solution at pH 6.5 contains only $[H_2NC_6H_4NH_2]$ and $[H_2NC_6H_4NH_3^+]$, calculate the ratio of $\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$ in the solution. [2]

$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \text{pOH} &= 14 - 6.5 = 7.5 \end{aligned}$$

$$\text{pOH} = \text{p}K_1 + \lg \frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$$

$$7.5 = 7.7 + \lg \frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$$

$$\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]} = 0.63$$

- (vi) Calculate the pH of solution containing equimolar amount of $H_2NC_6H_4NH_3^+$ and $^+H_3NC_6H_4NH_3^+$. [2]

when equimolar amount of $H_2NC_6H_4NH_3^+$ and $H_3NC_6H_4NH_3^{2+}$ is formed,
 $[H_2NC_6H_4NH_3^+] = [^+H_3NC_6H_4NH_3^+]$

This is the maximum buffer capacity at second stage of neutralization.
 Hence

$$\text{pOH} = \text{p}K_2 + \lg \frac{[H_3NC_6H_4NH_3^{2+}]}{[H_2NC_6H_4NH_3^+]}$$

$$\begin{aligned} \text{pOH} &= \text{p}K_2 \\ \text{pOH} &= 11 \\ \text{pH} &= 3 \end{aligned}$$

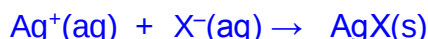
(b) Ammonia is commonly used in qualitative analysis of halides in aqueous solutions, such as detecting the presence of chloride and bromide ions in natural water sources such as rivers, lakes and streams.

- (i) 5 cm³ of 0.0100 mol dm⁻³ of silver nitrate is added to a 30 cm³ sample of river water containing chloride ions.

What is the minimum concentration, in mol dm⁻³, of chloride ions present in the river water when the first trace of precipitate appears?

Given solubility product of the silver chloride is $2.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

[2]



The ppt is AgX.

$$\begin{aligned} [\text{Ag}^+] \text{ at point of mixing} &= \text{no. of moles of Ag}^+ \text{ before mixing} \div \text{total vol} \\ &= (0.0100 \times 5/1000) \div 35/1000 \\ &= 1.428 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{Cl}^-] \text{ at point of mixing} &= \text{no. of moles of X}^- \text{ before mixing} \div \text{total vol.} \\ &= ([\text{Cl}^-]_{\text{initial}} \times 30/1000) \div 35/1000 \text{ mol dm}^{-3} \end{aligned}$$

For precipitation to take place,

$$\text{ionic product (AgCl)} \geq K_{\text{sp}}(\text{AgCl})$$

$$([\text{Ag}^+][\text{Cl}^-]) \text{ at point of mixing} \geq 2.0 \times 10^{-10}$$

$$(1.428 \times 10^{-3}) \times \left(\frac{[\text{Cl}^-]_{\text{initial}} \times \frac{30}{1000}}{\frac{35}{1000}} \right) \geq 2.0 \times 10^{-10}$$

$$[\text{Cl}^-]_{\text{initial}} \geq 1.63 \times 10^{-7}$$

Hence, minimum concentration is $1.63 \times 10^{-7} \text{ mol dm}^{-3}$

- (ii) To a test tube containing another river sample containing bromide ions, describe what you would see when aqueous silver nitrate is added to the sample, followed by excess aqueous ammonia to the resulting mixture

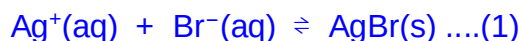
[1]

Br: cream ppt of AgBr observed; insoluble in excess NH₃(aq)

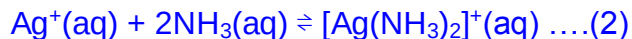
- (iii) Explain, with aid of appropriate equation(s), the observations in (b)(ii).

You should use the concepts of Le Chatelier's Principle and solubility product, K_{sp} , to explain your answer.

[4]



Precipitate of AgBr is observed when $I.P > K_{sp}$



When excess NH_3 is added (high $[\text{NH}_3]$) to $\text{AgBr}(\text{s})$, the position of equilibrium (2) shifts to the right in order to reduce the effect of excess $\text{NH}_3(\text{aq})$. OR complex $[\text{Ag}(\text{NH}_3)_2]^+$ is formed

$[\text{Ag}^+]$ decreases hence equilibrium (1) shifts to the left.
but the ionic product of AgBr is still larger than $K_{sp}(\text{AgBr})$,
AgBr remains insoluble.

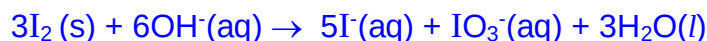
OR



- (c) (i) When iodine reacts with sodium hydroxide, iodide and iodate(V) are formed.

Write a balanced ionic equation, with state symbols, for the formation of IO_3^- when iodine reacts with sodium hydroxide. Name the type of reaction taking place.

[2]



Disproportionation

- (ii) When Group II iodates(V), $\text{M}(\text{IO}_3)_2$, are heated at high temperature, it form the metal oxide, iodine vapour and a colourless gas that relights glowing splinter.

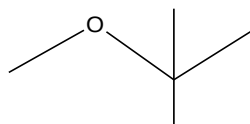
It was observed that Group II iodates(V) down the group have to be heated more strongly before the iodine vapour appears. Explain why thermal stability increases down the group for Group II iodate(V).

[3]

[Total: 20]

- Cationic size of M^{2+} increases down Group II resulting in decreasing charge density and/or hence decreasing polarising power.
- Thus the electron cloud of the IO_3^- is less distorted and thus less weakening effect on the I-O bond in IO_3^- .
- More energy required to bring about decomposition of $\text{M}(\text{IO}_3)_2$, resulting in higher temperature required for the purple iodine vapour to be observed.
- Thermal stability of $\text{M}(\text{IO}_3)_2$ increases down the group.

- 3 (a) Methyl t-butyl ether, **MTBE**, is a fuel additive that is used as an oxygenate to raise the octane number in fuel. This will help the fuel to burn more completely and reduce air pollution.



Methyl t-butyl ether, **MTBE**

- (i) What is meant by the term *standard enthalpy change of formation* of **MTBE**?

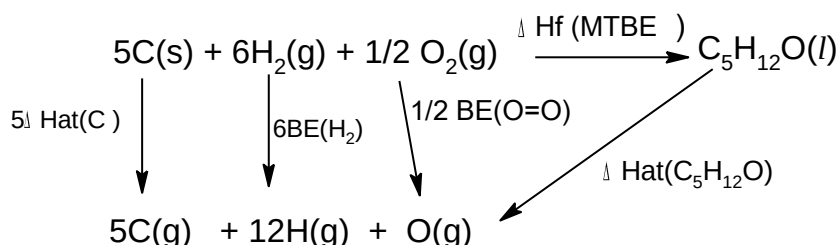
[1]

Standard enthalpy change of formation of MTBE is the heat change when 1 mole of a MTBE is formed from its constituent elements in their standard states under standard conditions of 298 K and 1 atmospheric pressure.

- (ii) Use the following data and relevant data from *Data Booklet* to construct an appropriate energy cycle, find the standard enthalpy change of formation of **MTBE**.

Standard enthalpy change of atomisation of C(s)	+715 kJ mol ⁻¹
Standard enthalpy change of atomisation of MTBE (l)	+6822 kJ mol ⁻¹

[4]



By Hess' Law,

$$\Delta H_f^\theta(\text{MTBE}) = 5\Delta H_{\text{at}}^\theta(\text{C}) + 6\text{BE}(\text{H}_2) + \frac{1}{2}\text{BE}(\text{O}_2) - \Delta H_{\text{at}}(\text{C}_5\text{H}_{12}\text{O})$$

$$\Delta H_f^\theta(\text{MTBE}) = 5(715) + 6\text{BE}(\text{H-H}) + \frac{1}{2}\text{BE}(\text{O}=\text{O}) - 6822$$

$$\Delta H_f^{\theta\theta}(\text{MTBE}) = 3575 + (6 \times 436) + \frac{1}{2}(496) - 6822$$

$$\Delta H_f^\theta(\text{MTBE}) = -383 \text{ kJ mol}^{-1}$$

- (iii) Given that the standard enthalpy change of vaporisation of **MTBE** is +30.4 kJ mol⁻¹ and using relevant data from the *Data Booklet* and (a)(ii), calculate the bond energy of C-O in **MTBE**.

Bond energy of C₅H₁₂O involves breaking a total of:

2(C-O), 3(C-C) and 12(C-H) bonds.

$$\Delta H_{\text{at}}^\theta(\text{C}_5\text{H}_{12}\text{O}) = \Delta H_{\text{vap}}^\theta(\text{C}_5\text{H}_{12}\text{O}) + 2\text{BE}(\text{C-O}) + 3\text{BE}(\text{C-C}) + 12\text{BE}(\text{C-H})$$

$$6822 = 30.4 + 2\text{BE}(\text{C-O}) + 3\text{BE}(\text{C-C}) + 12\text{BE}(\text{C-H})$$

$$6791.6 = 2\text{BE}(\text{C-O}) + (3 \times 350) + (12 \times 410)$$

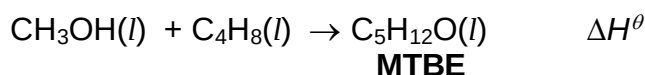
$$6791.6 = 2\text{BE}(\text{C-O}) + 5970$$

$$\text{BE}(\text{C-O}) = \underline{\underline{+411 \text{ kJ mol}^{-1}}}$$

- (iv) Suggest a reason for the difference in the C-O bond energy in (a)(iii) from the value given in the *Data Booklet*. [1]

The bond energy values from the Data Booklet are average values. The actual bond dissociation energy values depend on the specific chemical and electronic environment that a bond is in.

- (b) **MTBE** can be produced from methanol and but-1-ene by the following equation. The reaction has a standard entropy change of reaction of $-281 \text{ J mol}^{-1} \text{ K}^{-1}$.



The table below lists the ΔH_f^θ (standard enthalpy change of formation) values for some compounds.

compound	$\Delta H_f^\theta / \text{kJ mol}^{-1}$
$\text{CH}_3\text{OH}(l)$	-239
$\text{C}_4\text{H}_8(l)$	-0.4

- (i) Calculate the ΔH^θ for the reaction in (b) using the values from the table above and your answer to (a)(ii). [1]

$$\begin{aligned} \Delta H^\theta &= \sum m \Delta H_f^\theta(\text{products}) - \sum n \Delta H_f^\theta(\text{reactants}) \\ &= -383 - (-239 - 0.4) \\ &= -143.6 \text{ kJ mol}^{-1} \\ &= -144 \text{ kJ mol}^{-1} \end{aligned}$$

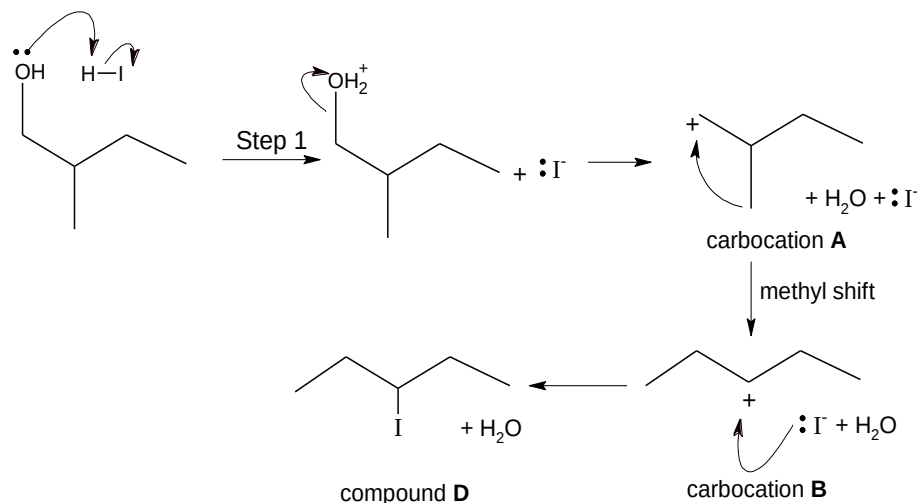
- (ii) Determine the feasibility of the production of **MTBE** from methanol and but-1-ene at 298 K. [2]

$$\begin{aligned} \Delta G^\theta &= \Delta H^\theta - T \Delta S^\theta \\ &= -143.6 - 298(-281 \times 10^{-3}) \\ &= -59.9 \text{ kJ mol}^{-1} < 0, \text{ reaction is energetically feasible at 298 K.} \\ &\quad \text{(ECF)} \end{aligned}$$

Final answer and statement on energetically feasible.

- (c) Methyl shift can occur in organic chemistry reactions in reactions involving carbocation intermediates.

An example of a methyl shift in a reaction between an alcohol and HI is shown below. In this reaction compound **D** is produced as the major product.



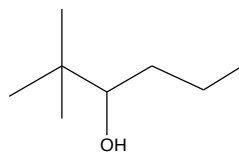
- (i) What is the role of HI in step 1?

acid

- (ii) Suggest a reason for the methyl shift to produce carbocation **B** from carbocation **A**. [1]

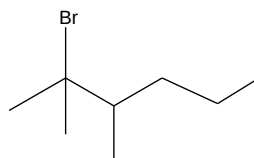
B is a secondary carbocation which is more stable than the **A** which is a primary carbocation. Hence, a more stable carbocation **B** is formed as an intermediate during the reaction.

- (iii)

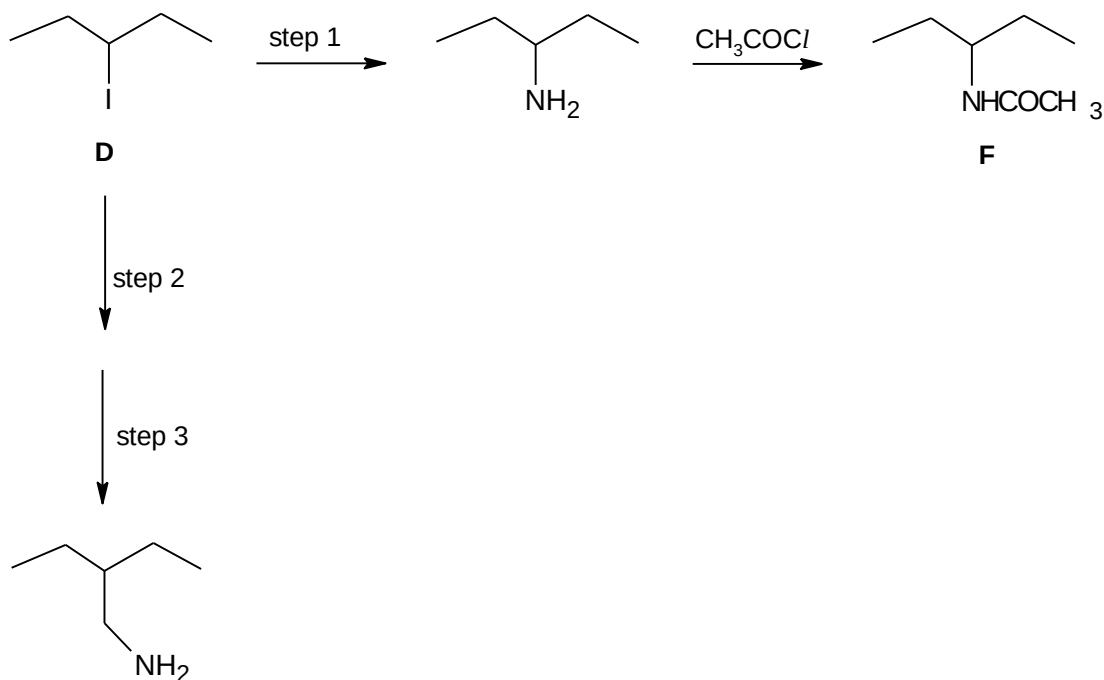


The structure of compound **E** is

Predict the major final product formed when compound **E** reacts with HBr based on the methyl shift reaction in (c). [1]



(iv) Compound **D** undergoes the following reactions.



Suggest suitable reagents for steps 1, 2 and 3.

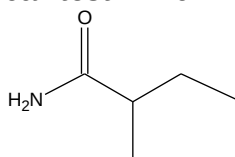
[3]

step 1: excess NH_3 in ethanol and heat it in sealed tube.

step 2: NaCN in ethanol, heat

step 3: LiAlH_4 in dry ether / H_2 , Ni cat, 200°C .

(v) Suggest one simple chemical test which would enable you to distinguish

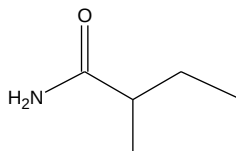


between compound **F** and

You should state the reagents and conditions for the test and describe the observations.

[Total: 20]

Reagents and conditions: NaOH(aq) , heat



Observation:
litmus paper blue.

the gas liberated which is NH_3 turns moist red

For **F**, moist red litmus paper remains red

- 4 (a) Compound **G**, $C_{10}H_{15}NO_3$, is a natural stimulant made in the adrenal gland of the kidney and is carried in the bloodstream and affects the autonomous nervous system, which controls functions such as heart rate, dilation of the pupils.

G is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate.

G undergoes reaction with hot acidified potassium dichromate(VI) to form **J**. **J** gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give a silver mirror with Tollens' reagent. Upon heating with concentrated H_2SO_4 , **G** forms **K**, $C_{10}H_{13}NO_2$. **K** does not react with PCl_5 . On heating with acidified potassium manganate(VII), **K** forms three compounds, **L**, $C_7H_6O_4$, **M**, $C_2H_4O_2$, and an ammonium salt, $CH_3NH_3^+$.

Deduce the structures for each compound, **G** to **M**, and give an account of the chemistry involved.

[10]

G is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate. **G** contains basic/amine groups and phenol

G undergoes oxidation with acidified potassium dichromate(VI) to form **J**, which undergoes condensation with 2, 4 - DNPH.

=> **J** is a ketone

=> **G** contains secondary alcohol

G undergoes elimination with concentrated H_2SO_4 , heat to form **K**, $C_{10}H_{14}NO_2$

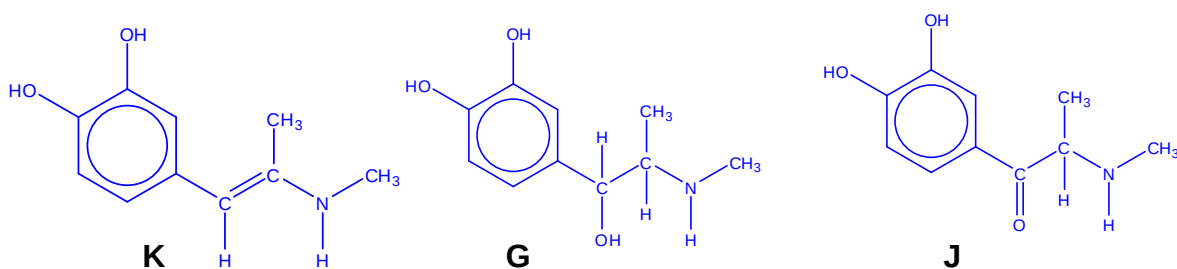
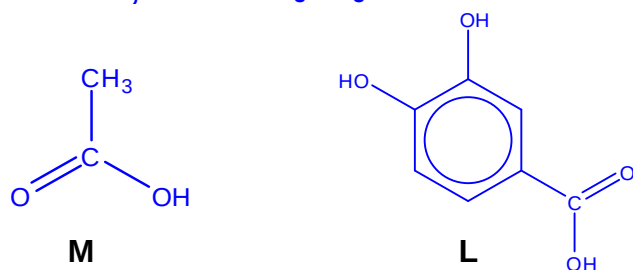
=> **G** is confirmed to be a secondary alcohol.

=> **K** is an alkene

K does not react with PCl_5

=> **K** is a has 2 phenol groups

K undergoes oxidation and acidic hydrolysis with acidified potassium manganate to form **L**, **M** and $CH_3NH_3^+$.

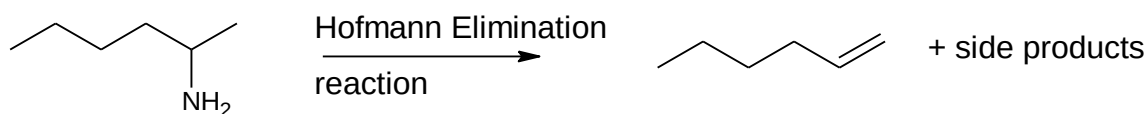


*The position of the substituent is not important in this question.

[1 for each of the compound]

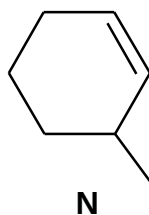
- (b) Like alcohols and halogenoalkanes, amines can be converted into alkenes by an elimination reaction known as Hofmann elimination.

For example, 1-methyl-pentylamine is converted into hex-1-ene as shown.

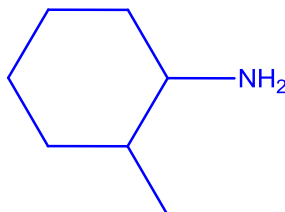


An interesting feature of the Hofmann elimination is that it gives a **less substituted alkene** compared to other elimination reactions.

- (i) Draw the likely structure of the starting amine if the following alkene **N** is the main product formed when the amine undergoes a Hofmann elimination reaction.



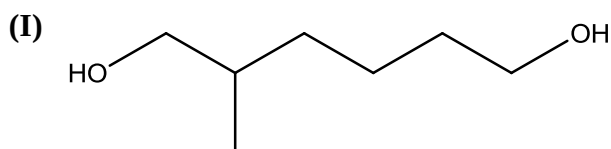
[1]



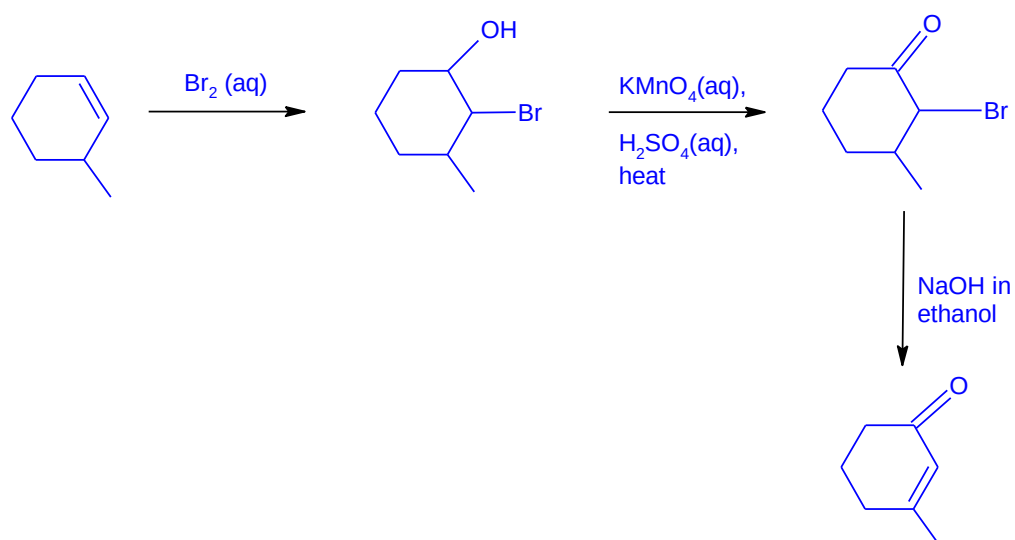
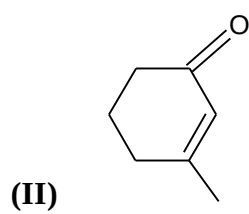
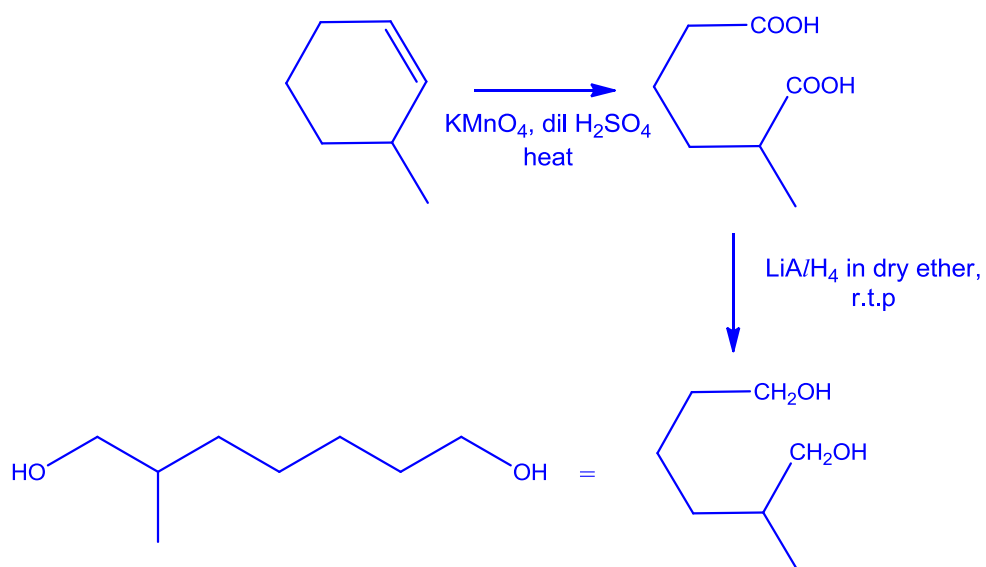
- (ii) Suggest, in no more than 3 steps, a suitable synthetic pathway to convert **N** into the following compounds.

For each step, state clearly the reagents and conditions, indicating the structural formula of all intermediate compounds formed.

[5]

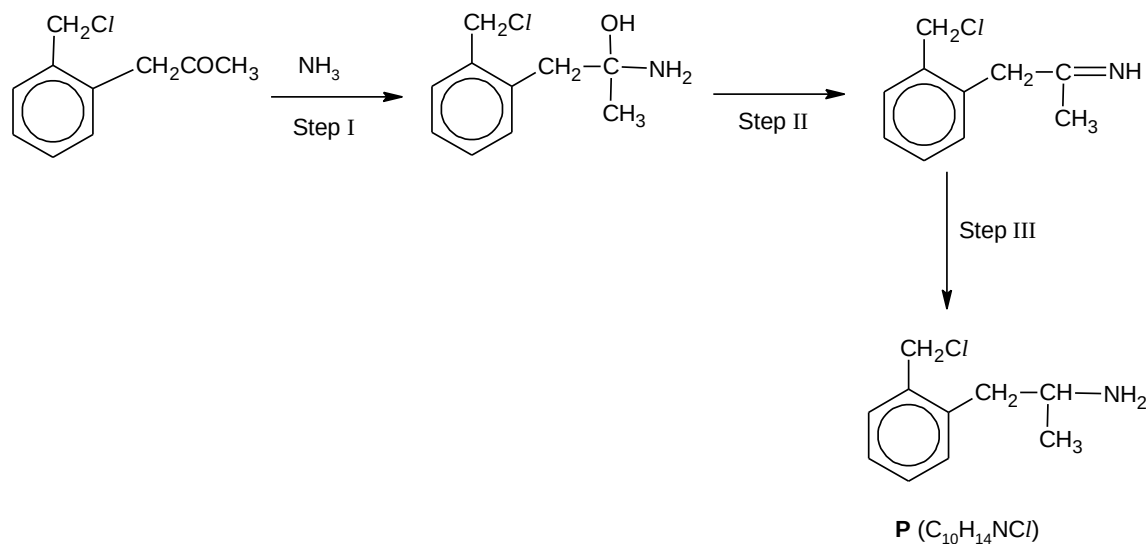


16



- (c) Amines can be formed by reductive amination of an aldehyde or ketone with ammonia or amine in the presence of reducing agent.

A reductive amination to produce an amine **P** takes place in the pathway shown.



- (i) Suggest the type of reaction that occurs at steps I and II.

[2]

Step I – Nucleophilic addition

Step II - Elimination

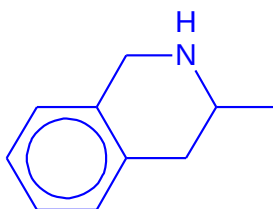
- (ii) Suggest the reagents and conditions for step III.

[1]

H_2 in nickel catalyst, 200°C , LiAlH_4

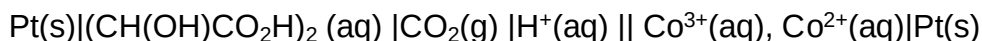
- (iii) On heating, **P** forms **Q**, $\text{C}_{10}\text{H}_{13}\text{N}$. Suggest a structure for **Q**.

[1]



[Total: 20]

- 5 (a) An electrochemical cell involving tartaric acid, $(\text{CH}(\text{OH})\text{CO}_2\text{H})_2$, has the following cell diagram notation.



- (i) Given that the e.m.f of the cell is +0.80 V and using relevant data from the *Data Booklet*, determine the standard electrode potential of the $\text{CO}_2(\text{g}) | (\text{CH}(\text{OH})\text{CO}_2\text{H})_2(\text{aq})$ half-cell.

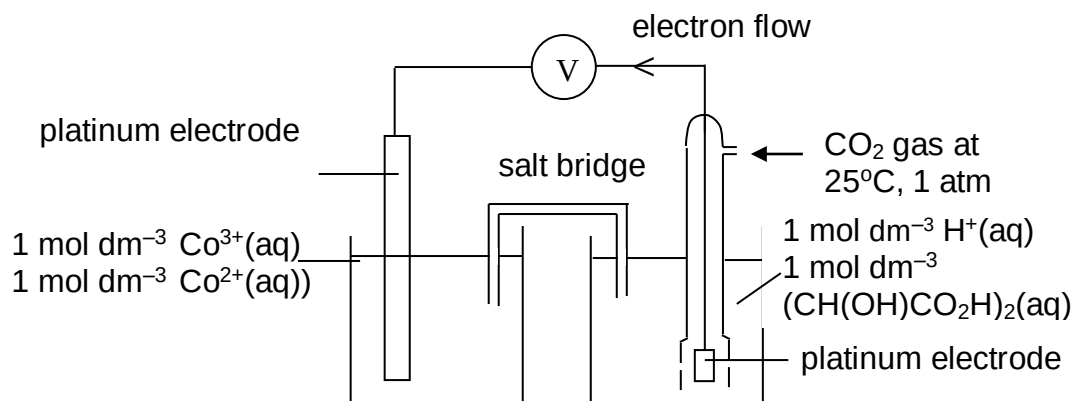
At the cathode, $E^\ominus_{\text{red}} (\text{Co}^{3+}(\text{aq}), \text{Co}^{2+}(\text{aq})) = +1.82 \text{ V}$

Since e.m.f. of cell = +0.80 V, and $E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} + E^\ominus_{\text{oxid}}$

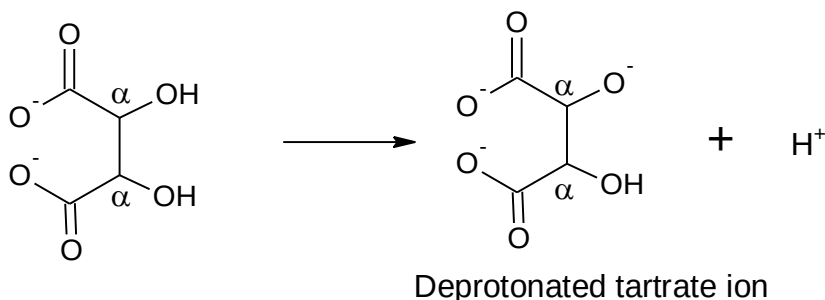
$$\begin{aligned} \therefore E^\ominus_{\text{oxid}} &= E^\ominus_{\text{cell}} - E^\ominus_{\text{red}} \\ &= +0.80 - (+1.82) = -1.02 \text{ V} \end{aligned}$$

At the anode, $E^\ominus_{\text{red}} = +1.02 \text{ V}$

- (ii) Draw a labelled diagram of the electrochemical cell.



- (b) Fehling's solution is made by adding equal volumes of a blue solution **A** containing aqueous copper(II) sulfate and a colourless solution **B** containing potassium sodium tartrate and sodium hydroxide. In a strong base, an alpha-hydroxy group in the tartrate ion, $(\text{CH}(\text{OH})\text{CO}_2^-)_2$, deprotonates as shown in the diagram below.



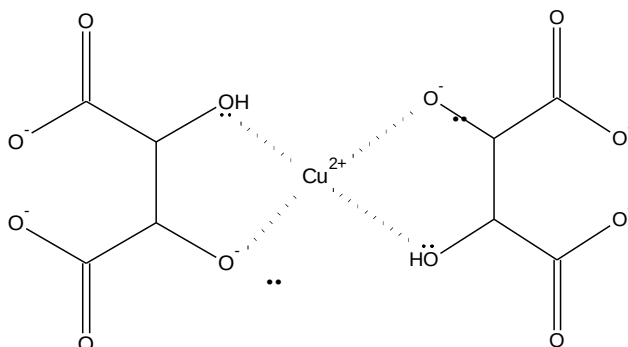
The deprotonated tartrate ion acts as a bidentate ligand and binds to the $\text{Cu}^{2+}(\text{aq})$ using both oxygen atoms from the **alpha-hydroxy groups**. A square planar bistartratocuprate(II) complex, $[\text{Cu}(\text{tart})_2]^{4-}$, forms, and a deep blue solution is seen.

[tart = deprotonated tartrate ion]

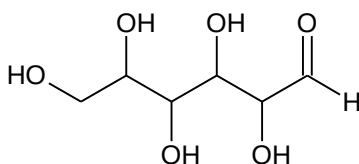
- (i) Draw the shape of $[\text{Cu}(\text{tart})_2]^{4-}$ complex, indicating clearly the type of bonds formed between the Cu^{2+} and the ligands.

(may want to include coordination number)

[2]



- (ii) The open straight chain form of D-glucose, a reducing sugar, is shown.



D-glucose

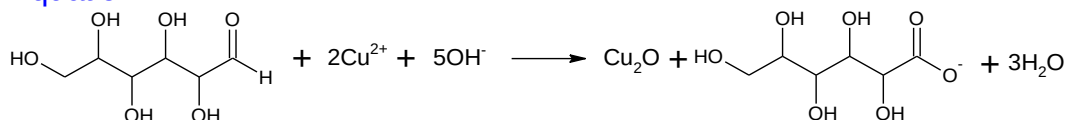
State what would be observed when D-glucose solution is warmed with a few drops of Fehling's solution.

Write the balanced equation for the reaction described above.

[2]

Observation: Brick-red/reddish-brown precipitate of Cu_2O observed

Equation:



- (iii) Explain why there is a need to form the $[\text{Cu}(\text{tart})_2]^{4-}$ complex in the Fehling's solution test.

[1]

The deprotonated tartrate ions, by complexing with Cu^{2+} prevents the precipitation of Cu^{2+} as solid $\text{Cu}(\text{OH})_2$ from the reaction of CuSO_4 and NaOH .

The Cu^{2+} in the complex can then be reduced to Cu^+ in the form of copper(I) oxide, Cu_2O .



- (iv) Explain why the Fehling's solution is deep blue while potassium sodium tartrate solution is colourless.

[4]

In the presence of ligands, the partially filled 3d-orbitals of Cu^{2+} split into 2 sets of different energy levels.

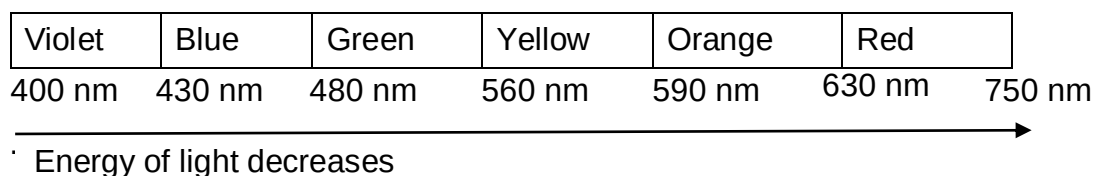
The small difference in energy between the two sets of orbitals corresponds to the energy of visible light in the electromagnetic spectrum

On absorbing energy from the visible light, an electron from a lower d-orbital gets promoted to a vacant / half-filled orbital of higher energy.

The colour observed is complementary to that absorbed.

For a compound of Group I, the metal ion does not have electrons in the 3d-orbitals and hence the d-d electron transitions would not occur. Hence, the solution of this compound is colourless.

- (v) Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.



To test for proteins, Biuret reagent which also contains the $[\text{Cu}(\text{tart})_2]^{4-}$ complex is used. In the presence of peptides, it undergoes ligand exchange to form $[\text{Cu}(\text{peptide})_2]^{2+}$. The deep blue solution turns violet.

Using the above electromagnetic spectrum of visible light, state the relative ligand field strength of peptides and deprotonated tartrate ions. Explain your answer.

[3]

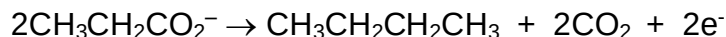
Peptides are stronger field ligands than the deprotonated tartrate ions.

$[\text{Cu}(\text{tart})_2]^{4-}$ appears blue because it absorbs orange light. $[\text{Cu}(\text{peptide})_2]^{2+}$ appears violet because it absorbs yellow light.

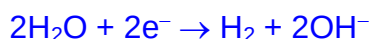
Yellow light has higher energy than orange light, the energy gap between the d orbitals of $[\text{Cu}(\text{peptide})_2]^{2+}$ is larger than that of $[\text{Cu}(\text{tart})_2]^{4-}$.

- (c) Adolf Kolbe first published a method describing the preparation of an alkane from the electrolysis of an aqueous solution of sodium salt of a monoprotic acid, using inert electrodes.

In the Kolbe electrolysis of sodium propanoate, butane was formed at the anode in the following reaction.



- (i) Write the half equation for the reaction at the cathode during the electrolysis of sodium propanoate. Hence write an equation for the **overall** reaction. [2]



Overall reaction:



- (ii) A student tried to synthesise another hydrocarbon using an aqueous solution of a sodium salt of a diprotic acid, succinic acid, $(\text{CH}_2\text{CO}_2\text{H})_2$. The succinate ion, $(\text{CH}_2\text{CO}_2^-)_2$, undergoes a similar reaction as propanoate ion at the anode.

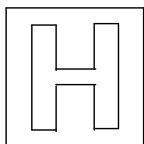


Suggest an identity of the hydrocarbon **R**.



[Total : 20]

End of Paper



**RAFFLES INSTITUTION
2016 YEAR 6 PRELIMINARY EXAMINATION**

Higher 2



CHEMISTRY

9647/01

Paper 1 Multiple Choice

26 September 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write in **soft pencil**.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, class and index number in the spaces provided on the Answer Sheet.

There are **forty** questions in this paper. Answer **all** questions.

For each question there are four possible answers **A, B, C** and **D**.

Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in the question booklet.

This document consists of **18** printed pages.

Section A

For each question, there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1** Which of the following statements best explains why helium has the highest first ionisation energy among all the elements in the Periodic Table?

A It is unreactive.
B It is the least electronegative element.
C It has only one completely filled principal quantum shell.
D Its valence electron is poorly shielded and is very close to the nucleus.

- 2** When a beam of protons travelling at the same speed passes through an electric field of constant strength, the protons, ${}^1\text{H}^+$, are deflected through an angle of $+12^\circ$.

Under identical conditions, which particle would be deflected through an angle of $+8^\circ$?

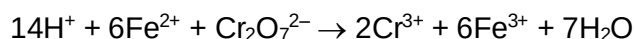
A ${}^2\text{H}^+$ **B** ${}^3\text{He}^{2+}$ **C** ${}^6\text{Li}^{2+}$ **D** ${}^{12}\text{C}^{3+}$

- 3** *Use of the Data Booklet is relevant to this question.*

Which particle has three unpaired electrons?

A V^{3+} **B** F^{2+} **C** Ni **D** S^-

- 4** FeSO_4 reacts with $\text{K}_2\text{Cr}_2\text{O}_7$ in acid solution according to the following equation.

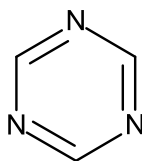


A 20.0 cm^3 sample of FeSO_4 solution required 13.10 cm^3 of 0.100 mol dm^{-3} acidified $\text{K}_2\text{Cr}_2\text{O}_7$ for complete reaction.

What was the concentration of the FeSO_4 solution?

A 0.0655 **B** 0.153 **C** 0.393 **D** 0.916

- 5 1,3,5-triazine is an aromatic compound and its structure resembles that of benzene.



1,3,5-triazine

Which statement about 1,3,5-triazine is correct?

- A Its empirical formula is CN.
 B A molecule of 1,3,5-triazine has six σ bonds.
 C The C–N π bond is formed by $2sp^2$ – $2sp^2$ overlap.
 D All the carbon-nitrogen bonds have equal bond lengths.
- 6 Which of the following shows the correct shape and bond angle of the molecule given?

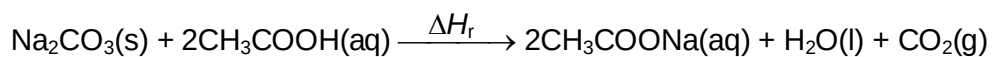
	molecule	shape	bond angle
A	OF ₂	bent	117°
B	BH ₃	trigonal pyramidal	120°
C	XeF ₄	tetrahedral	109.5°
D	SF ₆	octahedral	90°

- 7 At 25 °C and 101 kPa, a 1.00 g sample of dry air contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon and 0.03% carbon dioxide by volume.

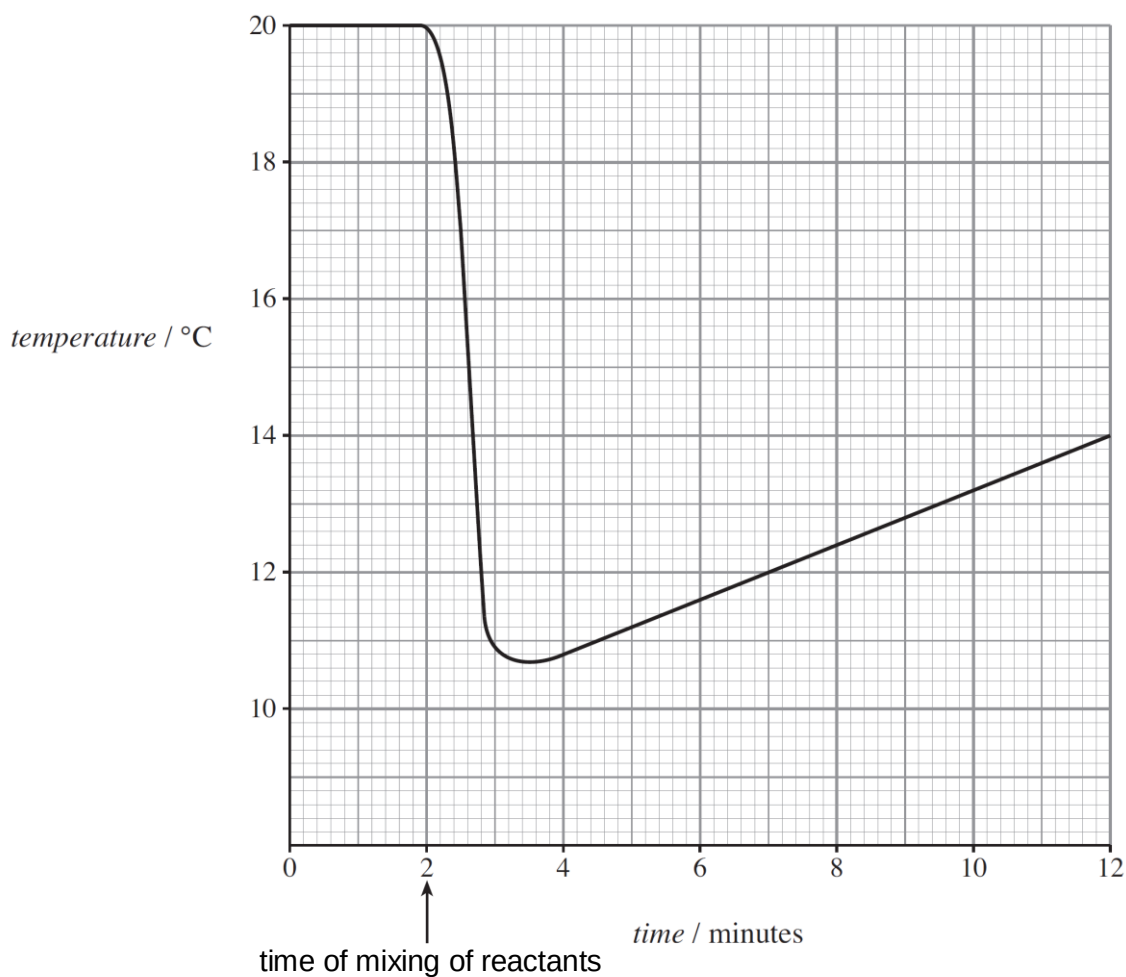
What is the average relative molecular mass of the air sample?

- A 14.67 B 24.52 C 28.95 D 30.26
- 8 Which of the following statements about an ideal gas is correct?
- A The total volume of the individual molecules is significant when compared to the volume of the container which the gas occupies.
 B An ideal gas can liquefy at low temperature and high pressure.
 C The gas molecules are in constant, random motion.
 D The gas molecules have no mass.

- 9 Sodium carbonate reacts with ethanoic acid according to the equation below.



In an experiment to determine the enthalpy change of reaction, ΔH_r , 7.5 g of solid sodium carbonate ($M_r = 106$) was added to 50 cm³ of excess aqueous ethanoic acid. The temperature of the resultant solution was monitored at various time intervals and the following graph was obtained.

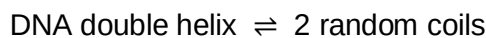


Given that the specific heat capacity of the solution is 4.18 J cm⁻³ K⁻¹, what is the enthalpy change of reaction, ΔH_r ?

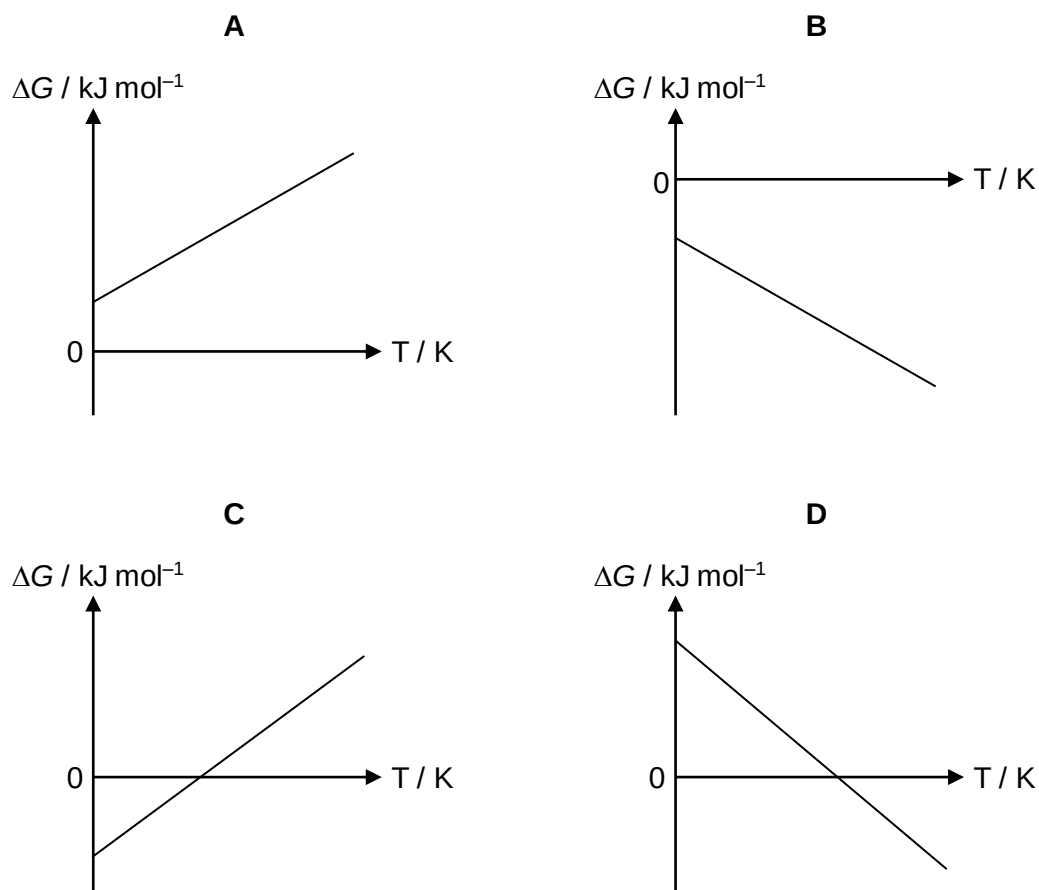
- A +27.5 kJ mol⁻¹
- B +29.5 kJ mol⁻¹
- C +31.6 kJ mol⁻¹
- D +34.0 kJ mol⁻¹

- 10 The DNA double helix consists of two DNA strands held together by hydrogen bonding.

When heated, the DNA double helix separates into two random-coil single strands. When cooled, the random coils reform the double helix.



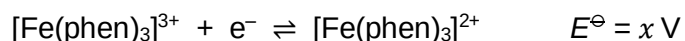
Which of the following graphs corresponds to the forward process?



- 11 Use of the Data Booklet is relevant to this question.

1,10-phenanthroline (phen) is an organic compound that is used as a ligand in coordination chemistry. It forms complexes with metal ions such as Fe^{3+} and Fe^{2+} .

The redox equilibrium between $[\text{Fe}(\text{phen})_3]^{3+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ is shown below.



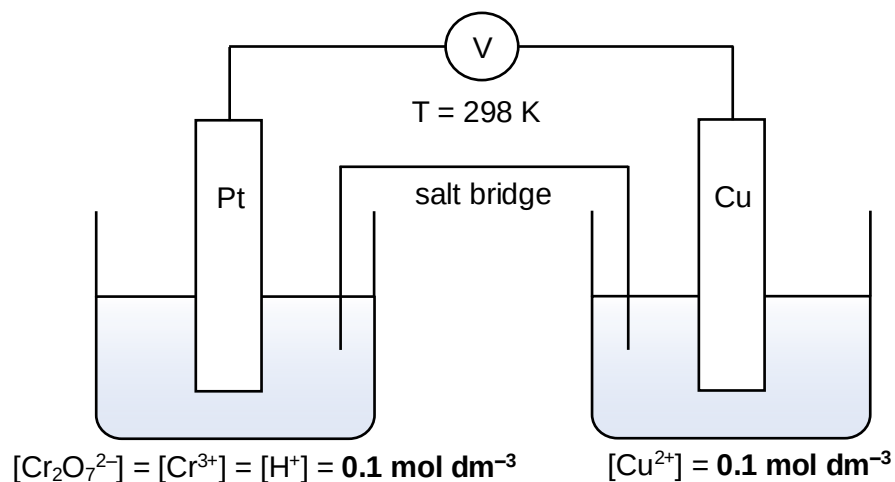
Aqueous chlorine oxidises $[\text{Fe}(\text{phen})_3]^{2+}$ to $[\text{Fe}(\text{phen})_3]^{3+}$, but both aqueous bromine and iodine do not.

What could be the value of x ?

- A -0.88 B -1.18 C +0.88 D +1.18

12 Use of the Data Booklet is relevant to this question.

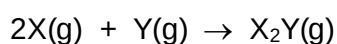
An electrochemical cell is set up as shown:



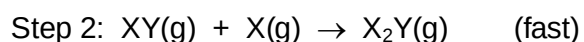
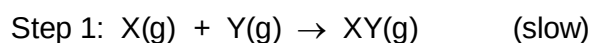
Which statement about the e.m.f. of the above cell is correct?

- A** The e.m.f. of the cell is +0.99 V.
- B** Addition of water to the $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ half-cell decreases the e.m.f. of the cell.
- C** Addition of $\text{H}^+(\text{aq})$ to the Cu^{2+}/Cu half-cell decreases the e.m.f. of the cell.
- D** Addition of excess $\text{NH}_3(\text{aq})$ to the Cu^{2+}/Cu half-cell decreases the e.m.f. of the cell.

13 The two-step mechanism for the reaction



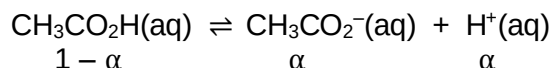
is shown below.



Which of the following is the rate equation for the reaction?

- A** rate = $k[\text{X}]^2$
- B** rate = $k[\text{X}][\text{Y}]$
- C** rate = $k[\text{XY}][\text{X}]$
- D** rate = $k[\text{X}]^2[\text{Y}]$

- 14** Ethanoic acid dissociates in aqueous solution as follows, where α is the degree of dissociation.



Which of the following statements is correct?

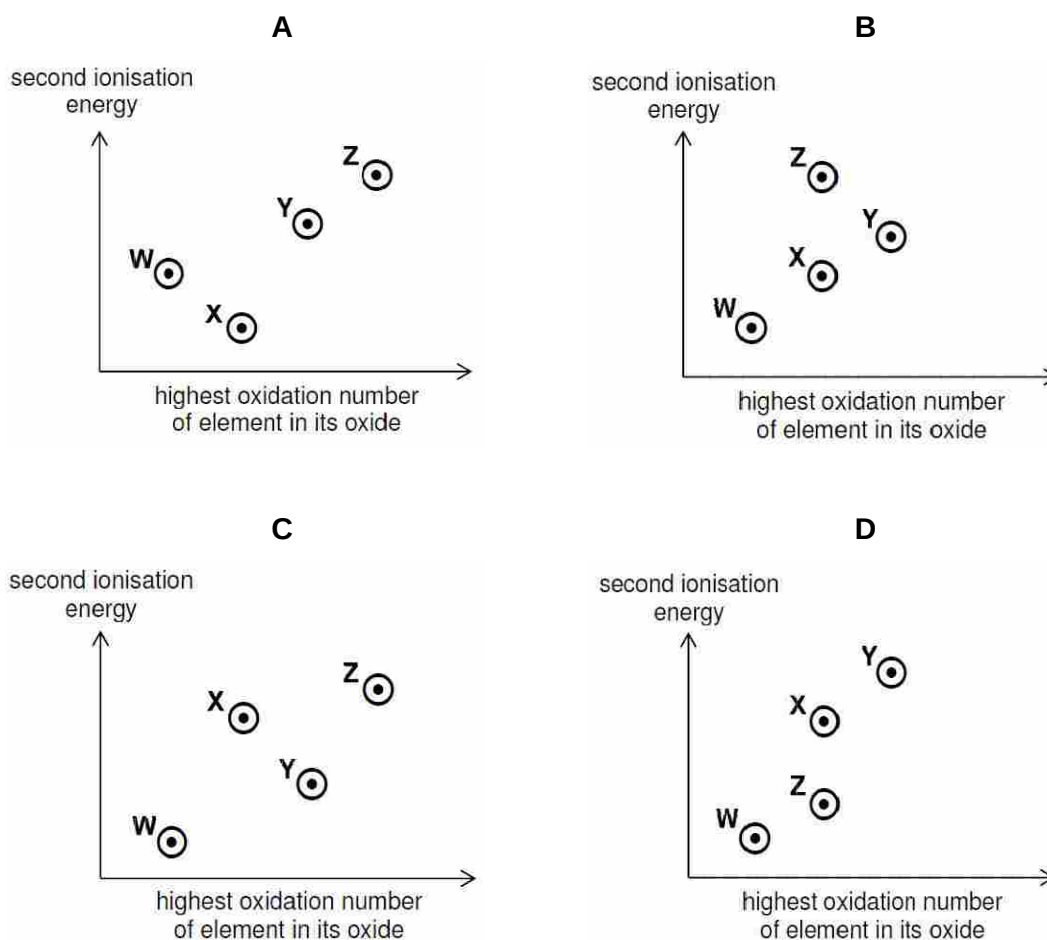
- A** The K_a , in terms of α and initial concentration C , is $\frac{\alpha^2 C}{1-\alpha}$.
- B** pH decreases with decreasing concentration of ethanoic acid.
- C** K_a increases with increasing concentration of ethanoic acid.
- D** α does not change with the concentration of ethanoic acid.
- 15** The solubility product, K_{sp} , of magnesium hydroxide at 25 °C is **X**.
The solubility of magnesium hydroxide at 25 °C is **S**.
Which of the following statements is correct at 25 °C?
- A** The pH of a saturated solution of magnesium hydroxide is $14 + \lg(2X)^{1/3}$.
- B** The solubility of magnesium hydroxide in a solution of magnesium chloride is larger than **S**.
- C** When solid sodium hydroxide is dissolved in a saturated solution of magnesium hydroxide, K_{sp} of magnesium hydroxide becomes smaller than **X**.
- D** The K_{sp} of barium hydroxide is smaller than **X**.
- 16** Which property of the Period 3 elements, from Na to Cl, increases consistently across the period?
- A** enthalpy change of atomisation
- B** number of unpaired electrons
- C** electronegativity
- D** atomic radius

17 Use of the Data Booklet is relevant to this question.

W, X, Y and Z are four consecutive elements in the third period of the Periodic Table. The formula of the hydride formed by each element is given in the table below.

element	W	X	Y	Z
formula of hydride	WH ₂	XH ₃	YH ₄	ZH ₃

Which of the following shows the correct trends when the second ionisation energies of the elements are plotted against the highest oxidation numbers that the elements exhibit in their oxides?



18 An azide ion, N_3^- , is called a pseudohalide because it has some properties which are similar to those of chloride ions.

Which of the following statements is **not** likely to be correct?

- A $\text{CH}_3\text{CH}_2\text{N}_3$ reacts with hot, ethanolic KCN to give $\text{CH}_3\text{CH}_2\text{CN}$.
- B N_3^- ions react with a Cu^{2+} ion to give a complex, $[\text{Cu}(\text{N}_3)_4]^{2-}$.
- C HN_3 may be prepared by warming NaN_3 with concentrated H_2SO_4 .
- D AgN_3 is soluble in water.

19 Which chlorine-containing products are obtained when chlorine is bubbled into hot concentrated NaOH?

- A** NaClO₃ only
- B** NaClO only
- C** NaCl and NaClO₃
- D** NaCl and NaClO

20 A Lewis acid is an electron-pair acceptor, while a Lewis base is an electron-pair donor.

- 1** $\text{C}_6\text{H}_6 + \text{Br}^+ \rightarrow [\text{C}_6\text{H}_6\text{Br}]^+$
- 2** $\text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4^+$
- 3** $\text{CH}_3\text{CH}_2^+ + \text{Br}^- \rightarrow \text{CH}_3\text{CH}_2\text{Br}$

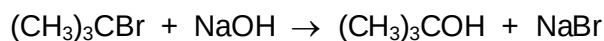
Which equations represent a Lewis acid-base reaction?

- A** 3 only
- B** 1 and 2
- C** 2 and 3
- D** 1, 2 and 3

21 What is the total number of isomers possible for C₃H₄?

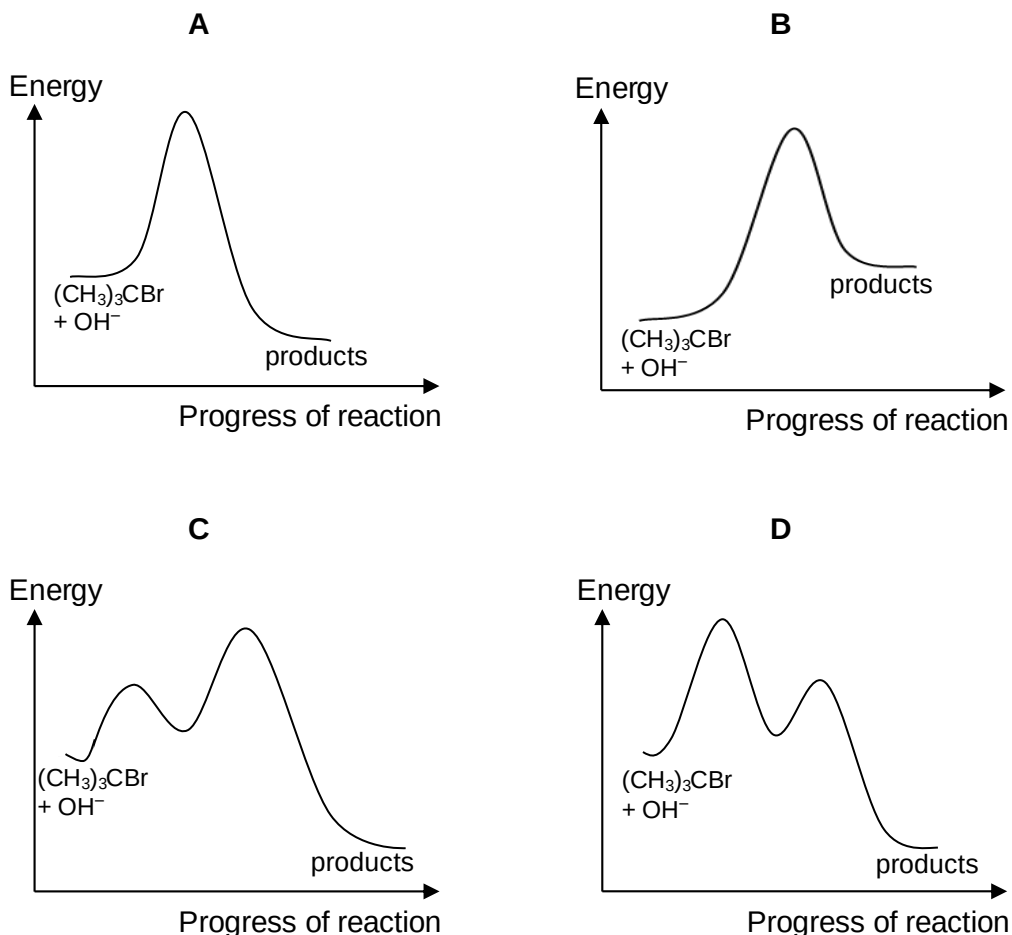
- A** 1
- B** 3
- C** 5
- D** 7

- 22 The following reaction was found to be exothermic.

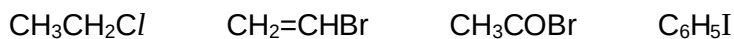


The rate equation of the reaction is: $\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$.

Which reaction profile fits the given information?



- 23 One gram of each of the following compounds was heated with NaOH(aq) , and then dilute $\text{HNO}_3\text{(aq)}$ and $\text{AgNO}_3\text{(aq)}$ were added.

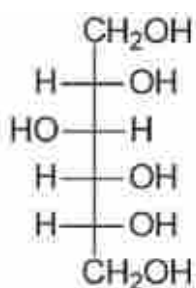


Which statement is correct?

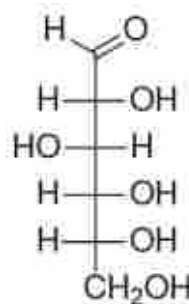
- A** The reaction with $\text{C}_6\text{H}_5\text{I}$ gave a pale yellow precipitate.
- B** The reaction with CH_3COBr gave a precipitate that dissolved completely in $\text{NH}_3\text{(aq)}$.
- C** The reaction with $\text{CH}_2=\text{CHBr}$ gave 1.76 g of precipitate.
- D** The reaction with $\text{CH}_3\text{CH}_2\text{Cl}$ gave the largest mass of precipitate.

- 24 Sorbitol is a sugar alcohol with a sweet taste, and is used as a sugar substitute.

The structures of sorbitol and glucose are given below.



sorbitol



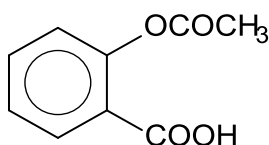
glucose

A sample containing a mixture of sorbitol and glucose reacts completely with 0.2 mol of hydrogen gas in the presence of nickel catalyst.

Another identical sample reacts with excess sodium metal to form 1.4 mol of hydrogen gas at room temperature and pressure.

What is the sorbitol : glucose ratio in the sample?

- A 3 : 2
 - B 3 : 1
 - C 6 : 1
 - D 7 : 1
- 25 Aspirin has the following structure.

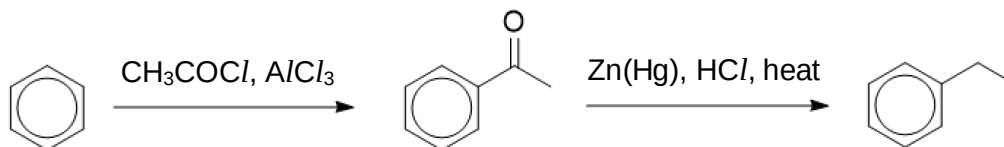


If 2-hydroxybenzoic acid is used as the starting material for making aspirin, which set of reagents and conditions will give the best yield?

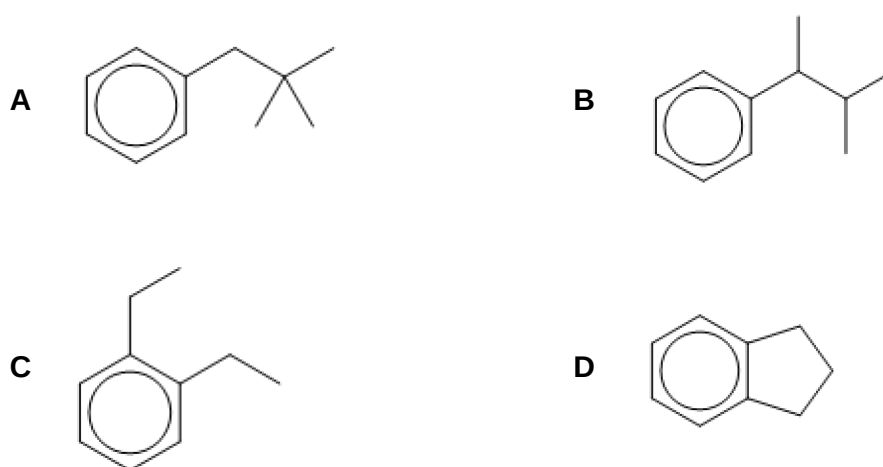
- A ethanoyl chloride at room temperature
- B phosphorus pentachloride at room temperature
- C heat with ethanol and a small amount of concentrated sulfuric acid
- D heat with ethanoic acid and a small amount of concentrated sulfuric acid

- 26 Alkylbenzenes can be synthesised from benzene by introducing an acyl group via electrophilic substitution, followed by the reduction of the carbonyl group with zinc amalgam and hydrochloric acid.

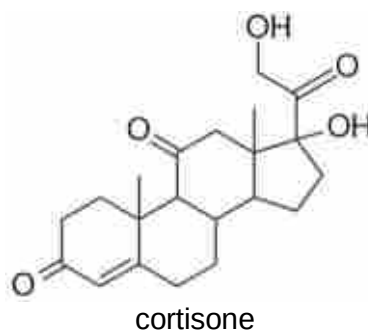
For example, ethylbenzene can be synthesised by the following route:



Which compound **cannot** be synthesised by the same method?



- 27 Cortisone is a hormone released by the adrenal gland in response to stress.



When cortisone is reacted with excess lithium aluminium hydride, how many chiral centres will be present in the product molecule?

- A 7 B 8 C 9 D 10

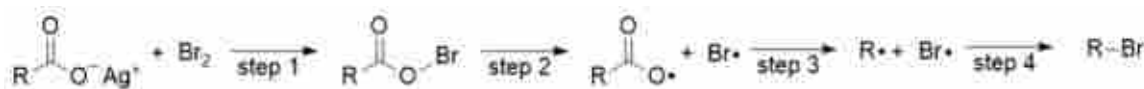
28 Consider the following four compounds, which are structural isomers of one another.

- 1 $\text{CH}_2\text{ClCHClCOOH}$
- 2 $\text{CHCl}_2\text{CH}_2\text{COOH}$
- 3 $\text{CHCl}_2\text{COCH}_2\text{OH}$
- 4 $\text{ClCH}_2\text{OCOCH}_2\text{Cl}$

Which sequence arranges the compounds in order of decreasing K_a ?

- A 1 2 3 4
- B 2 1 3 4
- C 4 3 1 2
- D 4 3 2 1

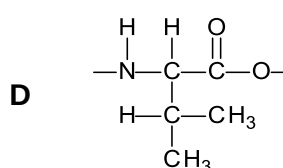
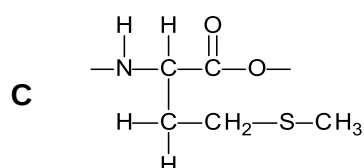
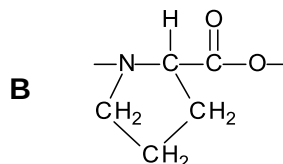
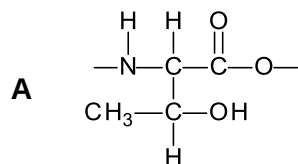
29 The Hunsdiecker reaction is a reaction in which halogenoalkanes can be produced from silver carboxylate salts, with the use of halogens. A proposed mechanism of the reaction is shown below.



Which statement is **not** correct?

- A Step 1 is favoured by the formation of a precipitate.
 - B Step 2 involves heterolytic fission.
 - C CO_2 is also a product in step 3.
 - D Alkane $\text{R}-\text{R}$ is a possible side-product of the reaction.
- 30 In the tertiary structure of a water-soluble globular protein, it was found that the types of amino acid residues present on the outer surface of the protein were different from those present on the inside.

Which of the following amino acid residues is most likely found on the outer surface of such proteins?



Section B

For each of the following questions, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

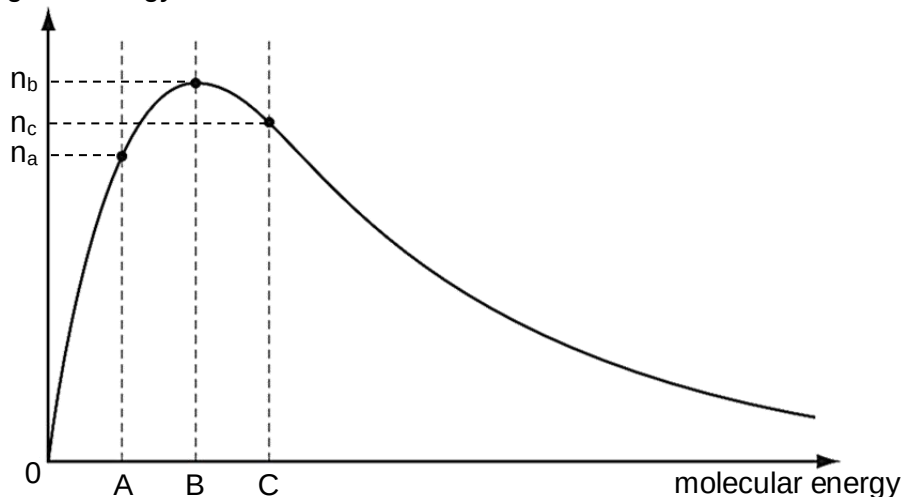
No other combination of statements is used as a correct response.

- 31** In which pairs does compound **1** have a higher melting point than compound **2**?

	compound 1	compound 2
1	$\text{CH}_3\text{CO}_2\text{NH}_4$	$\text{CH}_3\text{CH}_2\text{NH}_2$
2	SiCl_4	SiO_2
3	$\text{Ni}(\text{CO})_4$	NiSO_4

- 32** The Maxwell-Boltzmann distribution for gas **M** at a given temperature is shown below.

n = number of molecules
with a given energy



Which statements are correct for the number of molecules with molecular energies A, B and C?

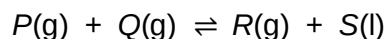
- 1** n_c decreases when more gas **M** is added at the same temperature.
- 2** n_a increases when temperature is lowered.
- 3** Addition of catalyst at the same temperature has no effect on n_a , n_b and n_c .

The responses **A** to **D** should be selected on the basis of

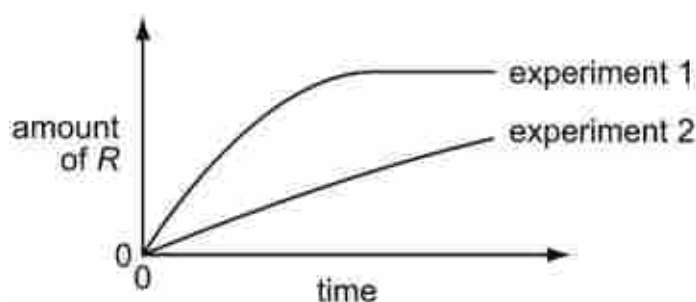
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 33** The stoichiometry of a catalysed reaction is shown by the equation below.



Two experiments were carried out in which the rate of production of *R* was measured. The results are shown in the diagram below.



Which changes in the conditions might explain the results shown?

- 1** A lower pressure was used in experiment 2.
 - 2** A different catalyst was used in experiment 2.
 - 3** Product *S* was continuously removed from the reaction vessel in experiment 2.
- 34** *Use of the Data Booklet is relevant to this question.*

Two catalysed reactions and their respective catalysts are shown below.

Reaction	Equation	Catalyst
I	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	Fe^{3+}
II	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	Mn^{2+}

Which statements about the reactions and the catalysts are correct?

- 1** Mn^{2+} is an auto-catalyst in reaction **II**.
- 2** Fe^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction **I**.
- 3** Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction **I**.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

35 *Use of the Data Booklet is relevant to this question.*

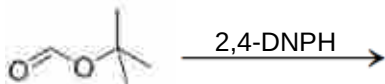
Element 117 is one of the most recently discovered elements in the Periodic Table.

In June 2016, the International Union of Pure and Applied Chemistry announced that the discoverers have proposed the name, Tennessine (${}_{117}\text{Ts}$), for this element.

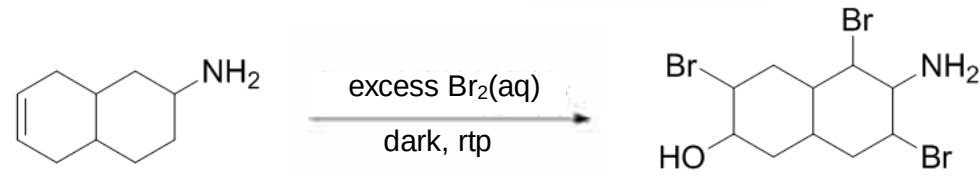
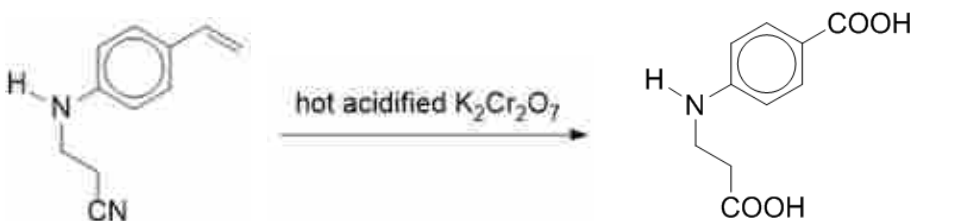
Which properties are Tennessine most likely to have?

- 1 Ts is a dark coloured solid at room temperature and pressure.
- 2 The covalent radius of Ts is greater than 0.140 nm.
- 3 The 6d and 7s orbitals of a Ts atom are completely filled with electrons.

36 Which of the following reactions will form a coloured product?

- 1 $\text{Ca}(\text{NO}_3)_2(\text{s}) \xrightarrow{\text{heat}}$
- 2 $\text{NaI}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \xrightarrow{\text{heat}}$
- 3 

37 In which reactions is the product shown a possible product?

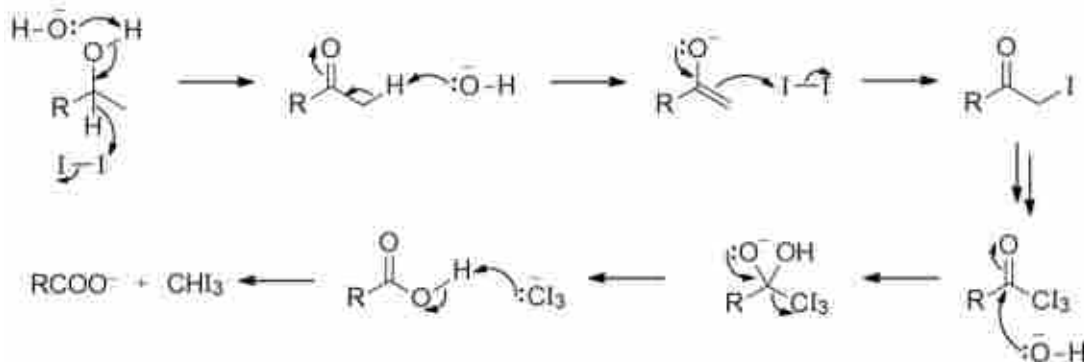
- 1 
- 2 
- 3 

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

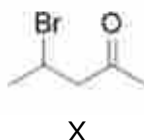
No other combination of statements is used as a correct response.

- 38** The reaction of methyl alcohols with alkaline aqueous iodine can be described by the following scheme:



Which of the following types of reactions are present?

- 1** oxidation
 - 2** acid-base reaction
 - 3** nucleophilic addition
- 39** Lithium acetylide, $\text{H}-\text{C}\equiv\text{C}^- \text{Li}^+$, is a useful nucleophilic reagent in organic synthesis. Lithium acetylide is reacted with compound X, followed by the addition of water.



Which of the following could be the products of the above reaction?

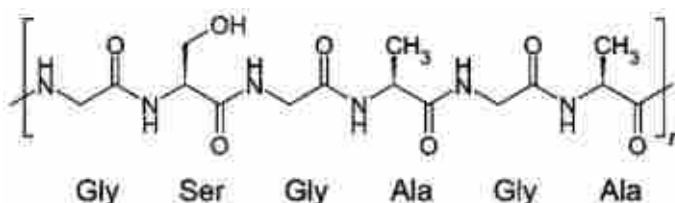
- 1**
- 2**
- 3**

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

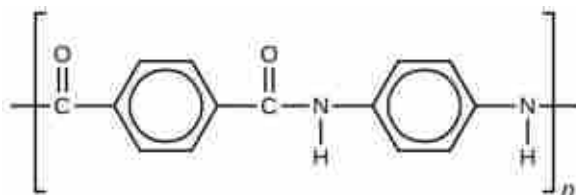
No other combination of statements is used as a correct response.

- 40** Fibroin, a protein present in Spiderman's web, consists of layers of anti-parallel beta-pleated sheets. Its primary structure consists of the amino acid sequence shown below:



Man-made Kevlar® can be stretched without snapping easily. Spiderman is impressed by the tensile strength of the man-made Kevlar® and intends to upgrade his spider silk so that it will not snap midway through his swings.

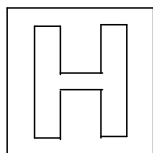
The primary structure of Kevlar® is shown below:



Which statements are correct?

- Both fibroin and Kevlar® have high tensile strength due to their ability to form intermolecular hydrogen bonding between adjacent strands.
- Kevlar's additional strength is derived from instantaneous dipole – induced dipole interactions between the aromatic rings of adjacent strands.
- Kevlar® is less water-absorbent than fibroin due to the non-polar aromatic rings, and thus could be used on rainy days.

– END OF PAPER –



RAFFLES INSTITUTION
2016 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9647/02

Paper 2 Structured Questions

14 September 2016
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

A Data Booklet is provided. Do not write anything in it.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	/ 12
2	/ 13
3	/ 13
4	/ 18
5	/ 16

Paper 1	Paper 2	Paper 3	Planning	Penalty	Total	Grade
/ 40	/ 60	/ 80	/ 12		/ 100	

This document consists of **24** printed pages.

1 Planning (P)

For
examiner's
use

Copper plating is a method employed to coat an object's surface with a thin layer of copper. The object to be plated is lowered into an electrolyte containing Cu^{2+} ions, which are reduced on the surface of the object to form a thin layer of copper when an electric current is passed through the set-up.

This set-up can also be used to determine the Faraday constant (F), which is the charge carried by 1 mol of electrons, as described below.

A pre-weighed metal object and a pure copper rod are placed in a copper(II) sulfate solution, and then connected to an electrical source. After a sufficient duration, the mass of copper plated onto the metal object is determined by taking the difference between the object's mass before and after plating.

The mass of copper plated is dependent on the amount of electrical charge flowing through the circuit. The value of the Faraday constant may be determined graphically by repeating the experiment several times using different amounts of electrical charge, and plotting the collected data on a graph.

- (a) The amount of electrical charge flowing through the circuit is dependent on time and electrical current.

Show that the relationship between the mass of copper plated onto the metal object and the time taken for the copper plating is given by:

$$m = \frac{63.5I}{2F} t$$

where
 m = mass of copper plated in grams (g),
 I = current of circuit in amperes (A),
 t = time in seconds (s)

[2]

- (b) The value of the Faraday constant (F) is widely accepted by chemists to be 96500 C mol^{-1} .

Using this value and given an electrical power source that supplies a constant current of 0.500 A , calculate the **maximum time** (to the nearest second) for which copper plating can be carried out so that the mass of copper plated onto the metal object will not exceed 1.00 g .

maximum time = ... [1]

- (c) By considering your answers to (a) and (b), write a plan for determining the value of the Faraday constant in a laboratory.

For
examiner's
use

You may assume that you are provided with:

- 0.0500 mol dm⁻³ copper(II) sulfate solution,
- 5 pieces of pure copper, each weighing **approximately** 1.5 g,
- 5 pieces of metal objects to be plated, each weighing exactly 2.00 g,
- an electrical power source that supplies a constant current of 0.500 A,
- distilled water,
- filter paper,
- the equipment and materials normally found in a school or college laboratory.

Your plan should include the following:

- a clearly labelled diagram of the set-up,
- details of how you would vary a variable of this experiment to collect 5 sets of data that will be used to calculate the Faraday constant,
- a sketch of the graph you would expect to obtain using the data collected and how the graph can be used to calculate the Faraday constant,
- the measures you would take to ensure the accuracy of the experiment.

Diagram for experimental set-up:

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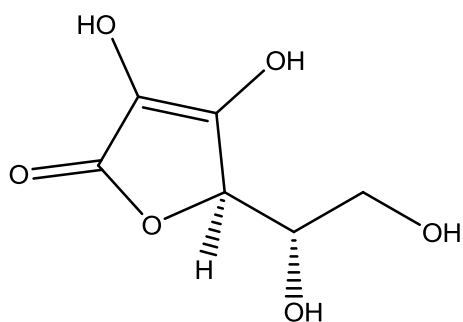
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This image shows a full page of white paper with horizontal dotted lines. The lines are evenly spaced and run across the width of the page, providing a guide for handwriting practice. There are no margins, text, or other markings on the page.

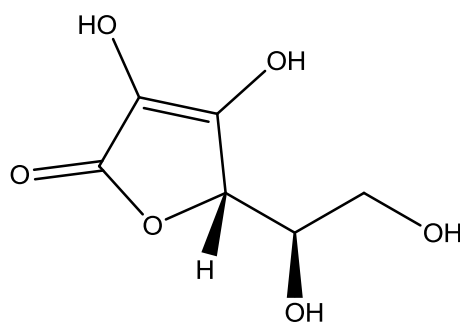
[Total: 12]

- 2 (a) "Vitamin C" refers to a group of compounds which includes ascorbic acid and its salts.

For
examiner's
use



ascorbic acid



compound A

Compound A is the mirror image of ascorbic acid.

- (i) Besides compound A, ascorbic acid has two other stereoisomers. Draw the structures of these two isomers.

[2]

- (ii) Pure ascorbic acid rotates plane-polarised light clockwise by 20° (or $+20^\circ$). Compound A was mixed with ascorbic acid, in an unknown proportion, in a beaker.

Plane-polarised light was shone through the beaker and it was found that the light had rotated 10° anti-clockwise (or -10°).

Calculate the percentage of ascorbic acid and compound A in the mixture.

% ascorbic acid = ...; % compound A = ... [2]

- (iii) Ascorbic acid is used as a food additive due to its solubility in water. Explain why ascorbic acid is soluble in water.

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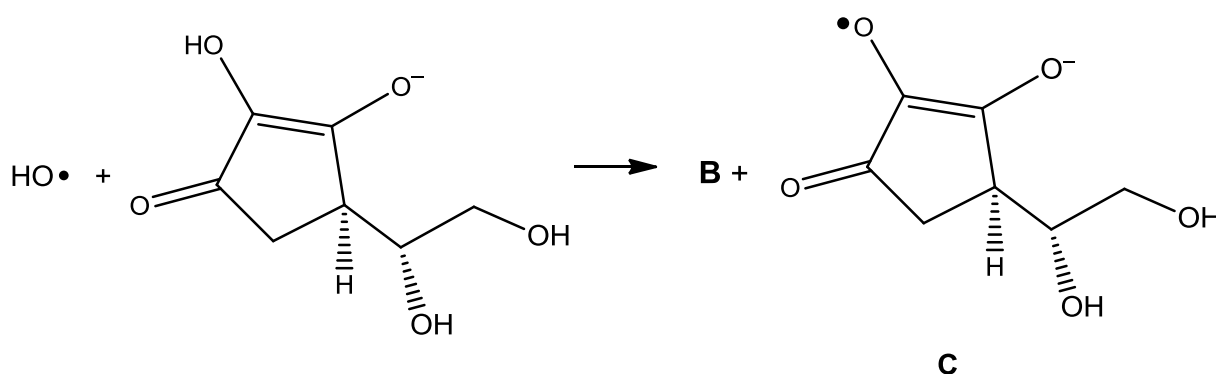
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[1]

- (b) Ascorbic acid has antioxidant properties and it exists mainly as the ascorbate ion at the physiological pH of 7.4.

An ascorbate ion reacts with a hydroxyl *free radical* in a 1:1 ratio to give product **B** and a radical anion **C** as shown below:



- (i) Explain what is meant by a *free radical*.

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[1]

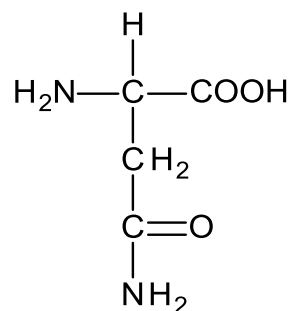
- (ii) Suggest the identity of **B**.

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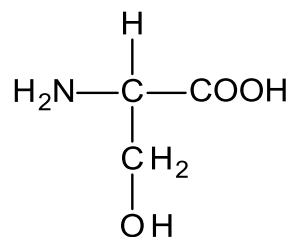
[1]

(c) Asparagine and serine are important α -amino acids in the synthesis of proteins.

For
examiner's
use



asparagine



serine

Suggest, with reagents and conditions, a simple chemical test to distinguish between the two α -amino acids.

Reagents and conditions:

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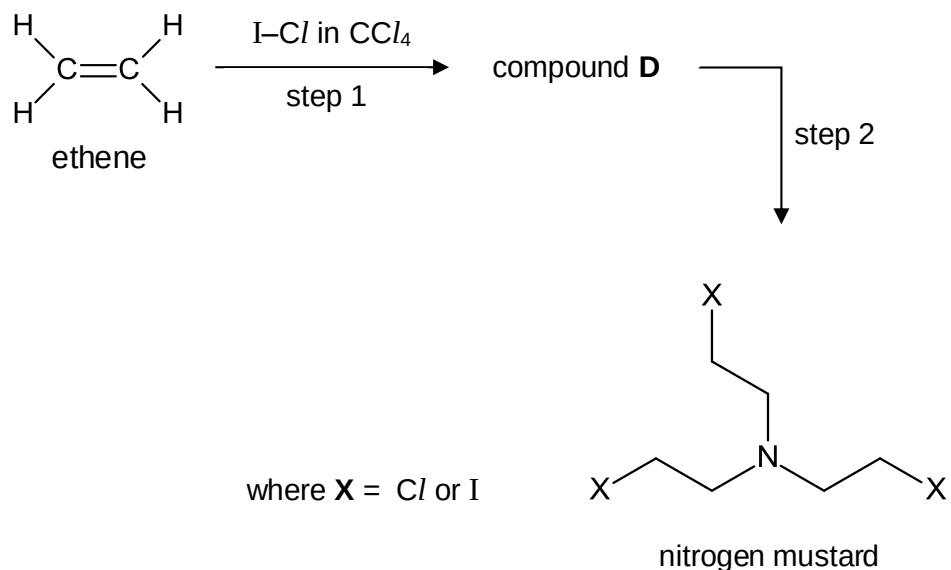
Observations:

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[2]

- (d) Nitrogen mustard gas is commonly used in chemotherapy for cancer.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:



- (i) Suggest the structure for compound **D**.

[1]

- (ii) State and explain whether **X** (in nitrogen mustard) is more likely to be Cl or I.

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[1]

- (iii) Suggest the reagents and conditions for step 2.

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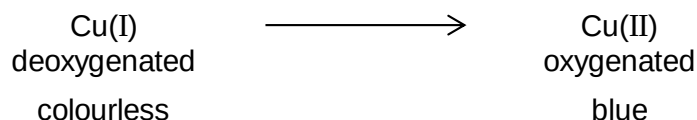
[2]

[Total: 13]

For
examiner's
use

(a) Haemocyanin is the primary oxygen transport molecule found in the blood stream of lobsters.

Unlike haemoglobin which contains iron, haemocyanin contains copper that binds reversibly to oxygen molecules. Oxygenation of haemocyanin results in an oxidation reaction, and a colour change as shown below:



-[1]

- (ii) By considering your answer to (a)(i), explain why oxygenated haemocyanin is coloured.

[illegible]

[3]

- (iii)** Account for the absence of colour in deoxygenated haemocyanin.

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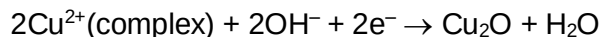
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[1]

- (b) Bis(tartrate) complex of Cu^{2+} , which is present in Fehling's solution, is used to test for aldehydes.

- (i) The reduction half-equation of bis(tartrate) complex of Cu^{2+} is given as:



Construct the half-equation for the oxidation of aldehyde (RCHO) under alkaline conditions, and hence, construct the overall equation.

Oxidation half-equation:

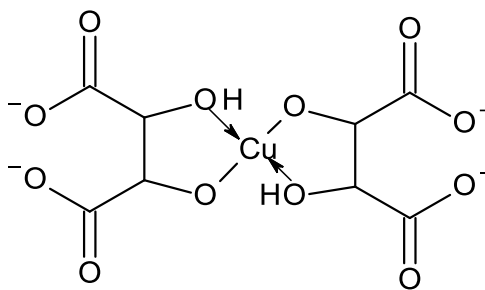
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Overall equation:

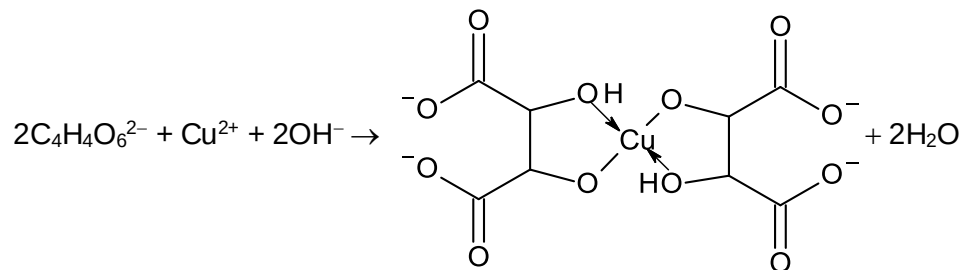
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[2]

- (ii) The bis(tartrate) complex of Cu^{2+} has the following structure:



It is synthesised by reacting aqueous Cu^{2+} ions with tartrate ions, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, in an alkaline medium as shown below:

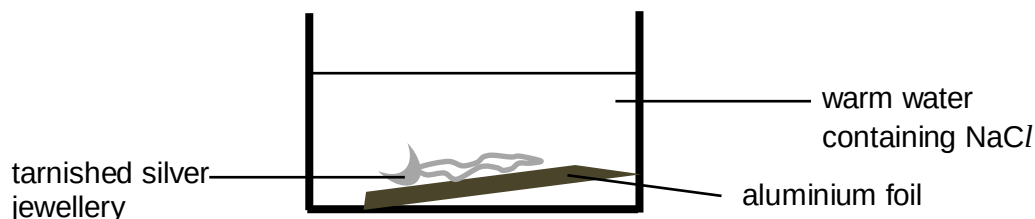


Draw the structure of the tartrate ion, $\text{C}_4\text{H}_4\text{O}_6^{2-}$.

[1]

- (c) Silver is a common metal used for jewellery. However, due to the increased amounts of hydrogen sulfide being released into the atmosphere by the combustion of fossil fuels, tarnishing of silver occurs relatively quickly, resulting in the formation of black silver sulfide.

Tarnished silver has a layer of silver sulfide, Ag_2S , on its surface. It may be restored easily by dipping it into warm water containing a piece of aluminium foil and a pinch of sodium chloride.



- (i) The piece of aluminium acts as the anode which reduces the silver sulfide; itself being oxidised to aluminium sulfide. Write the balanced equation for this reaction.

..... [1]

- (ii) A student calculated $E^\ominus_{\text{cell}}$ for this reaction using $E^\ominus(\text{Ag}^+/\text{Ag})$ and $E^\ominus(\text{Al}^{3+}/\text{Al})$.

However, the actual E_{cell} of this reaction is different from what he has calculated. Besides not being performed under standard conditions, suggest another reason to account for the difference.

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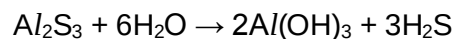
 [1]

- (iii) Suggest a purpose for the addition of sodium chloride in this reaction.

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 [1]

- (iv) While carrying out this procedure, a faint aroma of rotten egg smell is given off. This is due to the further reaction of aluminium sulfide with water, producing aluminium hydroxide and hydrogen sulfide gas.



17.1 cm³ of hydrogen sulfide gas was released at the end of the experiment, which was conducted at room temperature and pressure.

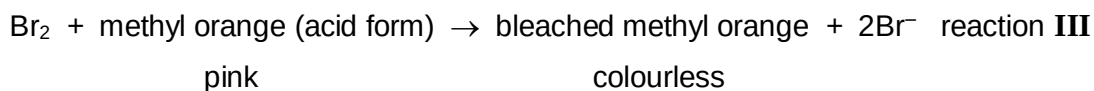
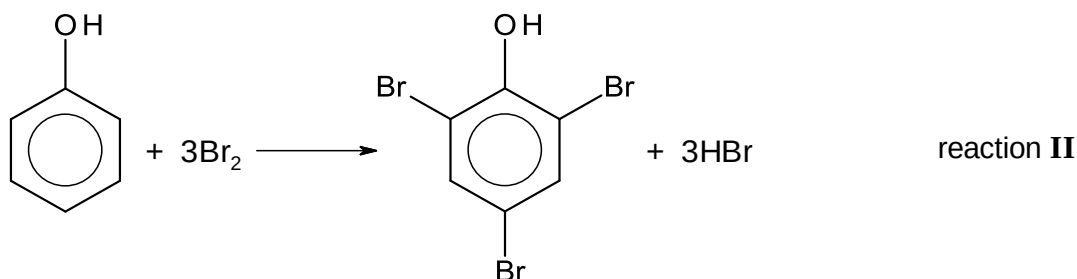
Using the information given and your answer to (c)(i), calculate the percentage of silver that was tarnished if the original jewellery contained 2.00 g of pure silver.

For
examiner's
use

[2]

[Total: 13]

(a) One use of phenol is in studying the kinetics of the reaction between bromide and bromate(V) ions in acid solution.

$$5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \quad \text{reaction I}$$


To study the kinetics of reaction I, KBr(aq) , $\text{KBrO}_3\text{(aq)}$ and $\text{H}_2\text{SO}_4\text{(aq)}$, each with an initial concentration of $0.100 \text{ mol dm}^{-3}$, are reacted with $0.00010 \text{ mol dm}^{-3}$ of phenol solution.

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[1]

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[1]

To find the order of reaction with respect to H^+ , five experiments are conducted.

In all the experiments, 10 cm^3 of KBr(aq) , 10 cm^3 of $\text{KBrO}_3(\text{aq})$, 5 cm^3 of phenol solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of $\text{H}_2\text{SO}_4(\text{aq})$ used and the time taken for the mixture to turn from pink to colourless for the 5 experiments are shown in the table below:

Experiment No.	Volume of $\text{H}_2\text{SO}_4(\text{aq})$, V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t} / \text{s}^{-1}$
1	24.00	576	10.0	0.100
2	20.00	400	14.4	0.069
3	16.00	256	22.5	0.044
4	12.00	144	40.0	0.025
5	8.00	64	90.0	0.011

- (iii) State the relationship between
- initial rate and t
 - concentration of H^+ and V .

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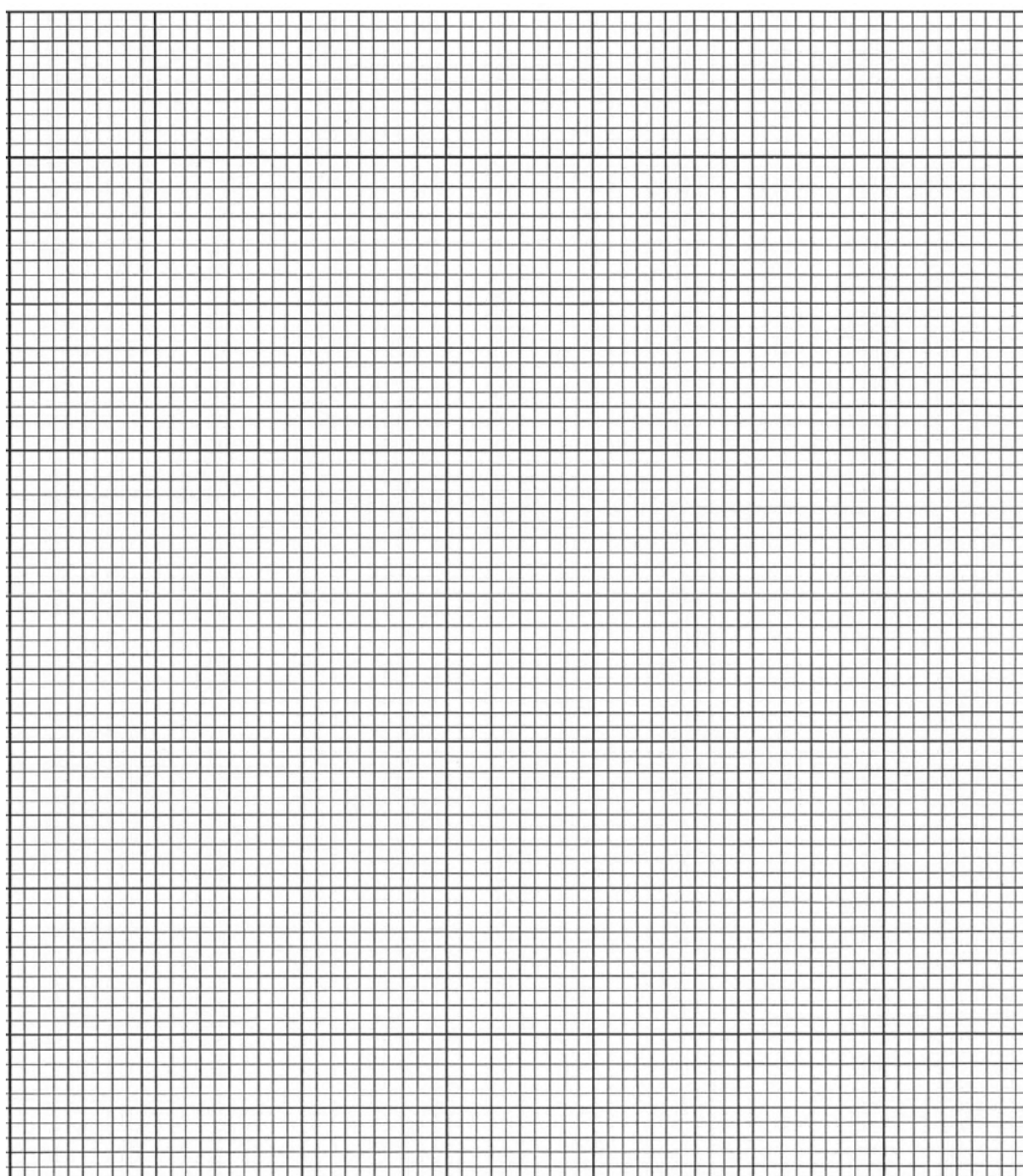
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[1]

- (iv) To determine the order of reaction with respect to H^+ , use the data in the table above to plot a straight line graph on the grid provided on page 15. Label the axes clearly.



[3]

- (v) With reference to the graph, state the order of reaction with respect to H^+ . Briefly explain your answer.

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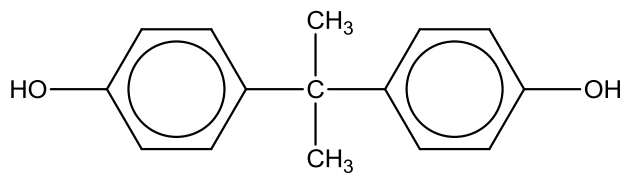
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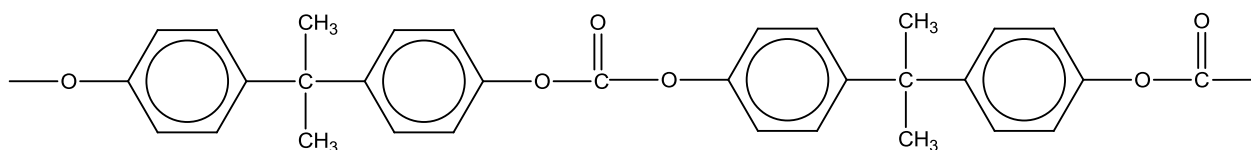
[2]

- (b) Bisphenol A, commonly known as BPA, has the structure shown below:



It is one of the two reactants used to make polycarbonate plastic which is a lightweight, high-performance polymer used in making containers, sports safety equipment and medical devices.

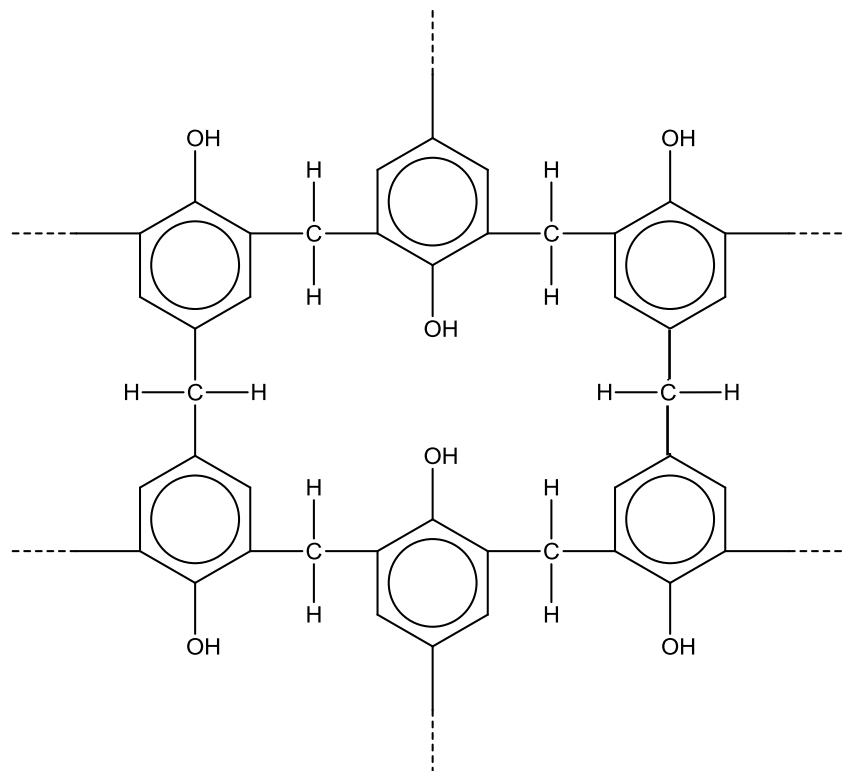
When reacted with compound **E**, BPA undergoes condensation to form polycarbonate plastic. The structure of the polycarbonate, showing two repeat units, is shown below:



- (i) Compound **E** contains carbon, oxygen and halogen only. It reacts with aqueous silver nitrate to give a white precipitate. Draw the displayed formula of compound **E**.

[1]

Bakelite, a polymer made from the condensation reaction of phenol and methanal, has the structure shown below:



- (ii) With reference to their structures, explain why Bakelite is more rigid than polycarbonate plastic.

*For
examiner's
use*

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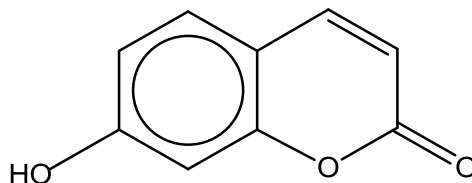
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[1]

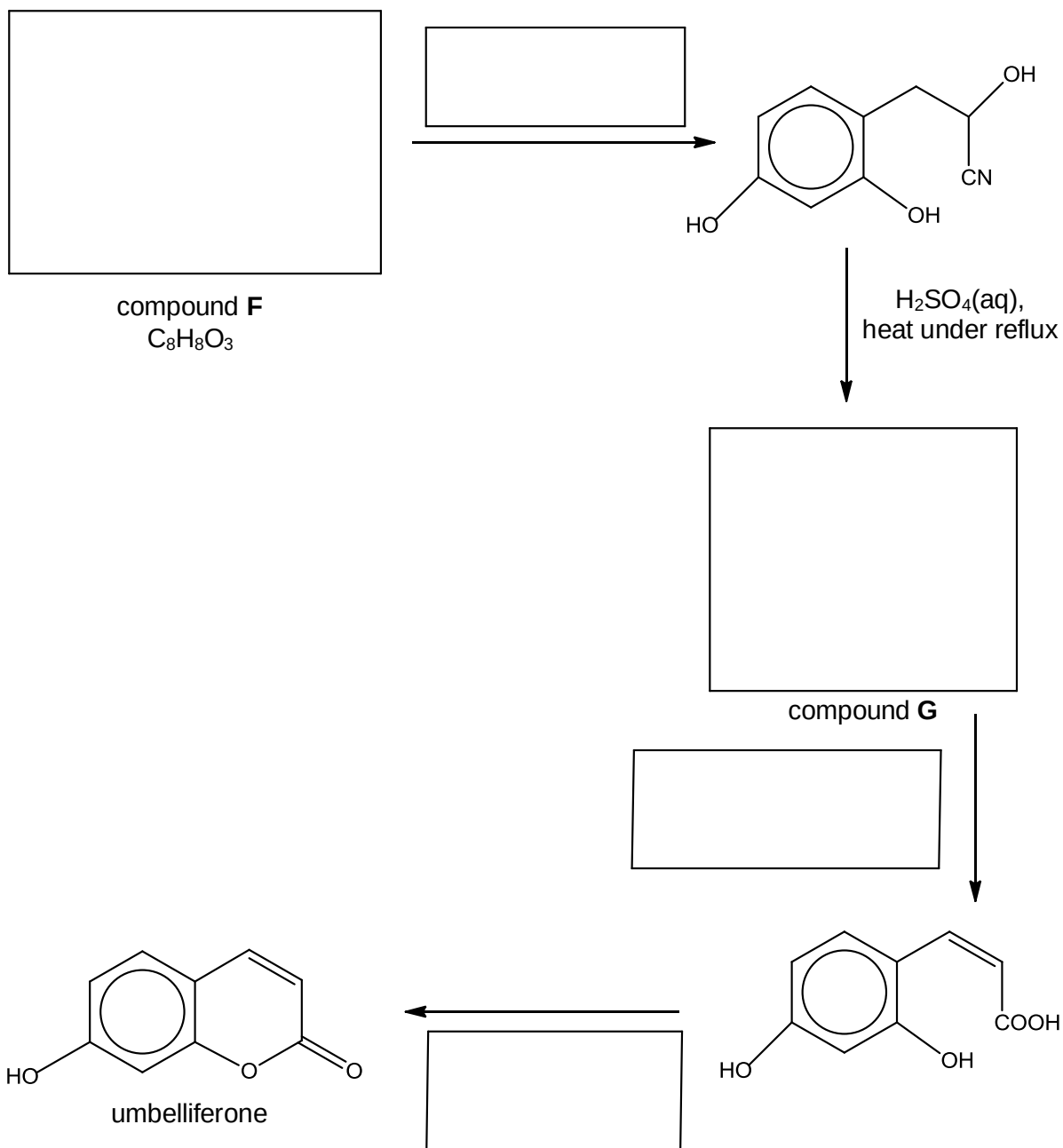
- (c) Umbelliferone is a yellowish-white crystalline solid occurring naturally in carrots and is used as a sunscreen agent. It has the structure shown below:

For
examiner's
use



The following reaction scheme shows how umbelliferone may be synthesised from compound **F**, which has a molecular formula of $C_8H_8O_3$.

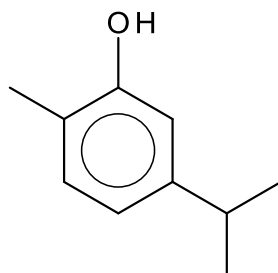
- In the boxes provided, fill in the missing
- reagents and conditions,
 - structures of compounds **F** and **G**.



[5]

- (d) Thymol is a white crystalline solid with a pleasant odour and provides the distinctive strong flavour of the herb thyme. It has the structure shown below:

For
examiner's
use



thymol

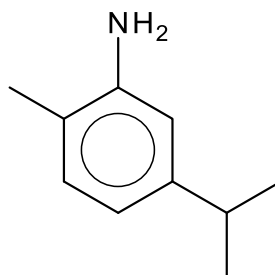
- (i) Carvacrol is a *positional* isomer of thymol.

When warmed with acidified aqueous potassium manganate(VII), both thymol and carvacrol gave the same organic product.

Draw the structure of carvacrol.

[1]

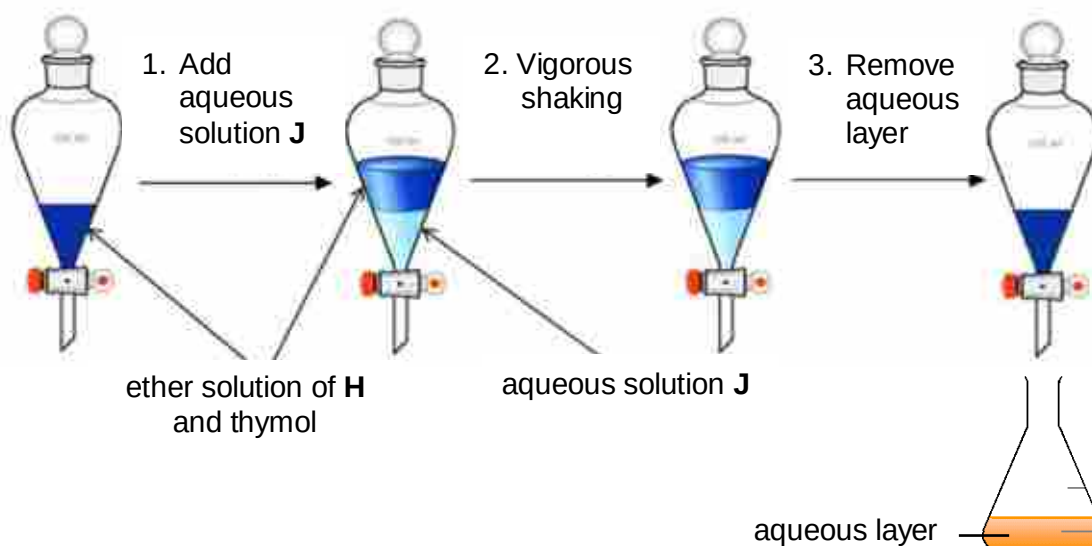
- (ii) Compound **H** has the structure shown below:



compound **H**

To separate **H** from a mixture of **H** and thymol, the following method is used.

Using a separatory funnel, an ether solution of **H** and thymol is shaken with an aqueous solution **J**, and the aqueous layer is separated from the organic layer.



If the organic layer contains only compound **H** after separation, suggest a suitable reagent which can be used as aqueous solution **J**. Give a reason for your answer.

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[2]

[Total: 18]

For
examiner's
use

- 5 The table below gives data about some physical properties of some Group I and II elements.

For
examiner's
use

property	potassium	calcium	strontium	barium	radium
relative atomic mass	39.1	40.1	87.6	137	—
atomic radius (metallic) / nm	0.227	0.197	0.215	0.217	0.220
ionic radius (2+) / nm	—	0.099	0.113	0.135	0.140
density / g cm ⁻³	0.890	1.55	2.60	3.50	5.50
1 st ionisation energy / kJ mol ⁻¹	418	590	548	502	509
2 nd ionisation energy / kJ mol ⁻¹	3070	1150	1060	966	979
solubility of sulfate in water (at 20 °C) / g per 100 cm ³	11.1	0.210	0.0130	0.000240	—

- (a) Explain why the atomic radius of barium is larger than that of strontium.

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[2]

- (b) Calcium and barium were separately added to cold water. Describe what you would observe and write equations for the reactions that occur.

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[3]

- (c) When added to water, potassium floats on the water surface. Explain whether calcium floats or sinks when it is first added to water.

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[1]

- (d) Determination of the relative atomic mass of an element depends on information like the relative isotopic masses of the isotopes and the relative abundance of each of the isotopes. Suggest why no value is quoted for the relative atomic mass of radium in the table.

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[1]

- (e) Write the expression for the solubility product, K_{sp} , of SrSO_4 .

Using data given in the table on page 21, calculate the solubility product of SrSO_4 and state its units.

[3]

- (i) State and explain the trend of the enthalpy change of hydration of Group II sulfates down the group.

[illegible]

(ii) The relationship between lattice energy, the enthalpy change of hydration and the enthalpy change of solution is given as follows:

Deduce the variation of the ΔH_{sol} of Group II sulfates down the group and hence explain the trend of the solubility of Group II sulfates shown in the table on page 21.

[illegible]

[2]

- (g) Barium forms barium peroxide, BaO_2 , on heating in oxygen.

The reaction involves the following energy change:



By using the following data and those given in the table on page 21, construct a Born-Haber cycle for barium peroxide in the grid below and calculate ΔH_1 .

enthalpy change of formation of barium peroxide	-630 kJ mol^{-1}
lattice energy of barium peroxide	$-3443 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of barium	$+176 \text{ kJ mol}^{-1}$

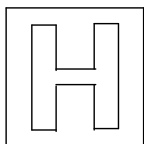


For
examiner's
use

[3]

[Total: 16]

– END OF PAPER –



RAFFLES INSTITUTION
2016 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CHEMISTRY

Paper 3 Free Response

9647/03

16 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything in it.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **12** printed pages.

Answer any **four** questions.

Begin **each** question on a **fresh sheet** of paper.

- 1 (a) Gallium trichloride, GaCl_3 , can be formed by direct combination of the elements. It has a melting point of 78°C .

Suggest the type of chemical bonding present in GaCl_3 and explain why gallium has a high tendency to form chlorides of this nature. [2]

- (b) Gallium hydride, with empirical formula GaH_3 , can be prepared from GaCl_3 . A 0.55 g sample of gaseous gallium hydride occupies a volume of 68 cm^3 at a temperature of 243 K and a pressure of $1.12 \times 10^5\text{ Pa}$.

Determine the M_r of gallium hydride and hence its molecular formula. [3]

- (c) GaH_3 reacts with $(\text{CH}_3)_3\text{N}$ at 178 K to give compound **A**, which has the following composition by mass:

H, 11.0%; C, 37.8%; N, 14.7%; Ga, 36.5%.

A molecule of compound **A** has only one Ga atom.

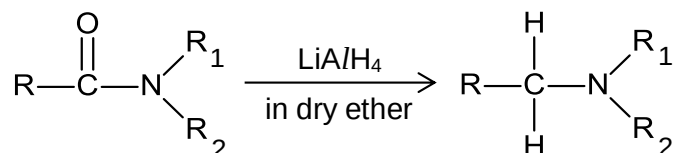
- (i) Determine the molecular formula of **A**. [1]

- (ii) Draw a structure to show clearly
- the shape of **A** around the gallium atom **and**
 - the types of bonds around the gallium atom. [2]

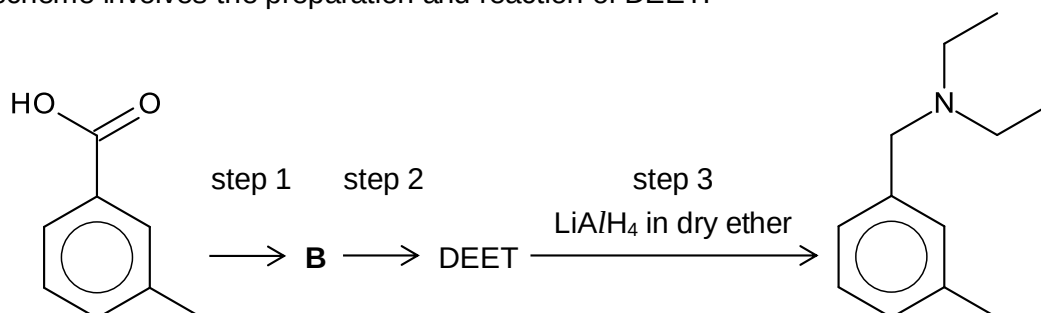
- (d) Lithium aluminium hydride, LiAlH_4 , and lithium gallium hydride, LiGaH_4 , are both donors of hydride, H^- . Thus, they are capable of reducing a large number of organic molecules.

Suggest a possible reason why LiAlH_4 is a stronger reducing agent than LiGaH_4 . [1]

- (e) LiAlH_4 can be used to reduce amides to amines as shown below:



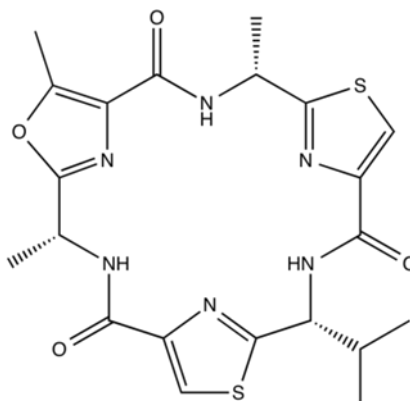
DEET is the active ingredient in many insect repellents. The following reaction scheme involves the preparation and reaction of DEET.



(i) Suggest the structures of compound **B** and DEET. [2]

(ii) Suggest the organic reactant used in step 2. [1]

(f) Venturamide A is a cyclic peptide with anti-malarial activity. It has the following structure.



Suggest reagents and conditions for the basic hydrolysis of Venturamide A and draw the structures of the organic products.

Assume that the 2 rings,  and , are inert in the reaction. [3]

(g) The identity of the side-chain and pK_a values associated with aspartic acid, asp, and alanine, ala, are as follows :

amino acid	aspartic acid, asp	alanine, ala
R	$-\text{CH}_2\text{COOH}$	$-\text{CH}_3$

amino acid	aspartic acid, asp	alanine, ala
pK_{a1}	2.10	2.35
pK_{a2}	3.86	9.87
pK_{a3}	9.82	

(i) Draw the structures of the major species present in a solution of the asp-ala dipeptide at **each** of the following pH values at room temperature.

pH = 1

pH = 3.86

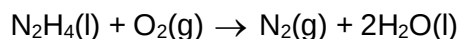
pH = 12

[3]

(ii) Draw the zwitterionic form of asp-ala and write an equation to show how it can remove small amounts of H^+ . [2]

[Total: 20]

- 2 (a) Hydrazine, N_2H_4 , is used as a rocket fuel.
It combusts in oxygen according to the equation:



Using the following data, calculate the enthalpy change of combustion of hydrazine.

compound	$\Delta H_f / \text{kJ mol}^{-1}$
$\text{N}_2\text{H}_4(\text{l})$	+51
$\text{H}_2\text{O}(\text{l})$	-286

[2]

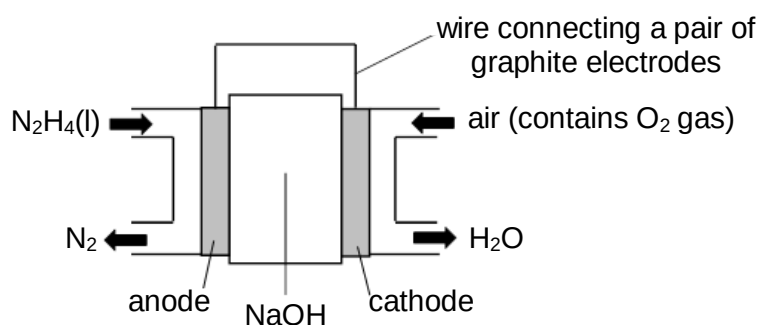
- (b) The standard electrode potential for the $\text{O}_2/\text{H}_2\text{O}$ half-cell was measured.



Draw a labelled diagram to show how the standard electrode potential of the $\text{O}_2/\text{H}_2\text{O}$ half-cell was measured. Include in your diagram the direction of electron flow.

[3]

- (c) (i) Hydrazine is increasingly used in fuel cells, and these direct hydrazine fuel cells are a more practical and viable source of energy as compared to hydrogen fuel cells.



Write balanced half-equations, with state symbols, for the reactions taking place at the anode and the cathode when the fuel cell, using aqueous sodium hydroxide as electrolyte, is in operation.

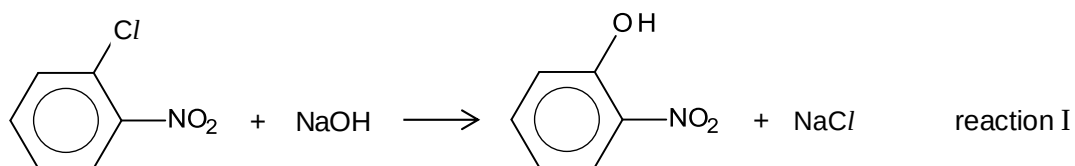
[2]

- (ii) Given that $E^\ominus_{\text{cell}}$ for the reaction that takes place in the fuel cell is +1.56 V, use values from the *Data Booklet* to calculate the standard electrode potential for the $\text{N}_2/\text{N}_2\text{H}_4$ half-cell.
- (iii) Suggest an advantage of using hydrazine as a fuel over hydrogen gas in a fuel cell.

[1]

[1]

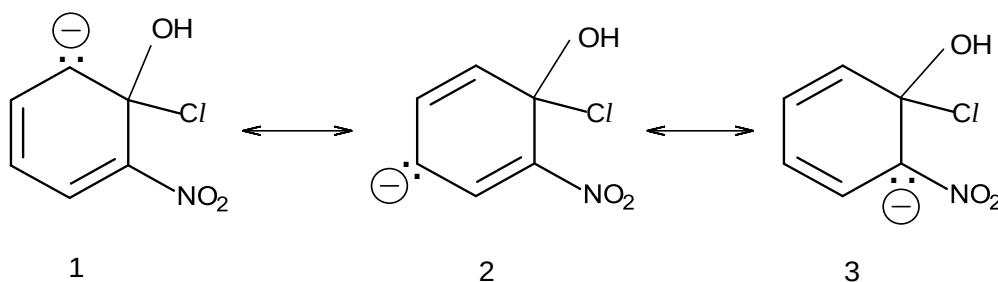
- (d) 2-chloronitrobenzene undergoes nucleophilic aromatic substitution when heated with aqueous NaOH at 100 °C.



2-chloronitrobenzene

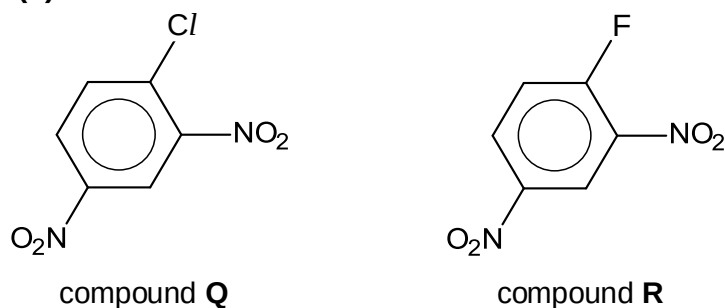
- (i) Suggest what is unusual about reaction I. [1]

The mechanism for reaction I involves a negatively charged anion intermediate. Three resonance structures of the anion intermediate are shown below:

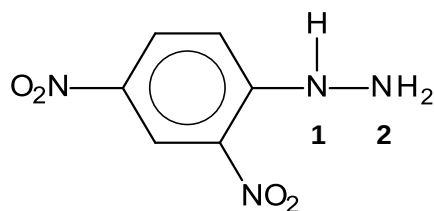


- (ii) Explain why structure 3 is the most stable resonance structure. [1]

Compounds **Q** and **R** can undergo nucleophilic aromatic substitution that is similar to reaction I in (d).

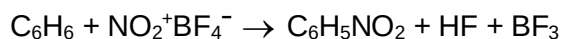


- (e) Despite the stronger C–F bond in **R** as compared to the C–Cl bond in **Q**, **R** is more reactive than **Q**. Suggest why this is so. [2]
- (f) The structure of 2,4-dinitrophenylhydrazine is given below.

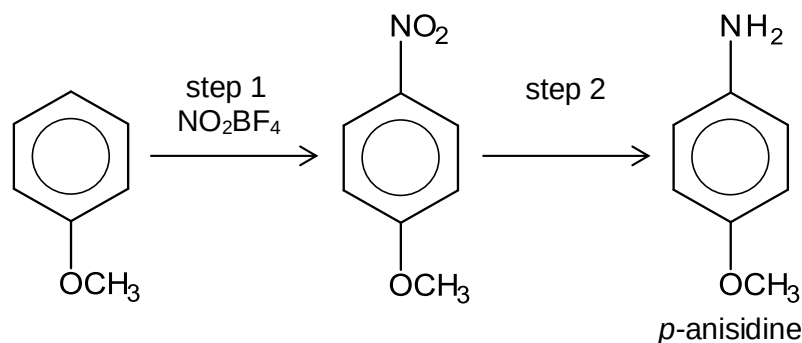


Suggest, with reasons, how the basicity of the N atoms labelled N-1 and N-2 on 2,4-dinitrophenylhydrazine compare with each other. [1]

- (g) Nitronium tetrafluoroborate, $\text{NO}_2^+\text{BF}_4^-$, is a nitronium salt which can be used as a nitrating agent for aromatic compounds.



p-anisidine may be prepared using the following route.
(Assume that the $-\text{OCH}_3$ group is unreactive.)



- (i) Name the type of reaction and describe the mechanism for the reaction in step 1. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [3]
- (ii) Suggest reagents and conditions for step 2. [1]

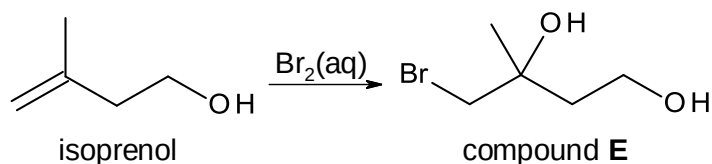
Fats and oils are sometimes oxidised to form aldehydes and ketones that cause a rancid smell in food. *p*-anisidine is widely used for detecting the presence of such aldehydes and ketones.

The reaction between an aldehyde and *p*-anisidine is similar to the reaction between an aldehyde and 2,4-dinitrophenylhydrazine.

- (iii) Name the type of reaction which RCHO , an aldehyde found in palm oil, undergoes with *p*-anisidine. [1]
- (iv) Draw the displayed formula of the product formed by the reaction between RCHO and *p*-anisidine. [1]

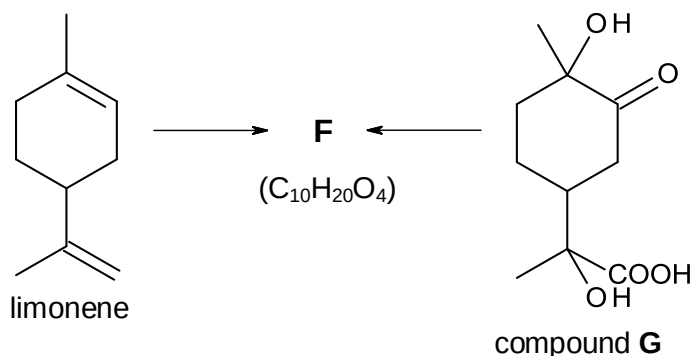
[Total: 20]

- 3 (a) Isoprenol is a terpenoid that can be used to prepare other useful compounds.



Name and draw a mechanism for the conversion of isoprenol to compound **E**. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]

- (b) Limonene is a compound used in perfumery because of its strong orange scent.



Compound **F** can be prepared from either limonene or compound **G**. One mole of **F** reacts with excess PCl_5 to produce 4 moles of gas.

- (i) Suggest a structure for compound **F**. [1]

- (ii) Suggest reagents and conditions for the preparation of compound **F** from
- limonene
 - compound **G**
- [2]

- (c) Compound **W**, $\text{C}_{10}\text{H}_{16}$, is a structural isomer of limonene. It is used in perfumery for its sweet herbal scent.

W exhibits geometric isomerism. When **W** is reacted with hydrogen in the presence of platinum catalyst, $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ is formed.

When **W** is treated with hot acidified $\text{KMnO}_4(\text{aq})$, it produces three organic compounds **X**, **Y** and **Z**, each having the same number of carbon atoms.

Both compounds **X** and **Z** react with 2,4-dinitrophenylhydrazine to give an orange precipitate.

Both compounds **Y** and **Z** react with excess magnesium to give an explosive gas.

Suggest structures for compounds **X**, **Y** and **Z**, and draw the geometric isomers of compound **W**. [5]

- (d) Platinum(IV) chloride reacts with ammonia to form a platinum(IV) salt with the formula, $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$. The cation in the salt is an octahedral complex.

When 0.100 mol of $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$ is dissolved in excess aqueous AgNO_3 , 28.7 g of white precipitate is formed.

Determine the formula of the cation present in $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$. [2]

- (e) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is a square planar complex which displays geometric isomerism.

Cisplatin, the cis-isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, kills cancer cells by altering the configuration of their DNA. The trans-isomer, transplatin, does not exhibit such anti-cancer activity.

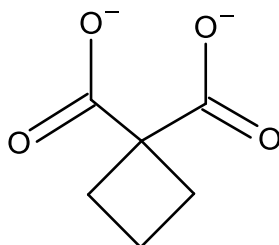
- (i) Draw the structures for both cisplatin and transplatin. [1]

- (ii) When cisplatin enters cancer cells, one of the chloride ligands in the complex is first replaced by a water molecule.

Write a balanced equation for this reaction. [1]

- (f) Carboplatin also exhibits anti-cancer activity, but it does not result in the severe side-effects which cisplatin causes.

Carboplatin has a square planar structure around Pt and it can be made by replacing the two chloride ligands in cisplatin with a bidentate cyclobutanedicarboxylate ion.



cyclobutanedicarboxylate ion

- (i) Explain what is meant by a *bidentate* ligand. [1]

- (ii) Draw the structure of carboplatin. [1]

- (g) Another method of killing cancer cells involves injecting concentrated ethanol directly into the tumour.

Explain, in terms of bonding, how ethanol may cause the denaturation of proteins in cancer cells. [2]

[Total: 20]

Use of the Data Booklet is relevant to this question.

- 4 (a) Phosphorus pentachloride, PCl_5 , is a solid which melts at 162°C .

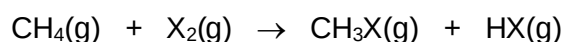
Describe how a **pure** solid sample of PCl_5 can be made from its elements. [2]

- (b) Phosphazenes are a group of P(V)/N(III) compounds with cyclic structures.

PCl_5 reacts with NH_4Cl to give phosphazene **S**, $\text{N}_3\text{P}_3\text{Cl}_6$, and steamy white fumes are evolved.

Write an equation for this reaction and suggest a structure for phosphazene **S**. [2]

- (c) Some halogens also react readily with methane.



- (i) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^\ominus$ of this reaction where X is iodine, I. [2]

- (ii) Hence, suggest why it is not possible to make iodomethane, CH_3I , by this reaction. [1]

- (d) Halogenoalkanes can undergo *homolytic fission* in the upper atmosphere.

- (i) Explain the term *homolytic fission*. [1]

- (ii) Suggest the most likely organic radical that would be formed by the homolytic fission of bromochloromethane, CH_2BrCl . Explain your answer. [1]

- (e) Methylene, $:\text{CH}_2$, is a neutral carbon electrophile containing **two unpaired** electrons.

Methylene has a few possible structures. In one of them, the centre carbon atom is sp^3 hybridised, with each unpaired electron occupying a hybrid orbital. The $\text{H}-\text{C}-\text{H}$ bond angle is 136° .

Explain why

- (i) methylene can act as an electrophile, [1]

- (ii) the $\text{H}-\text{C}-\text{H}$ bond angle is larger than a regular tetrahedral angle of 109.5° . [1]

- (f) Two moles of methylene combine to form one mole of ethene.

A **saturated** hydrocarbon **T**, C_4H_8 , can be formed by combining four moles of methylene.

Draw the structure of **T**. [1]

- (g) Methylene undergoes further homolytic fission to form a CH fragment with **three unpaired** electrons. In 1978, a symmetrical and saturated molecule, *tetrahedrane* (CH)₄, was made by a German chemist, by combining 4 CH fragments.

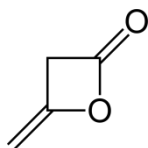
Draw the structure of *tetrahedrane*. [1]

- (h) Ketenes are very reactive organic compounds. A ketene **J** can be prepared by reacting methylene with carbon monoxide. **J** can also be prepared from ethanoyl chloride by an elimination reaction in which HCl is lost.

(i) Use the information to deduce the structure of **J**, and hence, draw its displayed formula. [1]

(ii) Identify the type of hybridisation of **each** carbon atom in **J**. [2]

- (i) Diketene **K** is formed by dimerisation of ketene **J**.



diketene **K**

Ethyl acetoacetate is used in perfume to achieve a sweet smell similar to that of green apples.

1 mole of diketene **K** reacts with 1 mole of ethanol to form 1 mole of ethyl acetoacetate as the only product.

Heating 1 mole of ethyl acetoacetate with alkaline aqueous iodine produces 1 mole of propanedioate ions and 2 moles of yellow precipitate.

(i) Determine the molecular formula of ethyl acetoacetate. [1]

(ii) Explain why one mole of ethyl acetoacetate forms two moles of yellow precipitate after heating with alkaline iodine solution, and hence suggest the structure of ethyl acetoacetate. [2]

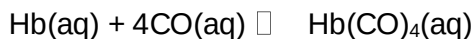
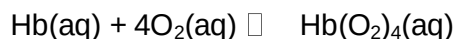
(iii) Ethylamine reacts with diketene **K** in the same way as ethanol.

Deduce the structure of the product formed when diketene **K** reacts with ethylamine. [1]

[Total: 20]

- 5 An oxocarbon is a chemical compound consisting of only carbon and oxygen, with the most common being carbon monoxide (CO) and carbon dioxide (CO₂).

- (a) Carbon monoxide is one of the most widespread and dangerous industrial hazards. The formation of carboxyhaemoglobin, Hb(CO)₄, takes place much more readily than the formation of oxyhaemoglobin, Hb(O₂)₄.



- (i) Draw a dot-and-cross diagram for CO. [1]
- (ii) With reference to haemoglobin, describe and explain what is meant by the *quaternary structure* of proteins. You should state the type of bonding or interaction involved. [2]
- (iii) A treatment method for carbon monoxide poisoning is to provide the patient with pure oxygen gas over a period of time.

With reference to the equations given above, explain why this is a suitable treatment method. [2]

- (b) The water-gas shift reaction is used to produce hydrogen gas industrially by reacting carbon monoxide with water vapour.



- (i) Write an expression for the equilibrium constant, K_p . [1]

An evacuated tank was initially filled with 0.0197 atm of CO and 0.0394 atm of H₂O at 600 K. It was sealed and left to stand. At equilibrium, the partial pressure of CO₂ was found to be 0.0191 atm.

- (ii) Calculate the value of K_p at 600 K. [2]

The table below shows how the value of K_p varies with temperature.

T / K	300	900	1500
value of K_p	1.170×10^5	1.978	0.2195

- (iii) Suggest whether the forward reaction of the water-gas shift reaction is an exothermic or an endothermic reaction. Explain your answer. [1]

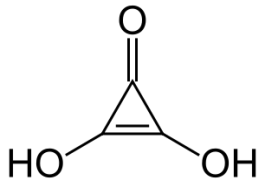
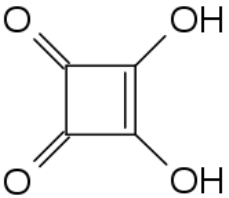
The Gibbs free energy, $\Delta G^\ominus$ (in J mol^{-1}), and the equilibrium constant, K_p , of a reaction are related by the following equation:

$$\Delta G^\ominus = -RT \ln K_p,$$

where R is the molar gas constant and T is the temperature in kelvins.

- (iv) Using the given values of K_p , calculate the values of $\Delta G^\ominus$ at 300 K and 900 K. Hence, determine the value of $\Delta S^\ominus$ for the water-gas shift reaction. (Assume that both $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of temperature.) [3]
- (v) Comment on the magnitude of the calculated value of $\Delta S^\ominus$. [1]

(c) Two organic acids which dissociate to form oxocarbon anions are shown below.

Name	Deltic acid	Squaric acid
Structure		
pK_{a1}	2.6	1.5
pK_{a2}	6.0	3.4

- (i) Sketch a clearly labelled titration curve to show how pH changes when a 10 cm^3 solution of $0.100 \text{ mol dm}^{-3}$ deltic acid is titrated against 30 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous sodium hydroxide. [3]
- (ii) Suggest a reason why squaric acid has a lower pK_{a1} value than deltic acid. [1]
- (d) An aromatic compound **X**, $\text{C}_{12}\text{H}_6\text{O}_{12}$, produces carbon dioxide when reacted with aqueous sodium carbonate.
- Heating **X** with concentrated sulfuric acid for several hours produces a neutral oxocarbon **Y**, C_{12}O_9 .
- When **Y** is heated strongly with ammonia, a compound **Z**, $\text{C}_{12}\text{H}_3\text{O}_6\text{N}_3$, is formed.
- When **Z** is heated strongly with dilute sulfuric acid, compound **X** is formed.
- Suggest structures for compounds **X**, **Y** and **Z**. [3]

[Total: 20]

– END OF PAPER –



RIVER VALLEY HIGH SCHOOL

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME

CLASS

6	

CENTRE NUMBER

S				

INDEX NUMBER

H2 CHEMISTRY

9647/01

Paper 1 Multiple Choice

23 September 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, class, centre number and index number on the Answer Sheet in the spaces provided.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the one you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1** For complete combustion of 20.0 g of heptane, what is the minimum volume of oxygen gas required at s.t.p.?
- A** 0.2 dm³
B 2.2 dm³
C 49.3 dm³
D 52.8 dm³
- 2** Element **X** exists as 3 different isotopes and has a relative atomic mass of 66.6. Which of the following compositions of isotopes is correct?
- A** 25% ⁶⁵**X**, 50% ⁶⁶**X** and 25% ⁶⁷**X**
B 30% ⁶⁵**X**, 60% ⁶⁶**X** and 10% ⁶⁷**X**
C 50% ⁶⁵**X**, 20% ⁶⁶**X** and 30% ⁶⁷**X**
D 10% ⁶⁵**X**, 20% ⁶⁶**X** and 70% ⁶⁷**X**
- 3** Which of the following does **not** contain a singly occupied orbital?
- A** N²⁺ **B** S⁻ **C** Br⁺ **D** Sc³⁺
- 4** Dinitrogen tetroxide, N₂O₄, has a simple covalent structure. Which of the following correctly describes the bonding within the dinitrogen tetroxide molecule?

	σ bond	π bond	dative bond
A	3	2	2
B	5	0	4
C	5	2	2
D	5	4	0

- 5 The Valence Shell Electron Pair Repulsion (VSEPR) theory is used to predict the shapes of molecules.

Which shape is correctly predicted by VSEPR?

	number of bonded electron pairs around central atom	number of lone pairs around central atom	shape
A	2	4	non-linear
B	3	2	T-shaped
C	4	1	square planar
D	3	2	see-saw

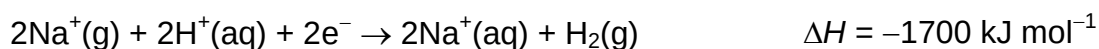
- 6 Equal masses of gaseous N_2 , NH_3 and N_2O are injected into an evacuated container to produce a total pressure of 3 atm.

How do the partial pressures of N_2 , NH_3 and N_2O compare?

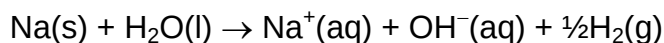
- A $p_{\text{N}_2} = p_{\text{NH}_3} = p_{\text{N}_2\text{O}}$ B $p_{\text{N}_2} < p_{\text{NH}_3} < p_{\text{N}_2\text{O}}$
 C $p_{\text{NH}_3} < p_{\text{N}_2} < p_{\text{N}_2\text{O}}$ D $p_{\text{N}_2\text{O}} < p_{\text{N}_2} < p_{\text{NH}_3}$

- 7 Use of the Data Booklet is relevant to this question.

The enthalpy changes for three reactions are given below:

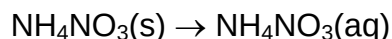


What is the enthalpy change for the following reaction?



- A -191 kJ mol^{-1}
 B -307 kJ mol^{-1}
 C -685 kJ mol^{-1}
 D $-1041 \text{ kJ mol}^{-1}$

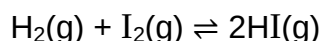
- 8 The dissolution of ammonium nitrate is a chemical reaction commonly used in cold packs that serve to relieve pain in sports injury. A thin plastic membrane separates powdered ammonium nitrate and water. When the cold pack is squeezed, the membrane breaks and the ammonium nitrate dissolves in water.



What are the signs of ΔH , ΔS , ΔG for the overall process?

	ΔH	ΔS	ΔG
A	–	–	+
B	–	+	–
C	+	+	–
D	+	+	+

- 9 Hydrogen reacts with iodine according to the equation:



P atm of hydrogen is allowed to react with Q atm of iodine at constant temperature.

At equilibrium, it is found that

- A** the partial pressure of hydrogen is greater than P .
 - B** the total pressure of the system is $(P + Q)$ atm.
 - C** the total pressure of the system is greater than $(P + Q)$ atm.
 - D** the total pressure of the system is less than $(P + Q)$ atm.
- 10 When 10 cm^3 of 0.02 mol dm^{-3} aqueous $\text{Ba}(\text{OH})_2$ is added to separate solutions of 10 cm^3 of 0.1 mol dm^{-3} MgCl_2 and 10 cm^3 of 0.1 mol dm^{-3} CaCl_2 , what would be observed?
- (K_{sp} of $\text{Mg}(\text{OH})_2 = 3.2 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$; K_{sp} of $\text{Ca}(\text{OH})_2 = 1.35 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$)
- A** Only $\text{Ca}(\text{OH})_2$ would be precipitated.
 - B** Only $\text{Mg}(\text{OH})_2$ would be precipitated.
 - C** Both $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ would be precipitated.
 - D** Neither $\text{Mg}(\text{OH})_2$ nor $\text{Ca}(\text{OH})_2$ would be precipitated.

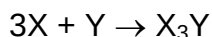
- 11** The auto-ionisation of water is represented by the following equation:



Given that the value of the equilibrium constant, K_w , is $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K, which of the following statements is true?

- A** Water is not a neutral liquid at a temperature lower than 298 K.
- B** When water is heated, the concentration of OH^- increases.
- C** The pH of water at temperatures higher than 298 K is greater than 7.
- D** The association of water molecules by hydrogen bonding increases as temperature rises.

- 12** Consider the following reaction:



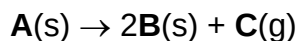
The mechanism involves the following steps:



Based on the information, what is the rate equation for this reaction?

A Rate = $k[\text{X}]^2$	B Rate = $k[\text{X}_2][\text{Y}]$
C Rate = $k[\text{X}]^2[\text{Y}]$	D Rate = $[\text{X}]^3[\text{Y}]$

- 13** The decomposition of compound **A** is a first order reaction which proceeds according to the equation:



A sample of **A** gave 80 cm^3 of **C** on complete decomposition and it took 40 min for 40 cm^3 of **C** to be evolved.

For another identical sample of **A**, how long would it take for 70 cm^3 of **C** to be evolved?

A 40 min	B 70 min
C 80 min	D 120 min

- 14** The Daniell Cell comprises two half-cells – a copper electrode dipped in copper(II) sulfate solution and a zinc electrode dipped in zinc sulfate solution – linked by a salt bridge.

Which of the following will increase the cell e.m.f. of the Daniell Cell?

- A** Adding solid copper(II) sulfate to the copper half-cell.
- B** Increasing the mass of copper electrode.
- C** Increasing the concentration of the zinc sulfate solution.
- D** Allow the system to reach equilibrium before measuring cell e.m.f.

- 15** Two separate electrolyses were performed as follows, under the same conditions of temperature and pressure.

1. When aqueous hydrochloric acid was electrolysed for five minutes, 100 cm^3 of hydrogen were collected from the cathode.
2. When aqueous sulfuric acid was electrolysed for five minutes, 200 cm^3 of oxygen were collected from the anode.

If the current used in electrolysis 1 was I , what was the current used in electrolysis 2?

- A** $4I$ **B** $2I$ **C** I **D** $0.5I$

- 16** Which of the following is a trend across Period 3 of the Periodic Table?

- A** The radii of ions decrease.
- B** The first ionisation energy decreases.
- C** The melting points of elements decrease.
- D** The compounds of elements become increasingly covalent.

17 Which of the following equations represents the reaction when calcium nitrate is heated strongly?

- A $\text{Ca}(\text{NO}_3)_2 \rightarrow \text{CaO} + \text{N}_2\text{O}_5$
B $\text{Ca}(\text{NO}_3)_2 \rightarrow \text{Ca}(\text{NO}_2)_2 + \text{O}_2$
C $2\text{Ca}(\text{NO}_3)_2 \rightarrow 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$
D $3\text{Ca}(\text{NO}_3)_2 \rightarrow \text{Ca}_3\text{N}_2 + 4\text{NO}_2 + 5\text{O}_2$

18 *Use of the Data Booklet is relevant to this question.*

Which of the following solutions of halide will **not** change the colour of acidified potassium dichromate(VI) ?

- A chloride B bromide C iodide D astatide

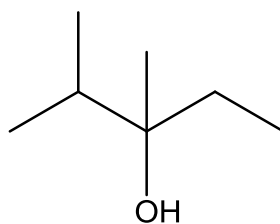
19 Which statement correctly **defines** a transition element?

- A Transition elements exhibit more than one oxidation state in their compounds.
B Transition elements or their compounds are widely used as catalysts.
C Transition elements form many coloured compounds.
D Transition elements have partially filled d orbitals.

20 Which of the following compounds **cannot** be obtained from propene in a single reaction?

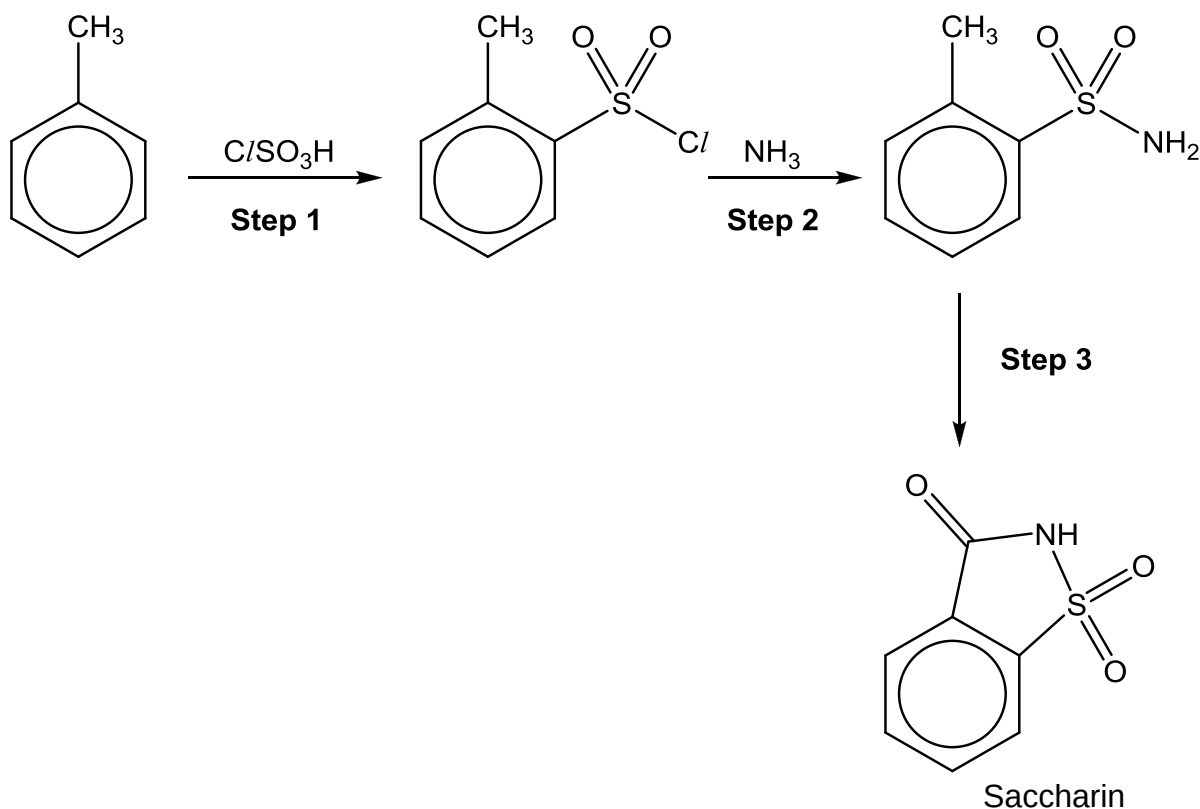
- A CO_2 B $\text{CH}_3\text{CH}_2\text{CH}_3$
C $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ D $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_3$

- 21 How many alkenes (including stereoisomers) can be formed when the following alcohol is heated with concentrated sulfuric acid?



- A 0 B 2 C 3 D 4

- 22 Saccharin, an artificial sweetening agent, can be synthesized from methylbenzene using the following reaction scheme:



What type of reactions do steps 1 and 2 illustrate?

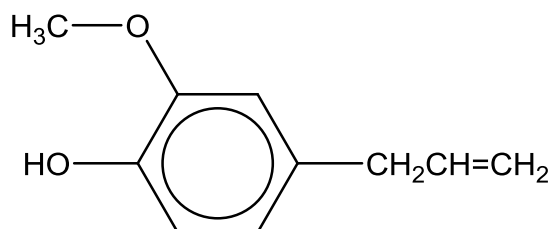
	Step 1	Step 2
A	Electrophilic substitution	Condensation
B	Electrophilic substitution	Nucleophilic Addition
C	Nucleophilic substitution	Condensation
D	Nucleophilic substitution	Nucleophilic Addition

23 Fluothane, CF_3CHBrCl , is a volatile liquid widely used as an anaesthetic.

Which of the following statements about fluothane is **not** correct?

- A** Fluothane may cause the depletion of the ozone layer.
- B** Weak van der Waals' forces hold molecules of fluothane together.
- C** Fluothane undergoes elimination when treated with hot ethanolic NaOH .
- D** When a sample of fluothane is heated with aqueous silver nitrate, a mixture of white and cream precipitate is formed.

24 Eugenol is a common component of perfumes and essential oils. It is also used as an antiseptic.



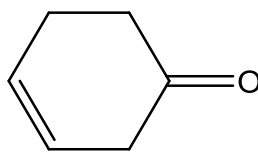
eugenol

(You may treat the $-\text{OCH}_3$ group attached to the benzene ring as inert.)

Which of the following statements about eugenol is correct?

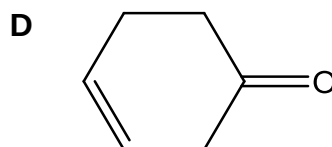
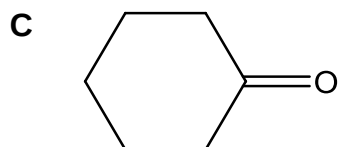
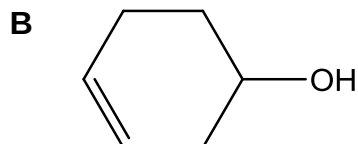
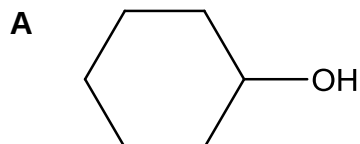
- A** It reacts with 2,4-DNPH to give an orange precipitate.
- B** It gives white fumes when reacted with thionyl chloride.
- C** It decolourises hot acidified potassium manganate(VII).
- D** It reacts with 2 moles of Br_2 in a suitable solvent to form a product with 4 bromine atoms incorporated.

- 25 Cyclohex-3-en-1-one has the following structure:



cyclohex-3-en-1-one

Which of the following compounds is formed when cyclohex-3-en-1-one is reacted with NaBH_4 dissolved in an organic solvent?



- 26 Compound **J** gives the following observations with Tollens' Reagent and $\text{Na}_2\text{CO}_3(\text{aq})$.

Reagent	Observation
Tollens' Reagent	Silver mirror observed
$\text{Na}_2\text{CO}_3(\text{aq})$	No effervescence observed

From the above observations, what could be a possible structure for **J**?

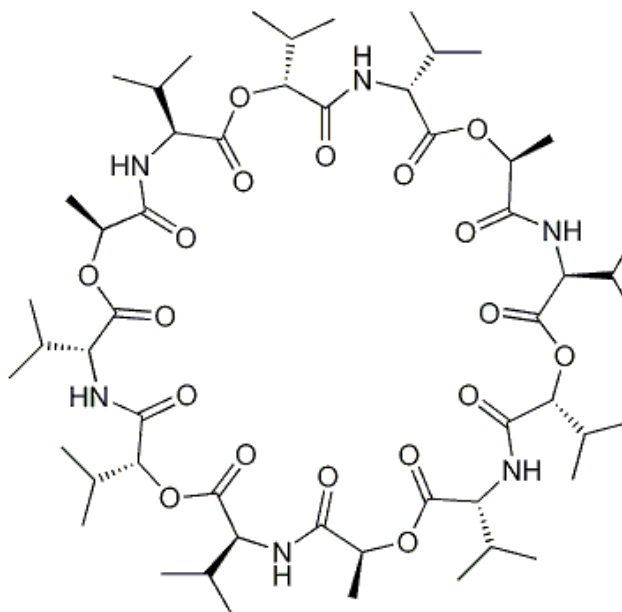
- A** $(\text{COOH})_2$
B CH_3COCHO
C CH_3COCOOH
D $\text{CH}_3\text{COCOCH}_3$

- 27** In the study of organic reaction mechanisms, radioactive oxygen-18, ^{18}O , is often used to tag organic molecules. The radioactivity of the products can then be detected to deduce which products contain ^{18}O .

When ^{18}O -tagged propan-1-ol is heated with ethanoic acid in the presence of a small amount of concentrated sulfuric acid, which of the following set of products will be obtained?

- A** $\text{CH}_3\text{CH}_2\text{CH}_2^{18}\text{OCOCH}_3$ and H_2O
- B** $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCOCH}_3$ and H_2^{18}O
- C** $\text{CH}_3\text{CH}_2\text{CH}_2^{18}\text{OCOCH}_3$ and H_2^{18}O
- D** $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCOCH}_3$ and H_2O
- 28** Which of the following correctly shows the compounds arranged in decreasing $\text{p}K_{\text{a}}$ values?
- A** $\text{CH}_2\text{FCOOH} > \text{CH}_2\text{ClCOOH} > \text{CH}_2\text{BrCOOH}$
- B** $\text{CH}_3\text{COOH} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{OH}$
- C** $\text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{CH}_2\text{ClCOOH}$
- D** $\text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{COOH}$

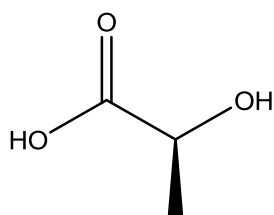
- 29 Valinomycin is a peptide-like molecule that disrupts plasma membrane formation in bacteria.



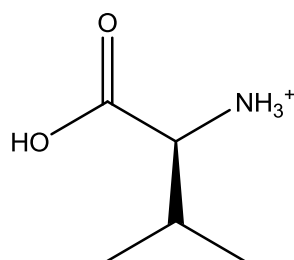
valinomycin

Which of the following will **not** be produced when valinomycin is heated with dilute $\text{H}_2\text{SO}_4(\text{aq})$ for a period of time?

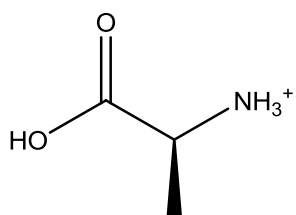
A



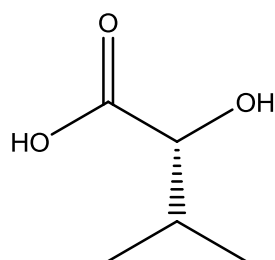
B



C



D



- 30** Denaturation of proteins occurs due to the destruction of the tertiary structure where various R group interactions are disrupted by external factors.

Which of the following correctly shows the R group interactions that will be affected by the corresponding external factor?

	R group interactions	External factor
A	disulfide bridges	extreme pH changes
B	ionic interactions	addition of alcohol
C	van der Waals' forces	addition of heavy metal ions
D	hydrogen bonding	extreme pH changes

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Which statements about aluminium are correct?

- 1** It forms amphoteric oxides.
- 2** It forms an ionic compound with oxygen.
- 3** It forms an ionic compound with chlorine.

32 Between ethanol molecules, there exists

- 1** hydrogen bonds.
- 2** instantaneous dipole-induced dipole interactions.
- 3** covalent bonds.

33 For a first order reaction, which of the following graphs will be a straight line passing through the origin?

- 1** Initial rate vs concentration of reactant
- 2** Initial rate vs time taken for complete reaction
- 3** Concentration of reactant vs time taken for complete reaction

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

34 Which statements correctly describe an electrolytic cell?

- 1 It is driven by an external battery.
- 2 The polarities of the cathode and anode are negative and positive respectively.
- 3 It is used to extract unreactive metals from the ores.

35 Which of the following statements are true for astatine, the element below iodine in Group VII of the Periodic Table?

- 1 Silver astatide is insoluble in concentrated aqueous ammonia.
- 2 Astatine oxidises potassium chloride to chlorine.
- 3 Hydrogen astatide is more stable to heat than hydrogen iodide.

36 When placed in a strong magnetic field, paramagnetic objects are attracted to the field. Paramagnetism arises when an element has unpaired electrons.

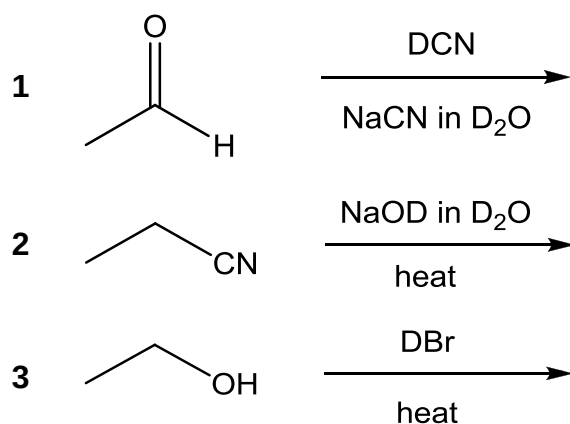
Which of the following chemical species would you expect to exhibit paramagnetism?

- 1 Cr
- 2 Mn
- 3 Cu^+

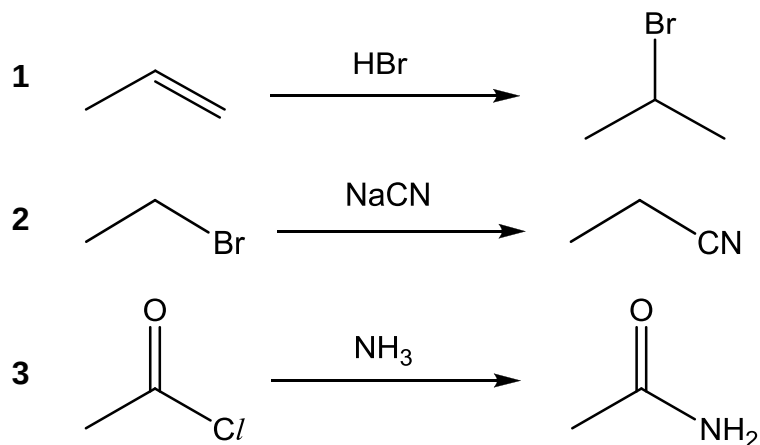
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

37 Deuterium, D, is the ^2H isotope of hydrogen.

Which of the following reactions could give an organic compound having a deuterium atom incorporated?

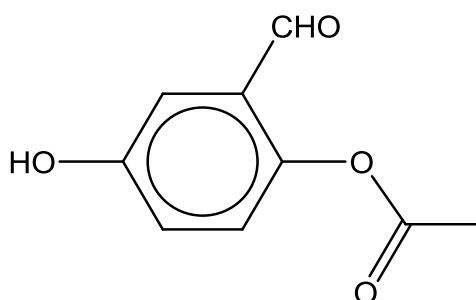


38 In which of the following reactions will the inorganic reagent act as the nucleophile?



A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

39 Compound X is a flavouring agent in food.



X

Which of the following reagents will cause a colour change when the reagent is added to a sample of compound X?

- 1 aqueous bromine
- 2 neutral iron(III) chloride solution
- 3 hot acidified potassium dichromate(VI)

40 Which of the following descriptions about haemoglobin are correct?

- 1 Both O₂ and CO can bind to haemoglobin.
- 2 The quaternary structure of haemoglobin consists of two α -helices and two β -pleated sheets.
- 3 A maximum of six oxygen molecules may be bound to each haemoglobin molecule.

- End of Paper -

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RIVER VALLEY HIGH SCHOOL

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE
NAME

CLASS

6	

CENTRE
NUMBER

S				

INDEX
NUMBER

H2 CHEMISTRY

9647/02

Paper 2 Structured Questions

13 September 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.

Write in dark blue or black pen on both sides of paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.

A Data Booklet is provided. Do NOT write anything on it.

The number of marks is given in brackets [] at the end of each question or part question.

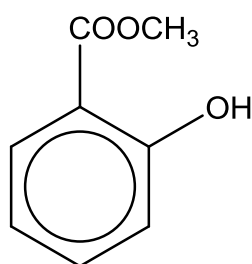
For Examiner's Use								
Paper 2								
Question Number	1	2	3	4	5	6		Total (Paper 2)
Marks	12	13	8	9	16	14		72
Paper 1	40		Paper 3		80	Total		192

This document consists of **18** printed pages and **2** blank pages.

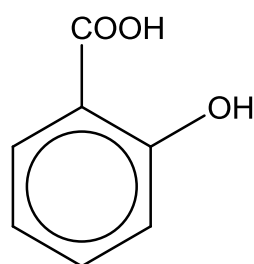
1 Planning (P)

Salicylic acid is known for its ability to ease aches and pains as well as reduce fevers. Its analgesic and anti-inflammatory properties makes it one of the most important medications needed in a basic health system, placing it on the World Health Organisation Model List of Essential Medicines.

It can be synthesised via the alkaline hydrolysis of methyl salicylate, followed by acidification.



methyl salicylate
($M_r = 152$)



salicylic acid
($M_r = 138$)

Methyl salicylate is a liquid with a density of 1.174 g cm^{-3} .

Aqueous sodium hydroxide used for the hydrolysis has a concentration of 6.0 mol dm^{-3} .

Like most organic reactions, the yield of this reaction is less than 100%. Using the procedure described below, a typical yield of pure salicylic acid is 60%.

Methyl salicylate is mixed with aqueous sodium hydroxide in a molar ratio of 1:2. The reaction is heated under reflux conditions for around 30 minutes to form a di-sodium salicylate salt.

When the reaction mixture has cooled down, concentrated hydrochloric acid is added until in excess to cause the crude salicylic acid to precipitate. This process is highly exothermic.

The crude salicylic acid is then purified by recrystallisation from water.

(a) Using the information given above:

- (i) write a balanced equation for the formation of the di-sodium salicylate salt;

[1]

- (ii) calculate the volumes of methyl salicylate and aqueous sodium hydroxide you would use to prepare 10 g of pure salicylic acid, showing your working.

[2]

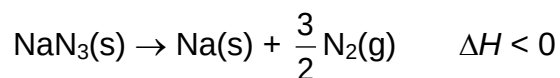
- (b) Write a plan for the preparation of 10 g of pure salicylic acid.

In your plan, you should:

- draw a diagram of the assembled apparatus you would use when heating the reaction mixture;
- give a full description of the procedures, including the capacities of the apparatus involved, you would use to prepare and purify the salicylic acid;
- explain how you would minimise a potential safety hazard.

[Total: 12]

- 2 Sodium azide is a chemical found in car safety airbags. When the car undergoes a head-on collision, a series of chemical reactions occur in the gas generator chamber. The first reaction produces nitrogen gas to fill the airbag. The equation for the reaction is shown below:



- (a) The volume of a fully inflated airbag is 60 dm^3 .
Calculate the mass of NaN_3 needed to fill such an airbag to an internal pressure of 150 kPa at 300°C .

[2]

- (b) (i) Given that $\Delta S_r = S(\text{products}) - S(\text{reactants})$ and the following information, calculate ΔS for the above reaction.

Molar entropy of $\text{NaN}_3(\text{s})$	$70.5 \text{ J mol}^{-1} \text{ K}^{-1}$
Molar entropy of $\text{Na}(\text{s})$	$51.3 \text{ J mol}^{-1} \text{ K}^{-1}$
Molar entropy of $\text{N}_2(\text{g})$	$191.6 \text{ J mol}^{-1} \text{ K}^{-1}$

[1]

- (ii) Explain why the reaction is feasible at all temperatures.

.....

[1]

- (iii) Suggest why the reaction in fact occurs only at temperatures above 300 °C.

.....

[1]

- (c) Sodium metal formed in the above reaction is very reactive and is made to react with potassium nitrate present in the airbag, forming sodium oxide as one of the products.

- (i) Explain what is meant by the lattice energy of sodium oxide.

.....

[1]

- (ii) Using the information given below and relevant information from the Data Booklet, construct an energy level diagram to calculate the lattice energy of sodium oxide.

Enthalpy change of formation of sodium oxide = -416 kJ mol^{-1}

Enthalpy change of atomisation of sodium = $+107 \text{ kJ mol}^{-1}$

Sum of 1st and 2nd electron affinity of oxygen = $+702 \text{ kJ mol}^{-1}$

[3]

- (iii) Given that the 1st electron affinity of oxygen is -142 kJ mol^{-1} , calculate the 2nd electron affinity of oxygen and explain the significance of its sign.

.....

.....

.....

.....

[2]

- (d) A working airbag should become fully inflated within 0.04 s of the initial collision. At this point, it is actually unsafe for the driver's body to hit the inflated airbag due to the high internal pressure (150 kPa). The airbag is hence designed to deflate immediately such that by the time the driver's body hit the airbag, usually 2 s after the initial collision, the internal pressure of the airbag would have dropped to 101 kPa, providing a softer cushioning for the driver.

An airbag at a safety test has a depressurisation rate of 23 kPa s^{-1} .

Explain if this airbag is safe for use, showing relevant calculations.

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.....

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.....

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[2]

[Total: 13]

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- 3 (a) What do you understand by the term standard electrode potential?

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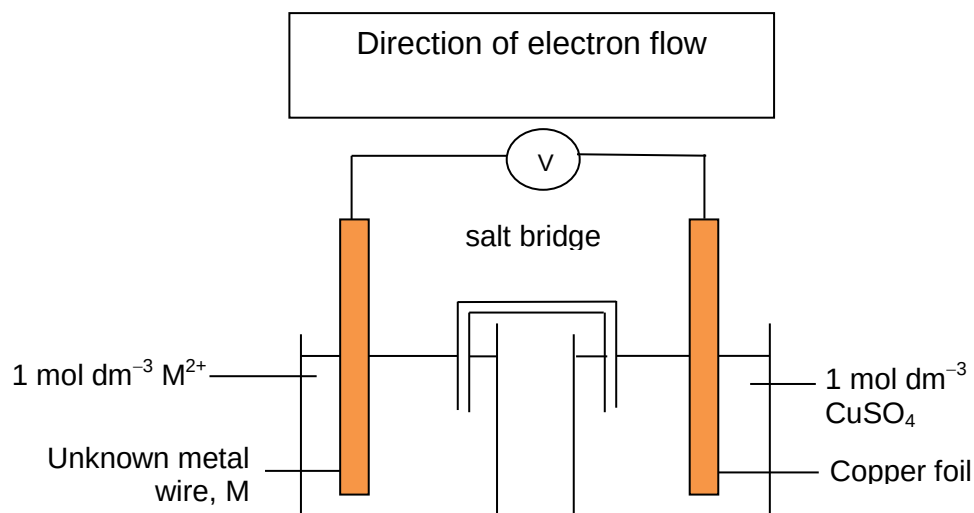
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[2]

- (b) The following cell was set up between a copper electrode and an unknown metal electrode $M^{2+}(aq)/M(s)$. The standard cell potential was found to be 0.76 V, and the copper foil was connected to the positive end of the voltmeter.



- (i) Use the Data Booklet to calculate the standard electrode potential of the $M^{2+}(aq)/M(s)$ system.

.....

.....

.....

.....

[1]

- (ii) Draw an arrow in the box above to show the direction of electron flow through the voltmeter.

[1]

- (iii) Predict the outcomes of the following situations. Describe what you will see and write ionic equations, with state symbols, for any reactions that occur.

I A rod of metal M is dipped into a solution of $1 \text{ mol dm}^{-3} \text{ CuSO}_4$.

.....
.....
..... [2]

II Dilute sulfuric acid is added into a beaker containing a powdered sample of metal M.

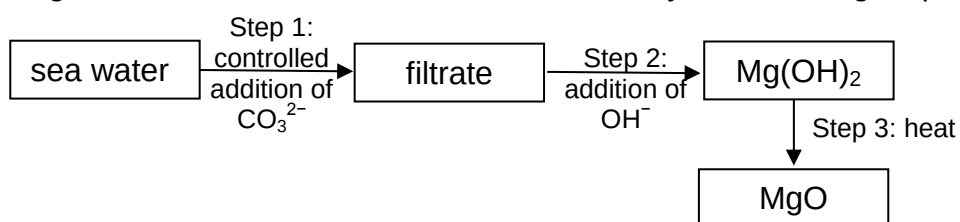
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..... [2]

[Total: 8]

- 4 The four most abundant salts in sea-water are as follows.

Salt	kg per m ³
Sodium chloride	27.5
Magnesium chloride	6.75
Magnesium sulfate	5.625
Calcium sulfate	1.80

Magnesium oxide is obtained from sea-water by the following steps.



The relevant numerical values of the solubility products are given below.

Salt	K_{sp}
Sodium carbonate	-
Calcium carbonate	5.0×10^{-9}
Magnesium carbonate	1.0×10^{-5}
Magnesium hydroxide	1.5×10^{-11}
Calcium hydroxide	7.9×10^{-6}

- (a) Explain why the addition of carbonate ions in Step 1 is necessary and has to be controlled.

.....

.....

.....

.....

.....

[2]

- (b) Suggest why the K_{sp} value of sodium carbonate is not provided.

.....
.....

[1]

- (c) Using the reaction scheme above, Barny used 1 dm^3 of sea water to extract magnesium oxide.

- (i) Calculate the concentration of Mg^{2+} in sea water.

[2]

- (ii) Barny chose a pH of 9.5 to carry out the extraction of $\text{Mg}(\text{OH})_2$.
Calculate the maximum mass of **magnesium oxide** that can be obtained at pH 9.5.
You may assume that negligible volumes of CO_3^{2-} and OH^- were used.

[3]

- (iii) Suggest how Barny can modify his experiment to improve on the yield of MgO ?

.....
.....

[1]

[Total: 9]

- 5 (a) In the periodic table, elements can exhibit either single or variable oxidation states. One example of an element which can exhibit variable oxidation state is manganese, Mn, while aluminium, Al is an example of an element which cannot exhibit variable oxidation state.

(i) Draw a dot and cross diagram for aluminium chloride, AlCl_3 .

[1]

- (ii) In the vapour state, the M_r of aluminium chloride was found to be 267. However, when aluminium chloride is in the solid state, its M_r was found to be 133.5.

With the aid of suitable diagram, explain this behaviour exhibited by aluminium chloride and the type of bonding involved.

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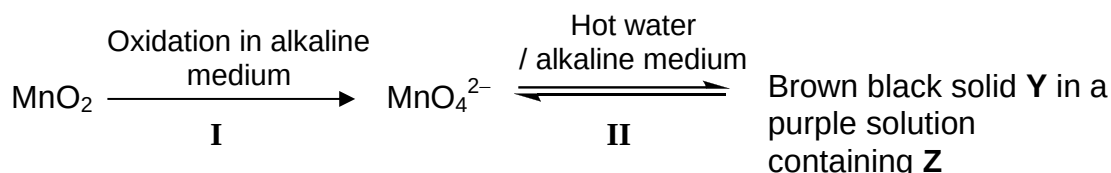
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[3]

- (b) Manganese is often found in minerals in combination with iron and is a metal with important industrial metal alloy uses, particularly in stainless steels. Manganese is found in various black minerals known as pyrolusite. Pyrolusite consists mainly of manganese(IV) oxide. Manganese(IV) oxide is the most common starting material for the production of compounds of manganese in other oxidation states.

Manganese(IV) oxide undergoes a 2-step reaction to produce Y and Z.



- (i) Define the term *transition element*.

.....

[1]

- (ii) Write the electronic configuration of Mn.

.....

[1]

- (iii) Explain why manganese can exhibit variable oxidation state.

.....

[1]

- (iv) The brown black solid Y contains 63.8% by mass of manganese and 36.2% by mass oxygen.

Determine the empirical formula of Y.

[1]

- (v) Suggest the identity of **Z** and state the type of reaction that occurs at step II.

Hence, construct a balanced equation for the reaction.

.....

 [3]

- (vi) With reference to your answer in (v), suggest how bubbling carbon dioxide gas into the hot solution of MnO_4^{2-} increases the yield of **Y** and **Z**.

.....

 [2]

- (c) Manganese(II) carbonate, MnCO_3 , undergoes thermal decomposition in a similar way to a Group II carbonate.

MnCO_3 decomposes at 200 °C while CaCO_3 decomposes at 840 °C.

- (i) Write an equation, with state symbols, for the thermal decomposition of MnCO_3 .

..... [1]

- (ii) Explain why MnCO_3 decompose at a lower temperature than CaCO_3 .

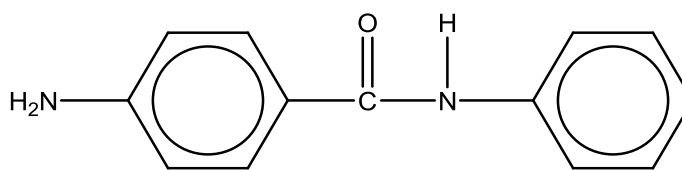
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 [2]

[Total: 16]

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- 6 (a) 4-Amino-N-phenylbenzamide, the structure of which is drawn below, is used in the treatment of epilepsy.



4-amino-N-phenylbenzamide

- (i) 4-Amino-N-phenylbenzamide is hydrolysed by warm aqueous sodium hydroxide. Draw the displayed formulae of the two hydrolysis products below.



A



B

[2]

- (ii) Which of the two hydrolysis product **A** & **B** is a liquid?

..... [1]

- (iii) When the other product is carefully neutralised with an aqueous mineral acid to pH 7, **C** is obtained.

Draw the structure of **C**.

[1]

- (iv) Upon evaporation of all the solvent from the solution of **C**, a white solid is obtained.

Suggest a physical property of the solid.

..... [1]

- (b) State the reagents and conditions required for the conversion of benzene into phenylamine in two steps. In your answer, identify the structure of the intermediate.

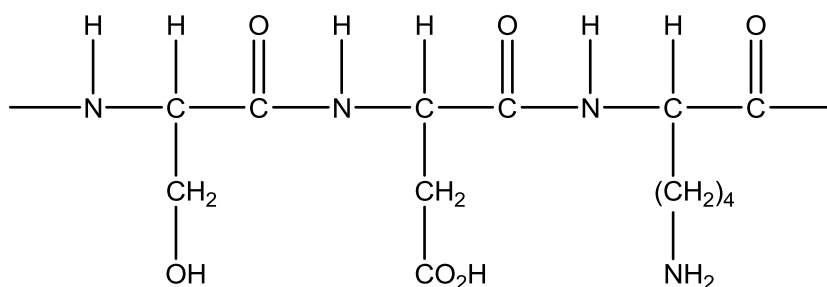
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[3]

- (c) The following structure shows part of a protein molecule.



- (i) Using suitable diagrams, describe **two** interactions that the protein fragment above can exhibit in its tertiary structure

[3]

- (ii) In solution, amino acids exist as zwitterions. Choose one of the amino acids that can be hydrolysed from the protein molecule above to illustrate what is meant by this term.

[1]

- (iii) Amino acids act as buffers in solution. By means of equations, show how your chosen amino acid can act as a buffer when:

(I) dilute hydrochloric acid is added to its solution;

[1]

(II) dilute sodium hydroxide is added to its solution.

[1]

[Total: 14]

– End of Paper –



RIVER VALLEY HIGH SCHOOL

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE
NAME

CLASS

6	

CENTRE
NUMBER

S				

INDEX
NUMBER

H2 CHEMISTRY

9647/03

Paper 3 Free Response

21 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper

Cover Page

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.

Write in dark blue or black pen on both sides of paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything on it.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together, with the cover page on top.

This document consists of **10** printed pages and **2** blank pages.

Answer any **four** questions.

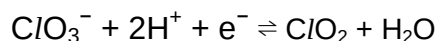
- 1** Many compounds of chlorine are manufactured from brine, NaCl(aq) . The electrolysis of brine produces $\text{Cl}_2(\text{g})$ and NaOH(aq) . In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction depend on the operating conditions used.

(a) Write balanced equations for the reaction between $\text{Cl}_2(\text{g})$ and

(i) cold aqueous NaOH ; [1]

(ii) hot aqueous NaOH . [1]

(b) Chlorine dioxide, ClO_2 , is used in the treatment of water. It is formed from ClO_3^- ions in an acidic solution.



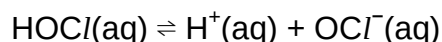
(i) Draw the dot-and-cross diagrams of ClO_2 and H_2O_2 .

You may assume that there is no dative bond in either compound. [2]

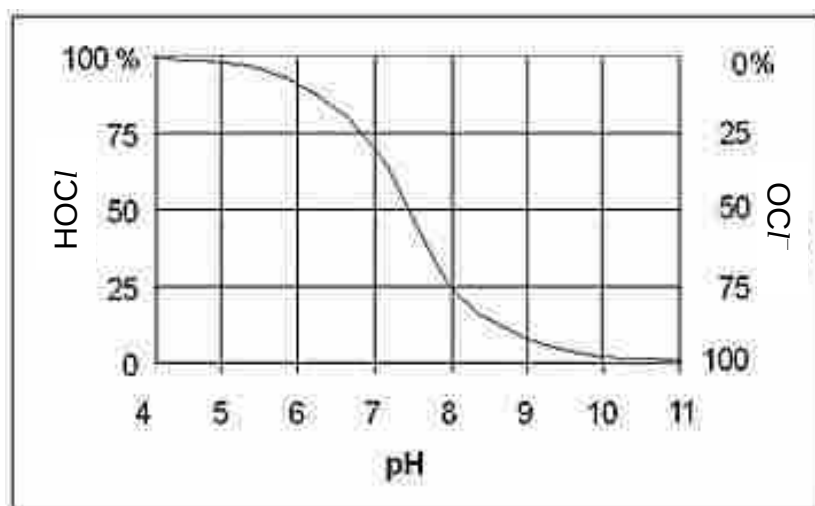
(ii) Construct the overall equation for the reaction of ClO_3^- ions with H_2O_2 in acidic solution. [1]

(iii) What is the role of H_2O_2 in the reaction? [1]

(c) Chlorine can also be used to disinfect water. When chlorine is added to water, it produces hypochlorous acid, HOCl . Hypochlorous acid is a weak acid that dissociates into hypochlorite ions, OCl^- , according to the following equation.



Free chlorine refers to the total chlorine content in HOCl and OCl^- . The dissociation curve below illustrates the ratio of hypochlorous acid to hypochlorite at different pH values.

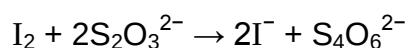


[Source: www.hach.com]

(i) Determine the pK_a of hypochlorous acid. [1]

(ii) Hence, calculate the pH of a $0.0025 \text{ mol dm}^{-3}$ hypochlorous acid solution. [2]

To determine whether the free chlorine in a sample of tap water meets the regulatory limit (4 mg Cl per litre), OCl^- is quantitatively reduced to Cl^- by I^- ions, which is in turn oxidised to I_2 . The I_2 is titrated with standard sodium thiosulfate. The following reaction takes place during the titration.



(iii) Construct a balanced equation between $OCl^-(aq)$ and acidified $KI(aq)$. [1]

(iv) When 2 dm^3 of tap water was tested, 6.0 cm^3 of $0.00455 \text{ mol dm}^{-3}$ sodium thiosulfate was required to discharge the colour of iodine. Calculate the concentration of OCl^- in the sample of water. [2]

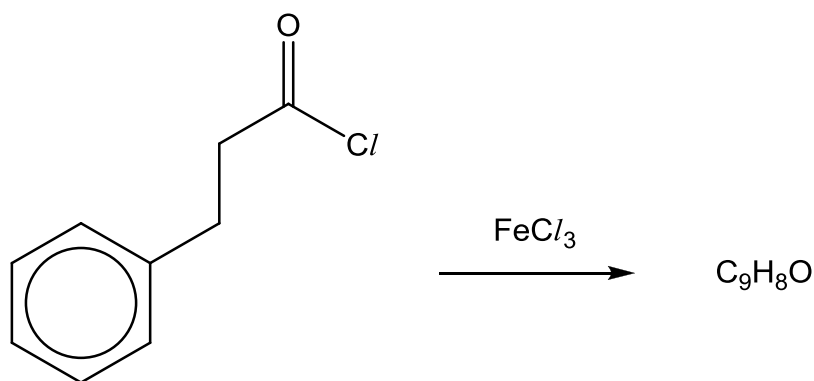
(v) Suggest why the calculated concentration of OCl^- has the same value as the concentration of *free* chlorine. [2]

(vi) Determine if the sample of tap water is safe for consumption. [2]

(d) Chlorine is also used in organic chemistry to produce the Lewis acid catalyst, $FeCl_3$, for the reaction between methylbenzene and chlorine.

(i) Describe the mechanism of the above reaction. [3]

(ii) $FeCl_3$ reacts in a similar way with acyl chlorides. Predict the structure of the product of the following reaction.



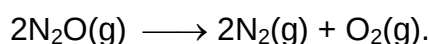
[Total: 20]

- 2 (a) Nitrous oxide or dinitrogen oxide, N_2O , is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anesthetic and analgesic effects. To produce N_2O , ammonium nitrate is decomposed at 170°C . Water is a by-product of this reaction.

(i) Write an equation for the production of dinitrogen oxide from ammonium nitrate. [1]

(ii) In the manufacturing of N_2O gas, 1 kg of N_2O gas is produced for every 2.1 kg of ammonium nitrate used. Determine the percentage yield of dinitrogen oxide. [2]

- (b) At 1200 K, in the presence of gold wire, dinitrogen oxide decomposes as shown:



To follow the rate of reaction, the change in concentration of a sample of N_2O is measure against time. The results are shown below:

Time, t / s	Concentration of $\text{N}_2\text{O} / \times 10^{-3} \text{ mol dm}^{-3}$
0	2.50
1000	2.01
2000	1.62
3000	1.31
4000	1.05
5000	0.85
6000	0.68
7000	0.55

(i) What do you understand by the term *half-life* of N_2O ? [1]

(ii) Plot the above data on a graph paper.

Use the following scale:

- 2 cm to represent 1000 s on the x-axis; and
- 2 cm to represent to represent $0.25 \times 10^{-3} \text{ mol dm}^{-3}$ on the y-axis.

(iii) From your graph, deduce the order of the reaction with respect to N_2O . [2]

- (iv) Calculate the rate constant for the reaction and state its units. [2]
- (v) The gold wire acts as a *heterogeneous catalyst* in this reaction.

Explain the terms *in italics* and outline the mode of action of the catalyst. [3]

- (c) Alkenes react with carbenes $R_2C:$ to yield cyclopropanes.

One way to generate a substituted carbene is by reacting chloroform, $CHCl_3$, with a strong base.

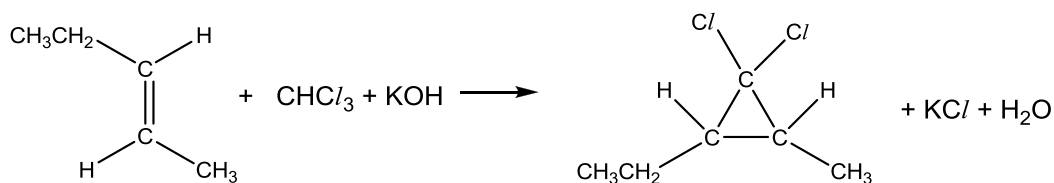
The mechanism to generate a carbene is described below.

- Potassium hydroxide, KOH, removes the proton from $CHCl_3$, leaving behind the electron pair. An anionic intermediate is formed.
- Cl^- is lost and a neutral dichlorocarbene is formed.

- (i) Based on the description above, draw a mechanism to show the generation of dichlorocarbene.

Show relevant lone pairs and use curly arrows to indicate the movement of electron pairs. [3]

An example of a reaction between an alkene and a carbene is as shown:



- (ii) Suggest the structure of the product formed when cyclohexene reacts with chloroform in the presence of KOH. [1]
- (iii) Suggest the role of carbene in its reaction with an alkene. Explain your answer. [2]
- (iv) Suggest the type of reaction when carbene reacts with an alkene. [1]

[Total: 20]

3 Copper is a rare element, constituting only 6.8×10^{-3} percent of the Earth's

crust by mass. However, it has a wide range of uses such as in alloys, plumbing and in electrical cables. The common oxidation states of copper are +2 and +1.

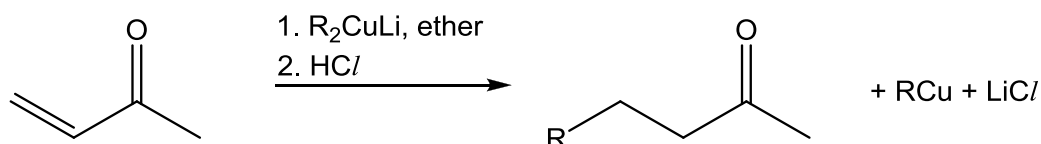
- (a) Copper can be obtained by roasting a copper ore, CuFeS_2 , to give Cu_2S , which is further oxidised to form metallic copper. This impure copper can be purified by electrolysis.
- (i) Draw a diagram to illustrate the electrolytic cell used in the purification of copper, using $\text{CuSO}_4(\text{aq})$ as the electrolyte. [2]
 - (ii) If a current of 0.8 A was passed through the cell, calculate the time required for 0.25 g of pure copper to be collected. [2]
- (b) Anhydrous copper(II) sulfate, $\text{CuSO}_4(\text{s})$, is a white powder. It dissolves in water to form a pale blue solution.
- (i) State the species responsible for the pale blue colour of the solution. [1]
 - (ii) Explain why the solution is pale blue in colour. [3]
 - (iii) Describe the colour changes observed when the following solutions are added to the pale blue solution, giving the formulae of all relevant species. [4]
 - I. Dilute $\text{NH}_3(\text{aq})$, until in excess;
 - II. $\text{KI}(\text{aq})$.
- (c) When Na_2CO_3 is added to a solution of CuSO_4 and the resultant mixture is filtered, a green solid, cupric carbonate, is obtained. The formula of this solid is $\text{Cu}_2(\text{OH})_a(\text{CO}_3)_b$.
 0.10 mol of $\text{Cu}_2(\text{OH})_a(\text{CO}_3)_b$ required 0.40 mol of hydrochloric acid for complete reaction. The products of this reaction include copper(II) chloride, carbon dioxide and water.
- (i) Given that 2.4 dm^3 of CO_2 was formed at room temperature and pressure, determine the values of **a** and **b**. [2]
 - (ii) Hence, write an equation for the reaction of cupric carbonate with hydrochloric acid. [1]

(d) Cu_2O , a brick red solid, is a compound where copper is in the oxidation

state of +1. It can be formed by reacting an alkaline solution of complexed Cu^{2+} with a particular organic functional group.

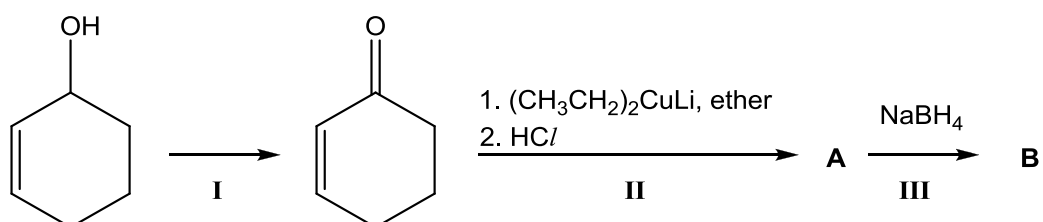
- (i) State the functional group that will produce Cu_2O with the alkaline solution of complexed Cu^{2+} . [1]
- (ii) Name the type of reaction undergone by the functional group in (i). [1]
- (e) Organocopper compounds are useful reagents in organic synthesis. One such class of compounds is the Gilman reagents, with the general formula R_2CuLi , where R represents an alkyl group.

Gilman reagents are effective nucleophiles used in conjugate addition reactions. Conjugate addition involves the addition of a nucleophile across a $\text{C}=\text{C}$ bond instead of across a $\text{C}=\text{O}$ bond. This is illustrated in the example below:



The Gilman reagent can be seen as providing the “ R^- ” nucleophile while a mineral acid (e.g. HCl) provides the proton that is added to one of the carbon atoms in the $\text{C}=\text{C}$ bond.

The following synthesis involves a Gilman reagent for one of the steps:



Suggest the reagent and conditions for Step I and the structures of compounds **A** and **B**. [3]

[Total: 20]

- 4 (a) Copper(I) chloride is used as a precursor of a fungicide and a catalyst for a variety of organic reactions. It is sparingly soluble in water.

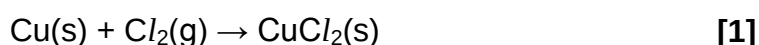
- (i) Define the standard enthalpy change of hydration of an ion. [1]
- (ii) Using the data given in the following table, draw an appropriate energy cycle and calculate the standard enthalpy change of solution for copper(I) chloride. [3]

$\Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+)$	-593 kJ mol^{-1}
$\Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)$	-378 kJ mol^{-1}
Lattice Energy of CuCl	-979 kJ mol^{-1}

- (b) (i) Explain what is meant by the term *entropy* of a chemical system. [1]

Describe and explain how the entropy of the following systems will change during the stated process. Assume the pressure of each system remains at 1 atm throughout.

- (ii) 1 mol of $\text{Cl}_2(\text{g})$ at 298 K is heated to 500 K. [1]
- (iii) 1 mol of $\text{Cl}_2(\text{g})$ at 298 K is reacted with copper according to the following equation. [1]



- (c) Copper(II) ions are pollutants found in water. One method of purification is via precipitation of $\text{Cu}(\text{OH})_2$ and CuS .

	$K_{\text{sp}} (298 \text{ K})$
CuS	6.3×10^{-36}
$\text{Cu}(\text{OH})_2$	2.0×10^{-19}

Using the above data, calculate:

- (i) the minimum concentration of Cu^{2+} for a precipitate of CuS to form in 10 ppm S^{2-} solution;
 (1 ppm = 1 mg dm⁻³) [2]
- (ii) the maximum pH of a solution containing 0.100 mol dm⁻³ Cu^{2+} ions. [3]

- (d) Many organic compounds also contain chlorine. An example would be 1,2-dichlorocyclohexane, which exhibits both geometrical and optical isomerism.

(i) Explain why 1,2-dichlorocyclohexane can exhibit geometrical isomerism. [1]

(ii) The effect of plane polarised light on 1,2-dichlorocyclohexane was investigated. Three different types of 1,2-dichlorocyclohexane was identified:

- Molecule **X** rotated plane polarised light to the left
- Molecule **Y** rotated plane polarised light to the right
- Molecule **Z** had no effect on plane polarised light

Suggest an explanation for these observations. [3]

(e) Compounds **C** and **D** both have the molecular formula C_7H_7Cl . In an experiment, both compounds are separately heated under reflux for some time with aqueous sodium hydroxide. The resulting solutions are cooled and acidified with dilute nitric acid. When aqueous silver nitrate is added subsequently, a white precipitate is formed with **C** while no precipitate is formed with **D**.

Suggest the structures of **C** and **D**. Explain your reasoning for **each** compound. [4]

[Total: 20]

5 (a) The electrical conductivities of some Period 3 elements are shown below.

Element	Na	Mg	Al	P	S	Cl

Electrical conductivity at 298 K / $\times 10^7 \text{ S m}^{-1}$	2.1	2.3	3.5	Non-conductors

(i) With reference to the data above, describe and explain the difference in electrical conductivities of the elements above. [3]

(ii) Silicon carbide (SiC), also known as carborundum and moissanite, is used in abrasive and cutting tools.

Suggest the structure and bonding of SiC. [2]

(b) Chlorides of Period 3 elements dissolve in water to give solutions of varying pH.

Explain the following pH values and write the chemical equations for any reactions that occur:

(i) AlCl_3 dissolves readily in water to form an acidic solution (pH = 3). [3]

(ii) $\text{SiCl}_4(\text{l})$ dissolves in water to form a strongly acidic solution (pH = 2). [2]

(c) Caffeic acid is an organic compound found in all plants as it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass.

Caffeic acid has the molecular formula $\text{C}_9\text{H}_8\text{O}_4$. Caffeic acid reacts with $\text{Br}_2(\text{l})$ to give $\text{C}_9\text{H}_8\text{O}_4\text{Br}_2$. When treated with hot KMnO_4 and H_2SO_4 , caffeic acid reacts to give **F**, $\text{C}_7\text{H}_6\text{O}_4$, and a colourless gas that produces a white solid with $\text{Ca}(\text{OH})_2(\text{aq})$. **F** reacts with PCl_5 to give **G**, $\text{C}_7\text{H}_5\text{O}_3\text{Cl}$, with the production of steamy white fumes. **G** reacts with water to form an acidic solution. When added to neutral $\text{FeCl}_3(\text{aq})$, **G** also forms a violet colouration. **G** reacts with $\text{Br}_2(\text{aq})$ to give **H**, $\text{C}_7\text{H}_3\text{O}_4\text{Br}_3$.

Use the information above to deduce the structures of caffeic acid and compounds **F** to **H**, explaining all the reactions involved. [10]

[Total: 20]

– End of Paper –

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RIVER VALLEY HIGH SCHOOL

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE
NAME

ANSWER KEY

CLASS

6

CENTRE
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4

4

INDEX
NUMBER

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H2 CHEMISTRY

9647/01

Paper 1 Multiple Choice

23 September 2016

1 hour

1.	C	11.	B	21.	D	31.	B
2.	D	12.	C	22.	A	32.	B
3.	D	13.	D	23.	C	33.	D
4.	C	14.	A	24.	C	34.	B
5.	B	15.	A	25.	B	35.	D
6.	D	16.	D	26.	B	36.	B
7.	A	17.	C	27.	A	37.	D
8.	C	18.	A	28.	D	38.	C
9.	B	19.	D	29.	C	39.	A
10.	C	20.	C	30.	D	40.	D



RIVER VALLEY HIGH SCHOOL

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE
NAME

CLASS

6	

CENTRE
NUMBER

S				

INDEX
NUMBER

H2 CHEMISTRY

9647/02

Paper 2 Structured Questions

13 September 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.

Write in dark blue or black pen on both sides of paper.

You may use a soft pencil for any diagrams, graphs or rough working.

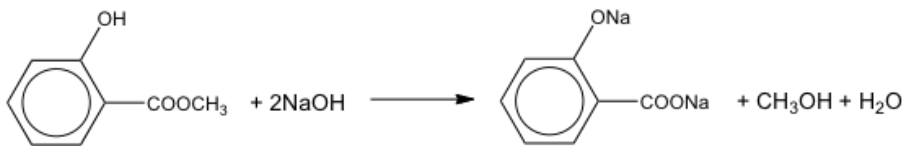
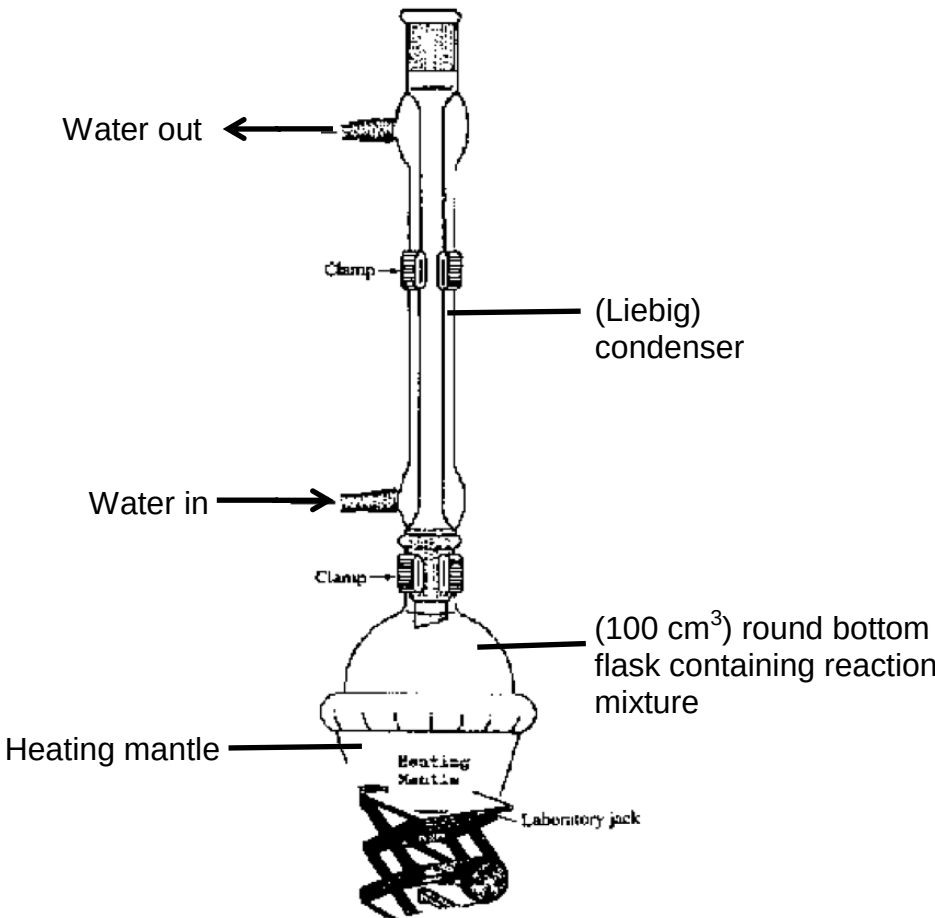
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.

A Data Booklet is provided. Do NOT write anything on it.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use								
Paper 2								
Question Number	1	2	3	4	5	6		Total (Paper 2)
Marks	12	13	8	9	16	14		72
Paper 1	40		Paper 3		80	Total		192

1	(a)	(i)		[1]
		(ii)	Amount of salicylic acid in 10 g = $\frac{10}{138} = 0.0725 \text{ mol}$ Theoretical amount of salicylic acid = $\frac{0.0725}{60} \times 100 = 0.121 \text{ mol}$ Amount of methyl salicylate required = 0.121 mol Mass of methyl salicylate required = $0.121 \times 152 = 18.4 \text{ g}$ Volume of methyl salicylate required = $\frac{18.4}{1.174} = \underline{15.7 \text{ cm}^3}$ Amount of sodium hydroxide required = $0.121 \times 2 = 0.242 \text{ mol}$ Volume of sodium hydroxide required = $\frac{0.242}{6.0} \times 1000$ $= \underline{40.3 \text{ cm}^3}$	[2]
	(b)			

		- Using a <u>25 cm³ measuring cylinder</u>, measure <u>16 cm³</u> (accept up to 20 cm³) of methyl salicylate and place it in a <u>100 cm³ round bottom flask</u>. - Using a <u>50 cm³ measuring cylinder</u>, measure <u>41 cm³</u> (accept up to 50 cm³) of aqueous sodium hydroxide and place it into the 100 cm³ round bottom flask. Add some <u>boiling chips</u> to the mixture. - Set up the reflux set-up shown in the above diagram and heat the mixture for 30 minutes. - Allow the reaction mixture to cool down to room temperature and remove the boiling chips. - Place the round bottom flask in an <u>ice bath</u>. - Add concentrated hydrochloric acid to the reaction mixture slowly, with stirring. - Test the acidity of the mixture with a blue <u>litmus paper</u>. - Filter the mixture and <u>wash</u> the residue (crude salicylic acid) with a <u>small amount of cold water</u>. - Transfer the crude salicylic acid to a <u>clean 100 cm³ conical flask</u>. Add a <u>small volume of water</u> and heat the mixture until all the crude product <u>dissolves</u>. - Filter the hot solution, using a <u>fluted filter paper</u>, into a <u>pre-warmed</u> clean and dry conical flask. Allow the solution to cool down slowly for crystals to form. - When the solution is cooled to room temperature, submerge the conical flask into an <u>ice bath</u> to allow more crystals to form. <u>Filter the mixture</u> to obtain the pure salicylic acid crystals and <u>pat dry</u> the crystals using <u>filter paper</u>.	[9]
			[Total: 12]

2	(a)	$pV = nRT$ $(150 \times 10^3)(60 \times 10^{-3}) = n(8.31)(300 + 273)$ Amount of nitrogen gas = <u>1.89 mol</u> Amount of sodium azide = $\frac{1.89}{3/2} = 1.26 \text{ mol}$ Mass of sodium azide = $1.26 \times 65.0 = \underline{81.9 \text{ g}}$		[2]
	(b)	(i)	$\Delta S = (51.3 + \frac{3}{2} \times 191.6) - 70.5 = \underline{+268.2 \text{ J mol}^{-1} \text{ K}^{-1}}$	[1]
		(ii)	ΔH is negative, ΔS is positive, <u>$-T\Delta S$ is negative</u> . Since $\Delta G = \Delta H - T\Delta S$, <u>ΔG is always negative</u> regardless of temperature.	[1]

		(iii)	The activation energy of the reaction is very high.	[1]
(c)	(i)		Lattice energy of sodium oxide is the enthalpy change when <u>one mole of solid sodium oxide</u> is formed from its <u>constituent gaseous ions Na⁺ and O²⁻</u> .	[1]
	(ii)		Energy / kJ mol⁻¹ $2\text{Na}^+(\text{g}) + \text{O}^{2-}(\text{g})$ $+702$ $2\text{Na}^+(\text{g}) + 2\text{e}^- + \text{O}(\text{g})$ $2(+494)$ $2\text{Na}(\text{g}) + \text{O}(\text{g})$ $2(+107) + \frac{1}{2}(+496)$ 0 $2\text{Na}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$ -416 $\text{Na}_2\text{O}(\text{s})$ LE (Na₂O) $\text{LE (Na}_2\text{O)} = -416 - 2(+107) - \frac{1}{2}(+496) - 2(+494) - (+702)$ $= \underline{-2568 \text{ kJ mol}^{-1}}$	
				[3]
	(iii)		2nd electron affinity = $+702 - (-142) = \underline{+844 \text{ kJ mol}^{-1}}$ The positive sign of 2nd EA means that <u>energy is required to overcome the repulsion between the anion and the electron to be added</u> since both are negatively charged.	[2]
(d)			Safe depressurisation rate = $\frac{(150 - 101)}{2 - 0.04} = 25 \text{ kPa s}^{-1}$ Since the airbag being tested depressurises <u>more slowly</u> than the safe depressurisation rate, it is <u>not safe</u> for use.	[2]
[Total: 13]				

3	(a)	What do you understand by the term standard electrode potential?	
		Standard electrode potential, $E^\ominus$, of an electrode is the <i>relative potential</i> of this electrode under <u>standard conditions compared with the standard hydrogen electrode</u> whose electrode potential is assigned as 0 V. The standard hydrogen electrode consists of <u>$\text{H}_2(\text{g})$ at 1 atm bubbling over platinum electrode coated with finely divided platinum which is dipped into $1 \text{ mol dm}^{-3} \text{H}^+(\text{aq})$ at 298 K.</u>	[2]
	(b)	The following cell was set up between a copper electrode and an unknown metal electrode $\text{M}^{2+}(\text{aq})/\text{M}(\text{s})$. The standard cell potential was found to be 0.76 V, and the copper foil was connected to the positive end of the voltmeter. Direction of electron flow	
	(i)	Use the Data Booklet to calculate the standard electrode potential of the $\text{M}^{2+}(\text{aq})/\text{M}(\text{s})$ system.	
		Since copper is the positive electrode of the galvanic cell, it is the cathode. Standard electrode potential of the $\text{M}^{2+}(\text{aq})/\text{M}(\text{s})$ $= 0.34 - 0.76 = -0.42 \text{ V}$	[1]
	(ii)	Draw an arrow in the box above to show the direction of electron flow through the voltmeter.	
			[1]
	(iii)	Predict the outcomes of the following situations. Describe what you will see and write ionic equations, with state symbols, for any reactions that occur.	

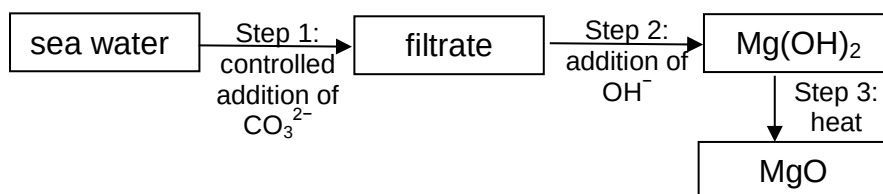
		I	A rod of metal M is dipped into a solution of $1 \text{ mol dm}^{-3} \text{ CuSO}_4$.	
			Metal M dissolves in (blue) solution and pink solid of Cu is formed. (Blue solution lightens in colour.) $\text{M(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Cu(s)} + \text{M}^{2+}(\text{aq})$	[2]
		II	Dilute sulfuric acid is added into a beaker containing a powdered sample of metal M.	
			Efferversence is observed; colourless odourless gas evolved that extinguishes a lighted splint with a pop sound. Metal M dissolves in (colourless) solution. $2\text{H}^+(\text{aq}) + \text{M(s)} \longrightarrow \text{M}^{2+}(\text{aq}) + \text{H}_2(\text{g})$	[2]
			[Total: 8]	

4

The four most abundant salts in sea-water are as follows.

Salt	kg per m^3
Sodium chloride	27.5
Magnesium chloride	6.75
Magnesium sulfate	5.625
Calcium sulfate	1.80

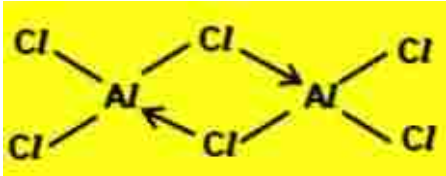
Magnesium oxide is obtained from sea-water by the following steps.



The relevant numerical values of the solubility products are given below.

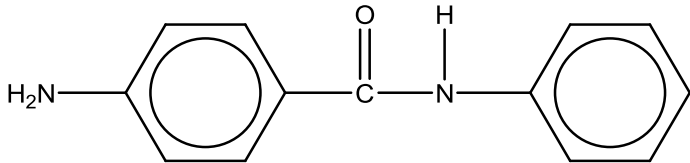
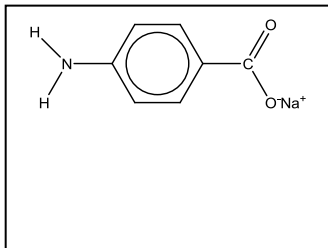
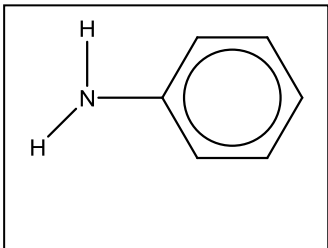
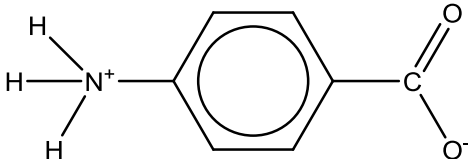
	Salt		K_{sp}	
	Sodium carbonate		-	
	Calcium carbonate		5.0×10^{-9}	
	Magnesium carbonate		1.0×10^{-5}	
	Magnesium hydroxide		1.5×10^{-11}	
	Calcium hydroxide		7.9×10^{-6}	
	(a)	Explain why the addition of carbonate ions in Step 1 is necessary and has to be controlled.		
		Both calcium carbonate and magnesium carbonate are <u>sparingly soluble salts</u> . Carbonate ions are added to <u>precipitate out calcium carbonate first</u> . In Step 1, the addition of carbonate must be controlled such that <u>little/no magnesium carbonate is precipitated/magnesium ions remain in the filtrate</u> .		[2]
	(b)	Suggest why the K_{sp} value of sodium carbonate is not provided.		
		Sodium carbonate is <u>not a sparingly soluble salt</u> /it is <u>very soluble in water</u> .		[1]
	(c)	Using the reaction scheme above, Barny used 1 dm^3 of sea water to extract magnesium oxide.		
		(i)	Calculate the concentration of Mg^{2+} in sea water.	
			In 1 dm^3 of sea water, Amount of $\text{MgCl}_2 = \frac{6.75 \times 10^3}{10^3} \div (24.3 + 35.5 \times 2)$ $= 7.08 \times 10^{-2} \text{ mol}$ Amount of $\text{MgSO}_4 = \frac{5.625 \times 10^3}{10^3} \div (24.3 + 32.1 + 16.0 \times 4)$ $= 4.67 \times 10^{-2} \text{ mol}$ $[\text{Mg}^{2+}] = 0.118 \text{ mol dm}^{-3}$	[2]

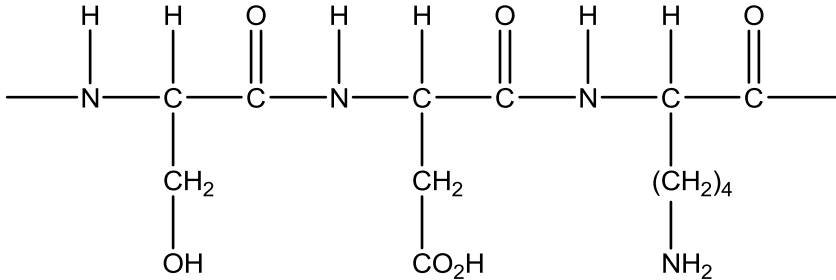
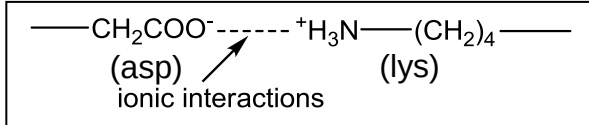
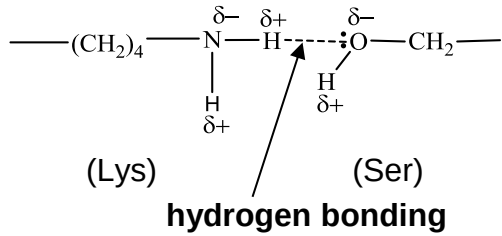
5	(a)	In the periodic table, elements can exhibit either single or variable oxidation states. One example of an element which can exhibit variable oxidation state is manganese, Mn, while aluminium, Al is an example of an element which cannot exhibit variable oxidation state.		
		(i)	Draw a dot and cross diagram for aluminium chloride, $AlCl_3$.	
				[1]
		(ii)	In the vapour state, the M_r of aluminium chloride was found to be 267. However, when aluminium chloride is in the solid state, its M_r was found to be 133.5. With the aid of suitable diagram, explain this behaviour exhibited by aluminium chloride and the type of bonding involved.	

		Aluminium chloride molecules can form dimers (between themselves) where one aluminium chloride molecule forms dative covalent bonds with another Aluminium chloride molecule. Hence, the observed M_r of the dimer is 267 at vapour state.  Dative bond is formed. The <u>lone pair on the Cl atom</u> of AlCl_3 is donated to the <u>empty orbital of the electron-deficient Al</u> in AlCl_3 to form a <u>dative (covalent) bond</u> so that Al can attain a stable octet configuration.	[3]
	(b)	Manganese is often found in minerals in combination with iron. Manganese is a metal with important industrial metal alloy uses, particularly in stainless steels. Manganese is found in various black minerals known as pyrolusite. Pyrolusite consists mainly of manganese(IV) oxide. Manganese(IV) oxide is the most common starting material for the production of compounds of manganese in other oxidation states. Manganese(IV) oxide undergoes a 2-step reaction to produce Y and Z. $\text{MnO}_2 \xrightarrow[\text{I}]{\text{Oxidation in alkaline medium}} \text{MnO}_4^{2-} \xrightleftharpoons[\text{II}]{\text{Hot water / alkaline medium}} \text{Brown black solid Y in a purple solution containing Z}$	
	(i)	Define the term <i>transition element</i> .	
		A transition element is a d-block element which forms at least one stable simple ion in which there is a partially-filled d subshell.	[1]
	(ii)	Write the electronic configuration of Mn.	
		$\text{Mn} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	[1]
	(iii)	Explain why manganese can exhibit variable oxidation state.	
		3d and 4s electrons are of similar energies, hence a variable number of 3d and 4s electrons can be involved in bonding (ionic or covalent).	[1]

		(iv)	The brown black solid Y contains 63.8% by mass of manganese and 36.2% by mass oxygen. Determine the empirical formula of Y .																
			<table><tr><td>element</td><td>Mn</td><td>O</td></tr><tr><td>mass ratio</td><td>63.8</td><td>36.2</td></tr><tr><td>mole ratio</td><td>$\frac{63.8}{54.9} = 1.16$</td><td>$\frac{36.2}{16.0} = 2.26$</td></tr><tr><td>simplest ratio</td><td>$\frac{1.16}{1.16} = 1.00$</td><td>$\frac{2.26}{1.16} = 1.94$</td></tr><tr><td></td><td>1</td><td>2</td></tr></table> Empirical formula: MnO ₂ .	element	Mn	O	mass ratio	63.8	36.2	mole ratio	$\frac{63.8}{54.9} = 1.16$	$\frac{36.2}{16.0} = 2.26$	simplest ratio	$\frac{1.16}{1.16} = 1.00$	$\frac{2.26}{1.16} = 1.94$		1	2	[1]
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	1	2																	
		(v)	Suggest the identity of Z and state the type of reaction that occurs at step II. Hence, construct a balanced equation for the reaction.																
			Z is MnO ₄ [−] Step II is a disproportionation/redox reaction. $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 4\text{OH}^-$	[3]															
		(vi)	With reference to your answer in (v), suggest how bubbling carbon dioxide gas into the hot solution of MnO ₄ ^{2−} increases the yield of Y and Z .																
			CO ₂ is <u>acidic</u> in nature. It can <u>remove the OH[−]</u> . <u>Equilibrium position</u> of $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^- + \text{MnO}_2 + 4\text{OH}^-$ <u>shifts to the right</u> to <u>replenish the OH[−]</u> , hence it helps in the disproportionation.	[2]															
	(c)		Manganese(II) carbonate, MnCO ₃ , undergoes thermal decomposition in a similar way to a Group II carbonate. MnCO ₃ decomposes at 200 °C while CaCO ₃ decomposes at 840 °C.																
		(i)	Write an equation, with state symbols, for the thermal decomposition of MnCO ₃ .																
			MnCO ₃ (s) → MnO(s) + CO ₂ (g)	[1]															
		(ii)	Explain why MnCO ₃ decompose at a lower temperature than CaCO ₃ .																

			The <u>ionic radius of Mn^{2+} is smaller</u>, hence <u>Mn^{2+} has a higher charge density than Ca^{2+}</u>. As a result, the <u>ability of Mn^{2+} to polarise the large CO_3^{2-} anion is greater</u> and the <u>C–O bonds are weakened to a larger extent</u>. Hence MnCO_3 decomposes at a lower temperature than CaCO_3.	[2]
			[Total: 16]	

6	(a)	4-Amino-N-phenylbenzamide, the structure of which is drawn below, is used in the treatment of epilepsy.  4-amino-N-phenylbenzamide	
	(i)	4-Amino-N-phenylbenzamide is hydrolysed by warm aqueous sodium hydroxide. Draw the displayed formulae of the two hydrolysis products below.	[2]
		 A  B	
	(ii)	Which of the two hydrolysis product A & B is a liquid?	[1]
		B	
	(iii)	When the other product is carefully neutralised with an aqueous mineral acid to pH 7, C is obtained. Draw the structure of C.	[1]
			

		(iv)	Upon evaporation of all the solvent from the solution of C , a white solid is obtained. Suggest a physical property of the solid.	[1]
			High melting and boiling point / conduct electricity in molten or aqueous state	
	(b)	State the reagents and conditions required for the conversion of benzene into phenylamine in two steps. In your answer, identify the structure of the intermediate.		[3]
		Step 1: concentrated H_2SO_4 , concentrated HNO_3 , 55°C Step 2: Sn , Concentrated HCl , heat, followed by NaOH(aq) Intermediate: nitrobenzene		
	(c)	The following structure shows part of a protein molecule.		
				
		(i)	Using suitable diagrams, describe two interactions that the protein fragment above can exhibit in its tertiary structure	[3]
			Hydrogen bonding between serine and aspartic acid/serine and lysine (reject aspartic acid and lysine) Ionic interactions between aspartic acid and lysine  E.g. of hydrogen bonding 	

		(ii)	In solution, amino acids exist as zwitterions. Choose one of the amino acids that can be hydrolysed from the protein molecule above to illustrate what is meant by this term.	[1]
			$ \begin{array}{c} \text{H} \\ \\ ^+\text{H}_3\text{N}-\text{C}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} \quad \text{OR} \quad \begin{array}{c} \text{H} \\ \\ ^+\text{H}_3\text{N}-\text{C}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{CO}_2\text{H} \end{array} \quad \text{OR} \quad \begin{array}{c} \text{H} \\ \\ ^+\text{H}_3\text{N}-\text{C}-\text{CO}_2^- \\ \\ (\text{CH}_2)_4 \\ \\ \text{NH}_2 \end{array} $	[1]
		(iii)	Amino acids act as buffers in solution. By means of equations, show how your chosen amino acid can act as a buffer when (I) dilute hydrochloric acid (II) dilute sodium hydroxide is added to its solution.	[2]
			$ \begin{array}{c} \text{H} \\ \\ ^+\text{H}_3\text{N}-\text{C}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} + \text{H}^+ \rightarrow \begin{array}{c} \text{H} \\ \\ ^+\text{H}_3\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} $ $ \begin{array}{c} \text{H} \\ \\ ^+\text{H}_3\text{N}-\text{C}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} + \text{OH}^- \rightarrow \begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2^- \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} + \text{H}_2\text{O} $	
			[Total: 14]	



RIVER VALLEY HIGH SCHOOL

YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE
NAME

CLASS

6	

CENTRE
NUMBER

S				

INDEX
NUMBER

H2 CHEMISTRY

9647/03

Paper 3 Free Response

21 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper

Cover Page

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.

Write in dark blue or black pen on both sides of paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin each question on a fresh sheet of paper.

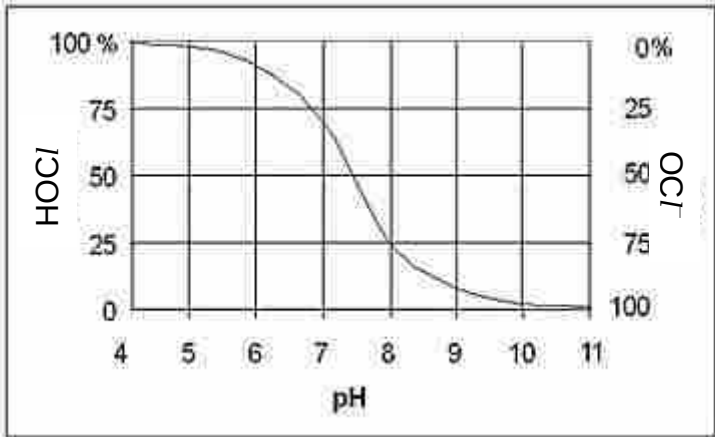
A Data Booklet is provided. Do not write anything on it.

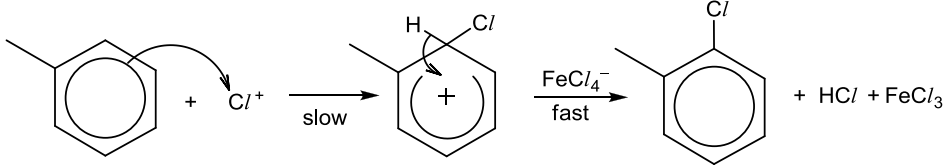
You are reminded of the need for good English and clear presentation in your answers.

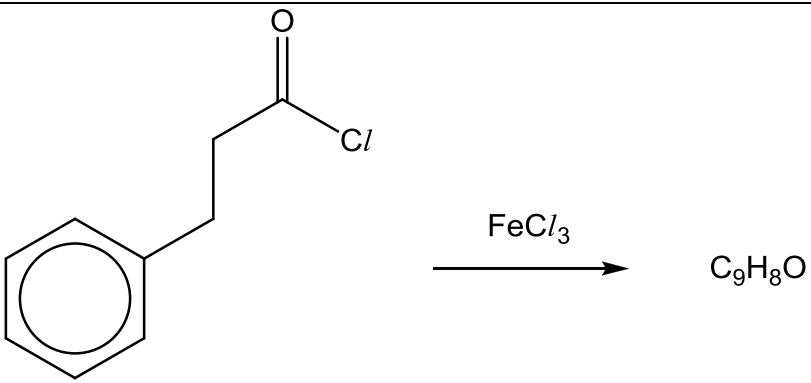
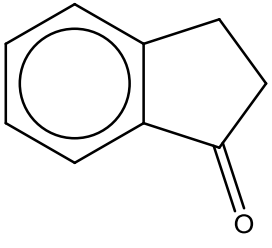
The number of marks is given in brackets [] at the end of each question or part question.

At the end of the examination, fasten all your work securely together, with the cover page on top.

	Answer any four questions.			
1	Many compounds of chlorine are manufactured from brine, NaCl(aq). The electrolysis of brine produces Cl ₂ (g) and NaOH(aq). In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction depends on the operating conditions used.			
	(a)	Write balanced equations for the reaction between Cl ₂ (g) and		
		(i)	cold aqueous NaOH;	[1]
			$\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$	
		(ii)	hot aqueous NaOH.	[1]
			$3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$	
	(b)	Chlorine dioxide, ClO ₂ , is used in the treatment of water. It is formed from ClO ₃ ⁻ ions in an acidic solution. $\text{ClO}_3^- + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{ClO}_2 + \text{H}_2\text{O}$		
		(i)	Draw the dot-and-cross diagrams of ClO ₂ and H ₂ O ₂ . <i>You may assume that there is no dative bond in either compound.</i>	[2]
			$ \begin{array}{c} \text{xx} \quad \cdot\cdot \quad \text{xx} \\ \text{x} \text{O} \text{x} : \text{Cl} : \text{x} \text{O} \text{x} \\ \text{x} \quad \cdot \quad \text{x} \end{array} $ $ \begin{array}{c} \text{xx} \quad \text{xx} \\ \text{H} \cdot \text{x} \text{O} \text{x} \text{x} \text{O} \text{x} \cdot \text{H} \\ \text{xx} \quad \text{xx} \end{array} $	
		(ii)	Construct the overall equation for the reaction of ClO ₃ ⁻ ions with H ₂ O ₂ in acidic solution.	[1]
			$2\text{ClO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{ClO}_2 + 2\text{H}_2\text{O} + \text{O}_2$	
		(iii)	What is the role of H ₂ O ₂ in the reaction?	[1]
			Reducing agent	

	(c)	Chlorine can also be used to disinfect water. When chlorine is added to water, it produces hypochlorous acid, HOCl. Hypochlorous acid is a weak acid that dissociates into hypochlorite ions, OCl^-, according to the following equation. $\text{HOCl(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OCl}^-(\text{aq})$ <i>Free chlorine</i> refers to the total chlorine content in HOCl and OCl^-. The dissociation curve below illustrates the ratio of hypochlorous acid to hypochlorite at different pH values.  [Source: www.hach.com]	
	(i)	Determine the pK_a of hypochlorous acid	[1]
		$\text{pH} = \text{pK}_a$ when $[\text{HA}] = [\text{A}^-]$. From the graph, $\text{pH} = 7.5$ when $[\text{OCl}^-] = [\text{HOCl}]$. Therefore, pK_a is 7.4 – 7.6.	
	(ii)	Hence, calculate the pH of a $0.0025 \text{ mol dm}^{-3}$ hypochlorous acid solution.	[2]
		$\text{pK}_a = 7.5$, $K_a = 10^{-7.5} = 3.16 \times 10^{-8} \text{ mol dm}^{-3}$ $[\text{H}^+] = (3.16 \times 10^{-8} \times 0.0025)^{1/2} = 8.89 \times 10^{-6} \text{ mol dm}^{-3}$ $\text{pH} = -\lg(8.89 \times 10^{-6}) = \underline{\underline{5.05}}$	
		To determine whether the free chlorine in a sample of tap water meets the regulatory limit (4 mg Cl per litre), OCl^- is quantitatively reduced to Cl^- by I^- ions, which is in turn oxidised to I_2. The I_2 is titrated with standard sodium thiosulfate. The following reaction takes place during the titration. $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	
	(iii)	Construct a balanced equation between $\text{OCl}^-(\text{aq})$ and acidified $\text{KI}(\text{aq})$	[1]
		$2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{I}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	

		(iv)	When 2 dm ³ of tap water was tested, 6.0 cm ³ of 0.00455 mol dm ⁻³ sodium thiosulfate was required to discharge the colour of iodine. Calculate the concentration of OCl ⁻ in the sample of water.	[2]
			Amount of S ₂ O ₃ ²⁻ = 2.73 × 10 ⁻⁵ mol Amount of iodine produced = 1.37 × 10 ⁻⁵ mol Amount of OCl ⁻ present = 1.37 × 10 ⁻⁵ mol Concentration = 6.83 × 10 ⁻⁶ mol dm ⁻³	
		(v)	Suggest why the calculated concentration of OCl ⁻ has the same value as the concentration of <i>free</i> chlorine.	[2]
			In the equilibrium, HOCl(aq) ⇌ H ⁺ (aq) + OCl ⁻ (aq), as OCl ⁻ is reduced by I ⁻ , [OCl ⁻] decreases and the equilibrium position shifts right to favour the formation of more OCl ⁻ until all the HOCl completely dissociates.	
		(vi)	Determine if the sample of tap water is safe for consumption.	[2]
			Mass concentration of free chlorine = 6.83 × 10 ⁻⁶ × 35.5 = 0.242 mg per litre. The tap water is safe for consumption.	
	(d)		Chlorine is also used in organic chemistry to produce the Lewis acid catalyst, FeCl ₃ , for the reaction between methylbenzene and chlorine.	
		(i)	Describe the mechanism of the above reaction.	[3]
			$\text{FeCl}_3 + \text{Cl}_2 \rightarrow \text{FeCl}_4^- + \text{Cl}^+$ 	
		(ii)	FeCl ₃ reacts in a similar way with acyl chlorides. Predict the structure of the product of the following reaction.	[1]

			 <chem>ClC(=O)CCc1ccccc1</chem> $\xrightarrow{\text{FeCl}_3}$ <chem>C9H8O</chem>	
			 <chem>O=C1C=CCc2ccccc21</chem>	
			[Total: 20]	

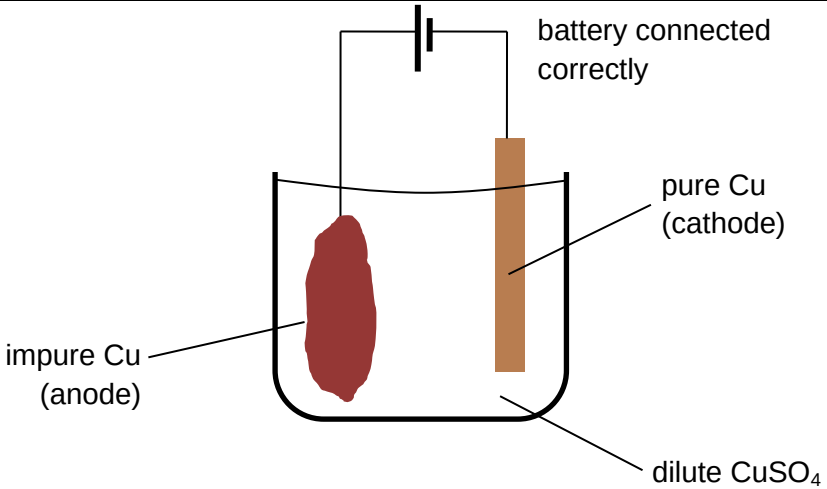
2	(a)	Nitrous oxide or dinitrogen oxide, N ₂ O, is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anesthetic and analgesic effects. To produce N ₂ O, ammonium nitrate is decomposed at 170 °C. Water is a by-product of this reaction.																				
	(i)	Write an equation for the production of dinitrogen oxide from ammonium nitrate.		[1]																		
		NH ₄ NO ₃ (s) → 2 H ₂ O (g) + N ₂ O (g)																				
	(ii)	In the manufacturing of N ₂ O gas, 1 kg of N ₂ O gas is produced for every 2.1 kg of ammonium nitrate used. Determine the percentage yield of dinitrogen oxide.		[2]																		
		Amount of NH ₄ NO ₃ used = $\frac{2.1 \times 1000}{14 \times 2 + 4 + 16 \times 3} = 26.3 \text{ mol}$ Theoretical amt of N ₂ O produced = 26.3 mol Theoretical mass of N ₂ O produced = 26.3 × (14 × 2+ 16) = 1157g % yield = $\frac{1000}{1157} \times 100\% = 86.4\%$																				
	(b)	At 1200 K, in the presence of gold wire, dinitrogen oxide decomposes as shown: $2\text{N}_2\text{O}(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}).$ To follow the rate of reaction, the change in concentration of a sample of N ₂ O is measure against time. The results are shown below: <table border="1"><thead><tr><th>Time, t / s</th><th>Concentration of N₂O / × 10⁻³ mol dm⁻³</th></tr></thead><tbody><tr><td>0</td><td>2.50</td></tr><tr><td>1000</td><td>2.01</td></tr><tr><td>2000</td><td>1.62</td></tr><tr><td>3000</td><td>1.31</td></tr><tr><td>4000</td><td>1.05</td></tr><tr><td>5000</td><td>0.85</td></tr><tr><td>6000</td><td>0.68</td></tr><tr><td>7000</td><td>0.55</td></tr></tbody></table>		Time, t / s	Concentration of N ₂ O / × 10 ⁻³ mol dm ⁻³	0	2.50	1000	2.01	2000	1.62	3000	1.31	4000	1.05	5000	0.85	6000	0.68	7000	0.55	
Time, t / s	Concentration of N ₂ O / × 10 ⁻³ mol dm ⁻³																					
0	2.50																					
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2000	1.62																					
3000	1.31																					
4000	1.05																					
5000	0.85																					
6000	0.68																					
7000	0.55																					

		(i)	What do you understand by the term <i>half-life</i> of N_2O ?	[1]
			Half-life is time taken for the concentration of N_2O to be halved.	
		(ii)	Plot the above data on a graph paper. Use the following scale: • 2 cm to represent 1000 s on the x-axis; and • 2 cm to represent to represent $0.25 \times 10^{-3} \text{ mol dm}^{-3}$ on the y-axis.	[2]
		(iii)	From your graph, deduce the order of the reaction with respect to N_2O .	[2]
			When concentration decreases from 2.5×10^{-3} to 1.25×10^{-3} , time taken is 3300 s. When concentration decreases from 1.25×10^{-3} to 0.7×10^{-3} , time taken is 3100 s. (to be shown on the graph) Since half-life is approximately constant, the <u>order of reaction with respect to N_2O is 1</u> . Show on graph that half time constant	
		(iv)	Calculate the rate constant for the reaction and state its units.	[2]
			Rate constant = $\frac{\ln 2}{t_{1/2}} = 2.17 \times 10^{-4} \text{ s}^{-1}$ Correct answer Correct units	
		(v)	The gold wire acts as a <i>heterogeneous catalyst</i> in this reaction.	[3]

			Explain the terms <i>in italics</i> and outline the mode of action of the catalyst.	
			A catalyst is a substance that provides an alternative pathway with lower activation energy, remaining chemically unchanged at the end of reaction. A heterogeneous catalyst is one that is in a different phases as the reactants. <u>Adsorption</u> The gold wire provides active sites whereby N_2O molecules may be adsorbed. The adsorption <u>weakens N–O bonds</u> so that the N_2O molecules are more reactive. <u>Reaction</u> The N_2O molecules on the gold surface are in <u>close proximity and the correct orientation</u> so that they can readily react together. <u>Desorption</u> The products, N_2 and O_2, formed diffuse away from the surface of the catalyst and the active sites become available again.	
	(c)		Alkenes react with carbenes $\text{R}_2\text{C:}$ to yield cyclopropanes. One way to generate a substituted carbene is by reacting chloroform, CHCl_3, with a strong base. The mechanism to generate a carbene is described below. 1. Potassium hydroxide, KOH, removes the proton from CHCl_3, leaving behind the electron pair. An anionic intermediate is formed. 2. Cl^- is lost and a neutral dichlorocarbene is formed.	
		(i)	Based on the description above, draw a mechanism to show the generation of dichlorocarbene. Show relevant lone pairs and use curly arrows to indicate the movement of electron pairs.	[3]

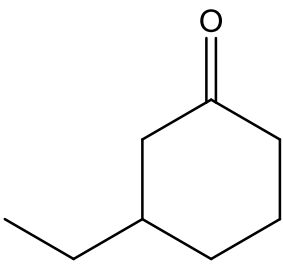
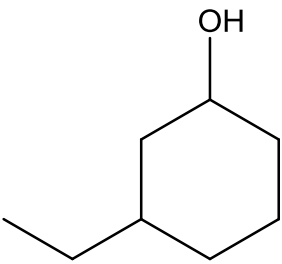
		An example of a reaction between an alkene and a carbene is as shown:		
	(ii)	Suggest the structure of the product formed when cyclohexene reacts with chloroform in the presence of KOH.	[1]	
	(iii)	Suggest the role of carbene in its reaction with an alkene. Explain your answer.	[2]	
		Carbene acts as an electrophile. Carbon in carbene is <u>electron deficient</u> as it is bonded to two electronegative chlorine atoms/it has only 6 valence electrons, hence it acts as an electrophile.		
	(iv)	Suggest the type of reaction when carbene reacts with an alkene.	[1]	

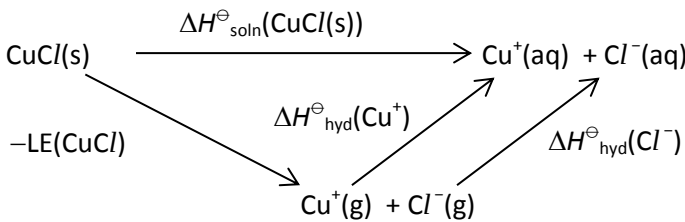
			Addition	
			[Total: 20]	

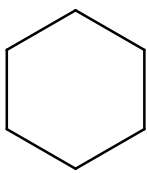
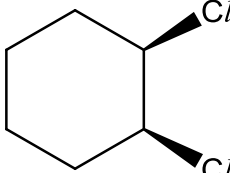
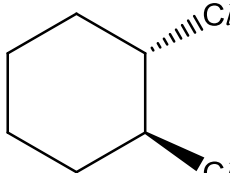
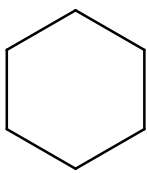
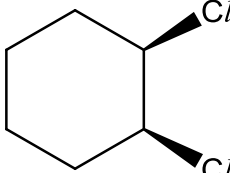
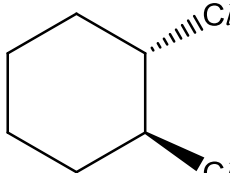
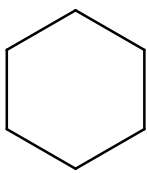
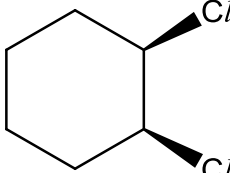
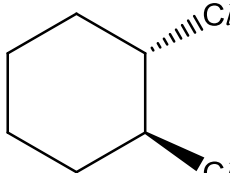
3	Copper is a rare element, constituting only 6.8×10^{-3} percent of the Earth's crust by mass. However, it has a wide range of uses such as in alloys, plumbing and in electrical cables. The common oxidation states of copper are +2 and +1.		
	(a)	Copper can be obtained by roasting a copper ore, CuFeS_2 , to give Cu_2S , which is further oxidised to form metallic copper. This impure copper can be purified by electrolysis.	
		(i)	Draw a diagram to illustrate the electrolytic cell used in the purification of copper, using $\text{CuSO}_4(\text{aq})$ as the electrolyte. [2]
			
		(ii)	If a current of 0.8 A was passed through the cell, calculate the time required for 0.25 g of pure copper to be collected. [2]
			Amt of Cu = $0.25 / 63.5 = 3.94 \times 10^{-3}$ mol $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ Amt of e^- required = $2(3.94 \times 10^{-3}) = 7.88 \times 10^{-3}$ mol Quantity of charge required = $nF = 7.88 \times 10^{-3} \times 96500 = 760 \text{ C}$ Time required = $Q / I = 760 / 0.8 = \underline{950 \text{ s}}$ (or 15.8 min)
	(b)	Anhydrous copper(II) sulfate, $\text{CuSO}_4(\text{s})$, is a white powder. It dissolves in water to form a pale blue solution.	
		(i)	State the species responsible for the pale blue colour of the solution. [1]
			$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
		(ii)	Explain why the solution is pale blue in colour. [3]
			Cu^{2+} has a <u>partially filled 3d subshell</u> (electronic configuration $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^9$). In the presence of H_2O ligands in

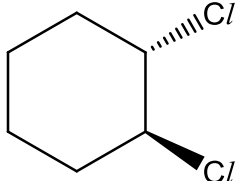
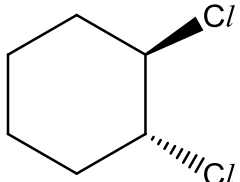
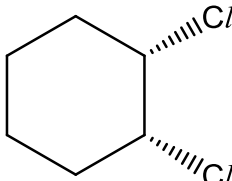
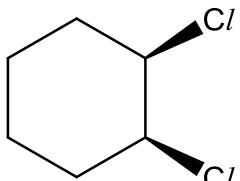
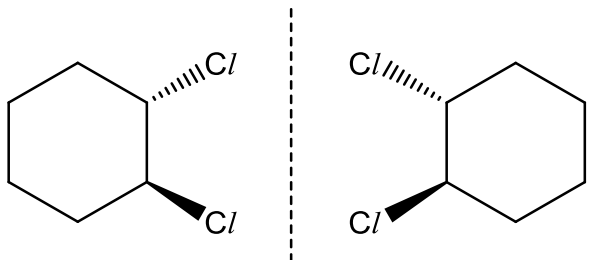
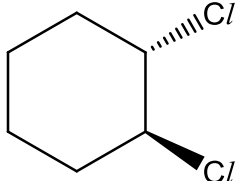
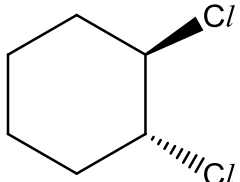
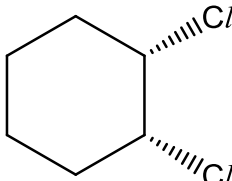
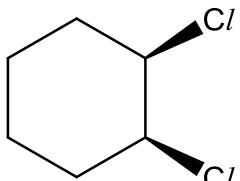
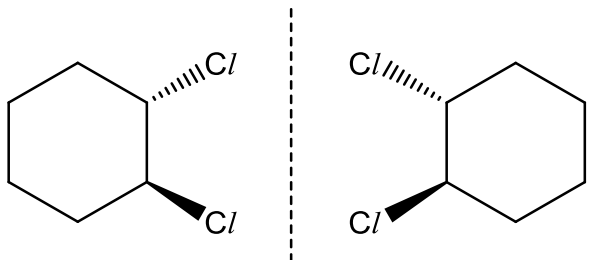
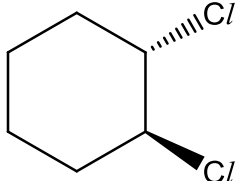
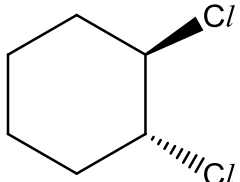
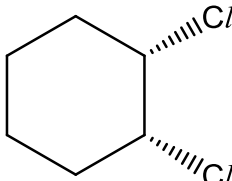
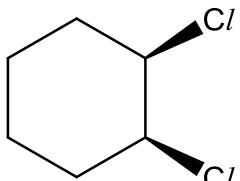
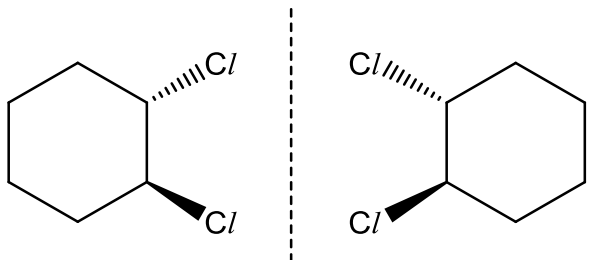
			[Cu(H ₂ O) ₆] ²⁺ , the <u>3d orbitals</u> of Cu ²⁺ are split into 2 sets of orbitals with different energies/become non-degenerate. The <u>difference in energies (ΔE)</u> between these 2 sets of non-degenerate 3d orbitals is <u>small</u> and <u>radiation from the visible region of the electromagnetic spectrum is absorbed</u> when an electron is promoted from a lower energy d-orbital to another unfilled/partially-filled <u>d orbital of higher energy</u> . The (blue) <u>colour</u> observed corresponds to the <u>complement of the (orange) light</u> absorbed.	
		(iii)	Describe the colour changes observed when the following solutions are added to the pale blue solution, giving the formulae of all relevant species. I. Dilute NH ₃ (aq), until in excess; II. KI(aq).	[4]
			I. A (pale) blue precipitate of Cu(OH)₂ is formed, which is soluble in excess NH ₃ (aq) to form a dark blue solution of [Cu(NH₃)₄(H₂O)₂]²⁺ . II. An off-white/cream precipitate of CuI (Accept: Cu ₂ I ₂) is formed in a brown solution of I₂ .	
	(c)		When Na ₂ CO ₃ is added to a solution of CuSO ₄ and the resultant mixture is filtered, a green solid, cupric carbonate, is obtained. The formula of this solid is Cu ₂ (OH) _a (CO ₃) _b . 0.10 mol of Cu ₂ (OH) _a (CO ₃) _b required 0.40 mol of hydrochloric acid for complete reaction. The products of this reaction include copper(II) chloride, carbon dioxide and water.	
		(i)	Given that 2.4 dm ³ of CO ₂ was formed at room temperature and pressure, determine the values of a and b .	[2]
			Cu ₂ (OH) _a (CO ₃) _b + (a + 2b)H ⁺ → 2Cu ²⁺ + bCO ₂ + (a + b)H ₂ O Amt of CO ₂ formed = 2.4 / 24 = 0.10 mol $\frac{1}{b} = \frac{0.10}{0.10} \Rightarrow b = \underline{1}$ $\frac{1}{a + 2b} = \frac{0.10}{0.40} \Rightarrow a + 2b = 4 \Rightarrow a = \underline{2}$	
		(ii)	Hence, write an equation for the reaction of cupric carbonate with	[1]

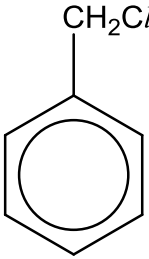
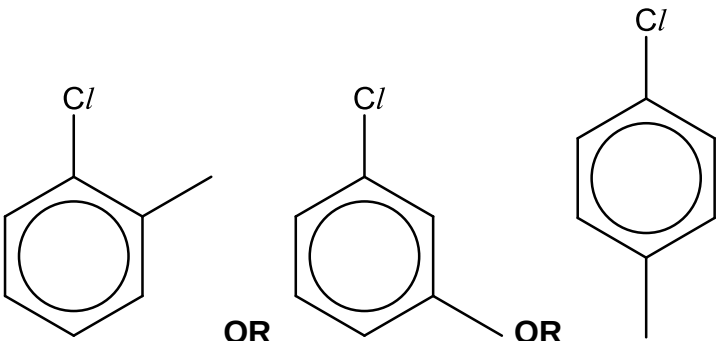
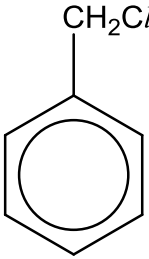
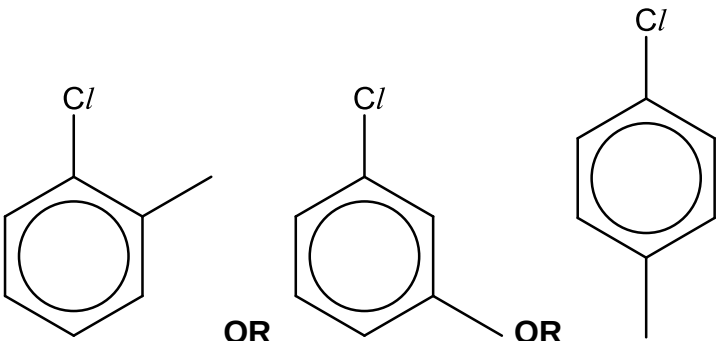
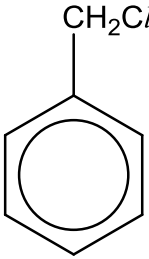
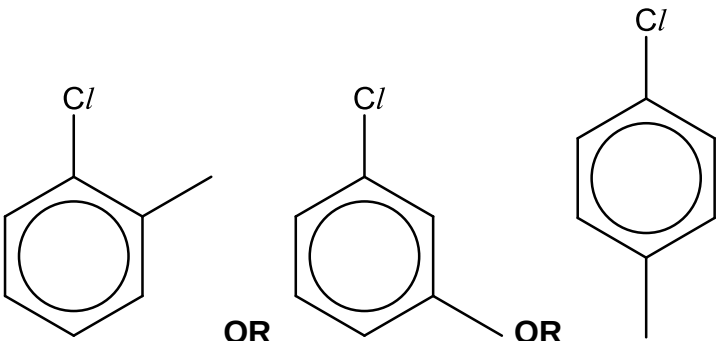
		hydrochloric acid.	
		$\text{Cu}_2(\text{OH})_2\text{CO}_3 + 4\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{CO}_2 + 3\text{H}_2\text{O}$	
	(d)	Cu_2O , a brick red solid, is a compound where copper is in the oxidation state of +1. It can be formed by reacting an alkaline solution of complexed Cu^{2+} with a particular organic functional group.	
	(i)	State the functional group that will produce Cu_2O with the alkaline solution of complexed Cu^{2+} .	[1]
		Aliphatic/Non-aromatic aldehyde	
	(ii)	Name the type of reaction undergone by the functional group in (i).	[1]
		Oxidation	
	(e)	Organocopper compounds are useful reagents in organic synthesis. One such class of compounds is the Gilman reagents, with the general formula R_2CuLi, where R represents an alkyl group. Gilman reagents are effective nucleophiles used in conjugate addition reactions. Conjugate addition involves the addition of a nucleophile across a $\text{C}=\text{C}$ bond instead of across a $\text{C}=\text{O}$ bond. This is illustrated in the example below: Reaction scheme: Methyl vinyl ketone $\xrightarrow[2. \text{HCl}]{1. \text{R}_2\text{CuLi, ether}}$ 4-methyl-2-pentanone + $\text{RCu} + \text{LiCl}$ The Gilman reagent can be seen as providing the "R^-" nucleophile while a mineral acid (e.g. HCl) provides the proton that is added to one of the carbon atoms in the $\text{C}=\text{C}$ bond.	
		The following synthesis involves a Gilman reagent for one of the steps: Reaction scheme: Cyclohex-2-en-1-ol (I) $\rightarrow$ Cyclohex-2-en-1-one $\xrightarrow[2. \text{HCl}]{1. (\text{CH}_3\text{CH}_2)_2\text{CuLi, ether}}$ A $\xrightarrow[\text{III}]{\text{NaBH}_4}$ B Suggest the reagent and conditions for Step I and the structures of compounds A and B.	[3]
		Reagents and conditions for Step I:	

		acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, heat (under reflux)		
		Structures:		
				
		A	B	
			[Total: 20]	

4	(a)	Copper(I) chloride is used as a precursor of a fungicide and a catalyst for a variety of organic reactions. It is sparingly soluble in water.								
	(i)	Define the standard enthalpy change of hydration of an ion.		[1]						
		The standard enthalpy change of hydration of an ion is the enthalpy change when one mole of gaseous ions is hydrated under standard conditions.								
	(ii)	Using the data given in the following table, draw an appropriate energy cycle and calculate the standard enthalpy change of solution for copper(I) chloride. <table border="1"><tr><td>$\Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+)$</td><td>$-593 \text{ kJ mol}^{-1}$</td></tr><tr><td>$\Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)$</td><td>$-378 \text{ kJ mol}^{-1}$</td></tr><tr><td>Lattice Energy of CuCl</td><td>-979 kJ mol^{-1}</td></tr></table>		$\Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+)$	-593 kJ mol^{-1}	$\Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)$	-378 kJ mol^{-1}	Lattice Energy of CuCl	-979 kJ mol^{-1}	[3]
$\Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+)$	-593 kJ mol^{-1}									
$\Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)$	-378 kJ mol^{-1}									
Lattice Energy of CuCl	-979 kJ mol^{-1}									
		$\Delta H^{\ominus}_{\text{soln}}(\text{CuCl(s)}) = \Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+) + \Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-) - \text{LE}(\text{CuCl})$ $= (-593) + (-378) - (-979) = +8 \text{ kJ mol}^{-1}$ 								
	(b) (i)	Explain what is meant by the term <i>entropy</i> of a chemical system.		[1]						
		Entropy is a measure of the disorder in a system. (The more disordered a system, the greater the number of ways for particles and energy to be dispersed, therefore the larger its entropy.)								
		Describe and explain how the entropy of the following systems will change during the stated process. Assume the pressure of each system remains at 1 atm throughout.								
	(ii)	1 mol of Cl ₂ (g) at 298 K is heated to 500 K.		[1]						
		Entropy increases/ΔS > 0. There is an increase in disorder as the particles have more kinetic energy on average and there are more ways to distribute the larger number of quanta of energy.								
	(iii)	1 mol of Cl ₂ (g) at 298 K is reacted with copper according to the following equation.		[1]						

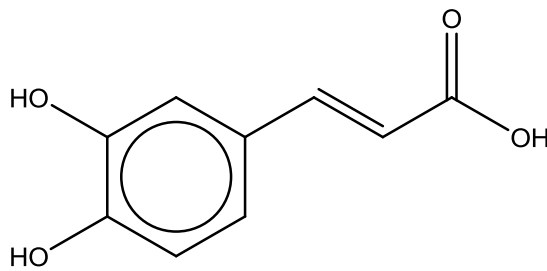
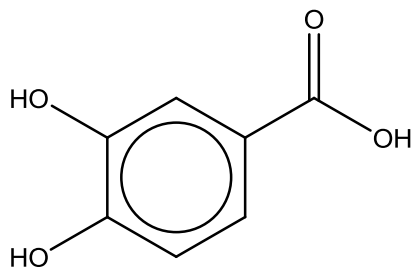
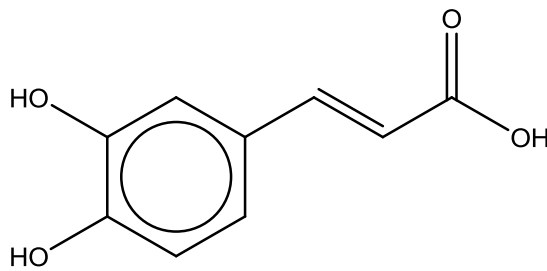
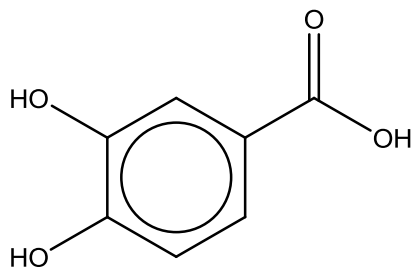
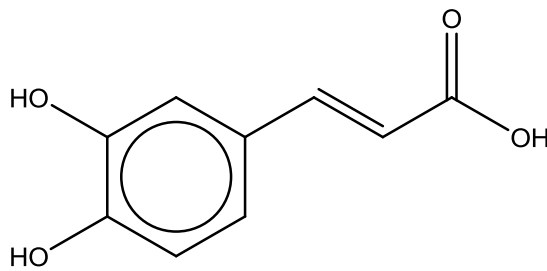
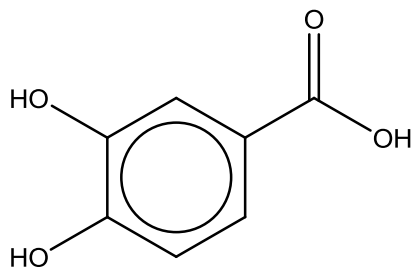
			$\text{Cu(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{CuCl}_2\text{(s)}$							
			Entropy decreases/$\Delta S < 0$. There is an decrease in disorder as the <u>number of gaseous molecules decreases</u> from 1 to 0.							
	(c)	Copper(II) ions are pollutants found in water. One method of purification is via precipitation of Cu(OH)_2 and CuS . <table><tr><td></td><td>K_{sp} (298 K)</td></tr><tr><td>CuS</td><td>6.3×10^{-36}</td></tr><tr><td>Cu(OH)_2</td><td>2.0×10^{-19}</td></tr></table> Using the above data, calculate:				K_{sp} (298 K)	CuS	6.3×10^{-36}	Cu(OH)_2	2.0×10^{-19}
	K_{sp} (298 K)									
CuS	6.3×10^{-36}									
Cu(OH)_2	2.0×10^{-19}									
	(i)	the minimum concentration of Cu^{2+} for a precipitate of CuS to form in 10 ppm S^{2-} solution; <i>(1 ppm = 1 mg dm⁻³)</i>								
		$[\text{S}^{2-}] = (0.01 / 32.1) = 3.12 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Cu}^{2+}] = (6.3 \times 10^{-36}) / (3.12 \times 10^{-4}) = \underline{\underline{2.02 \times 10^{-32} \text{ mol dm}^{-3}}}$								
	(ii)	the maximum pH of a solution containing 0.100 mol dm ⁻³ Cu^{2+} ions.								
		$K_{\text{sp}}(\text{Cu(OH)}_2) = [\text{Cu}^{2+}][\text{OH}^-]^2$ $2.0 \times 10^{-19} = (0.1)(x)^2$ $[\text{OH}^-] = 1.41 \times 10^{-9} \text{ mol dm}^{-3}$ $\text{pOH} = -\lg(1.41 \times 10^{-9}) = 8.85$ $\text{pH} = 14 - \text{pOH} = 14 - 8.85 = \underline{\underline{5.15}}$								
	(d)	Many organic compounds also contain chlorine. An example would be 1,2-dichlorocyclohexane, which exhibits both geometrical and optical isomerism.								
	(i)	Explain why 1,2-dichlorocyclohexane can exhibit geometrical isomerism.								
		There is <u>restricted rotation</u> about the carbon-carbon bond in the ring structure, resulting in cis- and trans-1,2-dichlorocyclohexane [1] . <table><tr><td></td><td>OR</td><td></td><td></td></tr></table>				OR				
	OR									

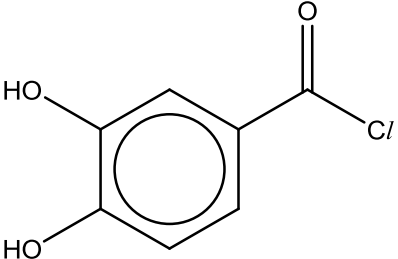
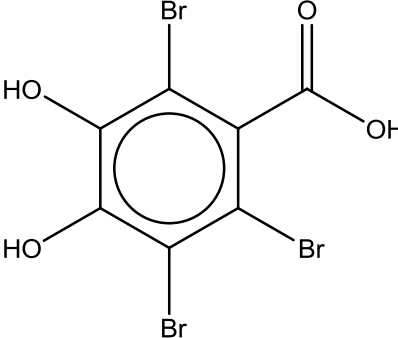
			cis isomer	trans isomer																						
		(ii)	The effect of plane polarised light on 1,2-dichlorocyclohexane was investigated. Three different types of 1,2-dichlorocyclohexane was identified: • Molecule X rotated plane polarised light to the left • Molecule Y rotated plane polarised light to the right • Molecule Z had no effect on plane polarised light Suggest an explanation for these observations.			[3]																				
			<table><tr><th>Molecule</th><th colspan="2">Explanation</th></tr><tr><td>X</td><td></td><td rowspan="2">Molecules possess two chiral carbons and no plane of symmetry. Hence, they are mirror images of each other that are non-superimposable (i.e. enantiomers of each other)</td></tr><tr><td>Y</td><td></td></tr><tr><td>Z</td><td> OR </td><td>Although the molecule has two chiral carbons, there is a plane of symmetry present. Hence, the mirror images are superimposable.</td></tr><tr><td colspan="3"></td><td colspan="2"></td></tr><tr><td colspan="3"> XY </td><td colspan="2"></td></tr></table>			Molecule	Explanation		X		Molecules possess two chiral carbons and no plane of symmetry . Hence, they are mirror images of each other that are non-superimposable (i.e. enantiomers of each other)	Y		Z	 OR 	Although the molecule has two chiral carbons, there is a plane of symmetry present . Hence, the mirror images are superimposable .						XY				
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XY																										

(e) Compounds C and D both have the molecular formula C_7H_7Cl. In an experiment, both compounds are separately heated under reflux for some time with aqueous sodium hydroxide. The resulting solutions are cooled and acidified with dilute nitric acid. When aqueous silver nitrate is added subsequently, a white precipitate is formed with C while no precipitate is formed with D. Suggest the structures of C and D. Explain your reasoning for each compound.	[4]								
<table border="1"> <tr> <td data-bbox="338 586 422 866">C</td> <td data-bbox="422 586 1401 866">  </td> </tr> <tr> <td data-bbox="338 866 422 1014"></td> <td data-bbox="422 866 1401 1014"> C undergoes <u>nucleophilic substitution</u> when heated with NaOH. <u>Free chloride ion then combines with Ag^+</u> to form white precipitate of AgCl. </td> </tr> <tr> <td data-bbox="338 1014 422 1395">D</td> <td data-bbox="422 1014 1401 1395">  </td> </tr> <tr> <td data-bbox="338 1395 422 1579"></td> <td data-bbox="422 1395 1401 1579"> C-Cl bond in D has <u>partial double bond character</u> due to the <u>delocalisation of a lone pair of electrons of chlorine into the benzene ring</u>. Hence, D does not undergo nucleophilic substitution with NaOH. </td> </tr> </table>	C			C undergoes <u>nucleophilic substitution</u> when heated with NaOH. <u>Free chloride ion then combines with Ag^+</u> to form white precipitate of AgCl.	D			C-Cl bond in D has <u>partial double bond character</u> due to the <u>delocalisation of a lone pair of electrons of chlorine into the benzene ring</u>. Hence, D does not undergo nucleophilic substitution with NaOH.	
C									
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D									
	C-Cl bond in D has <u>partial double bond character</u> due to the <u>delocalisation of a lone pair of electrons of chlorine into the benzene ring</u>. Hence, D does not undergo nucleophilic substitution with NaOH.								
[Total: 20]									

5	(a)	The electrical conductivities of some Period 3 elements are shown below.						
		Element	Na	Mg	Al	P	S	Cl
		Electrical conductivity at 298 K / $\times 10^7 \text{ S m}^{-1}$	2.1	2.3	3.5	Non-conductors		

		(i)	With reference to the data above, describe and explain the difference in electrical conductivities of the elements above.	[3]
			<u>Na, Mg & Al</u> They are metals / have giant metallic structure. Presence of delocalised valence electrons which act as mobile charge carriers thus making them good conductors. Electrical conductivity increases from Na ($2.1 \times 10^7 \text{ S m}^{-1}$) to Mg ($2.3 \times 10^7 \text{ S m}^{-1}$) to Al ($3.5 \times 10^7 \text{ S m}^{-1}$) as the number of valence electrons increases. <u>P₄, S₈ & Cl₂</u> They are non-metals / have simple covalent structure. Absence of mobile charge carriers thus they are non-conductors.	
		(ii)	Silicon carbide (SiC), also known as carborundum and moissanite, is used in abrasive and cutting tools. Suggest the structure and bonding of SiC.	[2]
			Giant covalent structure with strong electrostatic forces of attraction between the Si and C nuclei and the shared pair of electrons.	
	(b)		Chlorides of Period 3 elements dissolve in water to give solutions of varying pH. Explain the following pH values and write the chemical equations for any reactions that occur:	
		(i)	AlCl ₃ dissolves readily in water to form an acidic solution (pH = 3).	[3]
			Both hydration of ions and substantial hydrolysis of Al ³⁺ (aq) occurs. Due to its high charge density, Al ³⁺ is highly polarising and weakens the O–H bonds in the water molecules of the complex, causing the O–H bonds to break and hence release the hydrogen ions. $\text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^{-}(\text{aq})$ $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq})$	
		(ii)	SiCl ₄ (l) dissolves in water to form a strongly acidic solution (pH = 2)	[2]
			SiCl ₄ undergoes hydrolysis in water. This is because Si atom in SiCl ₄ has energetically accessible vacant 3d orbital for dative bonding with water molecules.	

		$\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{aq})$				
(c)	Caffeic acid is an organic compound found in all plants as it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass. Caffeic acid has the molecular formula $\text{C}_9\text{H}_8\text{O}_4$. Caffeic acid reacts with $\text{Br}_2(\text{l})$ to give $\text{C}_9\text{H}_8\text{O}_4\text{Br}_2$. When treated with hot KMnO_4 and H_2SO_4, caffeic acid reacts to give F, $\text{C}_7\text{H}_6\text{O}_4$, and a colourless gas that produces a white solid with $\text{Ca}(\text{OH})_2(\text{aq})$. F reacts with PCl_5 to give G, $\text{C}_7\text{H}_5\text{O}_3\text{Cl}$, with the production of steamy white fumes. G reacts with water to form an acidic solution. When added to neutral $\text{FeCl}_3(\text{aq})$, G also forms a violet colouration. G reacts with $\text{Br}_2(\text{aq})$ to give H, $\text{C}_7\text{H}_3\text{O}_4\text{Br}_3$. Use the information above to deduce the structures of caffeic acid and compounds F to H, explaining all the reactions involved.	[10]				
	Caffeic acid <u>C:H ratio $\approx 1:1$</u> which suggests <u>presence of benzene ring</u>. Caffeic acid <u>has a C=C double bond/has an alkene group</u> as it undergoes <u>electrophilic addition</u> with Br_2. Caffeic acid undergoes <u>oxidation/oxidative cleavage</u> with hot KMnO_4 to give <u>carbon dioxide gas</u>. Loss of 2 carbons as CO_2 suggests formation of <u>ethanedioic acid/$\text{HO}_2\text{CCO}_2\text{H}$</u> after oxidative cleavage. F contains a <u>carboxylic functional group</u> as it undergoes (nucleophilic) <u>substitution</u> with PCl_5 to give G, an acid chloride that hydrolyses in water, and fumes of <u>HCl</u>. G contains <u>phenol functional group</u> as it forms a <u>complex</u> with $\text{FeCl}_3(\text{aq})$. G undergoes <u>electrophilic substitution</u> with $\text{Br}_2(\text{aq})$. Substitution of 3 Br atoms suggests 3 positions on benzene ring that are available for substitution.					
	<table><tr><td>Caffeic acid</td><td></td></tr><tr><td>F</td><td></td></tr></table>	Caffeic acid		F		
Caffeic acid						
F						

		G		
		H		
		[Total: 20]		

– End of Paper –

ST ANDREW'S JUNIOR COLLEGE**JC2 Preliminary Examinations****Chemistry****9647/01****Higher 2****19th September 2016****Paper 1 Multiple Choice****1 hour**

Additional Materials: Multiple Choice Answer Sheet, Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil. Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **40** questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D. Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

This document consists of **27** printed pages **including** this page.

[Turn Over

Section A

For each question there are four possible answers, A, B, C and D. Choose the one you consider to be correct.

1. What volume of CO_2 will be liberated when $y \text{ cm}^3$ of 40:60 mixture of volume of methane and ethene are completely burnt in oxygen?

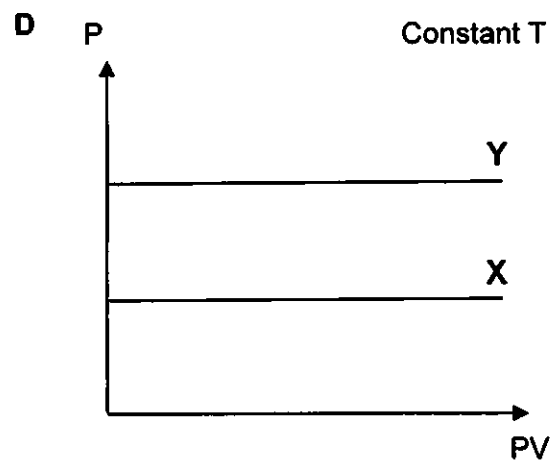
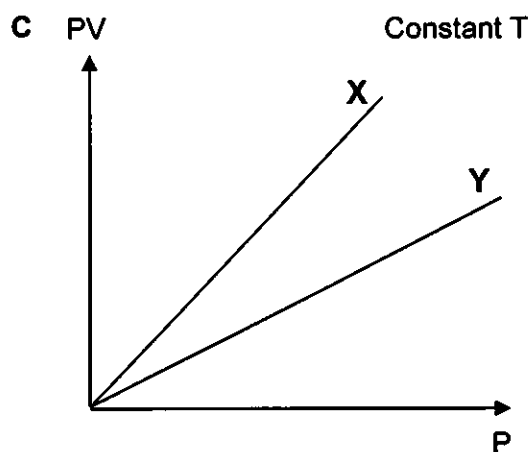
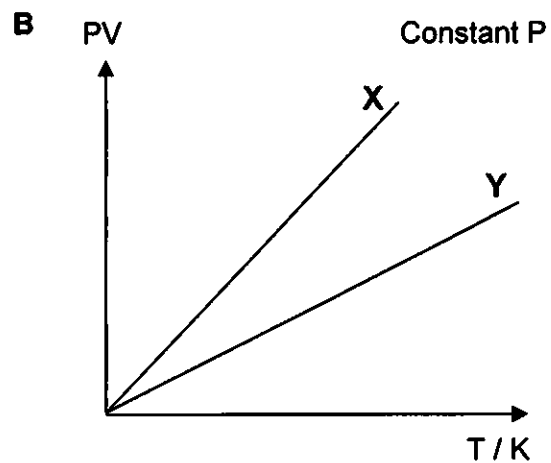
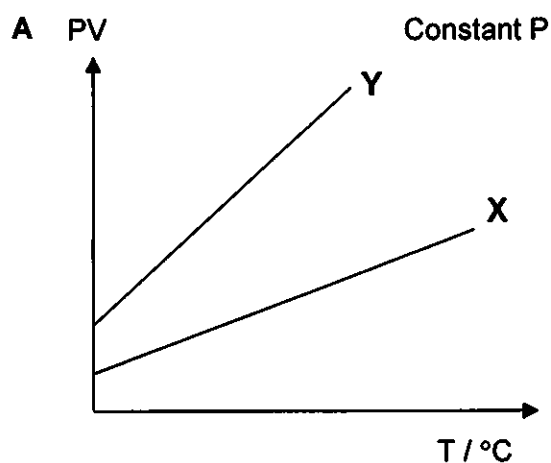
- A $y \text{ cm}^3$
B $\frac{2y}{5} \text{ cm}^3$
C $\frac{8y}{5} \text{ cm}^3$
D $2y \text{ cm}^3$

2. *Use of the Data Booklet is relevant to this question.*

Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, are oxidised by acidified, aqueous potassium manganate(VII) to give carbon dioxide. What volume of $0.020 \text{ mol dm}^{-3}$ potassium manganate(VII) is required to oxidise completely $1.0 \times 10^{-3} \text{ mol}$ of the salt $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$?

- A 20 cm^3
B 40 cm^3
C 50 cm^3
D 125 cm^3

3. Which graph correctly describes the behaviour of fixed masses of the ideal gases X and Y, where X has a higher M_r than Y?



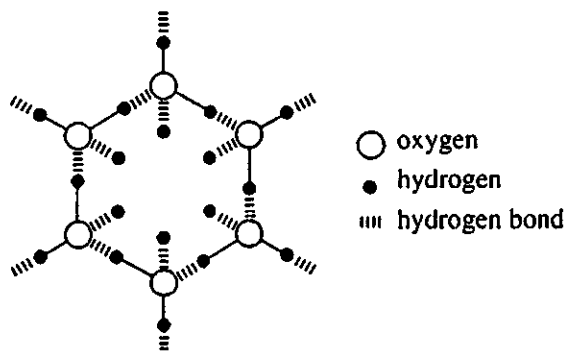
4. The table below shows the ionisation energy (in kJ mol^{-1}) of four elements labelled *A*, *B*, *C* and *D*.

Element	1 st I.E.	2 nd I.E.	3 rd I.E.	4 th I.E.	5 th I.E.	6 th I.E.
<i>A</i>	1012	1907	2914	4964	6274	21 267
<i>B</i>	787	1577	3232	4356	16 091	19 805
<i>C</i>	1521	2666	3931	5771	7238	8781
<i>D</i>	738	1451	7733	10 543	13 630	18 020

Which element above has no *p* electrons in the valence shell?

- A Element A
- B Element B
- C Element C
- D Element D

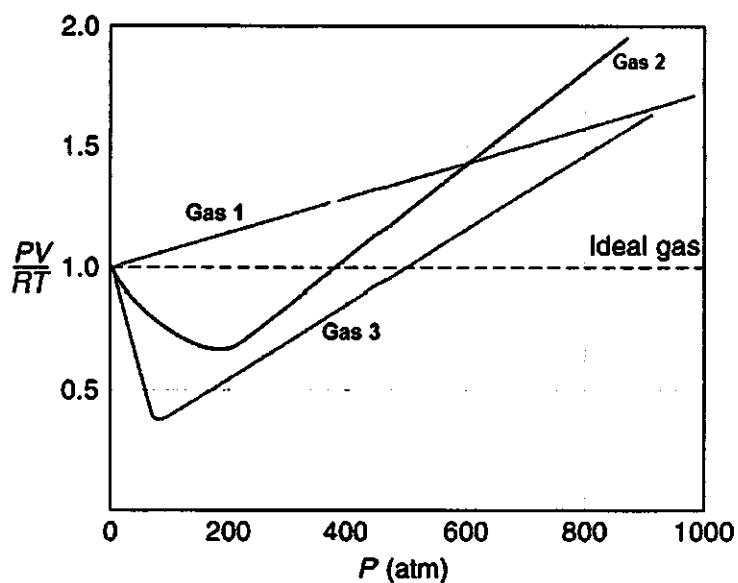
5. The diagram shows the structure of part of a crystal of ice.



Which of the following is **incorrect**?

- A All bond angles surrounding each oxygen atom are 109.5° .
- B Two electrons from each oxygen atom are involved in forming hydrogen bonds.
- C The hydrogen bonds are weaker than the O–H covalent bonds.
- D The open structure of ice causes ice to have a higher volume and lower density than water.
6. Which of the following has an exothermic enthalpy change?
- A $\text{Ba (g)} \rightarrow \text{Ba}^+ \text{ (g)} + \text{e}^-$
- B $\text{MgS (s)} \rightarrow \text{Mg}^{2+} \text{ (g)} + \text{S}^{2-} \text{ (g)}$
- C $\frac{1}{2} \text{N}_2 \text{ (g)} \rightarrow \text{N (g)}$
- D $\text{F (g)} + \text{e}^- \rightarrow \text{F}^- \text{ (g)}$

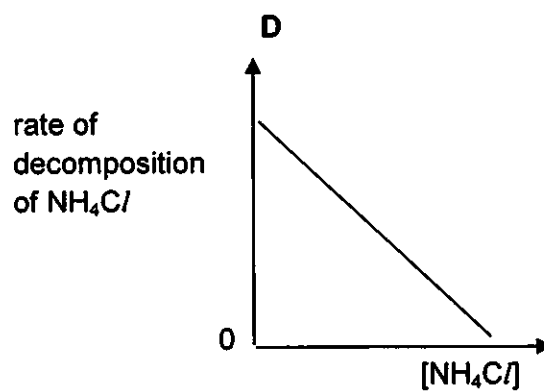
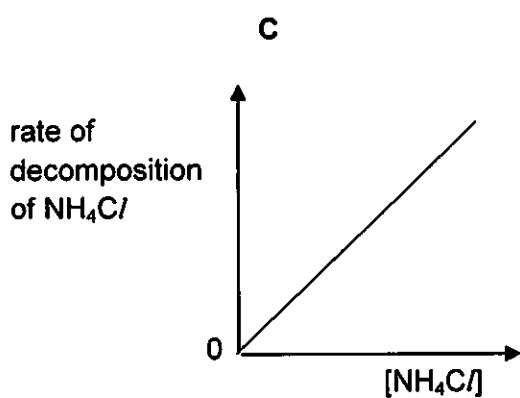
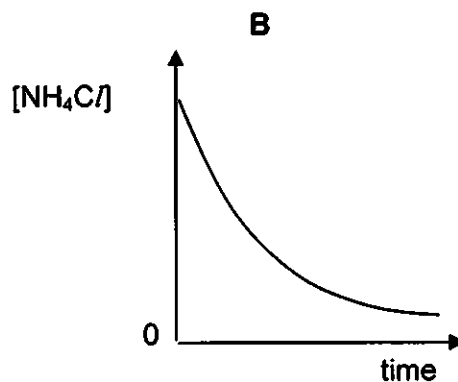
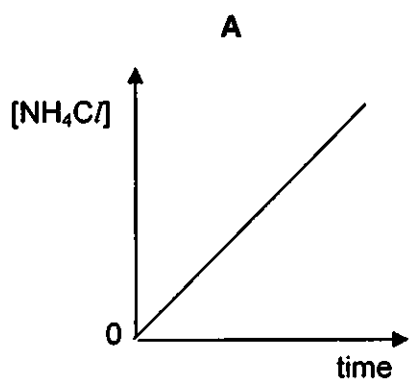
7. The value of $\frac{pV}{RT}$ is plotted against p at the same temperature for three gases – Ne, NH_3 and C_2H_6 , where p is the pressure and V is the volume of the gas.



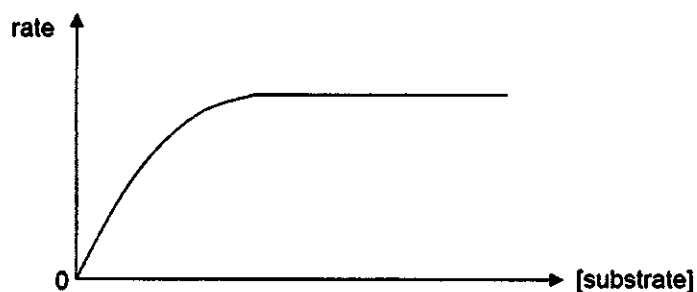
Which of the following correctly identifies the 3 gases?

	Gas 1	Gas 2	Gas 3
A	NH_3	C_2H_6	Ne
B	NH_3	Ne	C_2H_6
C	Ne	C_2H_6	NH_3
D	C_2H_6	Ne	NH_3

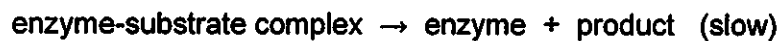
8. Which graph would confirm that the rate of decomposition of ammonium chloride is a first order reaction?



9. In an enzyme-catalysed reaction, the rate is affected by the concentration of substrate as shown in the graph below.



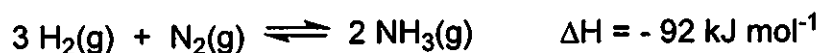
The mechanism for the reaction is as shown:



Which of the following is **incorrect**?

- A When [substrate] is low, the reaction is first order with respect to the substrate.
- B When [substrate] is high, the reaction is zero order with respect to the substrate.
- C The rate equation is given as: $\text{rate} = k [\text{enzyme-substrate complex}]$.
- D The reaction occurs in a two-step reaction.

10. The equation for the Haber Process is shown below.



Which of the following statements regarding the Haber Process is correct?

- A The use of Fe catalyst helps to lower the activation energy of the forward reaction more than that of the backward reaction.
 - B The use of a higher pressure increases the equilibrium constant.
 - C The rate constant of the backward reaction will decrease more than the rate constant of the forward reaction when temperature is decreased.
 - D The rate constant of the backward reaction will decrease less than the rate constant of the forward reaction when temperature is increased.
11. A student carried out a titration involving $0.10 \text{ mol dm}^{-3} \text{Ba(OH)}_2$ and $0.20 \text{ mol dm}^{-3} \text{HCOOH}$. Which of the following is a suitable indicator to indicate the end-point of this titration?
- A Phenolphthalein (pH range 8.2 – 10.0)
 - B Methyl red (pH range 4.8 – 6.0)
 - C Methyl orange (pH range 3.2 – 4.4)
 - D There is no suitable indicator.

12. Magnesium arsenate, $\text{Mg}_3(\text{AsO}_4)_2$, is a sparingly soluble salt commonly used to make insecticides. It dissociates in water according to the equation below.

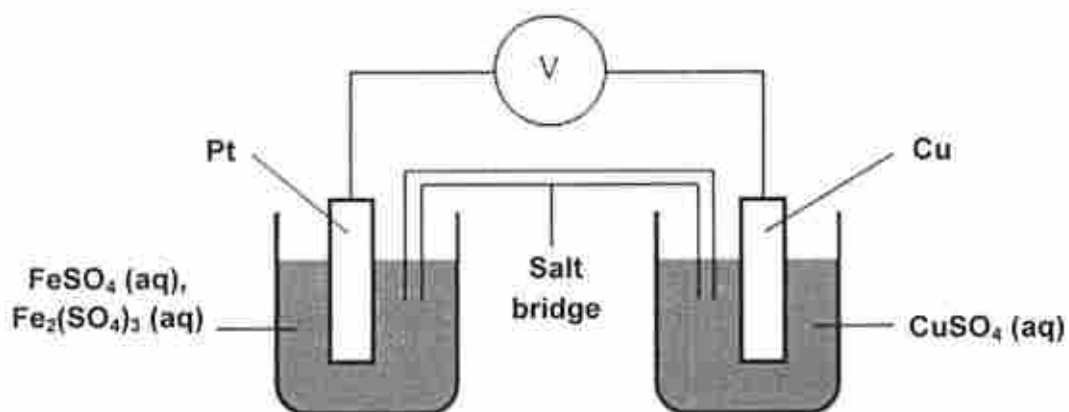


If the solubility product is S , what is the value of $[\text{AsO}_4^{3-} (\text{aq})]$ at equilibrium?

- A $S^{1/5}$
- B $(\frac{2}{3}S)^{1/5}$
- C $(\frac{2}{5}S)^{1/5}$
- D $(\frac{8}{27}S)^{1/5}$

13. Use of the Data Booklet is relevant to this question.

An electrochemical cell is set up as shown.



Which of the following correctly describes the cell?

- A $E_{\text{cell}}^{\ominus}$ is + 0.43 V when sodium cyanide is added to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half cell.
- B Cu is the positive electrode when sodium hydroxide is added to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half cell.
- C The reaction is less spontaneous when excess aqueous ammonia is added to Cu^{2+}/Cu half cell.
- D The cations in the salt bridge will move over to Cu^{2+}/Cu half-cell to prevent accumulation of positive charges.

14. The properties of each Period 4 element resemble those of the Period 3 element directly above it.

Which Period 4 elements form oxides that dissolve in water to give an acid solution?

- A As and Se
- B Ga and Ge
- C Ga and Se
- D Ca and Se

15. Elements W, X, Y and Z are in Period 3 of the Periodic Table.

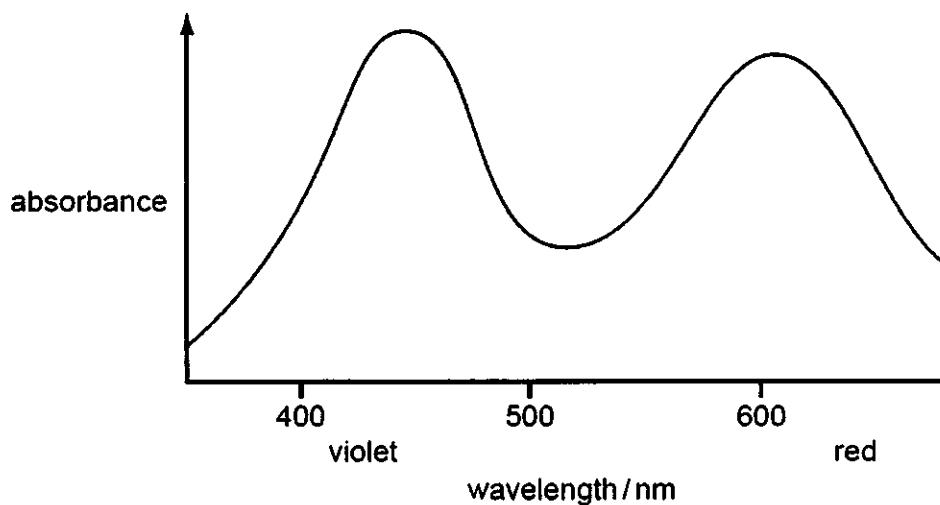
- W has the highest melting point among all the Period 3 elements.
- The chlorides of Y and Z are acidic while the chloride of X is neutral.
- The oxide of Y is basic while the oxide of Z is amphoteric.

Which of the following statements is correct?

- A The atomic radius increases in the following order: $W < Z < Y < X$.
- B The first ionisation energy decreases in the following order: $X > Y > Z > W$.
- C The pH of the chlorides decreases in the following order: $W > Z > Y > X$.
- D The electrical conductivity increases in the following order: $W < Z < Y < X$.

16. What can be seen when a piece of magnesium ribbon is placed in cold water?
- A A vigorous effervescence occurs.
 - B Bubbles of gas form slowly on the magnesium ribbon.
 - C The magnesium ribbon floats on the surface of the water and reacts quickly.
 - D The magnesium ribbon glows and a white solid is produced.
17. Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with tetrachloromethane, an organic solvent. What observation would be made?
- A A colourless layer forms on top of a reddish brown layer.
 - B The solution in the test-tube turns orange.
 - C A brown solid is seen in a colourless solution.
 - D A yellowish-green gas is produced.

18. A compound of chromium has the general formula of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. It is observed that 1 mole of this compound reacts with 3 moles of aqueous AgNO_3 . Also, this compound gives the following absorption spectrum.



Colour	Wavelength (nm)
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

Which of the following shows the correct structure of the chromium compound and its colour?

	Structure	Colour
A	$[\text{Cr}(\text{Cl})_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	Violet
B	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Green
C	$[\text{Cr}(\text{Cl})(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Orange
D	$[\text{Cr}(\text{Cl})_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$	Orange-violet

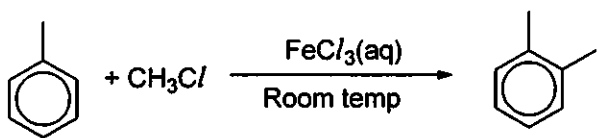
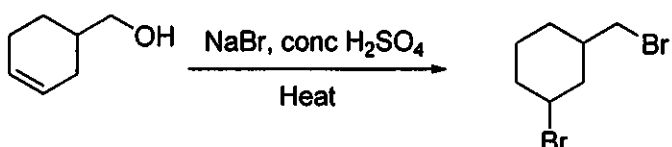
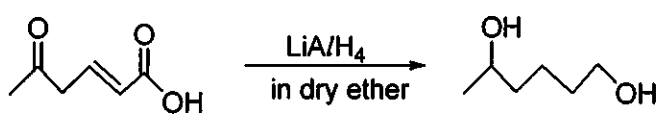
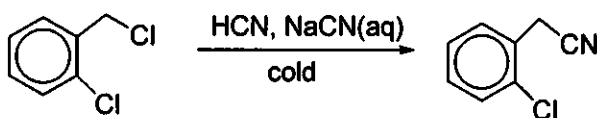
19. Compound X, $C_3H_6O_3$

- can be oxidised by sodium dichromate(VI);
- reacts with $NaBH_4$.

What could be X?

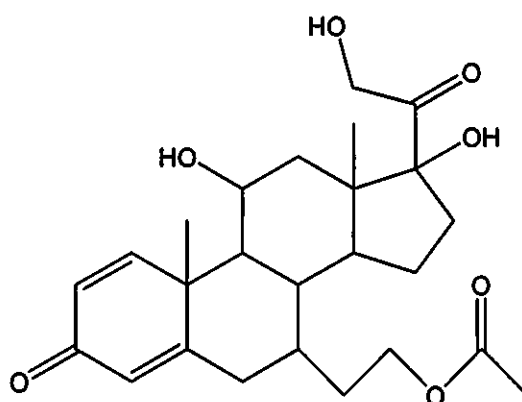
- A CH_3COOCH_2OH
- B $CH_3CH(OH)COOH$
- C CH_3OCOCH_2OH
- D $HOCH_2CH(OH)CHO$

20. Which transformation has a set of conditions that is correct?

- A 
Cc1ccccc1.CCl>>Cc1cccc(C)c1
- B 
C1CCC(CC1)CO.Br[Na].OS(=O)(=O)(O)O>>BrC1CCC(CC1)CBr
- C 
CC(=O)C=CC(=O)O>>CC(O)CCC(O)
- D 
ClCc1ccccc1Cl>>NCc1ccccc1Cl

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21. Compound **W** has the following structure.



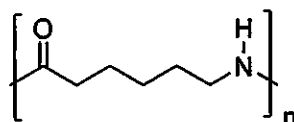
What reacts completely with 1 mole of **W**?

- A 4 mol of Na(s)
 - B 5 mol of HBr(g)
 - C 3 mol of NaOH(aq)
 - D 3 mol of 2,4-dinitrophenylhydrazine
22. Which liquid when shaken with AgNO_3 (aq) will give a precipitate in the shortest time?
- A tetrachloromethane
 - B propanoyl chloride
 - C 1-chlorobutane
 - D 2-chloropropene

23. For the following pairs of organic compounds, which reagent will be able to distinguish them?

			Reagent
A	$\text{CH}_3\text{CH}_2\text{CH}_3$	$\text{CH}_2=\text{CHCH}_3$	$\text{Cl}_2(\text{g})$
B	$\text{CH}_3\text{COCH}_2\text{I}$	$\text{CH}_3\text{CH}_2\text{CHO}$	I_2 in $\text{NaOH}(\text{aq})$
C	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	$\text{NaOH}(\text{aq})$
D	$\text{CH}_3\text{CH}_2\text{CHO}$	HCOOH	Tollens' reagent

24. Nylon 6 is a type of polyamide that is used for construction materials due to its high tensile strength and resistance. A section of nylon 6 molecule is shown below.



A sample of nylon 6 was subjected to a series of chemical reactions and Compounds P, Q and R were obtained at each step respectively.

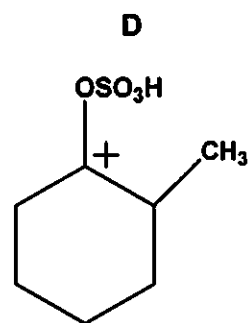
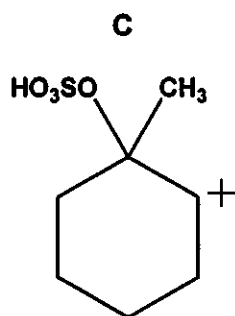
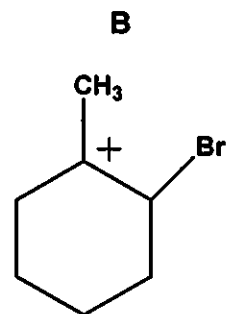
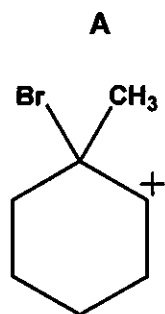
	Reagent	Organic Compound
Step 1	Hot concentrated NaOH , followed by careful acidification	P
Step 2	LiAlH_4 in dry ether	Q
Step 3	excess concentrated H_2SO_4 , heat	R

Which of the following statements is true?

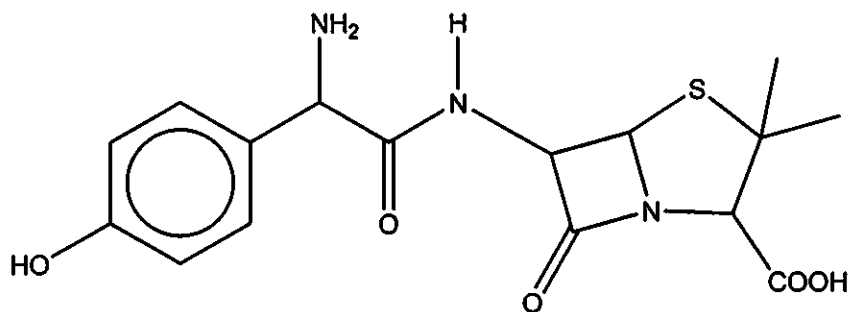
- A Compound P will react with 2,4-DNPH to produce orange precipitate.
- B Compound Q gives off white fumes with PCl_5 .
- C Step 3 is an addition reaction.
- D Compound P can undergo intramolecular nucleophilic substitution to form an amide.

[Turn Over

25. Which of the following is the major intermediate for the reaction of 1-methylcyclohexene and bromine in the presence of concentrated magnesium hydrogensulfate, $\text{Mg}(\text{OSO}_3\text{H})_2$?



26. The oxidation of alcohol **W** using hot acidified potassium manganate(VII) produced a compound of formula C_3H_6O . Which of the following reactions will produce the best yield of alcohol **W**?
- A Reacting 1-chloropropane with hot ethanolic NaOH
- B Reacting propanoic acid with $LiAlH_4$
- C Reacting 2-chloropropane with hot aqueous NaOH
- D Reacting propene with cold water
27. Amoxicillin is an antibiotic useful for the treatment of bacterial infections, such as middle ear infections.

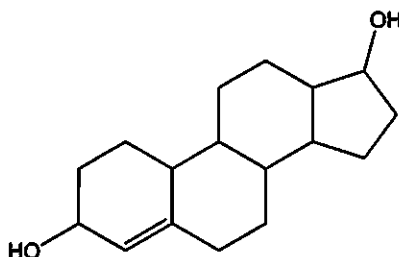


Amoxicillin

How many moles of NaOH(aq) will react with one mole of amoxicillin when it is heated under reflux with an excess of NaOH(aq)?

- A 3
- B 4
- C 5
- D 6

28. Bolandiol is a banned synthetic anabolic steroid.



Bolandiol

Which of the following statements is **not** true?

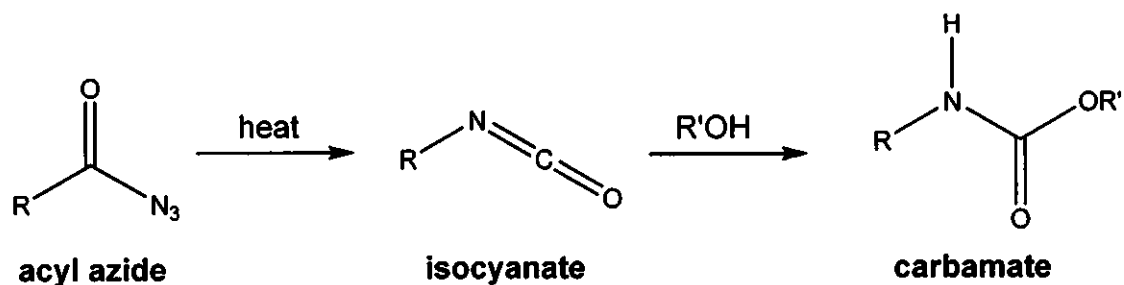
- A Bolandiol has 2^7 stereoisomers when reacted with liquid bromine.
- B Passing hot aluminium oxide over bolandiol produces a compound with three double bonds.
- C Orange potassium dichromate (VI) turns green when Bolandiol is heated with it.
- D Bolandiol produces one mole of hydrogen gas when reacted with sodium metal.
29. When alkane J, C_8H_{14} , is reacted with bromine under ultraviolet light, only three isomeric monobromo compounds, K, L, and M are produced. Only compound L is chiral. What are the structures of J and L?

J

L

A	$(CH_3)_3CCH_2CH_3$	$(CH_3)_3CCHBrCH_3$
B	$(CH_3)_2CHCH(CH_3)_2$	$(CH_3)CH(CH_2Br)CH(CH_3)_2$
C	$(CH_3)_2CHCH_2CH_2CH_3$	$(CH_3)_2CHCHBrCH_2CH_3$
D	$CH_3CH_2CH_2CH_2CH_2CH_3$	$CH_3CH_2CHBrCH_2CH_2CH_3$

30. The Curtius rearrangement can be used to produce carbamates from acyl azides. A general example of the Curtius rearrangement is shown below.



Which pair of compounds can be used to synthesise ethyl carbamate, CH₃CH₂OCONH₂?

- A**
-
- CH₃CH₂-C(=O)-N₃ + CH₃OH
- B**
-
- CH₃-C(=O)-N₃ + CH₃CH₂OH
- C**
-
- H-C(=O)-N₃ + CH₃CH₂OH
- D**
-
- H-C(=O)-N₃ + CH₃OH

Section B

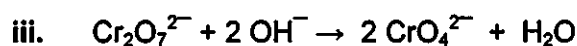
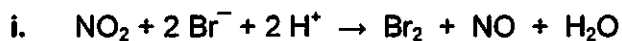
For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses A to D should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31. Which statements regarding the following reactions are true?

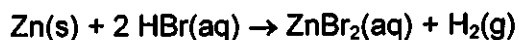


- 1 In reaction i, NO radical is produced.
- 2 NaH produced in reaction ii can act as an oxidising agent.
- 3 Reaction iii is a redox reaction as the number of oxygen atoms has decreased.

32. Which of the following sets of compounds consists of a giant ionic structure, a giant covalent structure and a simple covalent structure?

- 1 AlF_3 , graphite, BeCl_2
- 2 AlBr_3 , P_4O_{10} , Si
- 3 Al_2O_3 , BF_3 , SiCl_4

33. Zinc reacts readily with dilute hydrobromic acid to form zinc bromide and hydrogen.



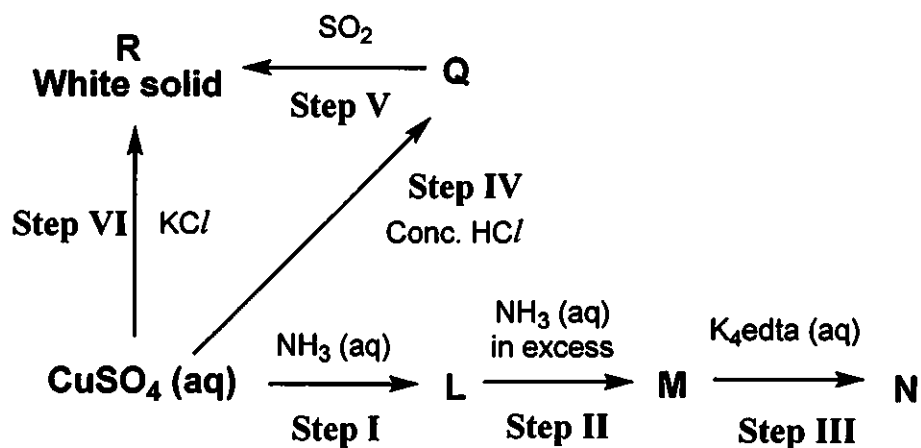
The standard enthalpy change for this reaction can be measured in the laboratory. What further information is needed in order to calculate the standard enthalpy change of formation of aqueous zinc bromide?

- 1 ΔH_f for HBr (aq)
 - 2 1st and 2nd electron affinity of Zn
 - 3 ΔH_f for H₂(g)
34. *Use of the Data Booklet is relevant to this question.*

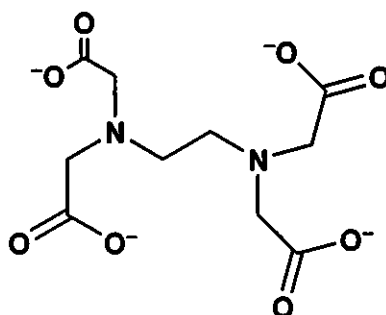
When chromium is heated separately with chlorine, bromine and iodine, which of the following can be obtained as the final product?

- 1 CrI₂
- 2 CrCl₃
- 3 CrBr₃

35. The following shows a reaction scheme involving aqueous CuSO_4 .



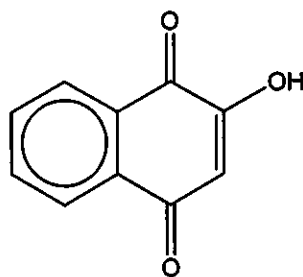
The structure of edta ion is as shown.



Which of the following statements regarding the reaction scheme are correct?

- 1 ΔS is positive for step III.
- 2 The d orbitals of Cu in species Q are degenerate.
- 3 Steps V and VI involve ligand exchange.

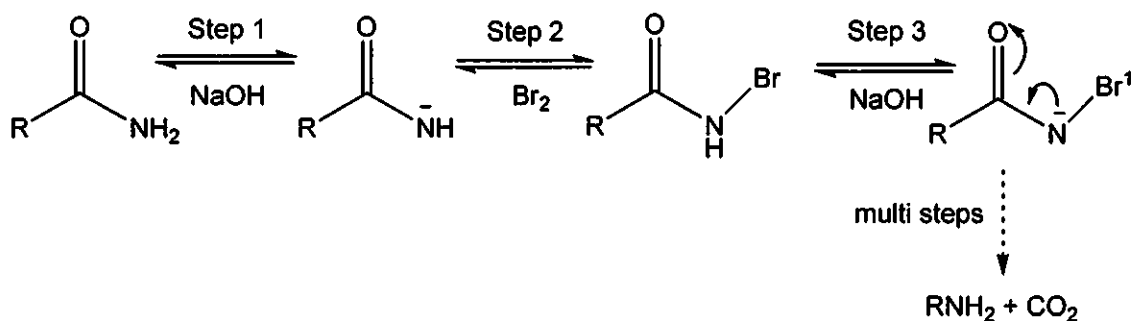
36. Lawsone is a dye which can be extracted from the henna plant, *Lawsonia inermis*.



Lawsone

Which of the following reagent will react with Lawsone?

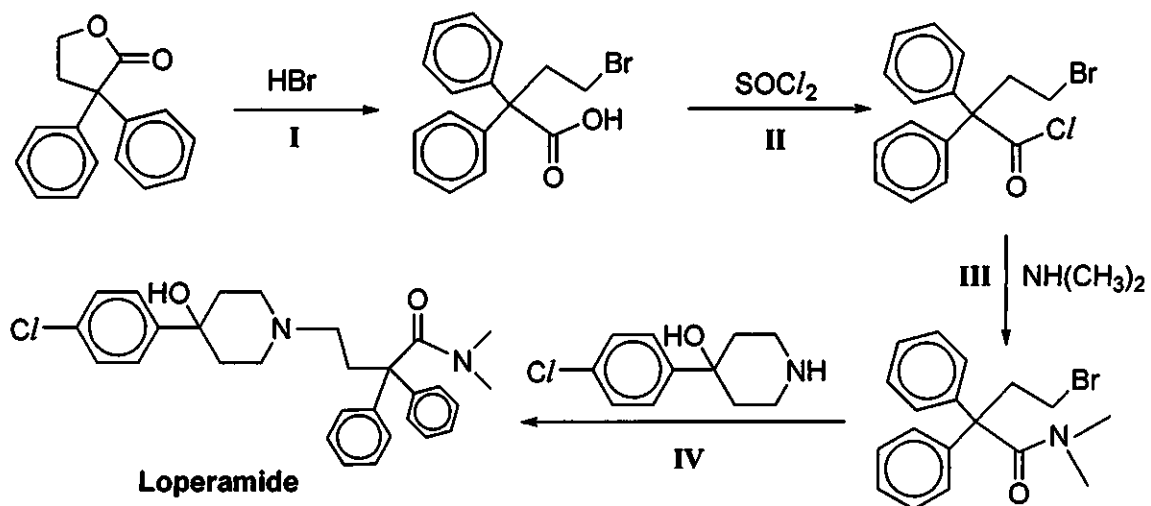
- 1 NH_2OH
 - 2 $[\text{Ag}(\text{NH}_3)_2]^+$
 - 3 Concentrated HNO_3
37. An amine may be derived from an amide in a reaction known as Hoffmann rearrangement. Part of the mechanism is as shown:



Which of the following statements is likely to be true?

- 1 NaOH is used as a base in Steps 1 and 3.
- 2 Br_2 is behaving as an electrophile in Step 2.
- 3 The oxidation state of Br^1 in Step 3 is -1 .

38. The active ingredient in anti-diarrhoea medicines is loperamide. The synthesis of loperamide is shown below.



What type of reaction is shown by at least one of the steps in the above route?

- 1 Hydrolysis
- 2 Nucleophilic substitution
- 3 Electrophilic substitution

39. Some of the amino acids found in soy protein are listed in the table below.

Amino acid	R-group
Cysteine	$-\text{CH}_2\text{SH}$
Threonine	$-\text{CH}(\text{OH})\text{CH}_3$
Glutamic acid	$-\text{CH}_2\text{CH}_2\text{COOH}$
Valine	$-\text{CH}(\text{CH}_3)_2$

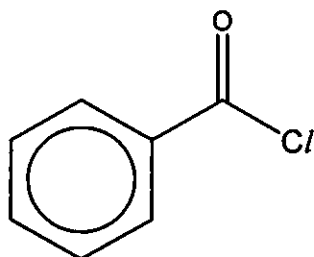
Which of the following statements are true?

- 1 Adding a reducing agent will disrupt the disulfide bonds and denature the protein.
- 2 The R-groups of glutamic acid and threonine will interact with each other through hydrogen bonds.
- 3 Adding $\text{NaOH}(\text{aq})$ will denature the protein.

40. Which of the following pairs of compounds would produce an amide when reacted together?

- 1 $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{NH}_2$ and $\text{CH}_3\text{COC}l$

2



and $(\text{CH}_3)_3\text{N}$

- 3 $\text{CH}_3\text{CH}(\text{CH}_3)\text{NH}_2$ and CH_3COOH

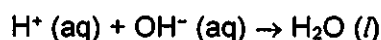
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ST ANDREW'S JUNIOR COLLEGE 																					
JC 2 Preliminary Exam																					
Chemistry Higher 2 Paper 2		9647/02 31 August 2016 2 hours																			
Candidates answer in the spaces provided on the question paper. Additional Materials: Data Booklet																					
READ THESE INSTRUCTIONS FIRST Write in dark blue or black pen. You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid. Answer all questions. You are reminded of the need for good English and clear presentation in your answers. The number of marks is given in brackets [] at the end of each question or part question.																					
For Examiner's Use: <table border="1" style="width: 40%; border-collapse: collapse; margin-top: 10px;"> <thead> <tr> <th style="width: 70%;">Question</th> <th style="width: 30%;">Marks</th> </tr> </thead> <tbody> <tr><td>1</td><td></td></tr> <tr><td>2</td><td></td></tr> <tr><td>3</td><td></td></tr> <tr><td>4</td><td></td></tr> <tr><td>5</td><td></td></tr> <tr><td>6</td><td></td></tr> <tr><td>7</td><td></td></tr> <tr> <td>Total (72 marks)</td> <td></td> </tr> </tbody> </table>				Question	Marks	1		2		3		4		5		6		7		Total (72 marks)	
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- 1 A student found a bottle of solid benzoic acid in the school laboratory. She was tasked to determine the standard enthalpy change of neutralisation of benzoic acid. The standard enthalpy change of neutralisation is when one mole of water is formed between an acid and a base.



You may assume you are provided with the following:

- FA 1, aqueous sodium hydroxide, NaOH
- Solid benzoic acid
- Polystyrene (styrofoam) cups
- Apparatus normally found in a school laboratory

Before carrying out the experiment, an aqueous solution of 2.00 mol dm^{-3} benzoic acid (FA 2) is first prepared. Subsequently, in separate experiments, different volumes of FA 2 and FA 1 are mixed while keeping the total volume of the reaction mixture constant. In each experiment, the temperature rise, ΔT , is to be determined. A graph of ΔT against volume of FA 1 used is then plotted.

Data from the graph can then be used to determine:

- the ΔT_{max} ,
- the concentration of FA 1,
- the enthalpy change of neutralisation between FA 1 and FA 2.

It is given that 4.18 J is required to raise the temperature of 1 cm^3 of any solution by 1°C .

- (a) Write an equation to represent the standard enthalpy change of neutralisation between sodium hydroxide and benzoic acid.

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[1]

[Turn Over

- 1 (b) (i) Write a detailed plan to prepare 2.00 mol dm^{-3} solution of FA 2.

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[3]

- (ii) It is predicted that the maximum temperature change for the neutralisation would occur when the volume of FA 1 mixed is between 25 cm^3 and 30 cm^3 . The total volume of any mixture should be kept constant at 50 cm^3 .

Write a detailed plan on how you could determine the temperature changes for the series of reactions between FA 1 and FA 2.

Your plan should include details of:

- all essential experimental details,
- appropriate volumes of solutions to be used,
- a tabulation of the experimental data to be collected (including volumes used),
- how these measurements can be used to obtain the temperature change, ΔT .

1 (b) (ii)

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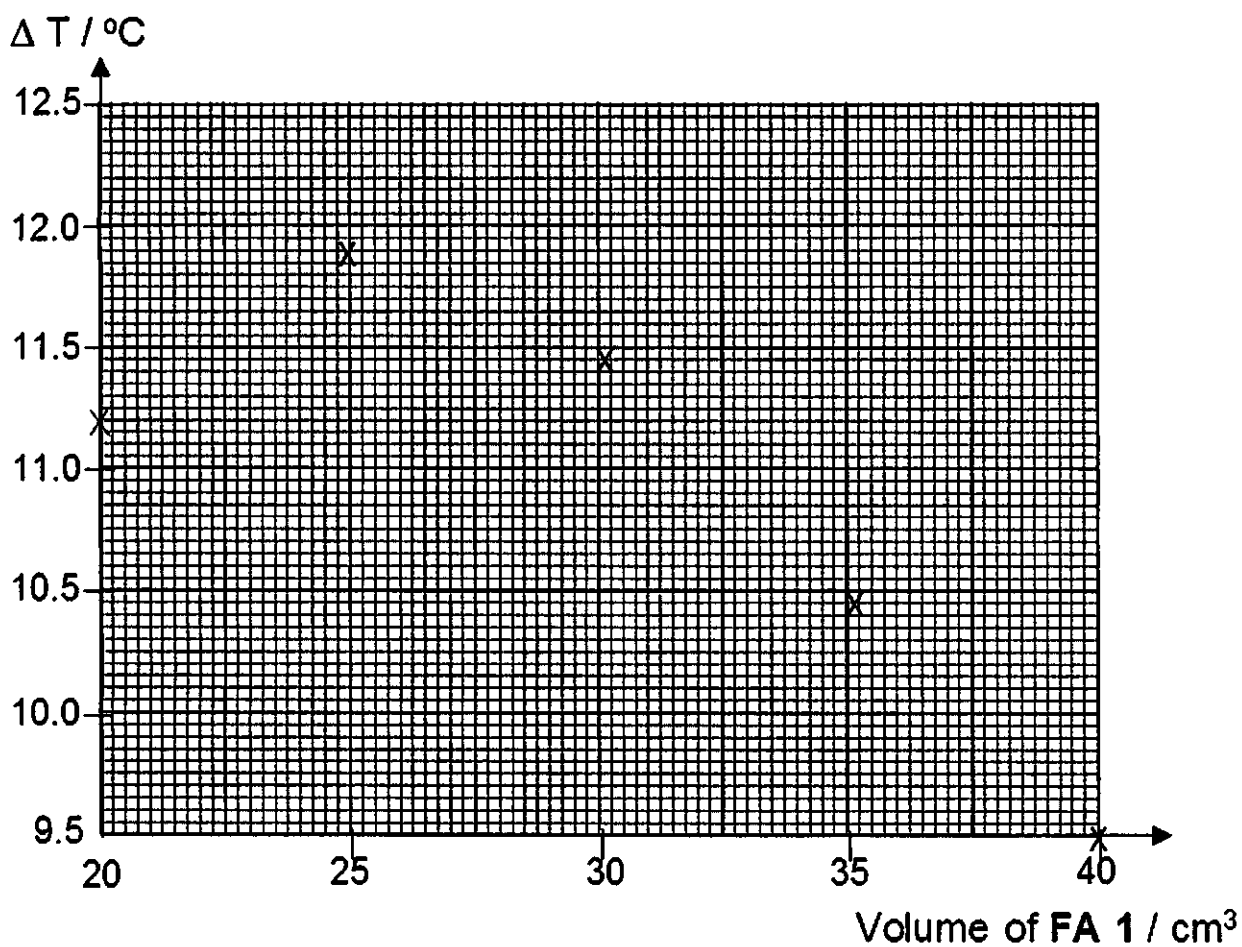
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[5]

[Turn Over

- 1 (b) (iii) The following plots were plotted on a grid after another similar experiment was conducted. Draw suitable graphs through the plotted points.

[1]



1 (c) By using the graph in (b)(iii), calculate

- the concentration of FA 1, given that the total volume of the mixture is 50 cm³.
- the enthalpy change of neutralisation for the reaction between FA 1 and FA 2.

[2]

[Total: 12]

[Turn Over

- 2 (a) Chromium carbonyl, also known as chromium hexacarbonyl, is a chemical compound with the formula $\text{Cr}(\text{CO})_6$. $\text{Cr}(\text{CO})_6$ is zerovalent, meaning that Cr has an oxidation state of 0. Draw the structure of the complex and state the shape and bond angle around the Cr atom in the complex.

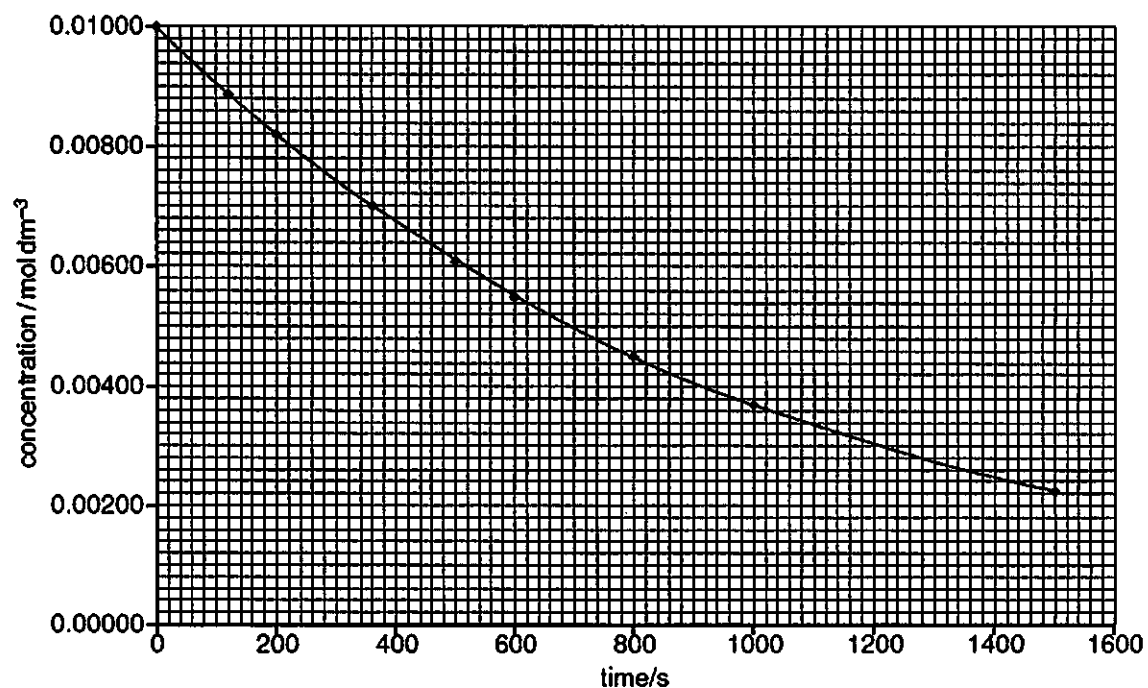
[2]

- (b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.



Two separate experiments were carried out to study the rate of this reaction.

In the first experiment, the ligand PR_3 was in a large excess and $[\text{Cr}(\text{CO})_6]$ was measured against time. The results are shown on the graph below.



- 2 (b) In the second experiment, $\text{Cr}(\text{CO})_6$ was in a large excess, and $[\text{PR}_3]$ was measured against time. The following results were obtained.

time / s	$[\text{PR}_3] / \text{mol dm}^{-3}$
0	0.0100
120	0.0076
200	0.0060
360	0.0028

- (i) On the graph, plot the data given in the table.

[1]

- (ii) Use the graphs to determine the order of reaction with respect to $\text{Cr}(\text{CO})_6$ and PR_3 . In each case explain how you arrived at your answer.

$\text{Cr}(\text{CO})_6$

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PR_3

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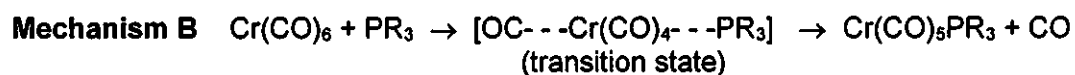
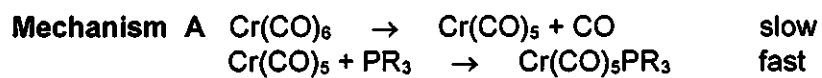
[2]

- (iii) Write the rate equation for the reaction, and calculate a value for the rate constant, stating the units of the rate constant.

[3]

[Turn Over]

- 2 (b) (iv) Two possible mechanisms for this reaction are given below. State the mechanism which is consistent with the rate equation you have written in (b)(iii) and explain your answer.



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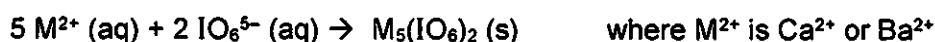
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[Total: 10]

3 This question refers to compounds of calcium and barium.

- (a) Oil paints contain traces of red Ca^{2+} and green Ba^{2+} ions which give them their characteristic red and green colours respectively. Oil painting is typically done on canvas. During the manufacturing process of canvas, hydrogen orthoperiodate ions, HIO_6^{4-} , is left on the canvas.

Orthoperiodate salts are formed when orthoperiodate ions, IO_6^{5-} , reacts with the Ca^{2+} and Ba^{2+} ions in the paint, causing the decolourisation of the red and green colour of the paint. The equations below show the formation of IO_6^{5-} and its salts.



Relevant K_{sp} values are given in the table below :

Salt	K_{sp}
$\text{Ca}_5(\text{IO}_6)_2$	4.0×10^{-9}
$\text{Ba}_5(\text{IO}_6)_2$	1.6×10^{-15}

The painting was stored in a display cabinet at a low pH environment. Over the weekend, the electrical supply of the display cabinet was disrupted which resulted in an increase of the environment's pH. It was found that the green portions of the painting were decolourised due to the formation of solid barium orthoperiodate, $\text{Ba}_5(\text{IO}_6)_2$.

[Turn Over

- 3 (a) Explain qualitatively why the green coloured areas of the painting were decolourised but not the red coloured areas when the pH increased.

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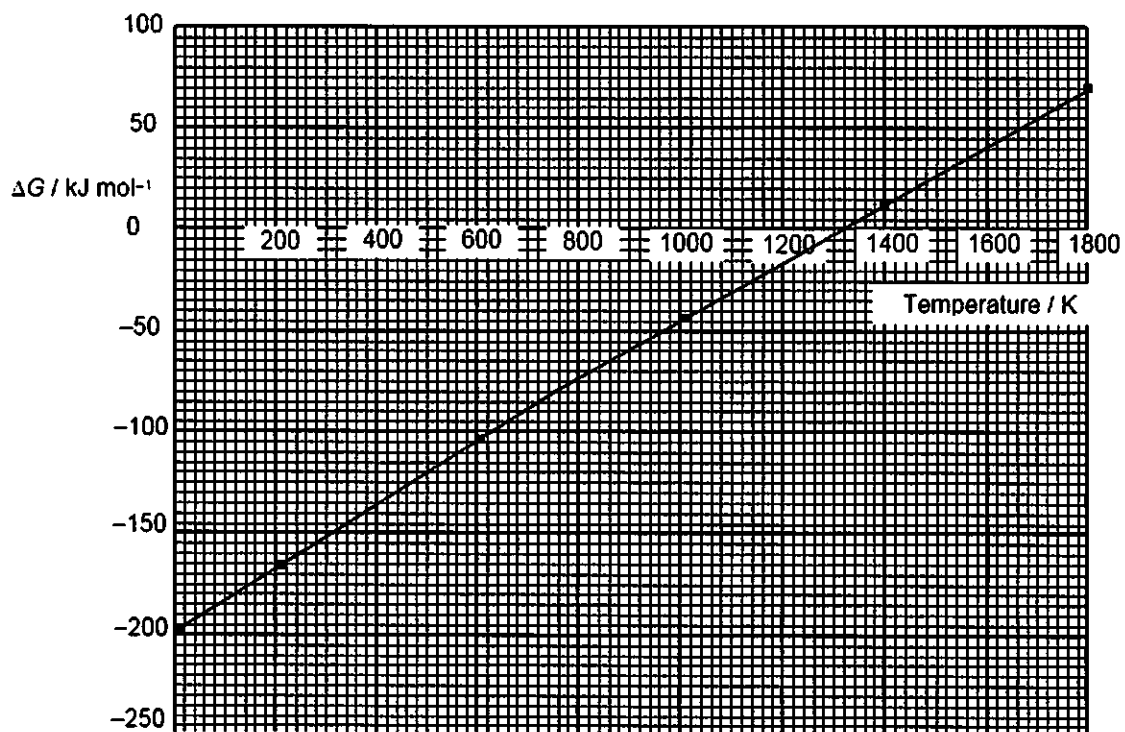
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[3]

- 3 (b) ΔG , ΔH and ΔS are related by the following equation.

$$\Delta G = \Delta H - T\Delta S$$

The Ellingham diagram below shows how ΔG changes between 0 K and 1800 K for the following reaction.



For the range of temperatures in the graph above, it can be assumed that the enthalpy change and the entropy change of the reaction remain approximately constant.

- (i) Predict the sign of ΔS for the reaction, showing your reasoning.

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[2]

[Turn Over]

3 (b) (ii) Using the graph, calculate ΔS .

[1]

(iii) Using the graph, determine ΔH .

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[1]

(iv) Determine the temperature above which the reaction become non-spontaneous.

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[1]

[Total: 8]

- 4 The table below gives data about some physical properties of the elements calcium, copper and chromium.

Physical Property	Calcium	Copper	Chromium
Relative atomic mass	40.1	63.5	52.0
Atomic radius / nm	0.197	0.128	0.117
Density / g cm ⁻³	1.54	8.92	7.20
First ionisation energy / kJ mol ⁻¹	590	745	653

- (a) (i) Explain why the first ionisation energy of copper and chromium are both higher than that of calcium.

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[2]

- (ii) Use relevant data from the table to explain qualitatively why the densities of copper and chromium are significantly greater than that of calcium.

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[Turn Over]

- 4 (b) Chromium (III) nitrate is more acidic than chromium (II) nitrate. Explain with the aid of a relevant equation.

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[2]

- (c) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with gold and chromium impurities. It contained no other metal. In order to purify it, the alloy was made the anode of an electrolytic cell, with a pure copper cathode and aqueous copper (II) sulfate as the electrolyte.

Explain, with reference to $E^\ominus$ values, what happens to the gold and chromium impurities during this purification process. The electrode reaction for the standard Au^{3+}/Au half cell is

$$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au}(\text{s}) \quad E^\ominus = +1.50 \text{ V}$$

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[3]

- 4 (d) A current of 1.8 A was passed through the cell described in (c) for 17 minutes, and the electrodes removed, washed, dried and weighed. It was found that some mass was lost from the anode.

After filtering it off and drying it, the deposit below the anode weighed 0.085 g. On adding an excess of hydroxide ions to the electrolyte, a grey-green precipitate was formed. Its mass was 0.304 g. (You may assume that negligible amount of copper ions remained in the electrolyte.)

- (i) Calculate the expected increase in mass of the cathode.

[2]

- (ii) Identify the grey-green precipitate.

grey-green precipitate:

[1]

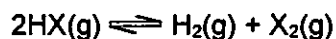
- (iii) It was found that the mass of copper removed from the alloy was 0.466 g. Calculate the masses of gold and chromium removed from the alloy. Hence calculate the total mass lost by the anode.

[3]

[Total: 14]

[Turn Over]

- 5 (a) A student conducted an experiment to identify the trend in thermal stability of hydrogen halides. The reaction occurred according to the following equation:



The approximate K_c values for the above equilibrium at various temperatures are shown in the table below.

Temperature /°C	K_c		
	HCl	HBr	HI
500	10^{-13}	10^{-9}	10^{-5}

- (i) Using the Data Booklet, explain the trend in thermal stability of hydrogen halides down the group.

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[2]

- (ii) Hence, deduce if the trend in (a)(i) agrees with the K_c data given above.

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[1]

- 5 (b) A student conducted another experiment to distinguish between samples of sodium chloride and phosphorus pentachloride. It was found that red onion water can be used as an indicator. The table below shows the colour of the indicator at various pH.

pH	Colour
Less than 7	Red
7	Violet

- (i) To each unknown sample of chlorides, he added a few drops of red onion water. He recorded the colour of the indicator. Predict the identities of the chlorides.

Colour of red onion water	Identity of chloride
Red	
Violet	

[1]

- (ii) With the aid of an equation, describe the action of water on phosphorus pentachloride.

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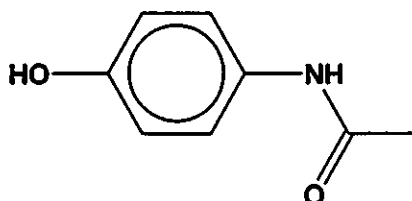
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[2]

[Total: 6]

[Turn Over]

- 6 Paracetamol is an effective analgesic discovered by Joseph von Mering in 1893. Its structure is as shown.

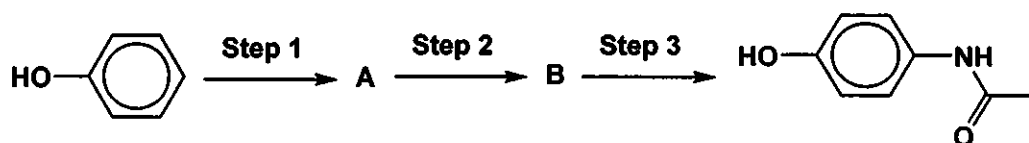


- (a) Explain why all the carbon-carbon bonds in benzene are of the same length.

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[1]

- (b) (i) Paracetamol may be synthesised from phenol as shown.



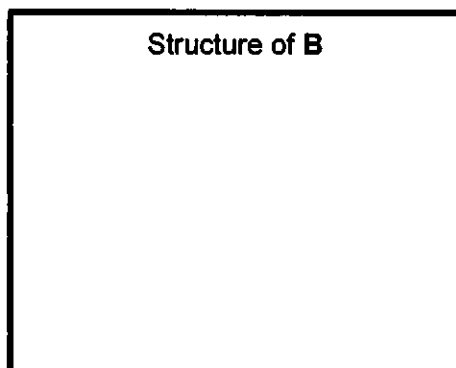
State the reagents and conditions for steps 1 to 3. Draw the structure of the intermediate product B.

Reagents and conditions:

Step 1:

Step 2:

Step 3:

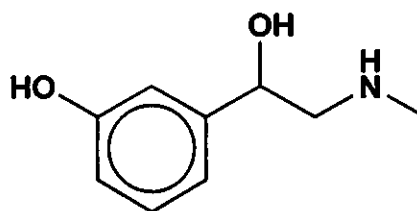


[4]

- 6 (b) (ii) Based on **Step 3** of the given reaction scheme, draw the structure of a possible side-product.

[1]

- (iii) Phenylephrine is a decongestant which may be taken with paracetamol when a person is suffering from cold. The structure of phenylephrine is as shown.



State and explain how the basicity of phenylephrine might compare with that of paracetamol.

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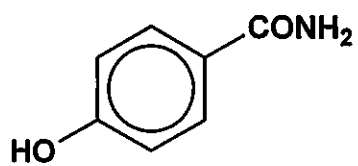
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[2]

[Turn Over]

- 6 (b) (iv) Suggest a simple chemical test to distinguish between paracetamol and compound A.



Compound A

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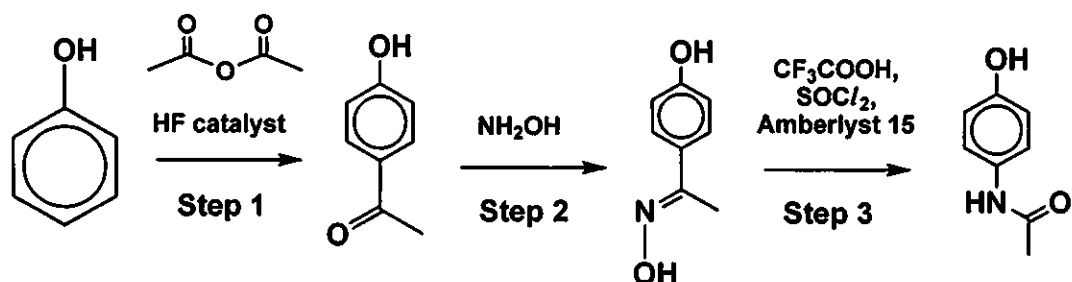
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[2]

- 6 (c) (i) Hoechst and Celanese discovered a simpler synthetic route for paracetamol as shown.



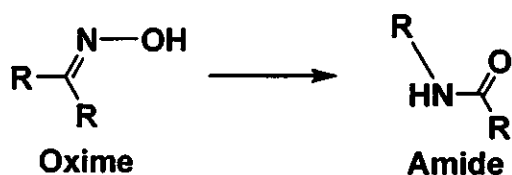
State the types of reaction for steps 1 and 2.

Step 1:

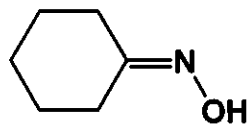
Step 2:

[2]

- (ii) Step 3 is known as the Beckmann arrangement, where an oxime is converted into an amide.



Draw the structure of the product formed when



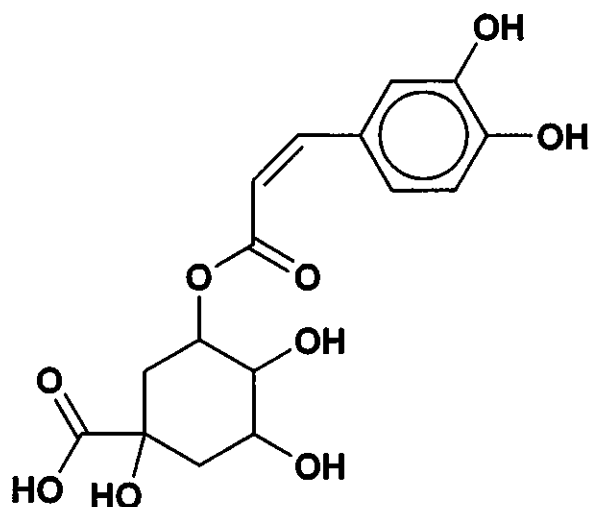
undergoes the Beckmann arrangement.

[1]

[Total: 13]

[Turn Over]

- 7 Coffee beans contain chlorogenic acid, which is an antioxidant and an important biosynthetic intermediate. The structure of chlorogenic acid is as shown.

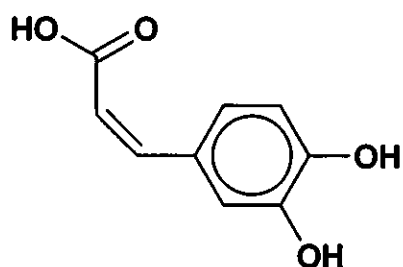


- (a) State the number of moles of hot NaOH (aq) that will react with 1 mole of chlorogenic acid.

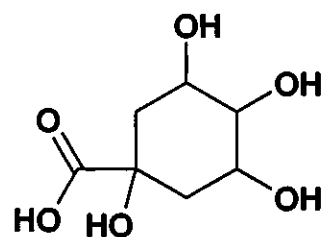
.....

[1]

- 7 (b) On heating with dilute acid, chlorogenic acid produces two compounds, X and Y.

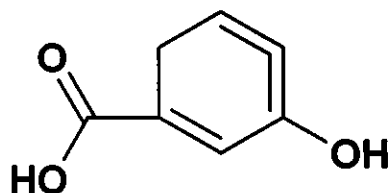


Compound X

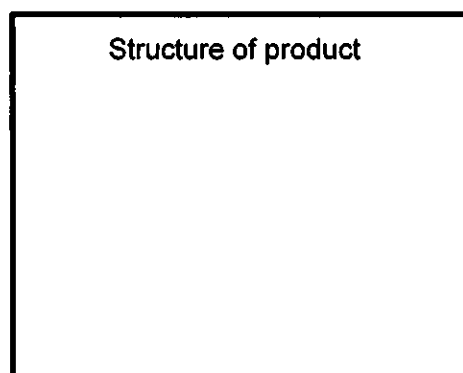


Compound Y

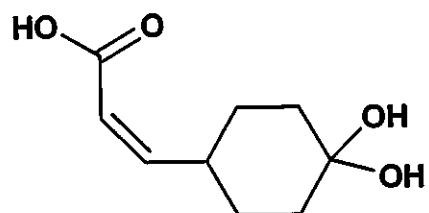
When compound Y reacts with hot excess concentrated sulfuric acid, a product with a molecular formula of $C_7H_6O_3$ is formed. A student claims that the product formed has the following structural formula but the teacher disagrees.



Draw the correct structure of the product and explain what is wrong with the student's answer.



7 (c)



Compound Z

- (i) Compound Z reacts with Br_2 (l) at room temperature and in the dark. Describe the mechanism showing curly arrows, charges, dipoles and any relevant lone pairs.

- 7 (c) (ii) The product of (c)(i) exists as a mixture of 4 stereoisomers. State the type of isomerism exhibited by the product and draw all the stereoisomers.

.....

[3]

[Total: 9]

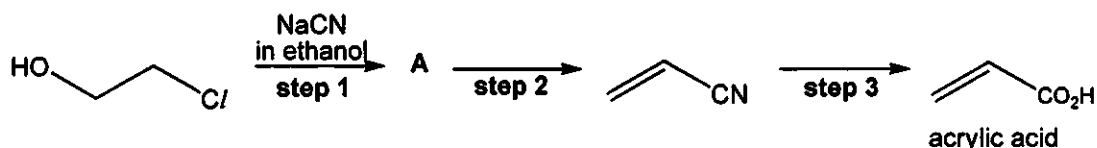
End of Paper

Name:		Class:	
ST ANDREW'S JUNIOR COLLEGE  JC2 Preliminary Examinations			
Chemistry			9647/03
Higher 2			16 September 2016
Paper 3			2 hours
Candidates answer on separate paper.			
Additional Materials: Writing paper, Data Booklet			
READ THESE INSTRUCTIONS FIRST Write your name and civics group on all the work you hand in. Write in dark blue or black pen. You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid. Answer any four questions. You are reminded of the need for good English and clear presentation in your answers. At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.			
This document consists of 14 printed pages including this page.			

[Turn over

1 Propenoic acid, also commonly known as acrylic acid, is used in the formation of many polymers.

(a) Acrylic acid can be synthesised from 2-chloroethanol in the laboratory by the following route.



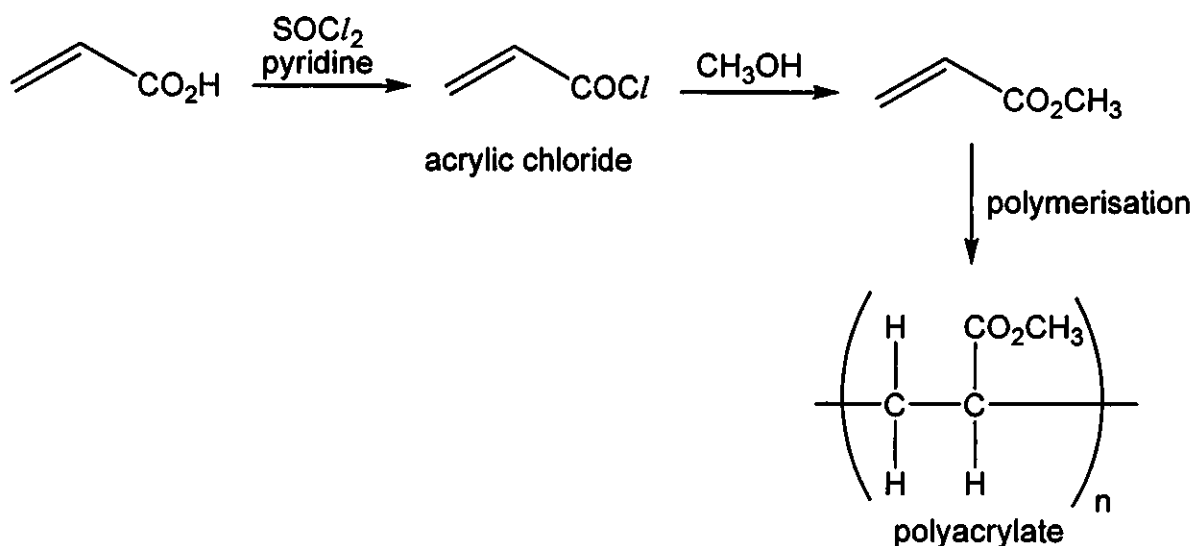
- (i) Suggest the structure for intermediate A. [1]
- (ii) Suggest reagents and conditions for **step 2** and for **step 3**. [2]
- (iii) What type of reaction is occurring in **step 2**? [1]

(b) Acrylic acid is manufactured industrially from the reaction of propene and oxygen gas.

- (i) Write a balanced equation for this reaction. [1]
- (ii) Propenal was isolated as an intermediate product in the reaction.
Draw the structure of propenal. [1]

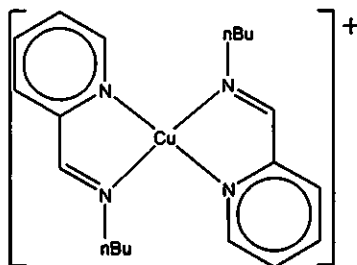
(c) Polyacrylate is used in environmentally-friendly detergents to remove calcium ions and magnesium ions in water.

In the manufacture of polyacrylate, acrylic acid was first converted into acrylic chloride, followed by reaction with an alcohol to form a monomer. Polyacrylate is formed when the monomer undergoes polymerisation.



- (i) Write a balanced equation for the conversion of acrylic acid into acrylic chloride. [1]
- (ii) Suggest the type of reaction occurring in the formation of the monomer from acrylic chloride. [1]
- (iii) Suggest how polyacrylate can remove magnesium ions from water through complex formation. [1]

- 1 (d) In the kinetic studies of polymerisation, *transition element-containing catalysts* were used. A copper(I)-containing catalyst is shown below.



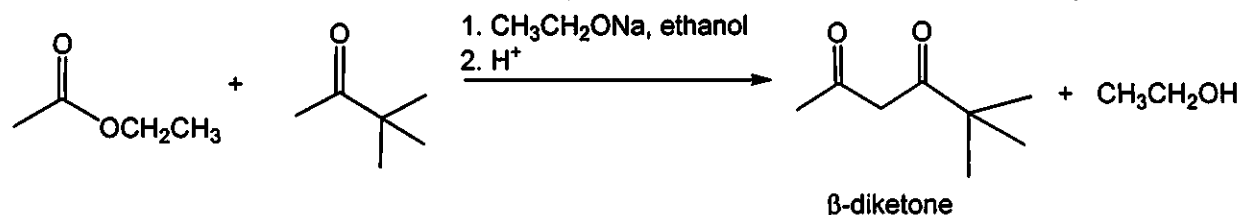
Cu(I)-nBuPCA catalyst

- (i) What is the co-ordination number of copper in the Cu(I)-nBuPCA catalyst? [1]
 - (ii) What is the electronic configuration of copper in Cu(I)-nBuPCA? [1]
 - (iii) Suggest whether copper in Cu(I)-nBuPCA catalyst can be classified as a *transition element*. [1]
- (e) Cu(I) undergoes disproportionation to form Cu and Cu(II).
- (i) Use relevant data from the *Data Booklet* to predict the spontaneity of this disproportionation reaction. [2]
 - (ii) Describe and explain what you would see when aqueous ammonia is added slowly to an aqueous solution of copper(II) chloride, until the aqueous ammonia is in excess. Write equations for any reactions that occur. [4]
 - (iii) Suggest an explanation for the difference in colour between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CuCl}_4]^{2-}$. [2]

[Total: 20]

[Turn Over]

- 2 In a Mixed Claisen Condensation Reaction, an ester and a ketone react to form a β -diketone.

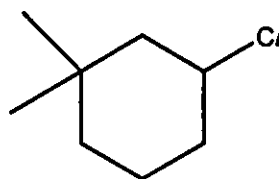


- (a) (i) Draw the β -diketone formed when 2,2-dimethylcyclohexanone reacts with ethyl ethanoate in the Mixed Claisen Condensation Reaction.



[1]

- (ii) In not more than 3 steps, propose the synthesis of 2,2-dimethylcyclohexanone from the following starting material.



[5]

- (b) Due to the presence of two ketone functional groups, β -diketones are a highly valuable substrate in several organic chemistry syntheses.

One of the many examples is selective reduction, in which only one of the ketone reduced.

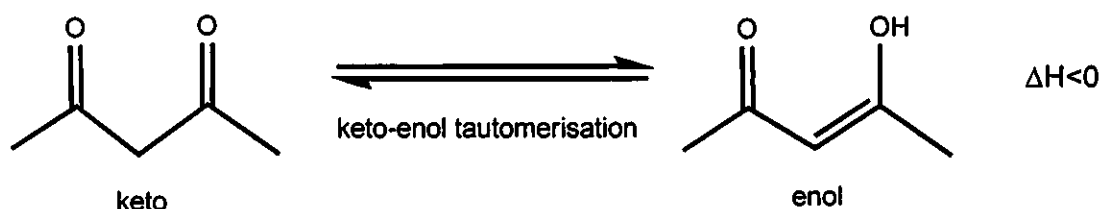


Draw the mechanism for the reaction between 4-hydroxypentan-2-one and HCN.

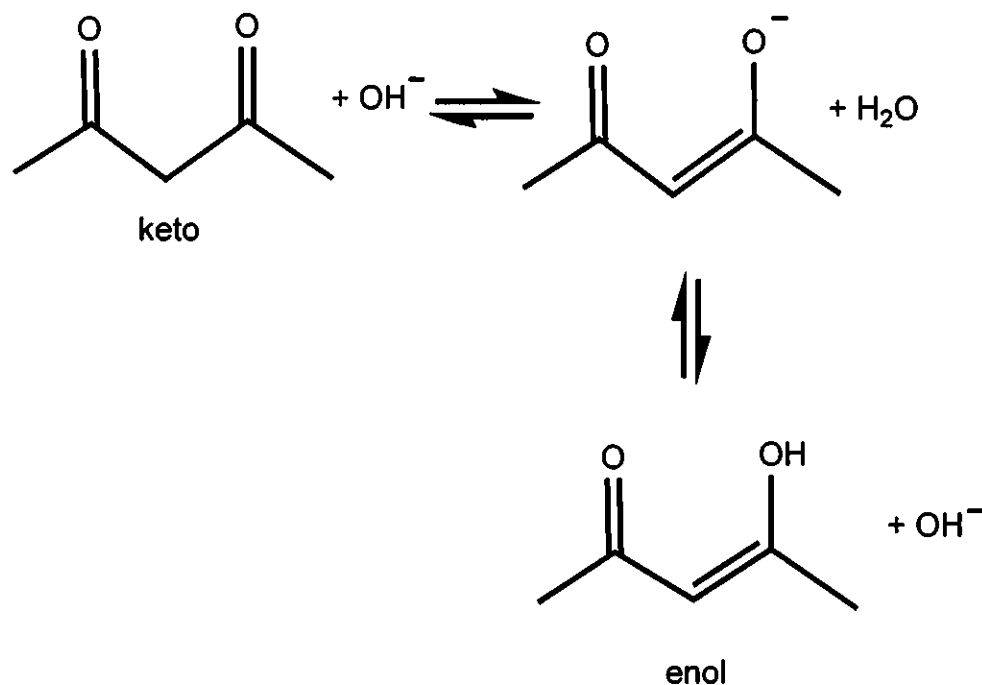
[3]

- 2 (c) β -diketones exist in equilibrium with a tautomeric form, known as an enol.

This is known as keto-enol tautomerisation. The keto-enol tautomerisation of pentan-2,4-dione is shown below.



- (i) Write an expression for K_c for the keto-enol tautomerisation of pentan-2,4-dione. [1]
 - (ii) In the case of pentan-2,4-dione, 76% of the mixture exists as an enol at room temperature and pressure. Calculate a value for K_c . [1]
 - (iii) Sketch a graph showing how the rates of the forward and reverse reactions change from the time pure keto is added to the time the reaction reaches equilibrium. Label your two lines clearly. [2]
- (d) The keto-enol tautomerisation is catalysed by the presence of an inorganic base, such as NaOH.



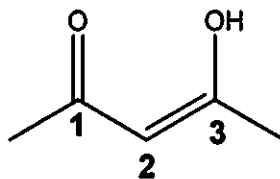
- (i) State how the presence of NaOH would affect the K_c , as calculated in (c)(ii). [1]
- (ii) On the same diagram in (c)(iii), show how the rates of the forward and reverse reactions change for the base catalysed keto-enol tautomerisation. Label your lines clearly. [1]
- (iii) Hence, explain the effect of NaOH on the reaction. [2]

[Turn Over]

- 2 (e) The enol form is more stable than the keto form due to two reasons

Reason I: Intramolecular hydrogen bonding

Reason II: Position of p orbitals



- (i) Draw an appropriate diagram to show how **reason I** contributes to the stability of [1]
the enol form.

- (ii) State the hybridisation of the carbon atoms at positions 1, 2 and 3.

Hence, explain how **reason II** contributes to the stability of the enol form. [2]

[Total: 20]

- 3 (a) Antiseptics and disinfectants are used to kill bacteria. The difference between antiseptics and disinfectants is that antiseptics are used on living skin and disinfectants are used on surfaces of objects.

Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is often used to sanitise public swimming pools. It is produced by treating calcium hydroxide with chlorine gas.



- (i) Write an equation for the decomposition of calcium hydroxide. [1]
- (ii) Deduce whether calcium hypochlorite would decompose at a higher or lower temperature than calcium hydroxide. Explain your reasoning. [2]
- (iii) In order to test the percentage purity of the calcium hypochlorite granules, 1 g of the calcium hypochlorite granules above was dissolved in water and the solution was then reacted with excess iodide in an acidic medium.



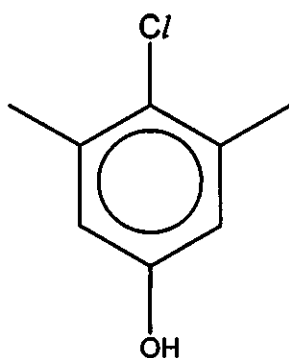
The resulting solution was then titrated with $0.500 \text{ mol dm}^{-3}$ sodium thiosulfate. 22.5 cm^3 of thiosulfate was required to reach the end-point.

Calculate the percentage purity of the granules. [2]

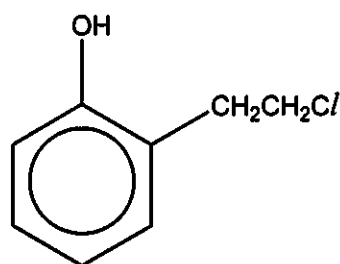
- (iv) Commercially, calcium hypochlorite is available as granules. Using your answer in (a)(iii), calculate the volume of chlorine gas (measured at room temperature and pressure) required to manufacture 1 kg of calcium hypochlorite granules. [2]

[Turn Over

- 3 (b) Chloroxylenol is commonly used in antibacterial soaps due to its disinfecting and sanitising properties. It is also responsible for the distinctive odour of Dettol. An isomer of chloroxylenol is compound X.



chloroxylenol



compound X

When hot ethanolic silver nitrate was added to chloroxylenol and compound X separately, the observations were different. State what you would observe for each compound and explain the difference in observations.

[3]

- (c) Compounds **A** and **B** are structural isomers of chloroxylenol. Both **A** and **B** give a violet colouration with neutral FeCl_3 .

A rotates plane-polarised light, but **B** does not. When **B** is treated with hot alcoholic sodium hydroxide, a compound of molecular formula $\text{C}_8\text{H}_8\text{O}$ is formed. When **A** is treated carefully with hot aqueous sodium hydroxide, compound **C**, $\text{C}_8\text{H}_{10}\text{O}_2$, is formed.

C reacts with hot concentrated potassium dichromate(VI) to form compound **D**.

C reacts with hot concentrated potassium manganate(VII) to form compound **E** and carbon dioxide gas.

D gives an orange precipitate with 2,4-dinitrophenylhydrazine, but **E** does not.

Suggest structures for **A** to **E**, and explain the observations described above.

[10]

[Total: 20]

4 The table below summarises the different types of acids found in various types of beverages.

Beverage	Acid	Formula	pK_{a1}	pK_{a2}	pK_{a3}
Beer	Carbonic	H_2CO_3	6.37	10.3	–
Fruit Juices	Malic	$HO_2CCH_2CH(OH)CO_2H$	3.46	5.10	–
Soda	Phosphoric	H_3PO_4	2.12	7.21	12.3

(a) (i) Explain why the pK_{a1} of malic acid is so much lower than the pK_{a1} of carbonic acid. [2]

(ii) Explain why the pK_{a3} of phosphoric acid is so much higher than the pK_{a2} of malic acid. [1]

(b) (i) 50.0 cm³ of 0.5 mol dm⁻³ aqueous H_3PO_3 was mixed with 30 cm³ of excess aqueous NaOH. It was found that the temperature of the solution rose by 8.4 °C after mixing. Calculate the enthalpy change of reaction per mole of H_3PO_3 (aq).

Given: Specific heat capacity of water = 4.18 J g⁻¹ K⁻¹;

Density of water = 1.0 g cm⁻³. [2]

(ii) Hence, given that the enthalpy change of neutralisation of HCl (aq) by NaOH (aq) is -57.3 kJ mol⁻¹, suggest the basicity of H_3PO_3 . [1]

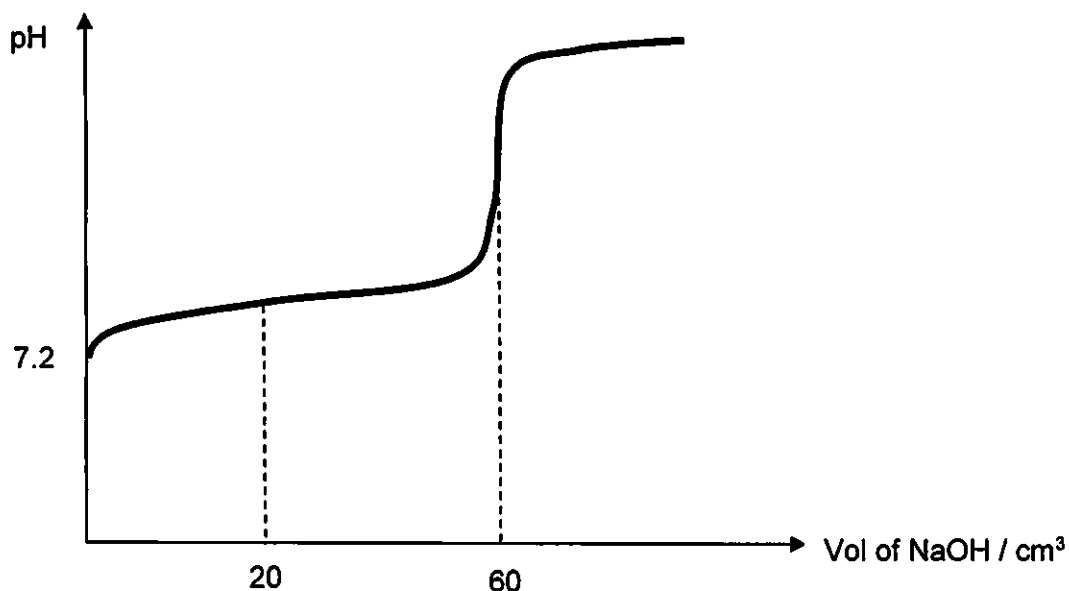
(c) A medical student wanted to investigate the buffer solution in fluids for intravenous injection. He needed to prepare a buffer of pH 7.2. Of the pK_a values given in the table above, suggest a conjugate acid–base pair which is most suitable as the buffer solution. [1]

[Turn Over

- 4 (d) A student titrated 20 cm³ of the buffer sample in (c) containing an acid and its salt, with 0.1 mol dm⁻³ NaOH (aq) and obtained the titration curve below. The maximum buffer capacity is obtained when 20 cm³ of NaOH is added.

The equivalence point of the titration is obtained when 60 cm³ of aqueous sodium hydroxide is added.

[You may use HA and A⁻ to represent the species identified in (c) to answer part (d)].



- (i) Explain why the pH rises only slightly at the start of the titration when a small amount of sodium hydroxide is added. [1]
 - (ii) Determine the total amount of acid in the buffer. Hence, show that the ratio of concentrations of the [HA] and [A⁻] at the start of the titration is 3:1. [2]
 - (iii) Calculate the K_a of the acid at the start of the titration. [1]
- (e) An electrochemical cell is composed of two half-cells, namely the AgBr | Ag and Ag⁺ | Ag half-cells at 298K.



- (i) Using the data booklet and the half-equation of AgBr | Ag above, write the overall equation for the cell reaction and calculate the $E^\ominus_{\text{cell}}$. [2]

- 4 (e) (ii) The Nernst equation is used to calculate the voltage, E_{cell} , generated under non-standard conditions.

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{nF} \ln \left(\frac{1}{K_{sp}} \right)$$

where n is the number of moles of electrons transferred per mole of equation, R is the molar gas constant, F is the Faraday constant and K_{sp} is the solubility product of AgBr.

When $E_{cell} = 0$, the system has achieved equilibrium.

Decide on a suitable value of n and hence, use your answer in (e)(i) and the Nernst equation to calculate the solubility product of AgBr at 298 K, stating its units. [3]

- (iii) Predict how the voltage of the cell, E_{cell} , will change when $\text{NH}_3(\text{aq})$ is added to the $\text{Ag}^+|\text{Ag}$ cell. [2]

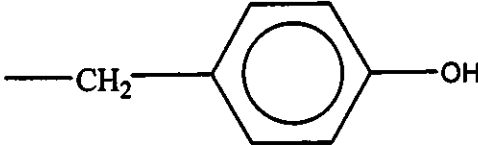
- (iv) Given that silver arsenate, Ag_3AsO_4 has a K_{sp} of 1.40×10^{-22} , show by calculation, if AgBr or Ag_3AsO_4 is the more soluble salt. [2]

[Total: 20]

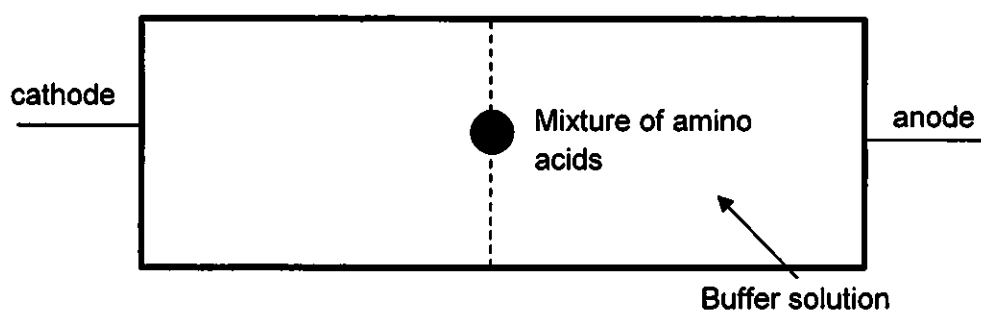
[Turn Over]

- 5 About 10% of the mass of a chicken egg is made up of proteins. The main protein in egg whites is ovalbumin.

Three of the amino acids obtained from the complete hydrolysis of ovalbumin and their isoelectric points are given in the table below.

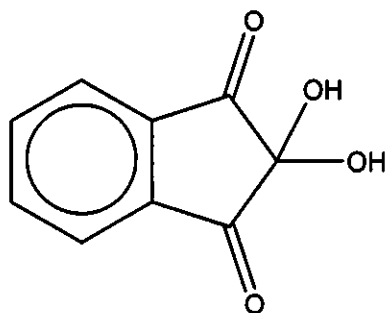
Amino acid	Formula of side chain	Isoelectric point
Aspartic acid (asp)	$-\text{CH}_2\text{CO}_2\text{H}$	2.77
Lysine (lys)	$-(\text{CH}_2)_4\text{NH}_2$	9.74
Tyrosine (tyr)		5.66

- (a) State how ovalbumin could be hydrolysed in the laboratory to form the amino acids in the table above. [1]
- (b) (i) Define the term isoelectric point. [1]
- (ii) Electrophoresis is an electrolytic method used to separate amino acids based on their isoelectric points. A simplified diagram of an electrophoresis set-up is shown below. Depending on the pH of the buffer solution used, the amino acids will move differently. The positions of the amino acids are ascertained by spraying the solution with ninhydrin solution. The colourless amino acid spots will turn blue.

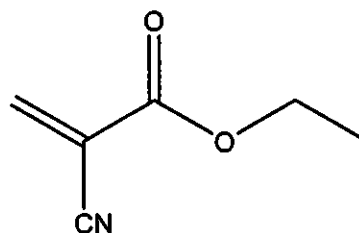


Using data from the table above, explain how electrophoresis can be used to separate and identify the constituent amino acids in a mixture of aspartic acid, lysine and tyrosine in a buffer solution of pH 8. You should include the structural formulae of the three amino acids at pH 8 in your answer. [3]

- 5 (c) With reference to protein structure, explain why egg white coagulates when cooked. [2]
- (d) Besides reacting with amino acids, ninhydrin is also commonly used in fingerprint analysis in criminal investigations. Another method to analyse fingerprints is called cyanoacrylate (Super Glue) fuming. One common cyanoacrylate used for this purpose is ethyl cyanoacrylate. The structures of ninhydrin and cyanoacrylate are given below.



ninhydrin



ethyl cyanoacrylate

Suggest a chemical test that could be used to distinguish ninhydrin and ethyl cyanoacrylate from each other. You should state what you would observe for each compound in the test.

[2]

- (e) Besides being rich in protein, eggs are also consumed widely as it contains vitamins and minerals needed on a daily basis. An example of a key nutrient that can be obtained from eating eggs is phosphorus, which is as important as calcium in building strong bones in our body.
- (i) Describe the reaction of phosphorus(III) oxide, P_4O_6 , with water. Include the pH value of the resulting solution, and write an equation for the reaction that occurs. [2]
- (ii) Write an equation to illustrate the acid-base nature of phosphorus(V) oxide, P_4O_{10} . [1]

[Turn Over

- 5 (f) Eggs are also rich in iodine which is a key component of hormones in the thyroid gland. Iodine deficiency results when we do not consume enough iodine in our diet. In order to combat iodine deficiency, table salt is mixed with various salts of iodine in the production of iodised salts.
- Potassium iodate, KIO_3 , is often used in iodised salts. With the aid of an equation, describe how potassium iodate can be prepared using iodine as a starting material. [2]
- (g) Describe what you would see if concentrated sulfuric acid is added to separate samples of solids KBr and KI . Suggest an explanation for the differences in reaction, and write equations for the reactions that occurred. [4]
- (h) Iodine has many isotopes. Only two of its isotopes are used in medicine, such as radiotherapy and imaging. In order to identify the mass of these two isotopes, they were first ionised to form singly-charged ions of +1 charge and passed through an electric field of constant strength. Their angles of deflection, along with a reference sample of helium nucleus, ${}^4_2\text{He}$, were recorded in the table below.

	Angle of deflection
Isotope X	1.07 °
Isotope Y	1.14 °
Helium nucleus, ${}^4_2\text{He}$	70.1 °

Calculate the mass of each isotope, giving your answer to the nearest whole number.

[2]

[Total: 20]

~ END OF PAPER ~



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

Candidate Name

Class

CHEMISTRY

JC2 Preliminary Examination

Paper 1 Multiple Choice

Additional Materials: Data Booklet
 Optical Mark Sheet (OMS)

9647/01

23 September 2016

1 hour

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.

Shade correctly your FIN/NRIC number.

There are **40** questions in this paper. Answer **all** questions.

For each question there are four possible answers **A, B, C** and **D**.

Choose the one you consider correct and record your choice using a **soft pencil** on the separate OMS.

Each correct answer will score one mark.

A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

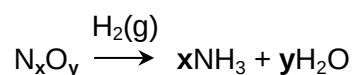
Answer all questions

- 1** The relative abundances of the isotopes of a sample of titanium are shown in the table below.

Relative Isotopic Mass	46	47	48	49	50
Relative Abundance	11.2	10.1	100.0	7.3	7.0

What is the relative atomic mass of titanium in this sample?

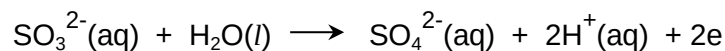
- A** 48.00
B 47.92
C 47.90
D 47.89
- 2** To identify an oxide of nitrogen, 0.10 mol of the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.



The water produced weighs 7.20 g. The ammonia produced is neutralised by 200 cm³ of 1.0 mol dm⁻³ HCl.

What is the formula of the oxide of nitrogen?

- A** N₂O
B NO
C NO₂
D N₂O₄
- 3** 50 cm³ of a 0.10 mol dm⁻³ solution of a metallic salt was found to react exactly with 25.0 cm³ of 0.10 mol dm⁻³ aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows.



What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

- A** +1
B +2
C +4
D +5

4 Of the following, which is the strongest oxidising agent?

- A O_2^+
- B O_2
- C O_2^-
- D O_2^{2-}

5 Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The greater the number of unpaired electrons in an atom, the greater the paramagnetism.

Which atom has the greatest paramagnetism?

- A Oxygen
- B Chlorine
- C Scandium
- D Arsenic

6 Which of the following is true of both real and ideal gases?

- A Molecules can be liquefied.
- B Molecules occupy a finite volume.
- C Molecules are in constant random motion.
- D Molecules behave identically at high pressure and low temperature.

7 The Valence Shell Electron Pair Repulsion Theory (VSEPR) is used to predict the shapes of molecules.

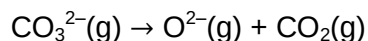
Which shape is correctly predicted by VSEPR?

	number of regions of electron density	number of lone pairs	shape
A	3	1	Tetrahedral
B	3	1	Trigonal pyramidal
C	5	1	See-saw
D	5	1	Square pyramidal

8 The magnitude of the lattice energy of calcium oxide and calcium carbonate is 3414 kJ mol^{-1} and 2814 kJ mol^{-1} respectively. The enthalpy change of

decomposition of calcium carbonate is $+176 \text{ kJ mol}^{-1}$.

Using the information provided, calculate the enthalpy change of the following reaction.



- A -424 kJ mol^{-1}
- B $+424 \text{ kJ mol}^{-1}$
- C -776 kJ mol^{-1}
- D $+776 \text{ kJ mol}^{-1}$

- 9 Primary, secondary and tertiary amine have similarly shaped molecules.

What is the predominant intermolecular force of attraction in methylamine, dimethylamine and trimethylamine?

	methylamine	dimethylamine	trimethylamine
A	hydrogen bonds	hydrogen bonds	hydrogen bonds
B	hydrogen bonds	permanent dipole – permanent dipole	Instantaneous dipole – induced dipole
C	permanent dipole – permanent dipole	permanent dipole – permanent dipole	permanent dipole – permanent dipole
D	hydrogen bonds	hydrogen bonds	permanent dipole – permanent dipole

- 10 The integrated form of first-order rate law is as shown.

$$\ln A = -kt + \ln A_0$$

where A is the activity at time t,
 A_0 is the initial activity,
 k is the rate constant,
 t is the time taken.

What is the half-life for a first order reaction if 68% of a substance is reacted within 66s?

- A 33 s
- B 40 s
- C 49 s
- D 119 s

- 11 For which equilibrium is $K_c = K_p$?

- A** $\text{C(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{(g)}$
- B** $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$
- C** $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$
- D** $2\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$

- 12** The ionic product of water, K_w , at two different temperatures is shown below,

$K_w / \text{mol}^2 \text{dm}^{-6}$	Temperature / K
1.00×10^{-14}	298
1.44×10^{-14}	303

Which statement is correct?

- A** Self-ionisation of water is an exothermic process.
- B** At 303 K, $[\text{H}^+] = 0.72 \times 10^{-14} \text{ mol dm}^{-3}$
- C**
$$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$
- D** At 303 K, $\text{pH} < 7$
- 13** Calculate the pH of the resulting solution when 10 cm^3 of potassium hydroxide with concentration at $7.5 \times 10^{-7} \text{ mol dm}^{-3}$ is mixed with an equal volume of hydrogen bromide with concentration at $8.5 \times 10^{-8} \text{ mol dm}^{-3}$.
- A** 4.18
- B** 6.36
- C** 7.64
- D** 9.82
- 14** Aqueous hydrochloric acid was electrolysed for ten minutes, 200 cm^3 of gas **A** was collected at the anode.
The same current was then applied to concentrated sodium chloride solution in another experiment and 400 cm^3 of a gas **B** is collected at the cathode.
- Which of these statements is correct?
- A** Gas **B** is pale yellow.
- B** The time taken for the second electrolysis is also ten minutes.
- C** Chlorine gas was collected initially in the first electrolysis system.
- D** Mercury electrodes can be used for the second electrolysis system if gas **B** is to be collected.
- 15** Which of the following properties could be predicted for strontium or its compounds?

- A It does not burn in air.
- B It forms a soluble sulfate.
- C It reacts with cold water, liberating hydrogen.
- D It forms a water-soluble carbonate which does not decompose on heating.

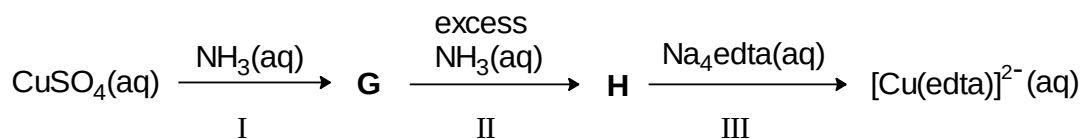
- 16 Equal volumes of chlorine gas were bubbled into hot and cold sodium hydroxide separately until reactions were complete.

Which of the following statements is incorrect about the above reactions?

- A Disproportionation reactions will occur.
 - B Greenish-yellow chlorine gas decolourises in both reactions.
 - C When aqueous silver nitrate is added to the resulting solutions, white precipitate is formed.
 - D Sodium chlorate(VII) and sodium chlorate(I) are formed in the reactions respectively.
- 17 Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of trichloromethane.

Which observation will be made?

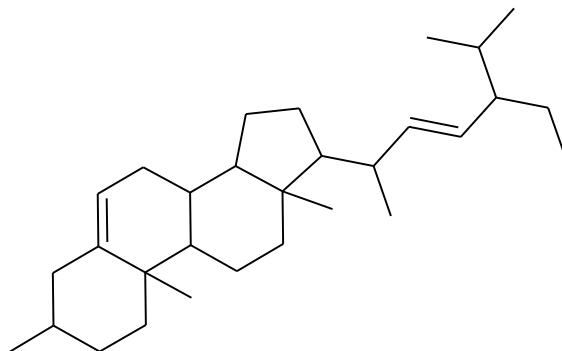
- A The solution in the test-tube turns colourless.
 - B The solution in the test-tube turns orange.
 - C A colourless layer forms on top of a purple layer.
 - D A colourless layer forms on top of an orange layer.
- 18 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **G** and **H** are copper-containing species.



Which of the following statements is correct?

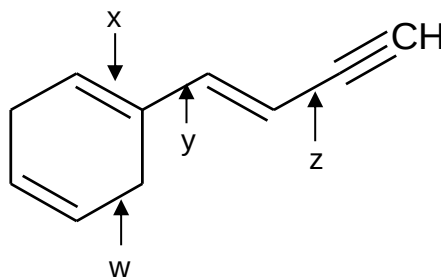
- A Reaction III is a redox reaction.
- B NH_3 acts as a ligand in reaction I.
- C **H** is a deep blue solution containing $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$.
- D The entropy of the system decreases when reaction III occurs.

- 19 Stigmasterol is an unsaturated plant sterol occurring in the plant fats of soybean.



How many stereoisomers does stigmasterol have?

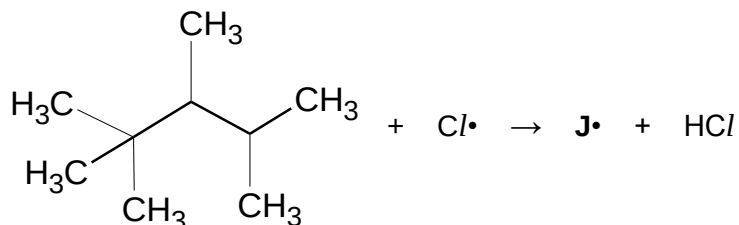
- A 2^9
 - B 2^{10}
 - C 2^{11}
 - D 2^{12}
20. Four carbon-carbon bonds are labelled in the diagram.



Which bonds are made up of a sp^2 - sp^2 overlap?

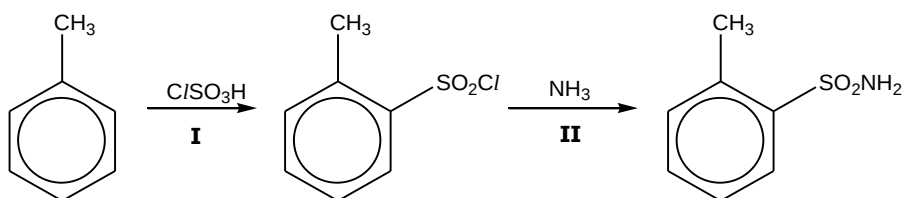
- A x only
- B x and y only
- C w, x and y only
- D w, y and z only

21. When heated with chlorine, the hydrocarbon 2,2,3,4-tetramethylpentane undergoes free radical substitution. In a propagation step, the free radical **J•** is formed by the loss of one hydrogen atom.



How many different forms of **J•** are theoretically possible?

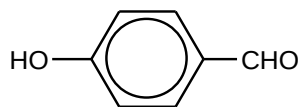
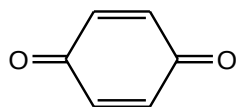
- A 3
B 4
C 5
D 6
22. *Saccharin* was an artificial sweetener used in some soft drinks. It was manufactured from methylbenzene by a series of reactions.



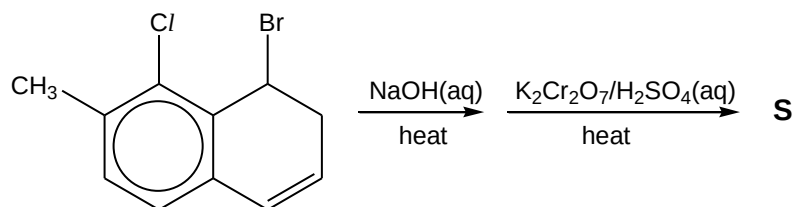
Which of the following shows the correct reaction type for steps **I** and **II**?

I	II
A Electrophilic substitution	Electrophilic addition
B Electrophilic substitution	Nucleophilic substitution
C Nucleophilic substitution	Nucleophilic substitution
D Nucleophilic substitution	Electrophilic substitution

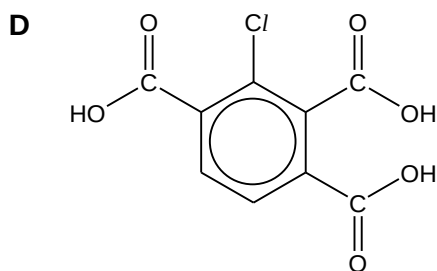
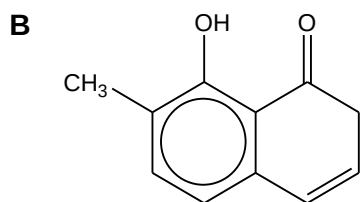
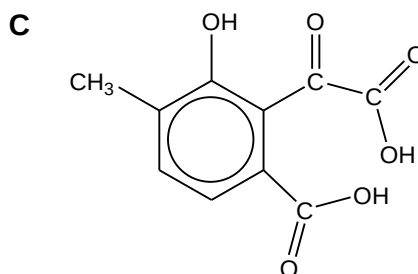
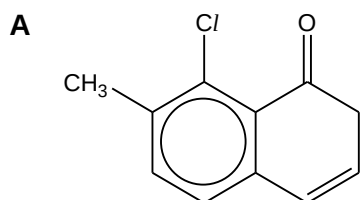
23 Which of the following **cannot** be used to distinguish between the following compounds?



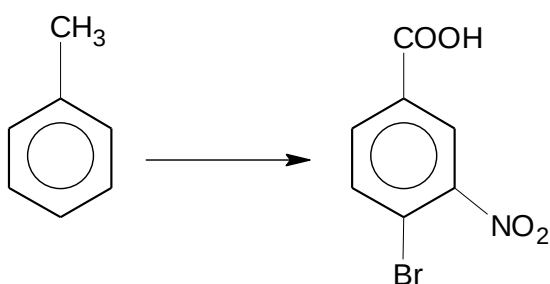
- A Hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$
 B Neutral iron(III) chloride
 C Diammine silver complex
 D Phenylhydrazine
- 24 The reaction scheme below shows the synthesis of compound **S**.



Which of the following can be **S**?



25 The following synthetic route consists of three steps.

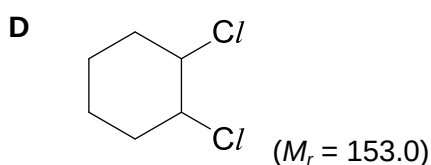
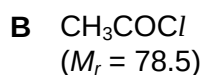
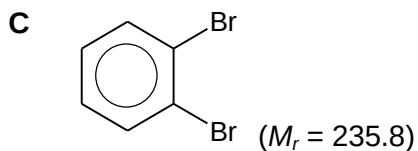
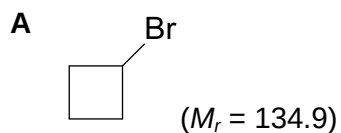


Which sequence of steps would give the highest yield?

	Step 1	Step 2	Step 3
A	KMnO ₄ , H ₂ SO ₄ , heat	conc HNO ₃ , conc H ₂ SO ₄ , heat	Br ₂ , Fe, r.t.p
B	conc HNO ₃ , conc H ₂ SO ₄ , heat	Br ₂ , Fe, r.t.p	KMnO ₄ , H ₂ SO ₄ , heat
C	Br ₂ , Al/Br ₃ , r.t.p	conc HNO ₃ , dilute H ₂ SO ₄ , heat	KMnO ₄ , H ₂ SO ₄ , heat
D	Br ₂ , Fe, r.t.p	KMnO ₄ , H ₂ SO ₄ , heat	conc HNO ₃ , conc H ₂ SO ₄ , heat

- 26 Ten grams of each of the following was heated with NaOH(aq) for a prolonged period of time. Subsequently, dilute HNO₃(aq) and AgNO₃(aq) were added.

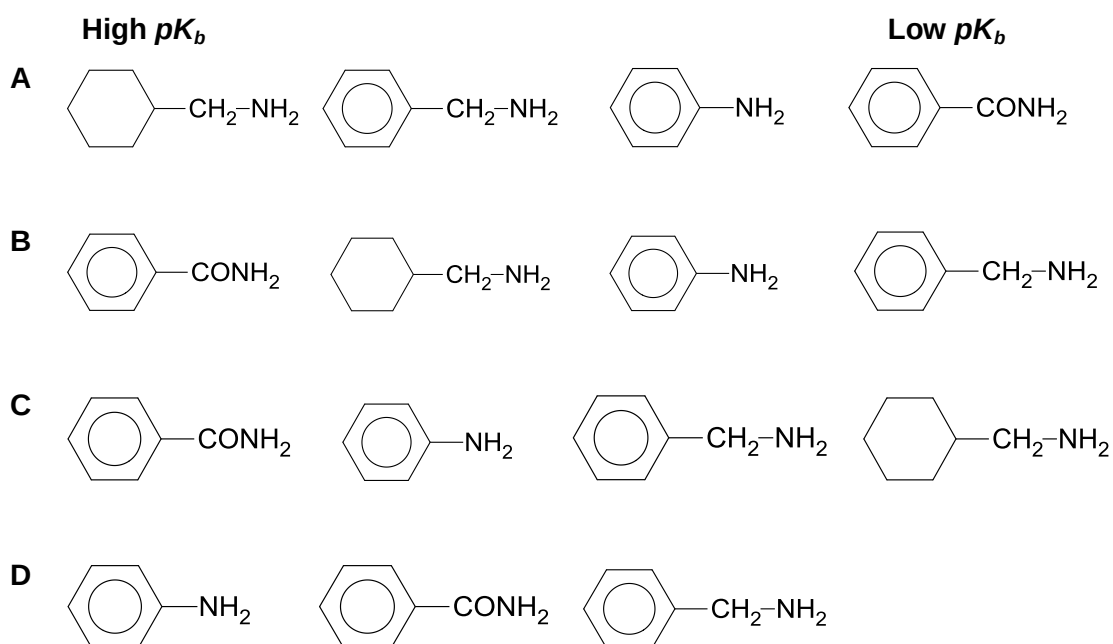
Which compound will produce the greatest mass of silver halide precipitate?

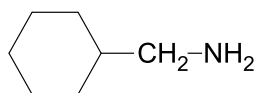


- 27 After the reduction using tin and concentrated acid of nitrobenzene to phenylamine, an excess of sodium hydroxide is added.

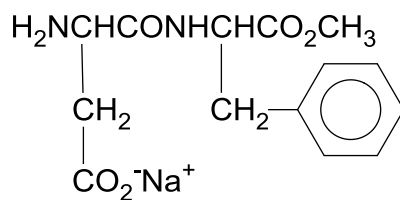
What is the purpose of the sodium hydroxide?

- A** to dry the product
 - B** to liberate the phenylamine
 - C** to neutralise the excess acid
 - D** to lower the boiling point for subsequent distillation
- 28 Which of the following shows the correct order of basicity?





- 29 Aspartame is a dipeptide derivatives used as an artificial sweetener. Its general usefulness is restricted because it loses its sweetness after hydrolysis.

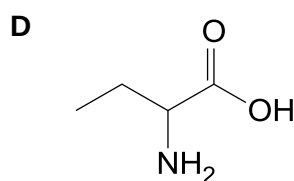
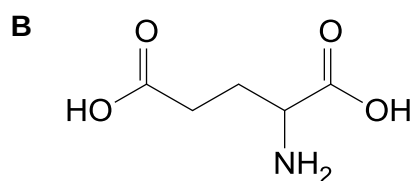
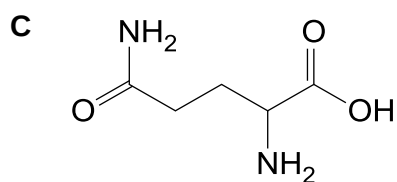
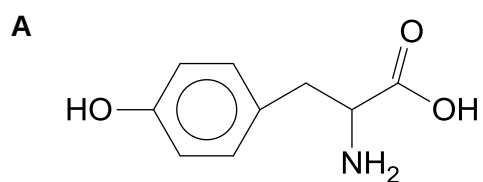


Which product would be formed after prolong acid hydrolysis.

- A** $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{CO}_2^-\text{Na}^+)\text{CO}_2\text{H}$ and $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$
- B** $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{COOH})\text{CO}_2\text{H}$ and $\text{H}_2\text{NCH}(\text{CH}_2\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$
- C** $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{COOH})\text{CO}_2\text{H}$ and $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{CO}_2\text{H}$ and CH_3OH
- D** $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{COOH})\text{CO}_2\text{H}$ and $\text{CH}_2\text{CO}_2\text{H}$ and CH_3OH

- 30** Electrophoresis is a technique of separating and identifying amino acids. amino acids is absorbed into paper that is moistened with a buffer stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species towards the anode.

With a buffer at pH 5, which amino acid will move most readily towards the cathode?

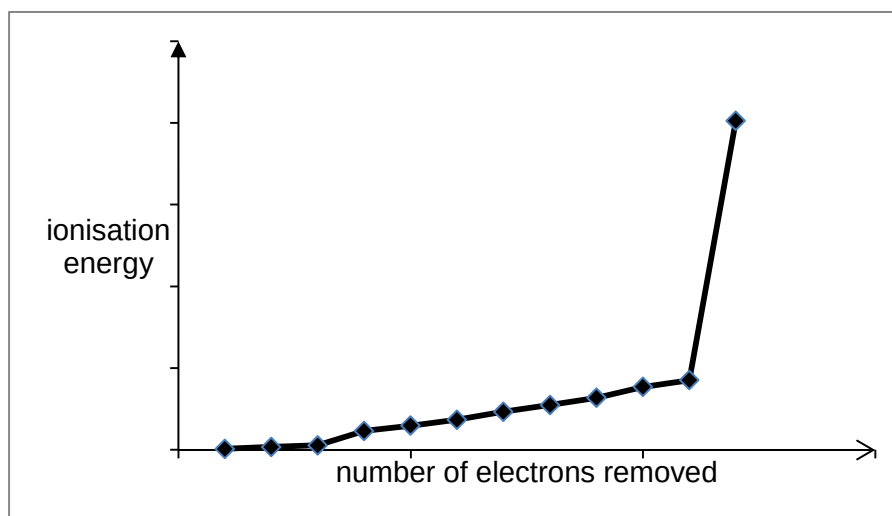


For **questions 31 – 40**, one or more of the numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct. The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is to be used as correct response.

31 The graph below shows the first twelve ionisation energies for element **T**.



Which of the following statements are true?

- 1** It is in Group I of the Periodic Table.
- 2** It forms an oxide which dissolves readily with acid.
- 3** It is in the third period (Na to Ar) of the Periodic Table.

32 The following chemical reactions are listed below.

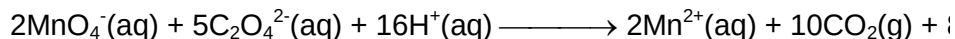
- Combustion of ethandioic acid
- Evaporation of water
- Atomisation of magnesium
- Photolysis of chlorine

Which of the following statements are correct?

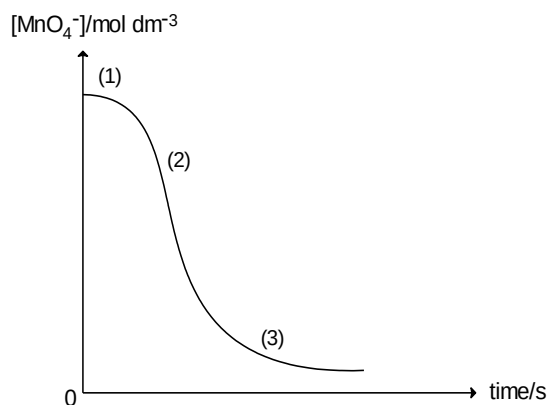
- 1** ΔS is positive for all reactions.
- 2** ΔG is negative for all reactions.

3 ΔH is positive for all reactions.

33 A reaction in which a product acts as a catalyst is said to be autocatalytic.



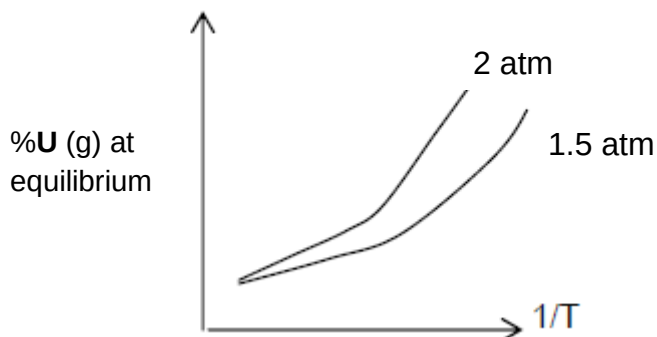
In the oxidation of ethanedioate ions by manganate(VII) ions, the reaction is accelerated by the Mn^{2+} ions produced during the reaction.



Which of the following statements can be deduced from the graph above?

- 1 Initial rate of reaction is the fastest at (1).
- 2 Reaction rate increases at (2) as Mn^{2+} is generated.
- 3 Reaction rate decreases at (3) as the concentration of the reactants decrease.

34 The graph below shows how the percentage of reactant $\text{U}(\text{g})$ that remained in an equilibrium mixture varies with $1/T$ at pressures of 1.5 atm and 2 atm.



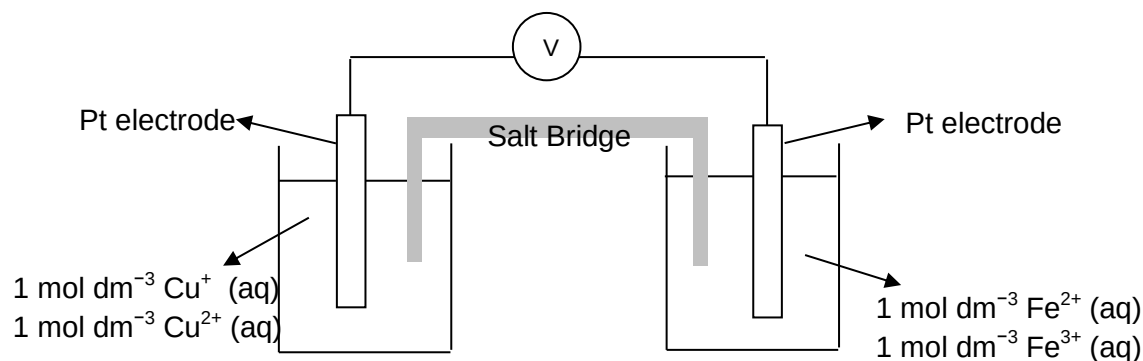
Which of the following statement can be deduced from this information?

- 1 The forward reaction is endothermic.

- 2 The equation for the above reaction could be $\mathbf{U(g)} \rightleftharpoons \mathbf{V(g)} + \mathbf{W(g)}$.
- 3 The equilibrium constant, K_p , increases as pressure increases in the system.

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

- 35 A student was investigating the possibility of an electrochemical cell using $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cells.



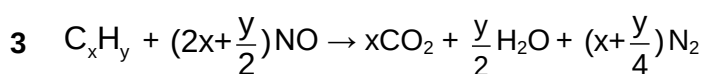
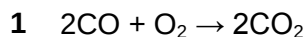
Which statements are true of the above set up?

- 1 $E_{\text{cell}}^{\ominus} = +0.62 \text{ V}$.
 - 2 Copper and iron electrodes cannot be used instead.
 - 3 When excess sodium hydroxide is added to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-cell, the polarity of the electrodes are reversed.
- 36 Barium sulfate is less soluble than magnesium sulfate.
- Which of these factors are needed to be considered in order to explain this observation?
- 1 ΔH_{hyd} of barium ion and magnesium ion.
 - 2 ΔH_f of barium sulfate and magnesium sulfate.
 - 3 Atomic radii of barium and magnesium.
- 37 Which observation about bromine or its compounds is correct?
- 1 When aqueous lead(II) nitrate is added to aqueous sodium bromide, a cream precipitate is observed.
 - 2 When sodium bromide is treated with concentrated sulfuric acid, a gas that turns moist blue litmus paper red is evolved.
 - 3 Silver bromide is soluble in both dilute and concentrated ammonia solution.

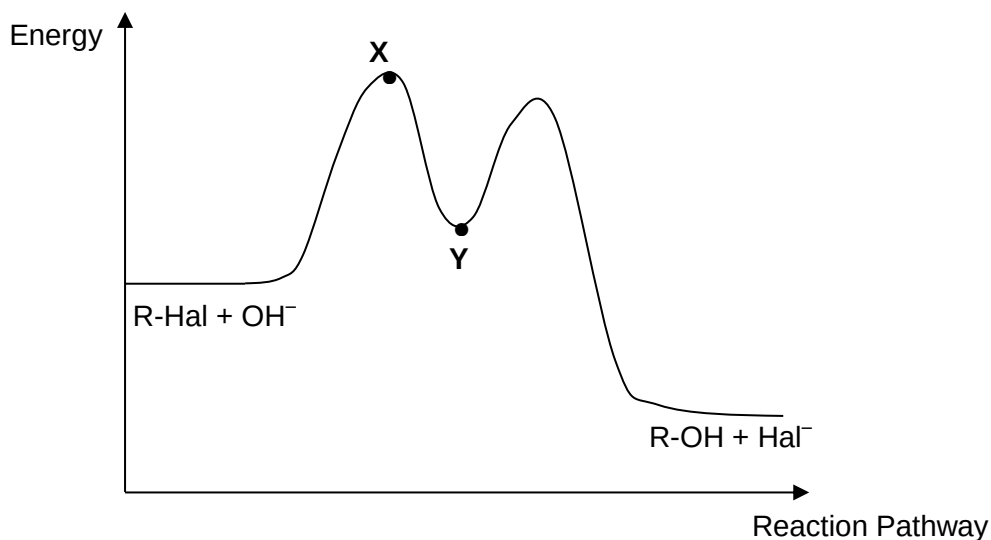
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

38 The catalytic converter is part of the exhaust system of modern cars.

Which reactions occur in the catalytic converter?

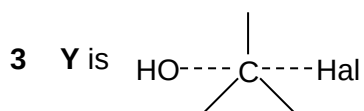
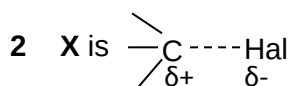


39 Halogenoalkanes react with aqueous alkali. One mechanism of this reaction has the reaction pathway diagram shown below.



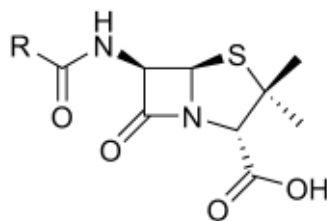
Which statements are true? (---- indicates a partial bond)

1 The reaction is a type of nucleophilic substitution.



40 Which of the following phenomena involves denaturation of proteins?

- 1** Heating of egg white.
- 2** Production of bean-curd from soy milk.
- 3** Dissolving Penicillin in a test tube of hot acid.



Penicillin

END OF PAPER 1



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

Candidate Name

Class

CHEMISTRY

JC2 Preliminary Examination

Paper 1 Multiple Choice

Additional Materials: Data Booklet
 Optical Mark Sheet (OMS)

9647/01

23 Sep 2016

1 hour

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.

Shade correctly your FIN/NRIC number.

There are **40** questions in this paper. Answer **all** questions.

For each question there are four possible answers **A, B, C** and **D**.

Choose the one you consider correct and record your choice using a **soft pencil** on the separate OMS.

Each correct answer will score one mark.

A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

Answer Key:

1	B	11	B	21	C	31	C
2	D	12	D	22	B	32	D
3	B	13	C	23	D	33	C
4	A	14	B	24	A	34	B
5	D	15	C	25	D	35	A
6	C	16	D	26	D	36	D
7	C	17	D	27	B	37	B
8	D	18	C	28	C	38	A
9	D	19	B	29	C	39	B
10	B	20	B	30	D	40	B

Suggested Worked Solution for MCQs

1	The relative abundances of the isotopes of a sample of titanium are shown in the table below.						
	Relative Isotopic Mass		46	47	48	49	50
	Relative Abundance		11.2	10.1	100.0	7.3	7.0
What is the relative atomic mass of titanium in this sample?							
	A	48.00					
	B	47.92					
	C	47.90					
	D	47.89					
Answer: B							
$\begin{aligned}\text{Relative atomic mass} &= \frac{(46 \times 11.2) + (47 \times 10.1) + (48 \times 100) + (49 \times 7.3) + (50 \times 7)}{11.2 + 10.1 + 100 + 7.3 + 7.0} \\ &= \frac{515.2 + 474.7 + 4800 + 357.7 + 350}{135.6} \\ &= \frac{6497.3}{135.6} = 47.92\end{aligned}$							

2	To identify an oxide of nitrogen, 0.10 mol of the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.	
	$\text{N}_x\text{O}_y \xrightarrow{\text{H}_2(\text{g})} x\text{NH}_3 + y\text{H}_2\text{O}$	
	The water produced weighs 7.20 g. The ammonia produced is neutralised by 200 cm ³ of 1.0 mol dm ⁻³ HCl.	
	What is the formula of the oxide of nitrogen?	
	A	N ₂ O
3	B	NO
	C	NO ₂
	D	N ₂ O ₄
	Answer: D Amt of H ₂ O = $\frac{7.2}{18} = 0.40 \text{ mol}$ Amt of NH ₃ = $\frac{200}{1000} \times 1 = 0.20 \text{ mol}$	
4	Assuming all gases and using Avogadro's Law Comparing mole ratio of N _x O _y with NH ₃ $\frac{1}{x} = \frac{0.10}{0.20}$ Hence, x = 2 Comparing mole ratio of N _x O _y with H ₂ O $\frac{1}{y} = \frac{0.10}{0.40}$ Hence, y = 4 Formula is N ₂ O ₄	

3	50 cm³ of a 0.10 mol dm⁻³ solution of a metallic salt was found to react exactly with 25.0 cm³ of 0.10 mol dm⁻³ aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows. $\text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$ What is the new oxidation number of the metal in the salt if its original oxidation number was +3?		
	<table border="1"> <tr> <td data-bbox="260 521 300 555">A</td><td data-bbox="300 521 1426 555">+1</td></tr> </table>	A	+1
A	+1		
	<table border="1"> <tr> <td data-bbox="260 555 300 589">B</td><td data-bbox="300 555 1426 589">+2</td></tr> </table>	B	+2
B	+2		
	<table border="1"> <tr> <td data-bbox="260 589 300 622">C</td><td data-bbox="300 589 1426 622">+4</td></tr> </table>	C	+4
C	+4		
	<table border="1"> <tr> <td data-bbox="260 622 300 656">D</td><td data-bbox="300 622 1426 656">+5</td></tr> </table>	D	+5
D	+5		

Answer: B

Amount of sulphite ions = $\frac{25}{1000} \times 0.10 = 0.0025 \text{ mol}$

Amount of metallic salt = $\frac{50}{1000} \times 0.10 = 0.005 \text{ mol}$

Let x be the new oxidation no of metal in salt.

[R]: $\text{M}^{3+} + (3-x)\text{e}^- \rightarrow \text{M}^x$

Since moles of electrons gained = moles of electrons lost in a redox reaction,

$$\frac{3-x}{2} = \frac{0.0025}{0.005}$$

$$x = +2$$

4	Of the following, which is the strongest oxidising agent?		
	<table border="1"> <tr> <td data-bbox="260 1364 300 1397">A</td><td data-bbox="300 1364 1426 1397">O_2^+</td></tr> </table>	A	O_2^+
A	O_2^+		
	<table border="1"> <tr> <td data-bbox="260 1397 300 1431">B</td><td data-bbox="300 1397 1426 1431">O_2</td></tr> </table>	B	O_2
B	O_2		
	<table border="1"> <tr> <td data-bbox="260 1431 300 1464">C</td><td data-bbox="300 1431 1426 1464">O_2^-</td></tr> </table>	C	O_2^-
C	O_2^-		
	<table border="1"> <tr> <td data-bbox="260 1464 300 1503">D</td><td data-bbox="300 1464 1426 1503">O_2^{2-}</td></tr> </table>	D	O_2^{2-}
D	O_2^{2-}		

Answer: A

Strongest oxidising agent means it will undergo reduction easily and as such will gain electrons.

O_2^+ is positively charged and hence is a stronger electron-acceptor than the other species.

5	Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The greater the number of unpaired electrons in an atom, the greater the paramagnetism. Which atom has the greatest paramagnetism?		
	<table border="1"> <tr> <td data-bbox="256 439 304 472">A</td><td data-bbox="304 439 1380 472">Oxygen</td></tr> </table>	A	Oxygen
A	Oxygen		
	<table border="1"> <tr> <td data-bbox="256 472 304 506">B</td><td data-bbox="304 472 1380 506">Chlorine</td></tr> </table>	B	Chlorine
B	Chlorine		
	<table border="1"> <tr> <td data-bbox="256 506 304 539">C</td><td data-bbox="304 506 1380 539">Scandium</td></tr> </table>	C	Scandium
C	Scandium		
	<table border="1"> <tr> <td data-bbox="256 539 304 573">D</td><td data-bbox="304 539 1380 573">Arsenic</td></tr> </table>	D	Arsenic
D	Arsenic		
Answer: D O: $1s^2 2s^2 2p^4 \rightarrow 2$ unpaired electrons in the 2p orbital Cl: $[\text{Ne}] 3s^2 3p^5 \rightarrow 1$ unpaired electron in the 3p orbital Sc: $[\text{Ar}] 3d^1 4s^2 \rightarrow 1$ unpaired electron in the 3d orbital As: $[\text{Ar}] 3d^{10} 4s^2 4p^3 \rightarrow \underline{\text{3 unpaired electrons}}$ in the 4p orbital			

6	Which of the following is true of both real and ideal gases?		
	<table border="1"> <tr> <td data-bbox="256 1039 304 1075">A</td><td data-bbox="304 1039 1380 1075">Molecules can be liquefied.</td></tr> </table>	A	Molecules can be liquefied.
A	Molecules can be liquefied.		
	<table border="1"> <tr> <td data-bbox="256 1075 304 1111">B</td><td data-bbox="304 1075 1380 1111">Molecules occupy a finite volume.</td></tr> </table>	B	Molecules occupy a finite volume.
B	Molecules occupy a finite volume.		
	<table border="1"> <tr> <td data-bbox="256 1111 304 1146">C</td><td data-bbox="304 1111 1380 1146">Molecules are in constant random motion.</td></tr> </table>	C	Molecules are in constant random motion.
C	Molecules are in constant random motion.		
	<table border="1"> <tr> <td data-bbox="256 1146 304 1180">D</td><td data-bbox="304 1146 1380 1180">Molecules behave identically at high pressure and low temperature.</td></tr> </table>	D	Molecules behave identically at high pressure and low temperature.
D	Molecules behave identically at high pressure and low temperature.		
Answer: C Molecules can be liquefied. (Not true - ideal gas do not exert attractive forces on one another) Molecules occupy a finite volume. (Not true - the size of the ideal gas molecule is assumed to be negligible compared to the volume of the container it occupies) Molecules are in constant random motion. (True) Molecules behave identically at high pressure and low temperature. (Not true – real gases behave most ideally at high temperature and low pressure)			

7	The Valence Shell Electron Pair Repulsion Theory (VSEPR) is used to predict the

	shapes of molecules.		
	Which shape is correctly predicted by VSEPR?		
		number of regions of electron density	number of lone pairs
	A	3	1
	B	3	1
	C	5	1
	D	5	1
			shape
			Tetrahedral
			Trigonal pyramidal
			See-saw
			Square pyramidal
Answer: C 5 regions of electron density consisting of 1 lone pair → see-saw shape $\begin{array}{c} \text{F} \\ \\ \text{:S} \\ \\ \text{F} \end{array}$ For example, SF_6 has a see-saw shape			

8	The magnitude of the lattice energy of calcium oxide and calcium carbonate is 3414 kJ mol^{-1} and 2814 kJ mol^{-1} respectively. The enthalpy change of decomposition of calcium carbonate is $+176 \text{ kJ mol}^{-1}$. Using the information provided, calculate the enthalpy change of the following reaction. $\text{CO}_3^{2-}(\text{g}) \rightarrow \text{O}^{2-}(\text{g}) + \text{CO}_2(\text{g})$		
	A	$- 424 \text{ kJ mol}^{-1}$	
	B	$+424 \text{ kJ mol}^{-1}$	
	C	$- 776 \text{ kJ mol}^{-1}$	
	D	$+776 \text{ kJ mol}^{-1}$	

Answer: D

$$\text{Ca}^{2+}(\text{g}) + \text{CO}_3^{2-}(\text{g}) \xrightarrow{\Delta H_{\text{reaction}}} \text{O}^{2-}(\text{g}) + \text{CO}_2(\text{g}) + \text{Ca}^{2+}(\text{g})$$

$\downarrow$
 $\text{LE}(\text{CaCO}_3)$
 $= - 2814$

$\downarrow$
 $\text{LE}(\text{CaO})$
 $= - 3414$

$$\text{CaCO}_3(\text{s}) \xrightarrow{\Delta H_{\text{decomposition}} = +176} \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

By Hess Law

$$\Delta H_{\text{reaction}} + \text{LE}(\text{CaO}) = \text{LE}(\text{CaCO}_3) + \Delta H_{\text{decomposition of CaCO}_3}$$

$$\Delta H_{\text{reaction}} = \text{LE}(\text{CaCO}_3) + \Delta H_{\text{decomposition of CaCO}_3} - \text{LE}(\text{CaO})$$

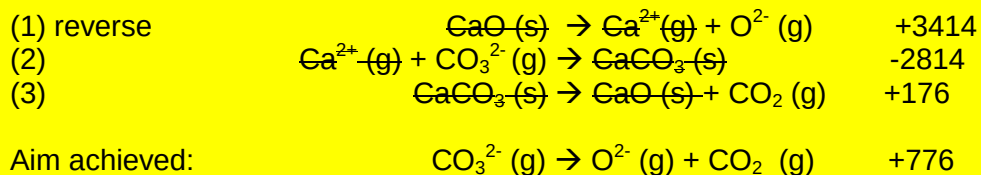
$$\Delta H_{\text{reaction}} = - 2814 + 176 + 3414 = +776 \text{ kJmol}^{-1}$$

Or

Using algebraic method:

(1) $\text{Ca}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \rightarrow \text{CaO}(\text{s})$	-3414
(2) $\text{Ca}^{2+}(\text{g}) + \text{CO}_3^{2-}(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$	-2814
(3) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	+176

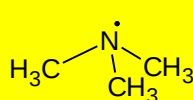
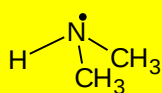
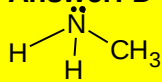
Objective : $\text{CO}_3^{2-}(\text{g}) \rightarrow \text{O}^{2-}(\text{g}) + \text{CO}_2(\text{g})$???



9 Primary, secondary and tertiary amine have similarly shaped molecules. What is the predominant intermolecular force of attraction in methylamine, dimethylamine and trimethylamine?

		methylamine	dimethylamine	trimethylamine
	A	hydrogen bonds	hydrogen bonds	hydrogen bonds
	B	hydrogen bonds	permanent dipole – permanent dipole	Instantaneous dipole – induced dipole
	C	permanent dipole – permanent dipole	permanent dipole – permanent dipole	permanent dipole – permanent dipole
	D	hydrogen bonds	hydrogen bonds	permanent dipole – permanent dipole

Answer: D



(from left to right) the strongest intermolecular force in methylamine, dimethylamine and trimethylamine are hydrogen bonds, hydrogen bonds and permanent dipole – permanent dipole respectively. Trimethylamine does not have hydrogen bonds because there are no hydrogen atoms directly bonded to the nitrogen atom.

10 The integrated form of first-order rate law is as shown.

$$\ln A = -kt + \ln A_0$$

where A is the activity at time t,

A_0 is the initial activity,

k is the rate constant,

t is the time taken.

What is the half-life for a first order reaction if 68% of a substance is reacted within 66s?

A	33 s
B	40 s
C	49 s
D	119 s

Answer: B

68% reacted means 32% remain

$$\ln 0.32 = -k(66) + \ln 1$$

$$k = 0.0172642 \text{ s}^{-1}$$

$$\text{Using } t_{1/2} = \frac{\ln 2}{k} \quad t_{1/2} = \frac{\ln 2}{0.0172642} \quad t_{1/2} = 40 \text{ second}$$

OR

$$C_t/C_0 = (1/2)^n$$

$$32/100 = (1/2)^n$$

$$n = 1.644 \quad \text{one half-life} = 66 / 1.644 = 40.15 \text{ s}$$

11	For which equilibrium is $K_c = K_p$?
A	$\text{C(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{(g)}$
B	$\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$
C	$\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$
D	$2\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$

Answer: B

When there are equal number of moles on each side of the stoichiometric equation
 $K_c = K_p$

considering ideal gases, $pV = nRT$ which implies

$$\text{Concentration of a gas: } \frac{n}{V} = \frac{p}{RT}$$

Consider the **reversible gaseous** system: $a\text{A(g)} + b\text{B(g)} \rightleftharpoons c\text{C(g)} + d\text{D(g)}$

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = \frac{\left(\frac{p_C}{RT}\right)^c \left(\frac{p_D}{RT}\right)^d}{\left(\frac{p_A}{RT}\right)^a \left(\frac{p_B}{RT}\right)^b} = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} (RT)^{(a+b)-(c+d)} = K_p \times (RT)^{(a+b)-(c+d)}$$

12	The ionic product of water, K_w , at two different temperatures is shown below, <table border="1" data-bbox="533 1160 1142 1267"> <thead> <tr> <th>$K_w / \text{mol}^2 \text{dm}^{-6}$</th><th>Temperature / K</th></tr> </thead> <tbody> <tr> <td>1.00×10^{-14}</td><td>298</td></tr> <tr> <td>1.44×10^{-14}</td><td>303</td></tr> </tbody> </table> Which statement is correct?	$K_w / \text{mol}^2 \text{dm}^{-6}$	Temperature / K	1.00×10^{-14}	298	1.44×10^{-14}	303
$K_w / \text{mol}^2 \text{dm}^{-6}$	Temperature / K						
1.00×10^{-14}	298						
1.44×10^{-14}	303						
A	Self-ionisation of water is an exothermic process.						
B	At 303 K, $[\text{H}^+] = 0.72 \times 10^{-14} \text{ mol dm}^{-3}$						
C	$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$						
D	At 303 K, $\text{pH} < 7$						

Answer: D

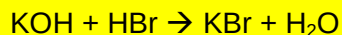
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ is an endothermic process.

At 303: $K_w = [\text{H}^+][\text{OH}^-]$, $1.44 \times 10^{-14} = x^2$ (where x is the $[\text{H}^+]$)
 $x = 1.2 \times 10^{-7} \text{ mol dm}^{-3}$
that means $[\text{H}^+] = 1.2 \times 10^{-7} \text{ mol dm}^{-3}$
 $\text{pH} = 6.92 (<7)$

13	Calculate the pH of the resulting solution when 10 cm^3 of potassium hydroxide with concentration at $7.5 \times 10^{-7} \text{ mol dm}^{-3}$ is mixed with an equal volume of hydrogen bromide with concentration at $8.5 \times 10^{-8} \text{ mol dm}^{-3}$.

	A	4.18
	B	6.36
	C	7.64
	D	9.82

Answer: C



Amt of KOH = 7.5×10^{-9} mol Amt of HBr = 8.5×10^{-10} mol

Since HBr is the limiting reagent and KBr is a neutral salt, the remaining KOH will account for the pH. Thus, the pH of the resulting solution must be greater than 7. Note that there is no buffer solution for strong acid vs strong base reaction.

Amt of KOH left = 6.65×10^{-9} mol

$$[\text{OH}^-] = 6.65 \times 10^{-7} / 0.02 = 3.32 \times 10^{-7}$$

$$\text{Total } [\text{OH}^-] = 3.32 \times 10^{-7} + \frac{1 \times 10^{-7}}{1} =$$

(dissociation of water must be considered as the concentration of the base and acid is very low)

$$\text{pOH} = 6.36$$

$$\text{pH} = 7.64$$

14	Aqueous hydrochloric acid was electrolysed for ten minutes, 200 cm ³ of gas A was collected at the anode. The same current was then applied to concentrated sodium chloride solution in another experiment and 400 cm ³ of a gas B is collected at the cathode. Which of these statements is correct?	
	A	Gas B is pale yellow.
	B	The time taken for the second electrolysis is also ten minutes.
	C	Chlorine gas was collected initially in the first electrolysis system.
	D	Mercury electrodes can be used for the second electrolysis system if gas B is to be collected.

Answer: B

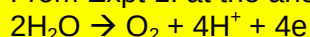
Option A is incorrect because the gas collected at the cathode is H₂.

Option C is wrong because the gas collected at the anode is O₂.

Option D is wrong because mercury electrodes will cause sodium to be selectively discharged at the cathode of the second electrolysis.

Option B is correct and the following shows the calculation:

From Expt 1: at the anode



$$\frac{0.2}{24} = \frac{I \times 10 \times 60}{4 \times 96500} \quad \text{solving } I = 5.361 \text{ A}$$

From Expt 2: At the cathode



Considering same current used in Expt 1

$$\frac{0.4}{24} = \frac{5.361 \times \text{time}}{2 \times 96500}, \quad \text{solving time} = 10 \text{ min}$$

15	Which of the following properties could be predicted for strontium or its compounds?	
	A	It does not burn in air.
	B	It forms a soluble sulfate.

	C	It reacts with cold water, liberating hydrogen.
	D	It forms a water-soluble carbonate which does not decompose on heating.
Answer: C Statement C is correct. Sr reacts vigorously with cold water. $\text{Sr(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Sr(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$ Sr burns very fast in air to produce a white oxide. $2\text{Sr(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{SrO(s)}$ SrSO_4 is not soluble in water as solubility of Group II sulfate decreases down the Group. SrCO_3 is not a water soluble compound and its reasoning is similar to its sulfate.		

16	Equal volumes of chlorine gas were bubbled into hot and cold sodium hydroxide separately until reactions were complete. Which of the following statements is incorrect about the above reactions?	
	A	Disproportionation reactions will occur.
	B	Greenish-yellow chlorine gas decolourises in both reactions.
	C	When aqueous silver nitrate is added to the resulting solutions, white precipitate is formed.
	D	Sodium chlorate(VII) and sodium chlorate(I) are formed in the reactions respectively.
Answer: D Hot: $3\text{Cl}_2 + 6\text{OH}^- \rightarrow 5\text{Cl}^- + \text{ClO}_3^-$ (chlorate (V)) + $3\text{H}_2\text{O}$ Cold: $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^-$ (chlorate (I)) + H_2O The reactions involved are disproportionation reaction and the greenish yellow chlorine gas will decolourised as it was reacted away. White ppt of silver chloride will be generated when AgNO_3 is added.		

17	Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of trichloromethane.

Which observation will be made?	
A	The solution in the test-tube turns colourless.
B	The solution in the test-tube turns orange.
C	A colourless layer forms on top of a purple layer.
D	A colourless layer forms on top of an orange layer.

Answer: D
 Chlorine is a strong oxidising agent and the bromide ion will be oxidised to bromine.
 $\text{Cl}_2 + \text{Br}^- \rightarrow \text{Cl}^- + \text{Br}_2$

When trichloromethane (an organic solvent) is added, the Br_2 will dissolve in this organic layer forming an orange layer. The aqueous layer may be pale yellow (if concentration of bromine formed is high) or colourless (if concentration of bromine is low).

Option C is out as iodine (which is purple) is not formed in this reaction.

Option A and B are out as water and trichloromethane exist as immiscible liquid.

18	A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both G and H are copper-containing species. $\text{CuSO}_4(\text{aq}) \xrightarrow[\text{I}]{\text{NH}_3(\text{aq})} \text{G} \xrightarrow[\text{II}]{\text{excess NH}_3(\text{aq})} \text{H} \xrightarrow[\text{III}]{\text{Na}_4\text{edta}(\text{aq})} [\text{Cu}(\text{edta})]^{2-}(\text{aq})$ Which of the following statements is correct?
A	Reaction III is a redox reaction.
B	NH_3 acts as a ligand in reaction I.
C	H is a deep blue solution containing $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$.
D	The entropy of the system decreases when reaction III occurs.

Answer: C

Reaction III is ligand exchange reaction, hence no redox occurs. Also, same no. of bonds are broken and formed, hence no change in entropy.

Reaction I is precipitation reaction, $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{NH}_4^+$

$\text{Cu}^{2+} + \text{OH}^- \rightleftharpoons \text{Cu}(\text{OH})_2$ (**identity of G**)

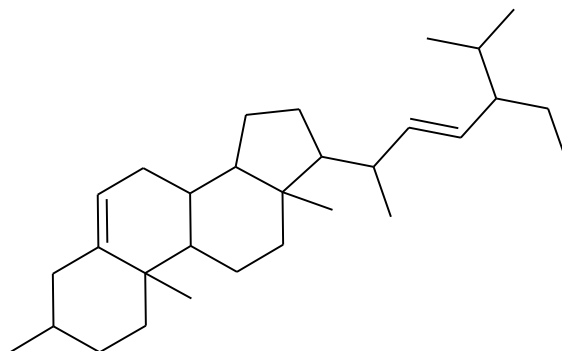
G, $\text{Cu}(\text{OH})_2$, is soluble in excess NH_3 to form **H**, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$, a deep blue solution.

When Na_4edta was added, ligand exchange reaction occurs

$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + \text{EDTA}^{4-} \rightarrow [\text{Cu}(\text{EDTA})]^{2-} + 4\text{NH}_3 + 2\text{H}_2\text{O}$

Entropy of the system increases due to the release of NH_3 and water molecules.

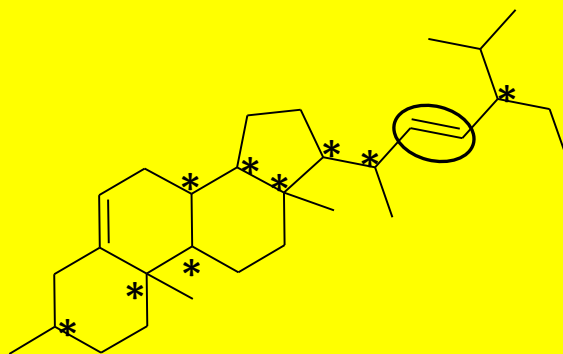
- 19** Stigmasterol is an unsaturated plant sterol occurring in the plant fats of soybean.



How many stereoisomers does stigmasterol have?

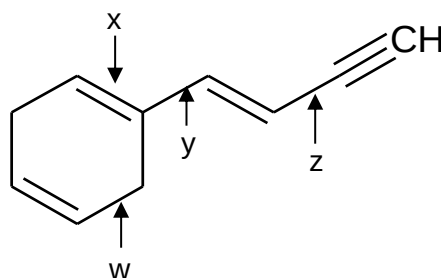
A	2^9
B	2^{10}
C	2^{11}
D	2^{12}

Answer: B



There are 9 chiral carbon centres and 1 double bond which can exhibit geometrical isomerism. Hence, the total number of stereoisomers is $2^{9+1} = 2^{10}$

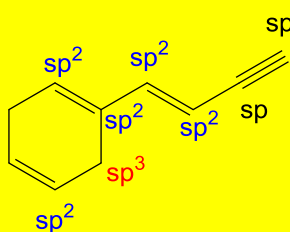
- 20.** Four carbon-carbon bonds are labelled in the diagram.



Which bonds are made up of a sp^2 - sp^2 overlap?

- A** x only
- B** x and y only
- C** w, x and y only
- D** w, y and z only

Answer: B

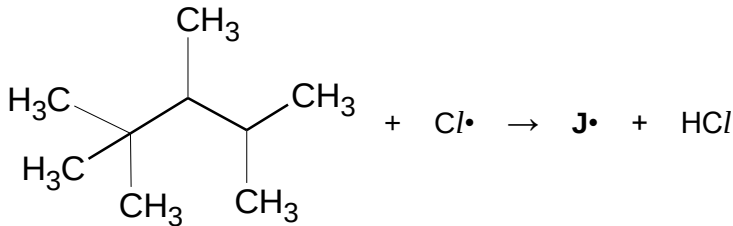
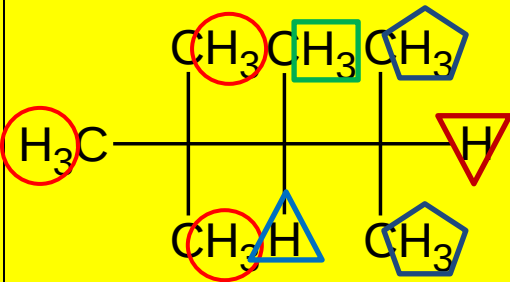


Bond x and y comprises of $sp^2 - sp^2$ overlap.

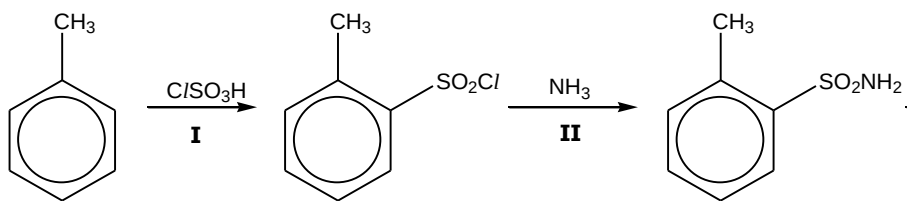
Bond w comprises of $sp^2 - sp^3$ overlap.

Bond z comprises of $sp^2 - sp$ overlap.

- 21.** When heated with chlorine, the hydrocarbon 2,2,3,4-tetramethylpentane undergoes free radical substitution. In a propagation step, the free radical **J•** is formed by the

	loss of one hydrogen atom.  How many different forms of J• are theoretically possible?
A	3
B	4
C	5
D	6
Answer: C  There are 5 possible sites (as indicated by the shapes) to lose one hydrogen to form different free radical.	

22	<i>Saccharin</i> was an artificial sweetener used in some soft drinks. It was manufactured from methylbenzene by a series of reactions.



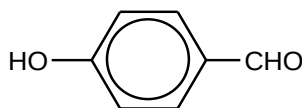
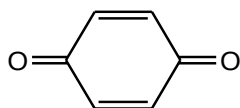
Which of the following shows the correct reaction type for steps I and II?

	I	II
A	Electrophilic substitution	Electrophilic addition
B	Electrophilic substitution	Nucleophilic substitution
C	Nucleophilic substitution	Nucleophilic substitution
D	Nucleophilic substitution	Electrophilic substitution

Answer: B

The first reaction involves the SO_2Cl^+ being substituted into the benzene ring.
The second reaction involves the NH_3 nucleophilic substitution with the RSO_2Cl .

23 Which of the following **cannot** be used to distinguish between the following compounds?



A	Hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$
B	Neutral iron(III) chloride
C	Diammine silver complex
D	Phenylhydrazine

Answer: D

Option A can be used. undergo oxidation with $\text{Cr}_2\text{O}_7^{2-}$ to form .

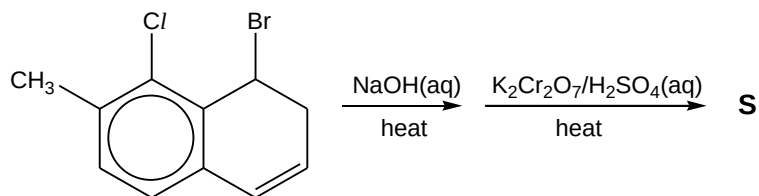
Option B is possible as will form a violet complex.

Option C, Tollen's reagent can be used to identify . A silver mirror will be formed upon heating.

Option D cannot be used as both compounds have carbonyl compound which can form orange ppt with phenylhydrazine.

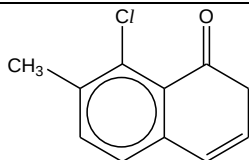
24

The reaction scheme below shows the synthesis of compound **S**.

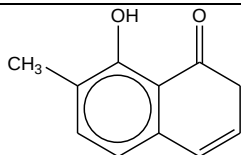


Which of the following can be **S**?

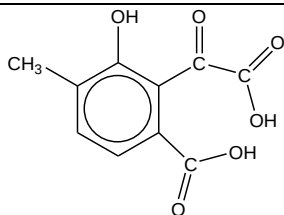
A



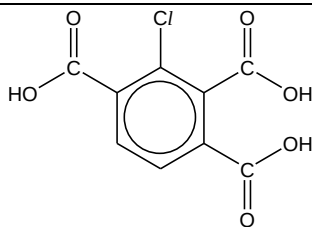
B



C

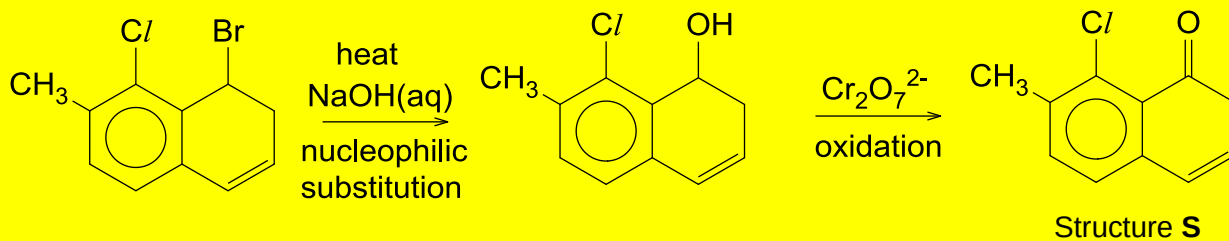


D



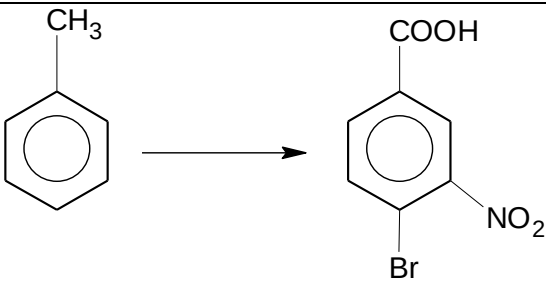
Answer: A

The reaction scheme for this question is shown below.

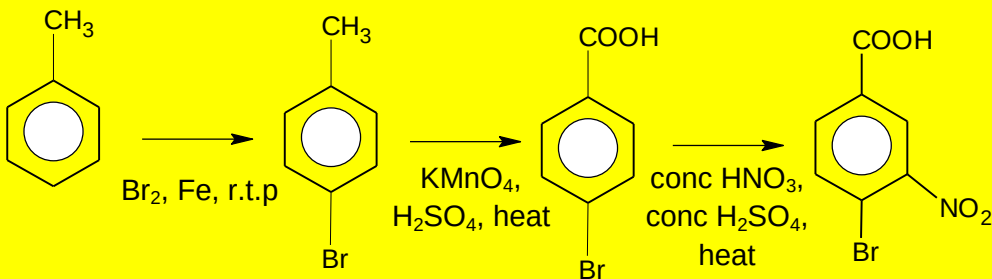


25

The following synthetic route consists of three steps.

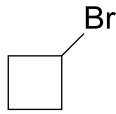
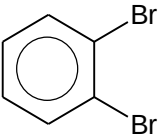
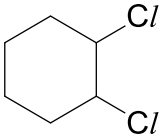
 Which sequence of steps would give the highest yield?				
		Step 1	Step 2	Step 3
	A	KMnO ₄ , H ₂ SO ₄ , heat	conc HNO ₃ , conc H ₂ SO ₄ , heat	Br ₂ , Fe, r.t.p
	B	conc HNO ₃ , conc H ₂ SO ₄ , heat	Br ₂ , Fe, r.t.p	KMnO ₄ , H ₂ SO ₄ , heat
	C	Br ₂ , Al/Br ₃ , r.t.p	conc HNO ₃ , dilute H ₂ SO ₄ , heat	KMnO ₄ , H ₂ SO ₄ , heat
	D	Br ₂ , Fe, r.t.p	KMnO ₄ , H ₂ SO ₄ , heat	conc HNO ₃ , conc H ₂ SO ₄ , heat

Answer: D



Please note that concentrated HNO₃ and concentrated H₂SO₄ must be used for electrophilic substitution of benzene ring.

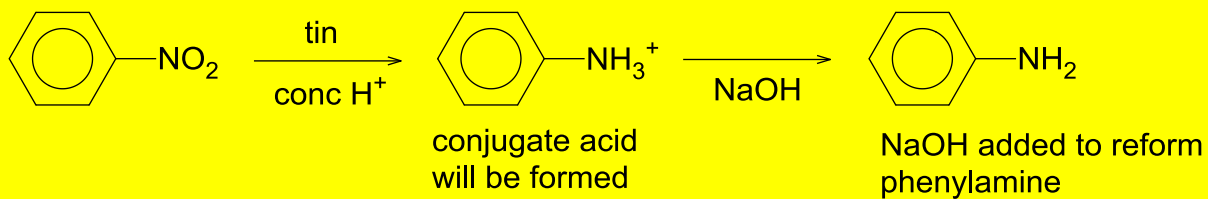
26	Ten grams of each of the following was heated for a prolong period of time with NaOH(aq). Subsequently, dilute HNO ₃ (aq) and AgNO ₃ (aq) were added.

Which compound will produce the greatest mass of AgBr(s)?	
A  $(M_r = 134.9)$	C  $(M_r = 235.8)$
B CH_3COCl $(M_r = 78.5)$	D  $(M_r = 153.0)$
Answer: D Upon heating with NaOH (aq), nucleophilic substitution will occur and all possible halogenoalkanes and acyl halides will undergo nucleophilic substitution. For Option A Amount of organic cpd = $10/134.9 = 0.074$ mol Amt of Br^- substituted = 0.074 mol Mass of AgBr ppted = $0.074 \times (108 + 79.9) = 13.9$ g For Option B Amount of organic cpd = $10/78.5 = 0.127$ mol Amt of Cl^- substituted = 0.127 mol Mass of AgCl ppted = $0.127 \times (108 + 35.5) = 18.3$ g For Option C No nucleophilic substitution took place. For Option D Amount of organic cpd = $10/153 = 0.0653$ mol Amt of Cl^- substituted = $0.0653 \times 2 = 0.131$ mol Mass of AgCl ppted = $0.131 \times (108 + 35.5) = \mathbf{18.8\text{ g}}$	

27	After the reduction using tin and concentrated acid of nitrobenzene to phenylamine, an excess of sodium hydroxide is added.

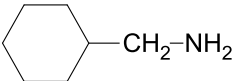
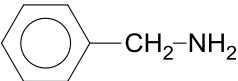
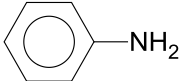
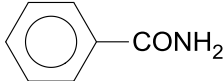
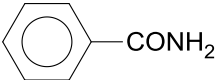
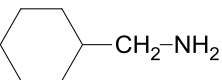
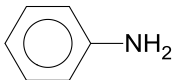
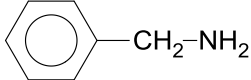
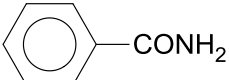
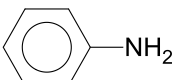
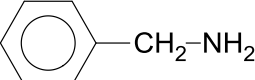
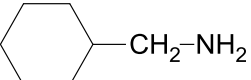
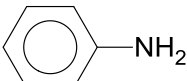
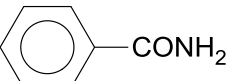
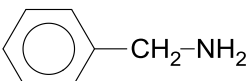
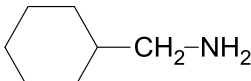
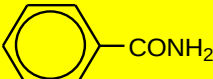
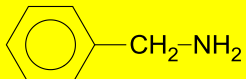
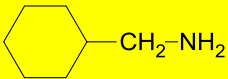
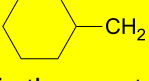
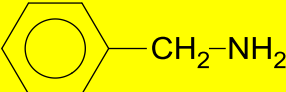
	What is the purpose of the sodium hydroxide?	
	A	to dry the product
	B	to liberate the phenylamine
	C	to neutralise the excess acid
	D	to lower the boiling point for subsequent distillation

Answer: B



The main role of NaOH is not to neutralise the concentrated acid but rather to react with the conjugate acid to form the phenylamine.

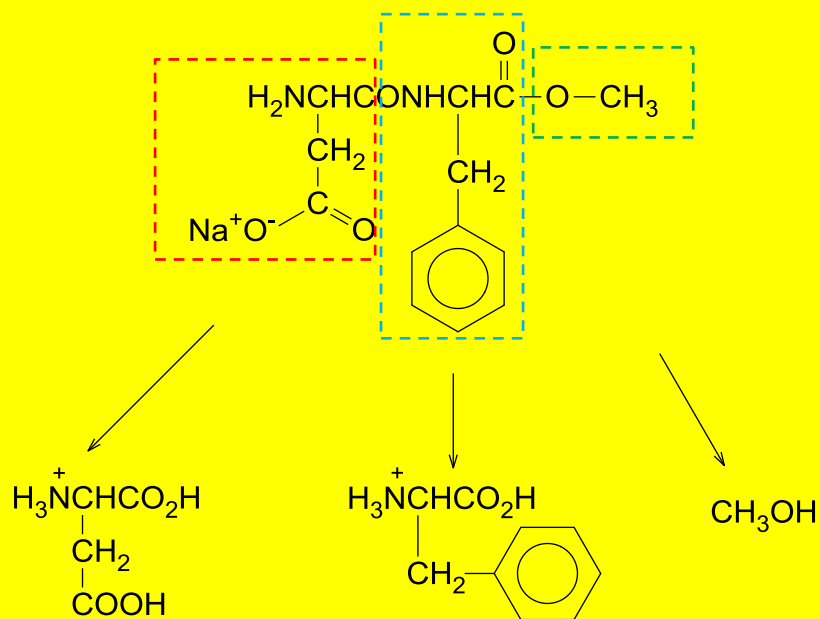
28	Which of the following shows the correct order of basicity?

	Weakest base (high pK_b)	Strongest base (Low pK_b)		
A	 $\text{CH}_2\text{-NH}_2$	 $\text{CH}_2\text{-NH}_2$	 NH_2	 CONH_2
B	 CONH_2	 $\text{CH}_2\text{-NH}_2$	 NH_2	 $\text{CH}_2\text{-NH}_2$
C	 CONH_2	 NH_2	 $\text{CH}_2\text{-NH}_2$	 $\text{CH}_2\text{-NH}_2$
D	 NH_2	 CONH_2	 $\text{CH}_2\text{-NH}_2$	 $\text{CH}_2\text{-NH}_2$
Answer: C				
	Weakest base		Strongest base	
	 CONH_2	 NH_2	 $\text{CH}_2\text{-NH}_2$	 $\text{CH}_2\text{-NH}_2$
	This is an amide and it is neutral	The lone pair of electron on the nitrogen atom can delocalised into the benzene ring making it less available for dative bond with the hydrogen protons.	The electron directing cause by the  is not as strong as the  due to the present of the benzene ring	The electron directing effect cause by the  group is the greatest. This cause the lone pair of electrons to be more available for dative bond with H^+ , resulting in a stronger base
For your knowledge, 2013 Paper 3 Q2(d)				
	 $\text{CH}_2\text{-NH}_2$			
	It is know that $(K_b = 2.18 \times 10^{-5})$ is less basic than CH_3NH_2 ($K_b = 5.6 \times 10^{-4}$).			
	The presence of the benzene ring affect the electron donating effect of the R-group.			

29	Aspartame is a dipeptide derivatives used as an artificial sweetener. Its general usefulness is restricted because it loses its sweetness after hydrolysis.

	$ \begin{array}{c} \text{H}_2\text{NCHCONHCHCO}_2\text{CH}_3 \\ \qquad \qquad \\ \text{CH}_2 \qquad \text{CH}_2 - \text{C}_6\text{H}_5 \\ \\ \text{CO}_2^-\text{Na}^+ \end{array} $ Which product would be formed after prolong acid hydrolysis.	
A	$ \begin{array}{c} \text{H}_3\text{N}^+\text{CHCO}_2\text{H} \\ \\ \text{CH}_2 \\ \\ \text{CO}_2^-\text{Na}^+ \end{array} $ and $ \begin{array}{c} \text{H}_3\text{N}^+\text{CHCO}_2\text{CH}_3 \\ \\ \text{CH}_2 - \text{C}_6\text{H}_5 \end{array} $	C
B	$ \begin{array}{c} \text{H}_3\text{N}^+\text{CHCO}_2\text{H} \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array} $ and $ \begin{array}{c} \text{H}_2\text{NCHCO}_2\text{CH}_3 \\ \\ \text{CH}_2 - \text{C}_6\text{H}_5 \end{array} $	D
	$ \begin{array}{c} \text{H}_3\text{N}^+\text{CHCO}_2\text{H} \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array} $ and $ \begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\ \\ \text{CH}_2 - \text{C}_6\text{H}_5 \end{array} $ and CH_3OH	

Answer: C



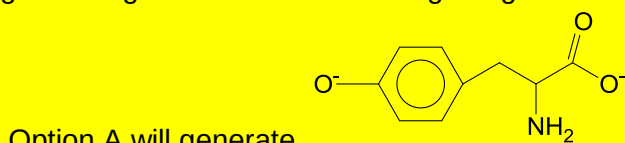
The diagram above shows the acidic hydrolysis reaction of the amide and ester group. Do note that since acid is present, all basic groups (the NH_2 , the COO^-Na^+) will be neutralised.

30	Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and

stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species towards the anode.	
With a buffer at pH 5, which amino acid will move most readily towards the cathode?	
A	
C	
B	
D	

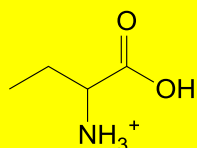
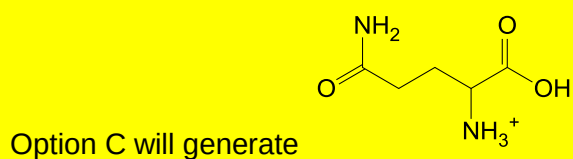
Answer: D

For A and B since its R-group are acidic, their isoelectric point will be lesser than 5. Thus in buffer at pH 5, they will be in an alkaline environment and will thus behave as an acid generating the anion and thus migrating to the anode.



Option B will generate

For C and D their R-group are neutral thus their isoelectric point reside around 7. Thus in buffer at pH 5, they will be in an acidic environment and thus will behave as an alkaline generating the cation and migrating to the cathode.



Option D will generate

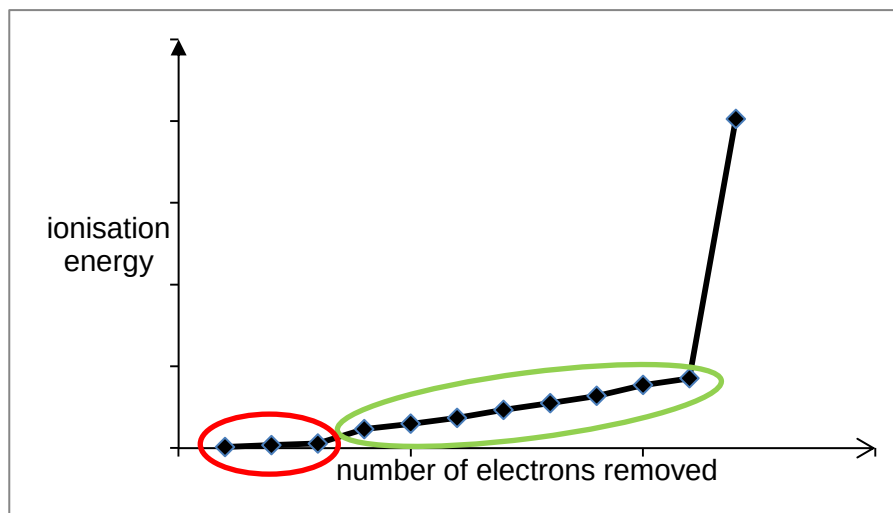
Since D has a lower M_r as compared to C, it will migrate more readily towards the cathode.

For **questions 31 – 40**, one or more of the numbered statements **1 to 3** may be correct. Decide whether each of the statements is or is not correct. The responses **A to D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is to be used as correct response.

31 The graph below shows the first twelve ionisation energies for element T.



Which of the following statements are true?

1	It is in Group I of the Periodic Table.
2	It forms an oxide which dissolves readily with acid.
3	It is in the third period (Na to Ar) of the Periodic Table.

Answer: C

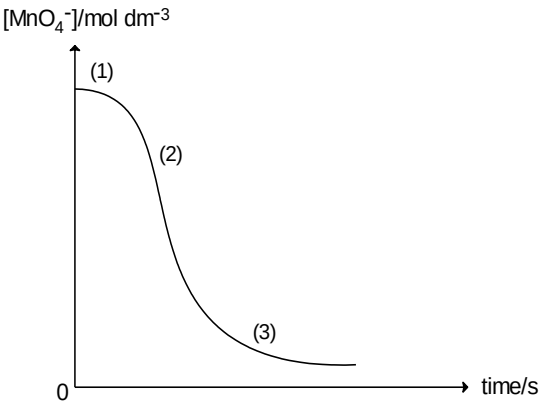
It is in group III of the Periodic Table as the first 3 consecutive electrons required lower energy. With this idea, Option 1 is definitely wrong and deploying MCQ skill, you should pick Option C (2 and 3) as the correct respond.

Being in group III, and having more than 10 electrons, it could be in the third period. The group III element could be aluminium whose oxide (Al_2O_3) can dissolve readily in acid.

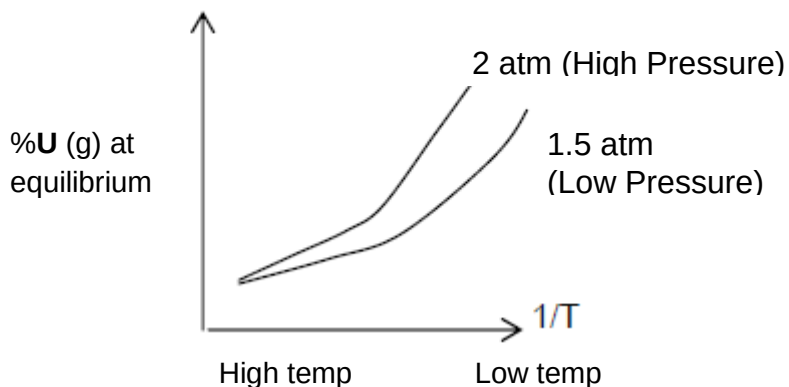
32	The following chemical reactions are listed below. - Combustion of ethandioic acid: $\text{C}_2\text{H}_2\text{O}_4(l) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(l)$ - Evaporation of water: $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ - Atomisation of magnesium: $\text{Mg}(s) \rightarrow \text{Mg}(g)$ - Photolysis of chlorine : $\text{Cl}_2(g) \rightarrow 2\text{Cl}\cdot(g)$ Which of the following statements are correct?
1	ΔS is positive for all reactions.
2	ΔG is negative for all reactions.
3	ΔH is positive for all reactions.

Answer: D

	ΔH	ΔS	ΔG
Combustion of ethandioic acid	Always negative (Exothermic) For combustion, energy is always released.	Positive There is more moles of product than reactant	Since ΔH is exothermic and ΔS is positive, ΔG will always be negative at all temperatures.
Evaporation of water	Always positive (Endothermic) Energy need to be absorbed to overcome the intermolecular H-bonding in water.	Positive	$\Delta G = \Delta H - T\Delta S$ Dependent on temperature. Since ΔH and ΔS is positive, ΔG will only be negative if temperature increases.
Atomisation of magnesium	Always positive (Endothermic) Energy need to be absorbed to change the magnesium solid into magnesium gaseous atoms	Positive	
Photolysis of chlorine	Always positive (Endothermic) Energy is absorbed when bonds are broken	Positive	

33	A reaction in which a product acts as a catalyst is said to be autocatalytic. $2\text{MnO}_4^-(\text{aq}) + 5\text{C}_2\text{O}_4^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) \longrightarrow 2\text{Mn}^{2+}(\text{aq}) + 10\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$ In the oxidation of ethanedioate ions by manganate(VII) ions, the reaction is accelerated by the Mn^{2+} ions produced during the reaction.  Which of the following statements can be deduced from the graph above?
1	Initial rate of reaction is the fastest at (1).
2	Reaction rate increases at (2) as Mn^{2+} is generated.
3	Reaction rate decreases at (3) as the concentration of the reactants decrease.
	Answer: C From the graph the gradient at (1) is not the steepest. It is only at region (2) that the reaction rate increases due to the auto-generation of catalyst Mn^{2+}. As the reaction progresses, the concentration of reactants decrease and that's when reaction rate starts to dwindle down gradually.

- 34** The graph below shows how the percentage of reactant **U(g)** that remained in an equilibrium mixture varies with $1/T$ at pressures of 1.5 atm and 2 atm.



Which of the following statement can be deduced from this information?

1	The forward reaction is endothermic.
2	The equation for the above reaction could be $\text{U(g)} \rightleftharpoons \text{V(g)} + \text{W(g)}$.
3	The equilibrium constant, K_p , increases as pressure increases in the system.

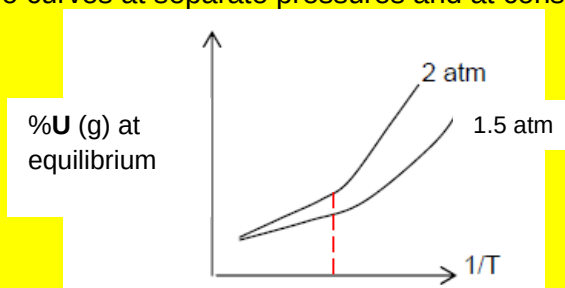
Answer: B

The first challenge is to deal with the $1/T$ axis. One word of advice is to label high temperature and low temperature on the question. This will make things easier. Do note that **U** is a **REACTANT!!**

Using any curve, as temperature increases while pressure is constant, % U decreases, this means there will be **less reactant U** and forward reaction is favoured. As increase in temperature by Le Chatelier's Principle always favour endothermic reaction, forward reaction is endothermic.

From the expression given in option 2 $\text{U(g)} \rightleftharpoons \text{V(g)} + \text{W(g)}$
 1 mol 2 mol

Considering the two curves at separate pressures and at constant temperature



An increase in pressure cause the %U to increase. This means the equilibrium position must shift left. As such the expression in option 2 matches this claim.

Option 3 is wrong as K_p is only temperature dependent.

35 A student was investigating the possibility of an electrochemical cell using $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cells.

Which statements are true of the above set up?

1	$E^\circ_{\text{cell}} = +0.62 \text{ V}$.
2	Copper and iron electrodes cannot be used instead.
3	When excess sodium hydroxide is added to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ half-cell, the polarity of the electrodes are reversed.

Answer: A (1 ,2 and 3 only)

Option 1 is true:

From Data Booklet

$$E^\circ(\text{Cu}^{2+}/\text{Cu}^+) = +0.15 \text{ V} \quad E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$$

$$E^\circ_{\text{cell}} = +0.77 - 0.15 = +0.62 \text{ V}$$

Option 2 is true: If copper and iron electrode are used. Other reaction will occur as equilibrium can be established between the metal and their ions.

Option 3 is true:

When OH^- is added to the iron half-cell, the half equation becomes



As compared to $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77\text{V}$

Thus the iron containing compound half-cell would now undergo oxidation and the $\text{Cu}^{2+}/\text{Cu}^+$ half-cell would now undergo reduction. Hence, the polarity of the electrodes are reversed

36 Barium sulfate is less soluble than magnesium sulfate.

Which of these factors are needed to be considered in order to explain this observation?

1	ΔH_{hyd} of barium ion and magnesium ion.
2	ΔH_{f} of barium sulfate and magnesium sulfate.
3	Atomic radii of barium and magnesium.

Answer: D (1 only)

$$\Delta H_{\text{solution}} = (\Delta H_{\text{hydration of cation}} + \Delta H_{\text{hydration of anion}}) - \Delta H_{\text{lattice energy}}$$

The more soluble the sulfate, the more exothermic the $\Delta H_{\text{solution}}$.

Note that for both $\Delta H_{\text{hydration}}$ and $\Delta H_{\text{lattice energy}}$, these terms are dependent on the ionic radii not the atomic radii.

Option 2 is not feasible as enthalpy change of formation is not required.

37	Which observation about bromine or its compounds is correct?	
	1	When aqueous lead(II) nitrate is added to aqueous sodium bromide, a cream precipitate is observed.
	2	When sodium bromide is treated with concentrated sulfuric acid, a gas that turns moist blue litmus paper red is evolved.
	3	Silver bromide is soluble in both dilute and concentrated ammonia solution.

Answer: **B (1 and 2 only)**

Option 1: $\text{Pb}^{2+}(\text{aq}) + \text{Br}^{-}(\text{aq}) \rightleftharpoons \text{PbBr}_2(\text{s})$

PbBr₂(s) is a cream ppt (same colour as AgBr ppt)

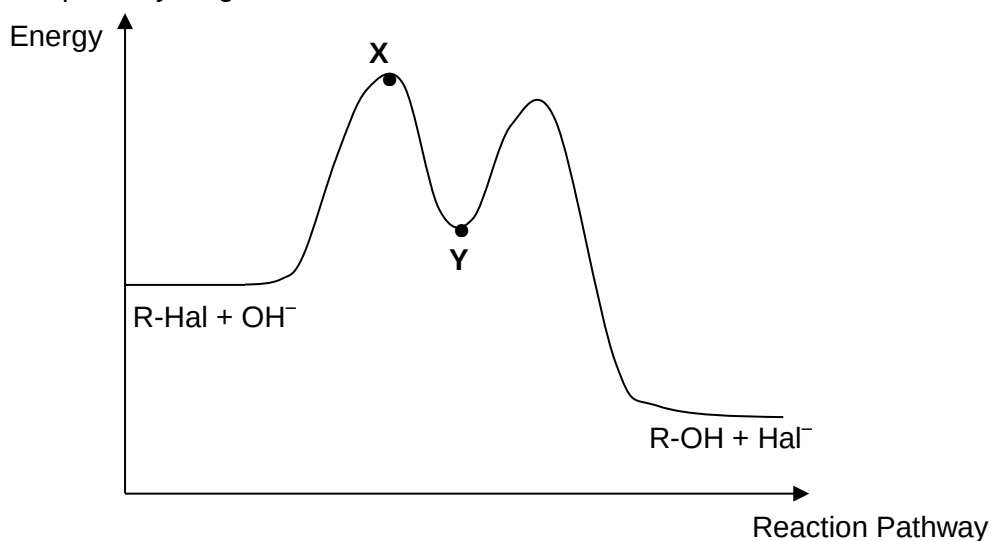
Option 2: $\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{HBr} + \text{NaHSO}_4$

$2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + 2\text{H}_2\text{O} + \text{Br}_2$ **SO₂ is acidic and turns moist blue litmus paper red**

Option 3: AgBr is only soluble in concentrated ammonia.

38	The catalytic converter is part of the exhaust system of modern cars. Which reactions occur in the catalytic converter?	
	1	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
	2	$2\text{NO} + \text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$
	3	$\text{C}_x\text{H}_y + (2x + \frac{y}{2})\text{NO} \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} + (x + \frac{y}{4})\text{N}_2$
Answer: A (1,2 and 3) Catalytic converter function to catalyse the 1. Oxidation of carbon monoxide to carbon dioxide 2. Reduction of nitrogen oxide to nitrogen and oxygen gas by carbon monoxide. 3. Complete combustion of hydrocarbons by oxygen or nitrogen oxide Reduction of nitrogen oxide to nitrogen and oxygen gas by carbon monoxide.		

- 39** Halogenoalkanes react with aqueous alkali. One mechanism of this reaction has the reaction pathway diagram shown below.



Which statements are true? (---- indicates a partial bond)

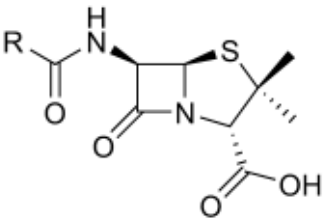
1 The reaction is a type of nucleophilic substitution.

2 X is $\begin{array}{c} \diagup \\ \text{C} \text{----} \text{Hal} \\ \diagdown \delta^+ \delta^- \end{array}$

3 Y is $\begin{array}{c} | \\ \text{HO} \text{----} \text{C} \text{----} \text{Hal} \\ | \end{array}$

Answer: B (1 & 2 only)

Y is a carbocation intermediate, not a pentavalent transition state.

40	Which of the following phenomena involves denaturation of proteins?	
	1	Heating of egg white.
	2	Production of bean-curd from soy milk.
	3	Dissolving Penicillin in a test tube of hot acid.
		 Penicillin
Answer: B (1 and 2 only) Option 1 involves denaturation: Heating during cooking causes the albumin (protein) in egg white to denature. Heating will disrupt the weak Van der Waals forces (and to a lesser extent, hydrogen bonds) holding the quaternary, tertiary and secondary structures, resulting in a more disordered arrangement. Option 2 involves denaturation: Extract from 2010 H2 Paper 3 Q3, "Dofu (bean curd) is made by coagulating soy milk and then pressing the curds between fine cloth to extrude most of the moisture. Coagulating agents that have been used include certain salts, acid or enzymes. Coagulation is due to the denaturation of the protein in the soy milk." Similar process in food preparation include cheese making, yogurt making and butter making. (Making of Margarine is not denaturation but addition of hydrogen into poly unsaturated alkenes) Option 3 does not involve denaturation as it is merely an acidic hydrolysis process.		

END OF PAPER 1



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY
JC2 Preliminary Examination
Paper 2 Structured Questions (SPA)

9647/02
16 September 2016
2hr

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
 Write in dark blue or black pen on both sides of the paper.
 You may use a soft pencil for any diagrams, graphs or rough work.
 Do not use staples, paper clips, highlighters, glue or correction fluid.

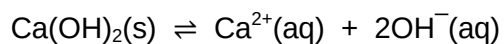
Answer **all** questions.
 A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
 The number of marks is given in the brackets [] at the end of each question or part questions.

For Examiner's Use	
P1	/ 40
P2	/ 72
P3	/ 80
GRAND TOTAL	/ 192
%	
GRADE	

For Examiner's Use	
1(P)	/ 12
2	/ 15
3	/ 13
4	/ 11
5	/ 12
6	/ 9
TOTAL P2	/ 72

- 1(P)** When a sparingly soluble salt, calcium hydroxide, Ca(OH)_2 , is added to water, an equilibrium is established between the undissolved salt and a saturated solution of the salt.



The solubility product at laboratory temperature can be found by determining the equilibrium concentration of the hydroxide ions in a saturated solution of calcium hydroxide. This equilibrium concentration can be found by titration with a standard solution of hydrochloric acid.

The numerical value of the solubility product of calcium hydroxide is approximately 5×10^{-6} .

- (a)** Write an expression for the solubility product of calcium hydroxide, stating its units.

.....
.....

[1]

You are required to write a plan to determine the solubility product of calcium hydroxide at laboratory temperature.

You may assume that you are provided with:

- Solid Ca(OH)_2
- $0.200 \text{ mol dm}^{-3}$ of stock solution of HCl
- deionised water
- indicators normally found in a school laboratory
- equipment normally found in a school laboratory

- (b) (i)** Calculate the minimum mass of Ca(OH)_2 that needs to be weighed in order to obtain 250 cm^3 of a saturated solution of Ca(OH)_2 at laboratory temperature.

[2]

- (ii)** Assuming that approximately 30.00 cm^3 of HCl was required to react with 25.0 cm^3 of saturated solution of Ca(OH)_2 , calculate an appropriate concentration of HCl required. Hence, calculate the volume of the given solution of HCl required to prepare 250 cm^3 of this solution.

[2]

Turn over]

- (iii)** Using the information given above and the answers in **b(i)** and **b(ii)**, you are required to write a plan to determine the solubility product of calcium hydroxide.

You are also required to explain how the data you obtain from this experiment may be used to determine the solubility product of calcium hydroxide.

Your plan should include:

- the preparation of 250 cm³ of the saturated solution of calcium hydroxide;
- the preparation of 250 cm³ of standard solution of hydrochloric acid from the stock solution of hydrochloric acid;
- titration procedure;
- how the results obtained can be used to determine the solubility product of calcium hydroxide.

[illegible]

[Total: 12]

- 2 The manufacture of ammonia from nitrogen and hydrogen takes place in two stages:

First Stage: The manufacture of hydrogen from methane.

Second Stage: The synthesis of ammonia (the Haber Process).

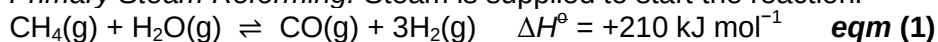
The First Stage occurs via a two-step process.

- *Steam Reforming*
- *Shift Reaction*

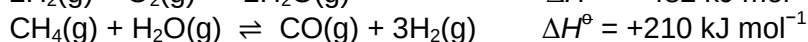
Both steps produce hydrogen gas that will be used in the Second Stage for the production of ammonia.

- (a) *Steam Reforming* is a reaction that converts methane and steam to a mixture of carbon monoxide and hydrogen. There are two possible routes for it:

Primary Steam Reforming: Steam is supplied to start the reaction.



Secondary Steam Reforming: Some hydrogen is burnt to form steam which then reacts with methane to generate more hydrogen.



- (i) State if the overall process of *Secondary Steam Reforming* is an exothermic or endothermic process.

..... [1]

- (ii) Suggest and explain which steam reforming process (*Primary* or *Secondary*) is favoured by high temperature.

.....

 [2]

(iii) The methane gas used usually contains some organic sulfur compounds, R-SH, and hydrogen sulfide, H_2S , both of which must be removed or it will poison the catalyst. Hence the methane mixture needs to be passed through a *desulfurisation unit* first.

- These organic sulfur compounds are first converted into hydrogen sulfide and a hydrocarbon by reduction with hydrogen gas.
- The hydrogen sulfide is reacted with zinc oxide (ZnO) to produce zinc sulfide (ZnS) as one of the products.

Construct two balanced chemical equations showing the reactions that occurred in the *desulfurisation unit*, using R-SH to represent organic sulfur compounds and RH to represent hydrocarbon.

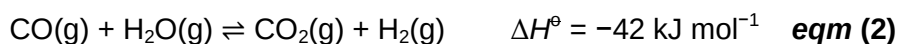
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[2]

(b) In the *Shift Reaction*, the carbon monoxide produced during the *Steam Reforming* process was converted to carbon dioxide and hydrogen gas. *Shift Reaction* is done via a two-step process:

- *High Temperature Shift Reaction* with iron(III) oxide catalyst.
- *Low Temperature Shift Reaction* with thermally unstable copper catalyst at 500 K. The carbon monoxide concentration is further reduced to 0.2%.

The reaction involved in the *Shift Reaction* is illustrated in the following equation.



(i) State the full electronic configuration of iron(III) ion and copper metal.

Fe³⁺: 1s².....

Cu: 1s².....

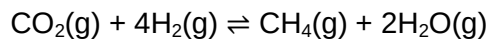
[2]

(ii) With reference to the *Shift Reaction*, state and explain if iron(III) oxide and copper is functioning as homogeneous or heterogeneous catalyst.

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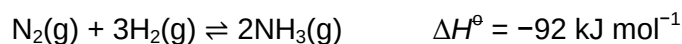
[2]

- (c) Traces of carbon dioxide produced in the *Shift Reaction* is subsequently removed by passing it with hydrogen gas over a nickel catalyst at 600 K, a process known as *Methanation*.



Using the enthalpy change values of **eqm(1)** and **eqm(2)**, determine the enthalpy change for this *Methanation* process.

- (d) The main process of the Haber Process occurs in a fixed bed reactor.



The proportion of ammonia in the equilibrium mixture increases with increasing pressure and with decreasing temperature. Quantitative data are given in the table below.

Pressure/atm	Percentage of ammonia present at equilibrium at a range of temperature		
	373 K	473 K	573 K
10	-	50.7	14.7
25	91.7	63.6	27.4
50	94.5	74.0	39.5
100	96.7	81.7	52.5
200	98.4	89.0	66.7
400	99.4	94.6	79.7
1000	-	98.3	92.6

- (i) To obtain a reasonable yield with favourable rate, high pressures, moderate temperatures and a catalyst are used. Using the data, select the temperature and pressure which will result in the highest yield of ammonia.

Temperature

Pressure

[1]

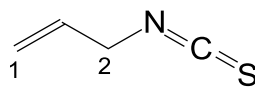
- (ii) Hence, using the data you have selected in (d)(i), determine the volume of ammonia gas, nitrogen gas and hydrogen gas at equilibrium when 10 cm³ of nitrogen gas is reacted with 30 cm³ of hydrogen gas in the Haber Process. Leave your answer to two decimal places.

[3]

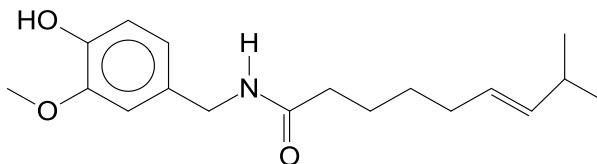
Turn over]

[Total: 15]

- 3 (a) Allyl isothiocyanate (AITC) is responsible for the pungent taste of wasabi while capsaicin is an active component of chilli pepper and is found in spiced products like curry.



AITC

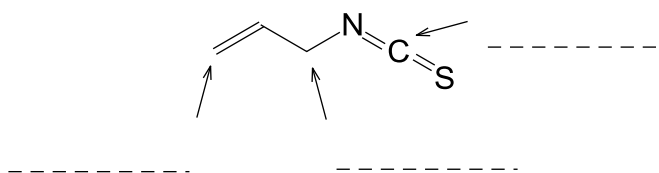


Capsaicin

- (i) Using your concept of VSEPR, state the shape about the carbon labelled 1 and 2 on AITC.

Carbon 1: Carbon 2: [2]

- (ii) State the type of hybridisation of carbons indicated in AITC.



[2]

- (iii) Besides the ether group , state the other functional groups that are present in Capsaicin.

.....[3]

- (iv) Ignoring the effect of the -N=C=S group, write an equation showing how AITC reacts with liquid IBr. Hence, with reference to the *Data Booklet* and given that the bond energy of I-Br to be 180 kJ mol^{-1} , determine the enthalpy change of reaction when AITC reacts with liquid IBr.

[2]

- (v) Using your knowledge in chemical bonding, suggest why the burning sensation of capsaicin cannot be washed away with water.

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[2]

- (vi) Draw the structural formula of the products formed when capsaicin is reacted with hot aqueous potassium hydroxide.

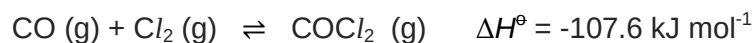
[You are to ignore the effect of the  group]

[2]

[Total: 13]

- 4 (a) Phosgene is a compound with the formula COCl_2 . It is not to be confused with cobalt(II) chloride with the formula CoCl_2 .

Phosgene is produced industrially with carbon monoxide and chlorine gas.



The K_p of this process is 0.05 atm^{-1} at 300 K. A mixture contains 2 mol of carbon monoxide and 2 mol of chlorine initially was reacted and allow to reach equilibrium. The equilibrium mixture is found to contain 1.5 mol of phosgene.

- (i) Draw the Lewis structure of phosgene.

[1]

- (ii) Write an expression for K_p for the equilibrium between CO , Cl_2 and phosgene and hence using the information provided calculate the total pressure of the system at equilibrium.

[3]

- (iii) Suggest if chlorine or phosgene will deviate more from ideal gas behaviour.

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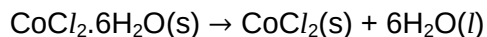
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[2]

- (b) Crystals of hydrated cobalt(II) chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, lose water when they are heated, forming anhydrous cobalt(II) chloride, CoCl_2 .



- (i) The standard enthalpy change for the reaction, $\Delta H^\ominus$, is $+88.1 \text{ kJ mol}^{-1}$. Given that the calculation for entropy change to be similar to that of enthalpy change, use the following entropy data to determine the standard entropy change of the reaction at 298 K. Give your answer to **four** significant figures.

Compound	$S^\ominus$ / $\text{J mol}^{-1}\text{K}^{-1}$
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} (\text{s})$	343.0
$\text{CoCl}_2 (\text{s})$	109.2
$\text{H}_2\text{O} (\text{l})$	69.9
$\text{H}_2\text{O} (\text{g})$	188.7

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[1]

- (ii) Hence, explain by using calculation, whether hydrated cobalt(II) chloride can be stored at 298K without decomposition.

[2]

- (c) With the aid of a chemical equation, explain why a solution of cobalt(II) chloride has a pH of 4.6.

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Turn over]

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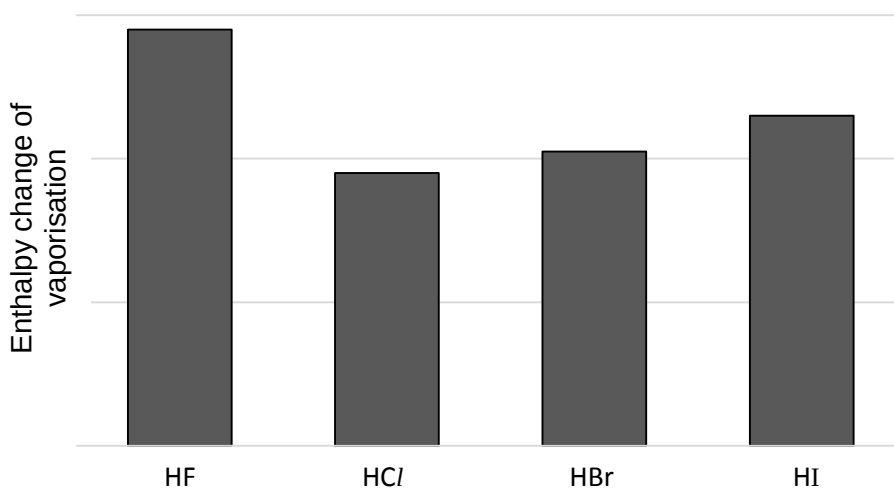
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[2]
[Total: 11]

- 5 Group VII hydrides are colourless gases at room temperature. The figures below shows the relative enthalpy change of vaporisation of the hydrides.

Figure 1: Enthalpy change of vaporisation of HX



- (a) With reference to **Figure 1**, explain the abnormally high enthalpy change of vaporisation of hydrogen fluoride.

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Turn over]

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[2]

- (b) The table below shows the pK_a of the respective compounds when they are dissolved in water.

Compounds	pK_a	Compounds	
		Hydrogen bromide	-9.00
Hydrogen chloride	-7.00	Hydrogen iodide	-10.00
Methanoic acid	3.77	Water	7.00

- (i) Using relevant information from the *Data Booklet*, rank the acid strength of aqueous solution containing HCl, HBr and HI, in increasing order. Explain your answer.

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Turn over]

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[2]

- (ii) Account for the relative acidities of methanoic acid and water.

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[2]

- (c) Unlike other Group VII hydrides, hydrogen fluoride, HF, behaves as a weak acid in water.

A solution of HF was titrated against aqueous potassium hydroxide until 25% of the HF present was neutralised.

- (i) Write the acid dissociation constant expression, K_a , for HF.

[1]

- (ii) Given that the pH of the resulting solution described above is 2.88, calculate K_a of HF.

Turn over]

[3]

(d) One of the most common ways to make hydrogen chloride is to react sodium chloride with concentrated sulfuric acid, H_2SO_4 or concentrated phosphoric(V) acid, H_3PO_4 . Both reactions occur similarly, releasing gas.

(i) Construct a balanced equation involving sodium chloride and concentrated phosphoric(V) acid.

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[1]

(ii) In the reaction with sodium bromide, concentrated sulfuric acid produces a reddish-brown solution while concentrated phosphoric(V) acid produces white fumes.

Suggest a reason for the observations above.

Turn over]

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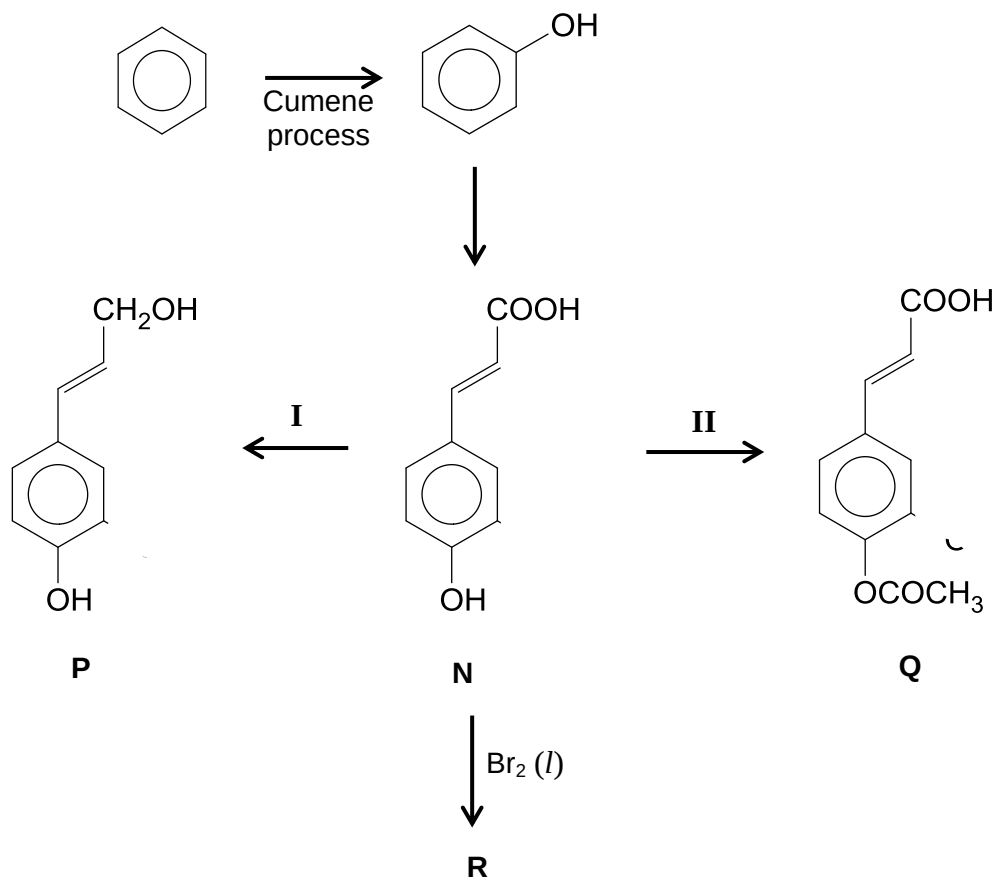
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[1]

[Total: 12]

- 6 (a) The chemical structure and some reactions involving compound **N** are shown below.



- (i) State the reagents and conditions involved in Steps **I** and **II**.

Step **I**:

Step **II**:

[2]

- (ii) Draw the structure of organic product **R**.

[1]

- (iii) Propose a chemical test to distinguish between **P** and **N**, in which a positive test is observed for **P only**. Write a balanced chemical equation for the reaction that has occurred.

Test:

Observation:

Equation:

[3]

- (b) In the cumene process one mole of benzene reacts with one mole of propene in the presence of oxygen from air to form phenol and organic substance **T**. Substance **T** does not give any positive observation with diammine silver complex or phosphorus pentachloride.

- (i) From the information provided, identify substance **T**.

[1]

- (ii) Hence, with an aid of a chemical equation, show how the functional group in substance **T** can be positively identified.

Observation:.....

Equation:

[2]

[Total: 9]

END OF PAPER



Serangoon Junior College

2016 JC2 H2 CHEMISTRY (9647) Paper 2 Suggested Solutions

1(P)	When a sparingly soluble salt, calcium hydroxide, Ca(OH)_2, is added to water, an equilibrium is established between the undissolved salt and a saturated solution of the salt. $\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$ The solubility product at laboratory temperature can be found by determining the equilibrium concentration of the hydroxide ions in a saturated solution of calcium hydroxide. This equilibrium concentration can be found by titration with a standard solution of hydrochloric acid. The numerical value of the solubility product of calcium hydroxide is approximately 5×10^{-6}.	
	(a)	Write an expression for the solubility product of calcium hydroxide, stating its units. [1]
		$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^{-}]^2$; units: $\text{mol}^3 \text{dm}^{-9}$
	You are required to write a plan to determine the solubility product of calcium hydroxide at laboratory temperature. You may assume that you are provided with: • Solid Ca(OH)_2 • $0.200 \text{ mol dm}^{-3}$ of stock solution of HCl • deionised water • indicators normally found in a school laboratory • equipment normally found in a school laboratory	
	(b)	(i) Calculate the minimum mass of Ca(OH)_2 that needs to be weighed in order to obtain 250 cm^3 of a saturated solution of Ca(OH)_2 at laboratory temperature. [2]
		$K_{\text{sp}} \approx 5.0 \times 10^{-6}$ Let the solubility be $x \text{ mol dm}^{-3}$. $(x)(2x)^2 = 5.0 \times 10^{-6}$ $4x^3 = 5.0 \times 10^{-6}$ $x = 0.01077 \text{ mol dm}^{-3}$ solubility in $\text{g dm}^{-3} = 0.01077 \times (40.1 + 16.0 \times 2 + 1.0 \times 2) = 0.7982 \text{ g dm}^{-3}$ Min mass of $\text{Ca(OH)}_2 = \frac{0.7982}{1000} \times 250 = 0.200\text{g}$
		(ii) Assuming that approximately 30.00 cm^3 of HCl was required to react with 25.0 cm^3 of saturated solution of Ca(OH)_2, calculate an appropriate concentration of HCl required. Hence, calculate the volume of the given solution of HCl required to prepare 250 cm^3 of this solution. [2]

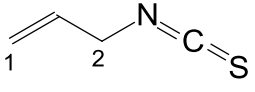
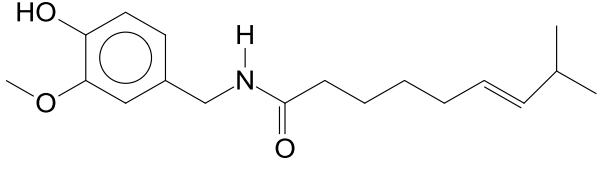
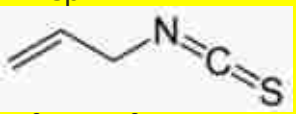
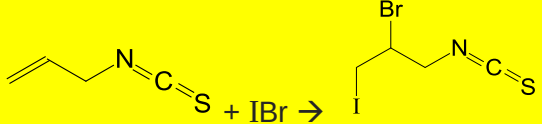
		$\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$ $\text{Amount of Ca(OH)}_2 = \frac{25}{1000} \times 0.01077 = 0.0002693\text{mol}$ $\text{Amount of HCl} = 0.0002693 \times 2 = 0.0005386\text{mol}$ $\text{Concentration of HCl required} = \frac{0.0005386}{30} \times 1000 = 0.0180\text{mol dm}^{-3}$ Vol of the given solution needed = $\frac{\frac{250}{1000} \times 0.0180}{0.2} = 0.0225\text{dm}^3 = 22.5\text{cm}^3$
	(iii)	Using the information given above and the answers in b(i) and b(ii), you are required to write a plan to determine the solubility product of calcium hydroxide. You are also required to explain how the data you obtain from this experiment may be used to determine the solubility product of calcium hydroxide. Your plan should include: - the preparation of 250 cm³ of the saturated solution of calcium hydroxide; - the preparation of 250 cm³ of standard solution of hydrochloric acid from the stock solution of hydrochloric acid; - titration procedure; - how the results obtained can be used to determine the solubility product of calcium hydroxide. [7]
		<u>Preparation of saturated solution of calcium hydroxide</u> <u>Weigh</u> approximately <u>0.200 g</u> of solid. - Using a <u>measuring cylinder</u>, place <u>250 cm³ of deionised water</u> into a <u>dry conical flask/beaker</u>. - Add <u>solid to water</u> and <u>stir with a glass rod</u> to dissolve the solid. <u>Weigh</u> and <u>add more solid</u> to the water until <u>excess solid remains / no more solid dissolves</u>. - Allow the mixture to <u>stand for a period of time</u> (e.g 30 mins) to establish equilibrium. <u>Filter</u> the mixture to obtain the filtrate.
		<u>Preparation of hydrochloric acid form the solution</u> - Fill a <u>burette</u> with the stock solution of <u>hydrochloric acid</u>. Drain <u>22.50 cm³</u> of the hydrochloric acid from the burette into a <u>250 cm³ volumetric flask</u>. Top-up the volumetric flask up <u>to the mark with de-ionised water</u>. Add the last few drops of de-ionised water using a dropper till the bottom of the meniscus coincides with the mark. <u>Stopper</u> the volumetric flask firmly and <u>shake it</u> to ensure complete mixing. This is to ensure that a homogeneous solution is obtained.

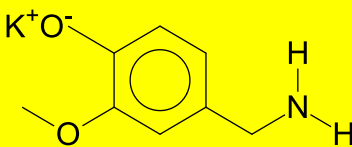
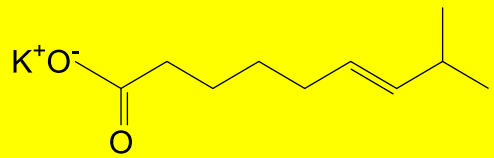
		<u>Titration procedure</u> 1. <u>Fill a clean burette</u> with the <u>hydrochloric acid</u> solution. 2. <u>Pipette 25.0 cm³ of calcium hydroxide</u> into a clean <u>conical flask</u>. 3. Add <u>2 or 3 drops of methyl orange indicator</u> into the conical flask and <u>titrate</u> this solution with the <u>hydrochloric acid in the burette</u> with <u>constant swirling</u>, and <u>add drop-wise</u> as the titration is <u>near the end-point</u>. 4. <u>Stop the titration</u> immediately when the first <u>drop of hydrochloric acid</u> added turns the solution from <u>yellow to orange</u>. 5. <u>Repeat the titration</u> until <u>two accurate titre readings fall within 0.10 cm³</u> of each other are obtained
		<u>Results</u> Assume that the volume obtained is <u>V cm³</u> Amount of Ca(OH)₂ in 25.0 cm³ = $\frac{1}{2} \times \left(\frac{V}{1000} \times 0.0180 \right) \text{mol}$ Concentration of saturated Ca(OH)₂ = $\left[\frac{1}{2} \left(\frac{V}{1000} \times 0.0180 \right) \div \frac{25}{1000} \right] = z \text{ mol dm}^{-3}$ [Ca²⁺] = z mol dm⁻³ [OH⁻] = 2z mol dm⁻³ K_{sp} = z × (2z)² = 4z³ mol³ dm⁻⁹
		[Total: 12]

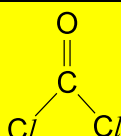
2	The manufacture of ammonia from nitrogen and hydrogen takes place in two stages: First Stage: The manufacture of hydrogen from methane. Second Stage: The synthesis of ammonia (the Haber Process). The First Stage occurs via a two-step process. • <i>Steam Reforming</i> • <i>Shift Reaction</i> Both steps produce hydrogen gas that will be used in the Second Stage for the production of ammonia..
	(a) <i>Steam Reforming</i> is a reaction that converts methane and steam to a mixture of carbon monoxide and hydrogen. There are two possible routes for it: <i>Primary Steam Reforming:</i> Steam is supplied to start the reaction. $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H^\ominus = +210 \text{ kJ mol}^{-1} \quad \text{eqm (1)}$ <i>Secondary Steam Reforming:</i> Some hydrogen is burnt to form steam which then reacts with methane to generate more hydrogen. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \quad \Delta H^\ominus = -482 \text{ kJ mol}^{-1}$ $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H^\ominus = +210 \text{ kJ mol}^{-1}$
	(i) State if the overall process of <i>Secondary Steam Reforming</i> is an exothermic or endothermic process. [1]
	Overall is exothermic.
	(ii) Suggest which steam reforming process (<i>Primary</i> or <i>Secondary</i>) is favoured by high temperature. [2]
	Primary steam reforming is favoured by high temperature. For primary steam reforming, process is endothermic. By Le Chatelier's Principle (LCP), high temperature favoured the endothermic reaction which is the forward reaction as excess heat energy is being absorbed.
	(iii) The methane gas used usually contains some organic sulfur compounds, R-SH, and hydrogen sulfide, H₂S, both of which must be removed or it will poison the catalyst. Hence the methane mixture needs to be passed through a <i>desulfurisation unit</i> first. • These organic sulfur compounds are first converted into hydrogen sulfide and a hydrocarbon by reduction with hydrogen gas. • The hydrogen sulfide is reacted with zinc oxide (ZnO) to produce zinc sulfide (ZnS) as one of the products. Construct two balanced chemical equations showing the reactions that occurred in the <i>desulfurisation unit</i>, using R-SH to represent organic sulfur compounds and RH to represent hydrocarbon [2]
	$\text{R-SH} + \text{H}_2 \rightarrow \text{RH} + \text{H}_2\text{S}$ $\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$

	(b) In the <i>Shift Reaction</i>, the carbon monoxide produced during the <i>Steam Reforming</i> process was converted to carbon dioxide and hydrogen gas. <i>Shift Reaction</i> is done via a two-step process: • <i>High Temperature Shift Reaction</i> with iron(III) oxide catalyst. • <i>Low Temperature Shift Reaction</i> with thermally unstable copper catalyst at 500 K. The carbon monoxide concentration is further reduced to 0.2%. The reaction involved in the <i>Shift Reaction</i> is illustrated in the following equation. $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \quad \Delta H^\circ = -42 \text{ kJ mol}^{-1} \quad \text{eqm (2)}$
	(i) State the full electronic configuration of iron(III) ion and copper metal. [2]
	Fe³⁺: 1s²2s²2p⁶3s²3p⁶3d⁵ Cu: 1s²2s²2p⁶3s²3p⁶3d¹⁰4s¹
	(ii) With reference to the <i>Shift Reaction</i>, state and explain if iron(III) oxide and copper is functioning as homogeneous or heterogeneous catalyst. [2]
	They are <u>heterogeneous catalysts</u> <u>The availability of partially-filled 3d orbitals allow reactant molecules to be adsorbed onto</u> the catalyst surface via van der Waals' interactions.
	(c) Traces of carbon dioxide produced in the <i>Shift Reaction</i> is subsequently removed by passing it with hydrogen gas over a nickel catalyst at 600 K, a process known as <i>Methanation</i>. $\text{CO}_2\text{(g)} + 4\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + 2\text{H}_2\text{O(g)}$ Using the enthalpy change values of eqm(1) and eqm(2) of this question, determine the enthalpy change for this <i>Methanation</i> process. [2]
	Using algebraic method: (1) $\text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + 3\text{H}_2\text{(g)} \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1}$ (2) $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \quad \Delta H^\circ = -42 \text{ kJ mol}^{-1}$ Reverse (1) + Reverse (2) $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1}$ $\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)} \quad \Delta H^\circ = +42 \text{ kJ mol}^{-1}$ Overall: $\text{CO}_2\text{(g)} + 4\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + 2\text{H}_2\text{O(g)} \quad \Delta H^\circ = -168 \text{ kJ mol}^{-1}$ OR Using energy cycle: <pre> graph TD A["CO2 (g) + 4 H2(g)"] -- "ΔH" --> C["CH4(g) + 2H2O"] A -- "+ 42" --> B["CO(g) + H2O(g) + 3H2(g)"] B -- "-210" --> C </pre> By Hess Law $\Delta H = +42 - 210 = -168 \text{ kJ mol}^{-1}$

	(d)	The main process of the Haber Process occurs in a fixed bed reactor. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H^\ominus = -92 \text{ kJ mol}^{-1}$ The proportion of ammonia in the equilibrium mixture increases with increasing pressure and with falling temperature. Quantitative data are given the table below. <table><tr><th>Pressure/atm</th><th colspan="3">Percentage ammonia present at equilibrium at a range of temperature</th></tr><tr><td></td><th>373 K</th><th>473 K</th><th>573 K</th></tr><tr><td>10</td><td>-</td><td>50.7</td><td>14.7</td></tr><tr><td>25</td><td>91.7</td><td>63.6</td><td>27.4</td></tr><tr><td>50</td><td>94.5</td><td>74.0</td><td>39.5</td></tr><tr><td>100</td><td>96.7</td><td>81.7</td><td>52.5</td></tr><tr><td>200</td><td>98.4</td><td>89.0</td><td>66.7</td></tr><tr><td>400</td><td>99.4</td><td>94.6</td><td>79.7</td></tr><tr><td>1000</td><td>-</td><td>98.3</td><td>92.6</td></tr></table>	Pressure/atm	Percentage ammonia present at equilibrium at a range of temperature				373 K	473 K	573 K	10	-	50.7	14.7	25	91.7	63.6	27.4	50	94.5	74.0	39.5	100	96.7	81.7	52.5	200	98.4	89.0	66.7	400	99.4	94.6	79.7	1000	-	98.3	92.6
Pressure/atm	Percentage ammonia present at equilibrium at a range of temperature																																					
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400	99.4	94.6	79.7																																			
1000	-	98.3	92.6																																			
	(i)	To obtain a reasonable yield with favourable rate, high pressures, moderate temperatures and a catalyst are used. Using the data, select the temperature and pressure which will result in the highest yield of ammonia. [1]																																				
		Temperature: 373 K Pressure: 400 atm																																				
	(ii)	Hence, using the data you have selected in (a)(i), determine the volume of ammonia gas, nitrogen gas and hydrogen gas at equilibrium when 10 cm³ of nitrogen gas is reacted with 30 cm³ of hydrogen gas in the Haber Process. Leave your answer to two decimal places. [3]																																				
		Let x be the volume of NH₃ at equilibrium <table><tr><td></td><td>N₂(g)</td><td>+</td><td>3H₂(g)</td><td></td><td>2NH₃(g)</td></tr><tr><td>Initial</td><td>10</td><td></td><td>30</td><td></td><td>0</td></tr><tr><td>Change</td><td>-0.5x</td><td></td><td>-1.5x</td><td></td><td>+x</td></tr><tr><td>Eqm</td><td>10 – 0.5x</td><td></td><td>30 – 1.5x</td><td></td><td>x</td></tr></table> Total volume of gas at eqm = 10 – 0.5x + 30 – 1.5x + x = 40 – x From (a)(i) Since at 373 K and 400 atm, percentage ammonia present is 99.4% $99.4 = \frac{x}{40-x} \times 100$ (0.994)(40-x) = x 39.76 – 0.994x = x x = 19.94 Hence at eqm: Volume of NH₃ = 19.94 cm³ Volume of N₂ = 10 – 0.997 = 0.03 cm³ Volume of H₂ = 30 – 1.5(19.94) = 0.09 cm³		N ₂ (g)	+	3H ₂ (g)		2NH ₃ (g)	Initial	10		30		0	Change	-0.5x		-1.5x		+x	Eqm	10 – 0.5x		30 – 1.5x		x												
	N ₂ (g)	+	3H ₂ (g)		2NH ₃ (g)																																	
Initial	10		30		0																																	
Change	-0.5x		-1.5x		+x																																	
Eqm	10 – 0.5x		30 – 1.5x		x																																	
		[Total: 15]																																				

3	(a)	Allyl isothiocyanate (AITC) is responsible for the pungent taste of wasabi while capsaicin is an active component of chilli pepper and is found in spiced products like curry.  AITC  Capsaicin
	(i)	Using your concept of VSEPR, state the shape about the carbon labelled 1 and 2 on AITC. [2]
		Carbon 1: Trigonal planar Carbon 2: Tetrahedral
	(ii)	Suggest the type of hybridisation for all carbons present in AITC. [2]
		sp^2  $sp^2 \quad sp^3 \quad sp$
	(iii)	Besides the ether group , state the other functional groups that are present in Capsaicin. [3]
		Alkene, secondary amide, phenol
	(iv)	Ignoring the effect of the $-N=C=S$ group, write an equation showing how AITC reacts with liquid IBr. Hence, with reference to the <i>Data Booklet</i> and given that the bond energy of I-Br to be 180 kJ mol^{-1}, determine the enthalpy change of reaction when AITC reacts with liquid IBr. [2]
		 $\Delta H = BE(C=C) + BE(I-Br) - BE(C-I) - BE(C-Br) - BE(C-C)$ $= 610 + 180 - 240 - 280 - 350$ $= -80 \text{ kJ mol}^{-1}$
	(v)	Using your knowledge in chemical bonding, suggest why the burning sensation of capsaicin cannot be washed away with water. [2]
		Capsaicin is a simple molecular structure. There is <u>no favourable solute-solvent interaction</u> between capsaicin and water. Hence, the burning effect could not be washed away with water.

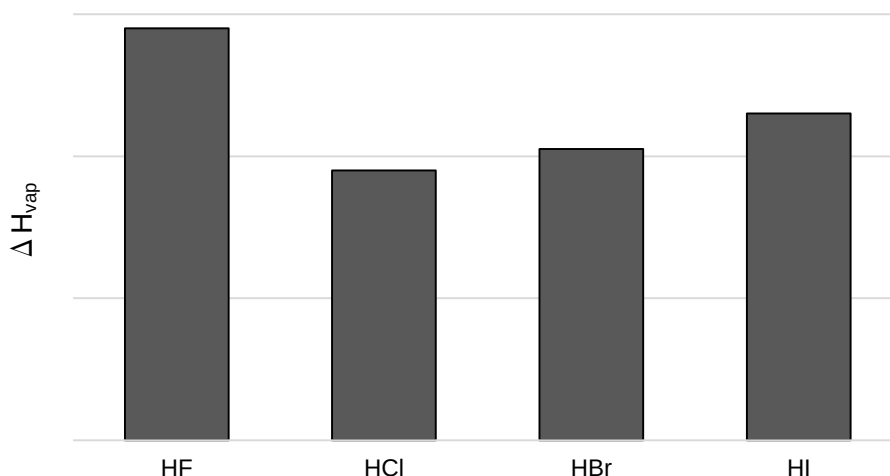
		(vi)	Draw the structural formula of the products formed when capsaicin is reacted with hot aqueous potassium hydroxide. [You are to ignore the effect of the  group] [2]
			 
			[Total: 13]

4	(a)	Phosgene is the chemical compound with the formula COCl_2. It is not to be confused with cobalt(II) chloride with the formula CoCl_2. Phosgene is produced industrially with carbon dioxide and chlorine gas. $\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)} \quad \Delta H^\circ = -107.6 \text{ kJ mol}^{-1}$ The K_p of this process is 0.05 atm^{-1} at 300 K. A mixture contains 2 mol of carbon monoxide and 2 mol of chlorine initially was reacted and allow to reach equilibrium. The equilibrium mixture is found to contain 1.5 mol of phosgene.																	
	(i)	Draw the Lewis structure of phosgene.	[1]																
																			
	(ii)	Write an expression for K_p for the equilibrium between CO , Cl_2 and phosgene and hence using the information provided calculate the total pressure of the system at equilibrium.																	
		$K_p = \frac{P_{\text{COCl}_2}}{P_{\text{CO}} P_{\text{Cl}_2}}$<table><tr><td></td><td colspan="2">$\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}$</td></tr><tr><td>Initial no. of moles</td><td>2</td><td>2</td><td>0</td></tr><tr><td>Change in no. of moles</td><td>-1.5</td><td>-1.5</td><td>+1.50</td></tr><tr><td>Eqm. no. of moles</td><td>0.5</td><td>0.5</td><td>1.50</td></tr></table> Total no. of moles of gases at eqm = $0.5 + 0.5 + 1.50 = 2.5$ $K_p = \frac{(P_{\text{COCl}_2})}{(P_{\text{CO}}) \times (P_{\text{Cl}_2})}$$0.05 = \left(\frac{1.50}{2.50} \times P_T \right) \div \left(\left(\frac{0.5}{2.50} \times P_T \right) \left(\frac{0.5}{2.50} \times P_T \right) \right)$$0.05 = 0.6 P_T \div (0.2 P_T \times 0.2 P_T)$$0.05 = 0.6 P_T \div (0.04 P_T^2)$$0.05 = 15/P_T$$P_T = 300 \text{ atm}$				$\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}$		Initial no. of moles	2	2	0	Change in no. of moles	-1.5	-1.5	+1.50	Eqm. no. of moles	0.5	0.5	1.50
	$\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}$																		
Initial no. of moles	2	2	0																
Change in no. of moles	-1.5	-1.5	+1.50																
Eqm. no. of moles	0.5	0.5	1.50																
	(iii)	Suggest if chlorine or phosgene will deviate more from ideal gas behaviour.																	
		<u>Phosgene gas deviates more from ideality</u> <u>The permanent dipole – permanent dipole interaction between phosgene molecules is stronger as compared to the instantaneous dipole – induced dipole between chlorine molecules.</u>																	

	(b)	Crystals of hydrated cobalt(II) chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, lose water when they are heated, forming anhydrous cobalt(II) chloride, CoCl_2 . $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightarrow \text{CoCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l})$										
	(i)	The standard enthalpy change for the reaction, $\Delta H^\ominus$, is $+88.1 \text{ kJ mol}^{-1}$. Given that the calculation for entropy change to be similar to that of enthalpy change, use the following entropy data to determine the standard entropy change of the reaction at 298 K. Give your answer to four significant figures. <table><tr><th>Compound</th><th>$S^\ominus$ / $\text{J mol}^{-1}\text{K}^{-1}$</th></tr><tr><td>$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} (\text{s})$</td><td>343.0</td></tr><tr><td>$\text{CoCl}_2 (\text{s})$</td><td>109.2</td></tr><tr><td>$\text{H}_2\text{O} (\text{l})$</td><td>69.9</td></tr><tr><td>$\text{H}_2\text{O} (\text{g})$</td><td>188.7</td></tr></table> [1]	Compound	$S^\ominus$ / $\text{J mol}^{-1}\text{K}^{-1}$	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} (\text{s})$	343.0	$\text{CoCl}_2 (\text{s})$	109.2	$\text{H}_2\text{O} (\text{l})$	69.9	$\text{H}_2\text{O} (\text{g})$	188.7
Compound	$S^\ominus$ / $\text{J mol}^{-1}\text{K}^{-1}$											
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$\text{H}_2\text{O} (\text{l})$	69.9											
$\text{H}_2\text{O} (\text{g})$	188.7											
		$\Delta S^\ominus = 109.2 + 6(69.9) - 343$ $= +185.6 \text{ J mol}^{-1}\text{K}^{-1} \text{ (to 4 s.f.)}$										
	(ii)	Hence, explain by using calculation, whether hydrated cobalt(II) chloride can be stored at 298K without decomposition. [2]										
		$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$ $= +88.1 \times 10^3 - 298(185.6)$ $= 88100 - 55308.8$ $= 32791.2$ $\approx +32800 \text{ J mol}^{-1}$ Yes it can be stored without decomposition as $\Delta G^\ominus$ is positive.										
	(c)	With the aid of a chemical equation, explain why a solution of cobalt(II) chloride has a pH of 4.6. [2]										
		(FYI for Co^{2+} : charge +2, ionic radius 0.065 nm) (FYI for Al^{3+} : charge +3, ionic radius 0.053 nm) (FYI for Mg^{2+} : charge +2, ionic radius 0.072 nm) <u>Co^{2+} ion</u> has <u>high charge density</u> or has <u>high polarising power</u> which can distort the electron cloud of the water ligand. $[\text{Co}(\text{H}_2\text{O})_6]^{2+} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}^+$ Thus, solution is acidic.										
		[Total: 11]										

- 5 Group VII hydrides are colourless gases at room temperature. The figures below shows the relative enthalpy change of vaporisation of the hydrides

Figure 1: ΔH_{vap} of HX



- (a) With reference to **Figure 1**, explain the abnormally high enthalpy change of vaporisation of hydrogen fluoride. [2]

HF molecules are held together by stronger **intermolecular hydrogen bonds** as compared to the other HX molecules held by weaker **permanent dipole-permanent dipole interactions**.

More energy is needed to overcome **stronger** intermolecular hydrogen bonds in HF, explaining its abnormally high enthalpy change of vaporisation.

- (b) The table below shows the pK_a of the respective compounds when they are dissolved in water

Compounds	pK_a	Compounds	pK_a
		Hydrogen bromide	-9.00
Hydrogen chloride	-7.00	Hydrogen iodide	-10.00
Methanoic acid	3.77	Water	7.00

- (i) Using relevant information from the *Data Booklet*, rank the acid strength of aqueous solution containing HCl, HBr and HI, in increasing order. Explain your answer. [2]

From Data Booklet, Bond energy: $\text{H}-\text{Cl}$ (431) > $\text{H}-\text{Br}$ (366) > $\text{H}-\text{I}$ (299)

Ease of cleavage of HX bond: $\text{H}-\text{Cl} < \text{H}-\text{Br} < \text{H}-\text{I}$

Or **energy needed to break HX bond:** $\text{H}-\text{Cl} > \text{H}-\text{Br} > \text{H}-\text{I}$

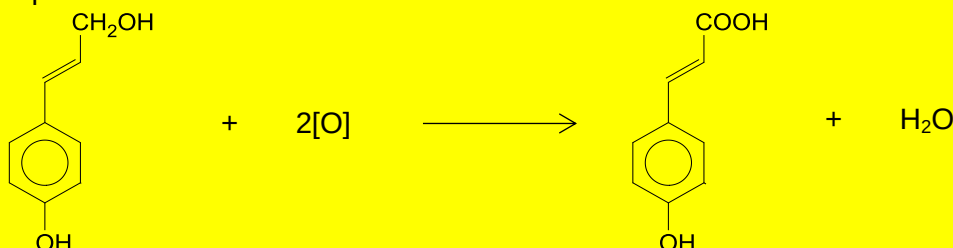
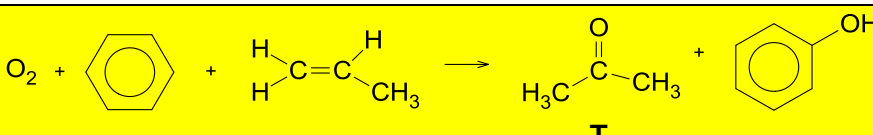
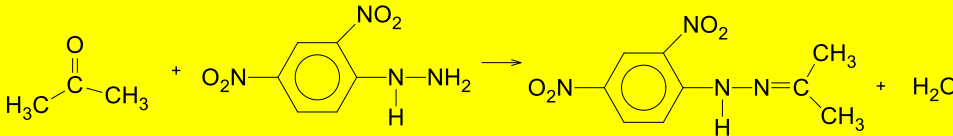
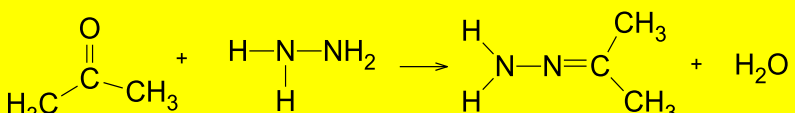
Ease of release of H^+ ion: $\text{HCl} < \text{HBr} < \text{HI}$

Acidity: $\text{HCl} < \text{HBr} < \text{HI}$

		(ii)	Account for the relative acidities of methanoic acid and water. [2]																								
			Methanoic acid is a stronger acid than water as its conjugate base / carboxylate anion (RCOO^-) is resonance stabilised by the delocalisation of the negative charge over the C atom and both oxygen atoms . As such, methanoic acid is less likely to accept a proton from HX than water.																								
	(c)		Unlike other Group VII hydrides, hydrogen fluoride, HF, behaves as a weak acid in water. A solution of HF was titrated against aqueous potassium hydroxide until 25% of the HF present was neutralised.																								
		(i)	Write the acid dissociation constant expression, K_a , for HF. [1]																								
			$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$																								
		(ii)	Given that the pH of the resulting solution described above is 2.88, calculate K_a of HF. [3]																								
			$\text{pH} = -\log_{10}[\text{H}^+]$ $[\text{H}^+] = 10^{-2.88} = \underline{1.32 \times 10^{-3} \text{ mol dm}^{-3}}$ Let x be the initial [HF] <table><tr><td></td><td>HF</td><td>$\rightleftharpoons$</td><td>H⁺</td><td>+</td><td>F⁻</td></tr><tr><td>Initial/mol dm⁻³</td><td>x</td><td></td><td>0</td><td></td><td>0</td></tr><tr><td>Change/mol dm⁻³</td><td>-0.25x</td><td></td><td>+0.25x</td><td></td><td>+0.25x</td></tr><tr><td>Eqm/mol dm⁻³</td><td>0.75x</td><td></td><td>0.25x</td><td></td><td>0.25x</td></tr></table> $K_a = \frac{[\text{H}^+][0.25x]}{[0.75x]} = \frac{(1.32 \times 10^{-3}) \times 1}{3}$ $= \underline{4.40 \times 10^{-4} \text{ mol dm}^{-3}}$ Alternative solution $\text{pH} = \text{p}K_a + \lg \{[\text{salt}]/[\text{acid}]\}$ $2.88 = \text{p}K_a + \lg \{[\text{F}^-]/[\text{HF}]\}$ $2.88 = \text{p}K_a + \lg (0.25/0.75)$ $K_a = 4.39 \times 10^{-4} \text{ mol dm}^{-3}$		HF	$\rightleftharpoons$	H ⁺	+	F ⁻	Initial/mol dm ⁻³	x		0		0	Change/mol dm ⁻³	-0.25x		+0.25x		+0.25x	Eqm/mol dm ⁻³	0.75x		0.25x		0.25x
	HF	$\rightleftharpoons$	H ⁺	+	F ⁻																						
Initial/mol dm ⁻³	x		0		0																						
Change/mol dm ⁻³	-0.25x		+0.25x		+0.25x																						
Eqm/mol dm ⁻³	0.75x		0.25x		0.25x																						

	(d)	One of the most common ways to make hydrogen chloride is to react sodium chloride with concentrated sulfuric acid, H_2SO_4 or concentrated phosphoric(V) acid, H_3PO_4 . Both reactions occur similarly, releasing white fumes of gas.
	(i)	Construct a balanced equation involving sodium chloride and concentrated phosphoric(V) acid. [1]
		$\text{NaCl} + \text{H}_3\text{PO}_4 \rightarrow \text{HCl} + \text{NaH}_2\text{PO}_4$
	(ii)	In reaction with sodium bromide, concentrated sulfuric acid produces reddish-brown solution while concentrated phosphoric(V) acid produces white fumes. Suggest a reason for the observations above. [1]
		Concentrated sulphuric acid is able to oxidise Br^- to reddish-brown Br_2 while concentrated phosphoric(V) acid cannot. Thus, concentrated phosphoric(V) acid is a <u>weaker oxidising agent</u> .
		[Total: 12]

6	(a)	The chemical structure and some reactions involving compound N are shown below. The diagram shows the following chemical transformations: - Benzene $\xrightarrow{\text{Cumene process}}$ Phenol - Phenol $\rightarrow$ 4-(hydroxymethyl)benzoic acid (N) N $\xrightarrow{\text{I}}$ 4-(hydroxymethyl)phenol (P) N $\xrightarrow{\text{II}}$ 4-(acetoxyvinyl)benzoic acid (Q) N $\xrightarrow{\text{Br}_2(l)}$ R
	(i)	State the reagents and conditions involved in Steps I and II. Step I: Step II: [2]
		Step I: <u>LiAlH_4 in dry ether, rtp</u> Step II: <u>CH_3COCl, rtp</u>
	(ii)	Draw the structure of organic product R. [1]

		(iii)	Propose a chemical test to distinguish between P and N , in which a positive test is observed for P only . Write a balanced chemical equation for the reaction that has occurred. [3]
			Test: Add <u>K₂Cr₂O₇ in dilute H₂SO₄, heat</u> Observation: <u>Orange K₂Cr₂O₇ turns green</u> <i>*KMnO₄ is not suitable as ferulic acid may be [O] as well due to presence of C=C and benzylic H</i> <i>*distillation with K₂Cr₂O₇ to form aldehyde is not preferred when carrying out simple chemical tests</i> Equation: 
	(b)		In the cumene process one mole of benzene reacts with one mole of propene in the presence of oxygen from air to form phenol and organic substance T . Substance T does not give any positive observation with diammine silver complex.
		(i)	From the information provided, identify substance T . [1]
			
		(ii)	Hence, with an aid of a chemical equation, suggest how the functional group in substance T can be positively identified. [2]
			<u>orange ppt</u> will be observed  Or 
			[Total: 9]

END



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY
JC2 Preliminary Examination
Paper 3 Free Response

9647/03
20 September 2016
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Papers

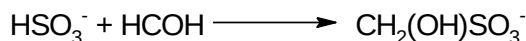
READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in the brackets [] at the end of each question or part question.
At the end of the examination, fasten all your work securely together with the cover page provided.

- 1 Sodium bisulfite (NaHSO_3) is a useful compound to treat chemical waste after organic synthesis. It reacts with methanal, converting it into a non-toxic compound which can be disposed safely. The overall equation is shown below.



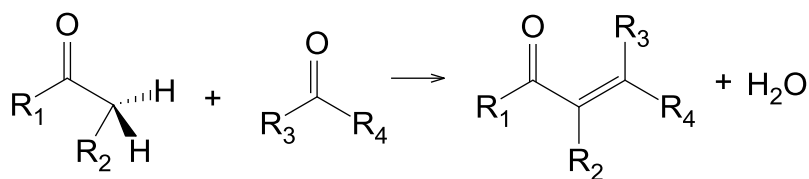
- (a) Draw the dot-and-cross diagram of the bisulfite ion, HSO_3^- . [1]
- (b) The initial rate of this reaction can be studied by the “clock” method, using phenolphthalein as a suitable indicator. The sudden appearance of the pink colour indicates the time to stop the stopwatch.

A series of experiments was carried out using different concentrations of HSO_3^- and HCOH . The following results were obtained.

experiment number	$[\text{HSO}_3^-]$ / mol dm^{-3}	$[\text{HCOH}]$ / mol dm^{-3}	time for the appearance of the pink colour/ s
1	0.040	0.040	60
2	0.040	0.050	48
3	0.050	0.060	40
4	0.040	0.070	34

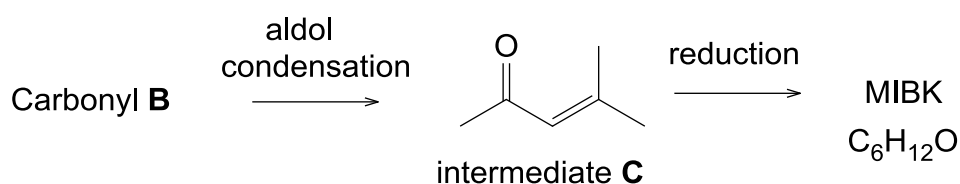
- (i) What is the simple relationship between the time taken for the pink colour to appear and the initial rate of reaction? [1]
- (ii) Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to the two reactants. Explain your reasoning. [2]
- (iii) Using your answer in (b)(ii), write the rate equation for the reaction, stating the units of the rate constant. [2]
- (iv) Sketch the graph of concentration against time for each reactant. [2]
- (c) Kinetic studies suggests that the mechanism involves the following two steps:
- Step 1: Bisulfite reacts with water via an acid-base reaction, forming sulfite, SO_3^{2-} .
- Step 2: The resulting sulfite reacts with methanal to produce the non-toxic compound, $\text{CH}_2(\text{OH})\text{SO}_3^-$ and hydroxide ion.
- (i) Write a balanced equation each for step 1 and step 2. [2]
- (ii) Suggest why phenolphthalein is a suitable indicator to determine the completion of the reaction. [1]

- (d) Aldol condensations are important in organic synthesis as a good way to form carbon-carbon bonds.



(where R_1 , R_2 , R_3 and R_4 can be alkyl group or hydrogen atom)

The following reaction sequence illustrate how MIBK, a solvent used on paints, could be synthesised from carbonyl compound **B**. It is known that MIBK does not undergo attack by electrophile.



- (i) Using the information provided, draw the displayed formula carbonyl **B**. [1]
- (ii) For each of the following reactions, describe the mechanism, showing curly arrows, dipoles and any relevant lone pairs. You are to state the condition required for reaction 2.

Reaction 1: Intermediate **C** with dry hydrogen bromide gas.

Reaction 2: Intermediate **C** with aqueous hydrogen cyanide.

Hence, suggest with explanation if the products formed from the two reactions could rotate plane polarised light.

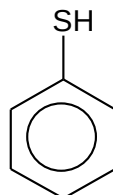
[6]

- (iii) Deduce the structure of MIBK.

[2]

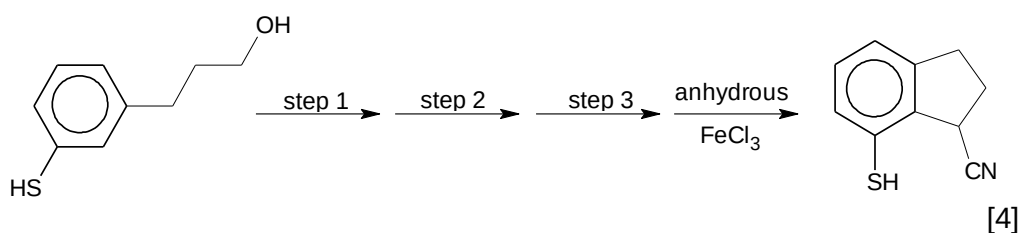
[Total: 20]

- 2(a)** Thiophenol is an organosulfur compound with the formula $\text{C}_6\text{H}_5\text{SH}$. The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom.



Thiophenol

- (i) Suggest if the C-S-H bond angle in thiophenol will be larger than the C-O-H bond angle in phenol [1]
- (ii) Explain why thiophenol has a lower pK_a value than phenol. [2]
- (iii) The reaction scheme below shows how one thiophenol derivative could be synthesised into another organic compound in **four** steps using inorganic reagents. Draw the structure of the intermediate compounds and state the reagents and conditions for each step 1, 2 and 3.



- (b)** The use of *Data Booklet* is relevant in this question.

In an experiment to determine the enthalpy change of combustion of thiophenol, 2.00 cm^3 of thiophenol with density of 1.08 g cm^{-3} was burnt as fuel to bring a calorimeter containing 170 cm^3 of water at 30°C to boil.

- (i) Define standard enthalpy change of combustion. [1]
- (ii) Calculate the enthalpy change of combustion of thiophenol, ΔH_c , given that the process is 80% efficient. [2]

- (c) The use of *Data Booklet* is relevant in this question.

In nuclear magnetic resonance (NMR) spectroscopy, the proton chemical shift can be used to diagnose the structure of an organic molecule.

Compound **D** has a molecular formula of $C_9H_{16}O_3$. When heated with hydrochloric acid, compound **E** and **F** are produced.

Compound **E** has a proton chemical shift of 2.1ppm. When 1 mole of **E** is warmed with alkaline aqueous iodine, 2 mole of yellow precipitates are formed, along with compound **G**. White fumes were also observed when **E** is reacted with thionyl chloride.

Compound **F**, $C_5H_xO_2$, rotates plane polarised light and has a proton chemical shift of 13.0ppm. Compound **F**, however, do not exhibit cis-trans isomerism and will not decolourise oxidising agents.

- (i) Suggest the structures of **D** to **F**, and explain the observations described above. [9]

- (ii) Construct a balanced chemical equation of the reaction between **E** and alkaline aqueous iodine. [1]

[Total: 20]

- 3 (a)** Haemoglobin is the iron-containing oxygen transport protein found in the red blood cells.

In general, haemoglobin can be saturated with oxygen molecules (oxyhaemoglobin) or desaturated with oxygen molecules (deoxyhaemoglobin).

The absorption spectra of oxyhaemoglobin and deoxyhaemoglobin differ. The oxyhaemoglobin has significantly lower absorption of the 660 nm wavelength as compared with deoxyhaemoglobin which is valued at 940 nm wavelength. This difference is used for the measurement of the amount of oxygen in a patient's blood by an instrument called a pulse oximeter.

- (i)** With reference to the haemoglobin molecule, describe and explain what is meant by the term *quaternary structure* of proteins. In your answer, you should state the type of bonding or interaction involved.

[2]

- (ii)** Haemoglobin is typically an all alpha-protein consisting of four subunits. However, some of the connecting loops between the helices can sometimes exist in a very short beta-stranded conformation.

With the aid of a diagram, describe how a polypeptide chain is held in the shape of a beta-stranded conformation.

[2]

- (iii)** Using the information from the question, explain if oxyhaemoglobin or deoxyhaemoglobin contain the larger energy gap, E , between its d-orbital.

[2]

- (b)** Carbon monoxide mainly causes adverse effects in humans by combining

with haemoglobin in the blood.

Human *cytochrome c oxidase* is composed of several subunits. Some of the amino acids found in *cytochrome c oxidase* are listed below.

Amino acid	Formula of side chain (R in $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$)
valine (val)	$-\text{CH}(\text{CH}_3)_2$
aspartic acid (asp)	$-\text{CH}_2\text{COOH}$
lysine (lys)	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
cysteine (cys)	$-\text{CH}_2\text{SH}$
asparagine (asp)	$-\text{CH}_2\text{CONH}_2$
threonine (thr)	$-\text{CH}(\text{OH})\text{CH}_3$

- (i) Explain how carbon monoxide affects the normal functioning of haemoglobin. [2]
- (ii) Using the dipeptide segment of **lys-thr** in *cytochrome c oxidase*, give the structural formulae of the products obtained when hot hydrochloric acid is added. [2]
- (iii) *Cytochrome c oxidase* can undergo denaturation due to various factors, resulting in loss of its biological function.

Identify the site whereby the R group interactions are broken under the following conditions and explain how these interactions are affected in each cases:

- 1) The addition of a reducing agent.
- 2) The addition of a base.

[2]

- (c) In cyanide poisoning, the enzyme *cytochrome c oxidase* which aid in respiration in human are thought to be adversely affected.

To treat this cases of poisoning, the United State standard cyanide antidote kit was developed and it comprises of a three step process.

Step 1: Inhale small dosage of amyl nitrite.

Step 2: Intravenous of sodium nitrite, NaNO_2 .

Step 3: Intravenous of sodium thiosulfate.

- (i) Sodium nitrite is part of the cyanide antidote kit. It decomposes to form an acidic brown gas, a solid residue and a free radical.

When the residual solid was placed in water, it forms a solution of pH 13.

Using the information provided, construct a balanced chemical equation for the decomposition of sodium nitrite. [1]

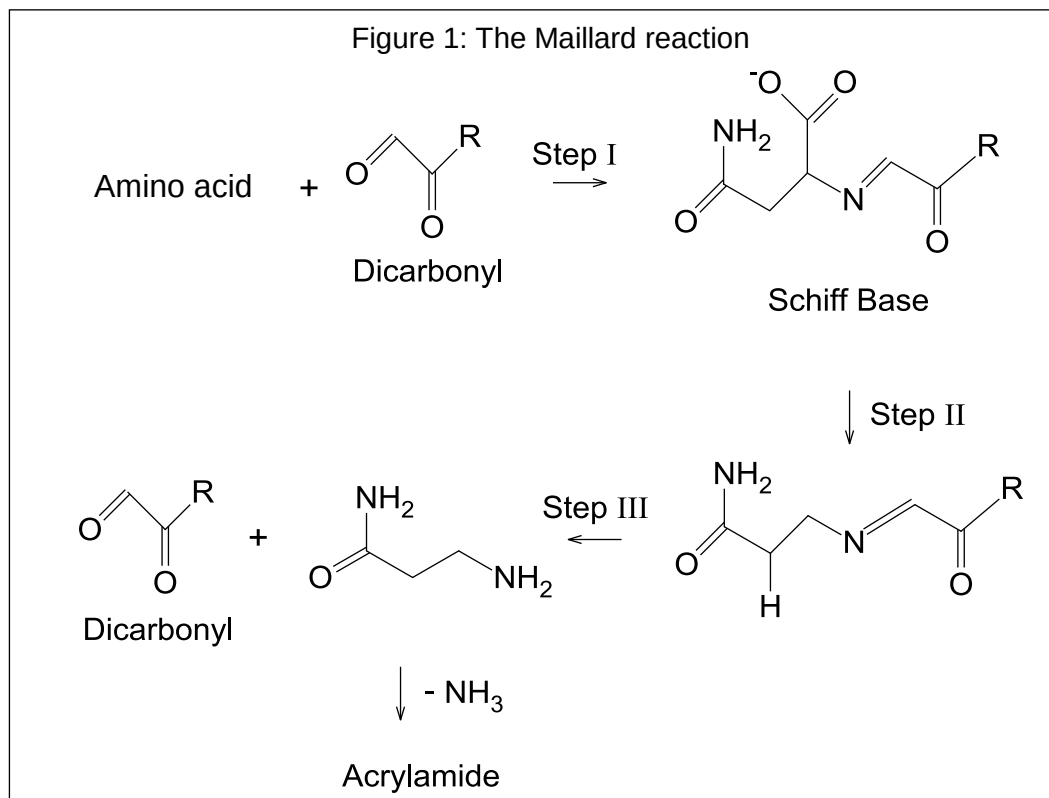
- (ii) Thiosulfate reacts differently with chlorine and iodine. Using equations only

Turn over]

suggest an explanation for this difference.

[2]

- (d) The Maillard reaction is a chemical reaction between amino acid and reducing sugar that gives browned food its desirable flavour. Pan-fried dumplings, french fries and toasted marshmallows undergo this reaction when heated at high temperature.



Acrylamide, $\text{C}_3\text{H}_5\text{NO}$, a possible human carcinogen, can be generated as a by-product of Maillard reaction between reducing sugars and amino acid.

- Using the table from (b), state the amino acid that is required in the synthesis of acrylamide. [1]
- Suggest the gas that was produced in Step II and propose how this gas can be identified. [1]
- Suggest the structural formula of acrylamide. [1]
- Propose an isomer of acrylamide which does not evolve ammonia gas on heating with aqueous sodium hydroxide. Hence, state the type of isomerism involved. [2]

[Total: 20]

Turn over]

- 4 (a) Limestone is mainly composed of calcite, CaCO_3 , and is usually white or transparent, shimmering crystals depending on how it is formed. It has a different colour when exposed to different impurities such as siderite, FeCO_3 .

(i) Using information from the *Data Booklet*, suggest if calcite or siderite has a lower decomposition temperature.

[2]

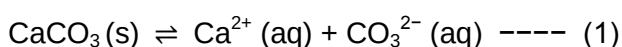
(ii) Dolomitization is a process by which dolomite, $\text{CaMg}(\text{CO}_3)_2$, is formed when magnesium ions replace calcium ions in calcite.

When 1.000 g of an impure sample of dolomite was completely dissolved in excess hydrochloric acid, the carbon dioxide evolved was bubbled into aqueous calcium hydroxide where 0.80 g of white insoluble solid was isolated. Calculate the percentage purity of the dolomite.

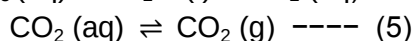
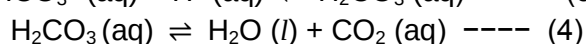
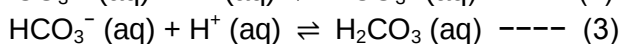
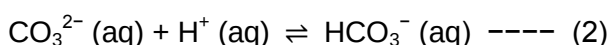
[2]

- (b) Stalagmites and stalactites in limestone caves are created when the calcite is dissolved in rain water and subsequently precipitated when the water drips off the ceiling of the cave to the cave floor.

Dissolution of calcite occurs mainly via the following equilibrium:



However, it is also affected by the amount of atmospheric carbon dioxide present, and it can be represented via these four additional equilibria:



- (i) Calculate the enthalpy change of solution of calcite using the information given below.

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{CaCO}_3(\text{s})$	-1206.9
$\text{Ca}^{2+}(\text{aq})$	-542.8
$\text{CO}_3^{2-}(\text{aq})$	-677.1

[1]

- (ii) Explain how the enthalpy change of solution of calcite would differ from siderite.

[3]

- (iii) Given that the enthalpy change of atomisation of calcium is $178.2 \text{ kJ mol}^{-1}$, and the lattice energy of calcite is $-2804 \text{ kJ mol}^{-1}$, calculate the enthalpy change of formation of gaseous carbonate ions using an energy level diagram and other relevant information from the *Data Booklet*.

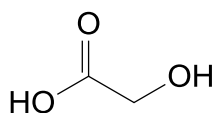
[3]

- (iv) With reference to the equilibriums given, suggest what would happen to the calcite formations in limestone caves when the acidity of rain and river water increases due to pollutants.

[3]

- (c) Limescale, which is primarily calcium carbonate is the off-white deposit that is commonly found in kettles. In addition to being unsightly and hard to clean, limescale impairs the operation of medical equipment.

Ethanoic acid and glycolic acid can serve as good descaling agent and are used to remove the limescale.



Glycolic acid

Both organic acids can be treated using the following steps to recover a carbonyl containing compound from limescale.

Step 1: Heat the limescale with the organic acid to ensure all the limescale has reacted.

Step 2: Evaporate the sample and collect the salt.

Step 3: Heat the salt in a test-tube and allow to cool to room temperature. Calcium carbonate will be formed together with a liquid carbonyl containing compound.

Step 4: Separate the calcium carbonate residue from the liquid carbonyl containing compound using vacuum filtration.

- (i) Propose chemical test to differentiate ethanoic acid and glycolic acid in the school laboratory. You are to state clearly the reagents and condition used and the expected observation to be made.

[2]

- (ii) Write a balanced equation, for the reaction of limescale and ethanoic acid. Include state symbols in your answer.

[1]

- (iii) With reference to structure and bonding, suggest why it is possible to isolate the salt via evaporation.
- (iv) With reference to Step 3, suggest the structural formulae of the organic products formed when calcium ethanoate and calcium glycolate is heated in separate test-tubes.

[2]

[Total: 20]

- 5 (a) The following table shows some common oxidation numbers of selected metals.

Metals	Oxidation Numbers		
Sc			+3
Ti			+3
V		+2	+3
Fe		+2	+3
Cu	+1	+2	
Zn		+2	

Table 1

- (i) From **Table 1**, state all the ions that are colored. [1]
- (ii) Using one of the ions stated in (a)(i), explain why it is colored. [3]
- (iii) When dilute aqueous ammonia is added to a solution that contains copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added.

Give an explanation for these observations using relevant equations.

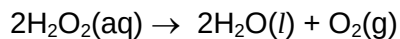
[3]

- (b) Iron by mass, is the most common element on Earth, forming much of Earth's outer and inner core. It forms compounds mainly in the +2 and +3 oxidation states. Iron and its compounds are widely used as catalyst.

- (i) Suggest why iron has the ability to exist in variable oxidation states.

[1]

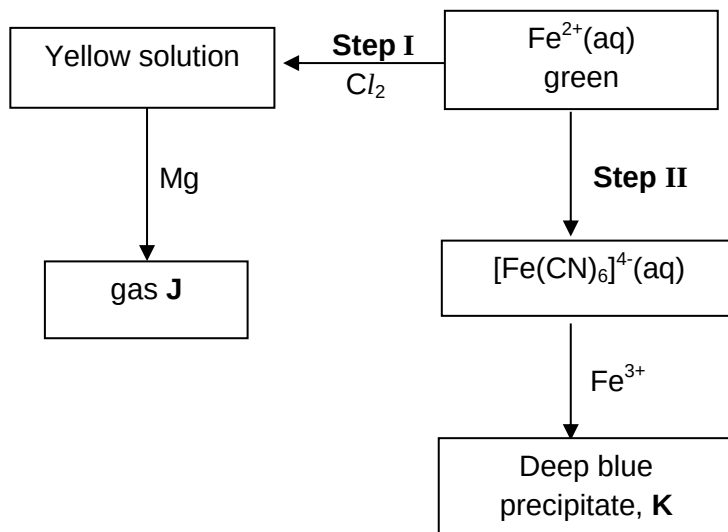
- (ii) Hydrogen peroxide decompose according to the following equation:



Iron(III) ions can be used to catalyse this decomposition. Using relevant data from the *Data Booklet*, suggest a mechanism for this catalysis, calculating the $E^\ominus$ values for each step.

[3]

(iii) The following diagram shows the reactions of some iron compounds.

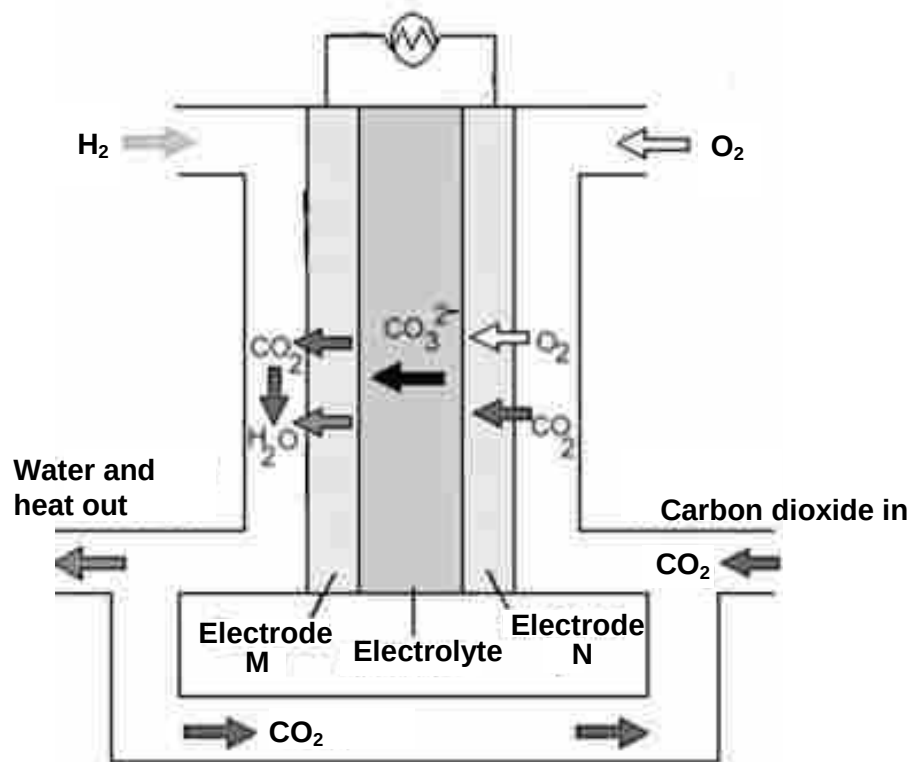


Name the type of reaction in **Step II** and identify gas J and precipitate K.

[3]

- (c) Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix.

The following diagram show a MCFC.



At the electrode **N**, carbon dioxide is reacted with oxygen to form carbonate as the only product. The carbonate ions move towards electrode **M** and react with hydrogen to form carbon dioxide and water.

- (i) Write half-equations for the reactions taking place at the electrodes of the fuel cell and hence, construct the overall equation for the fuel cell reaction. [3]
- (ii) State the direction of the electron flow with respect to the electrode. [1]
- (iii) Besides being high in efficiency and high operating cost, suggest one advantage and disadvantage of the molten carbonate fuel cell. [2]

[Total: 20]

END OF PAPER 3

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SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY
JC2 Preliminary Examination
Paper 3 Free Response

9647/03
20 Sept 2016
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Papers

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

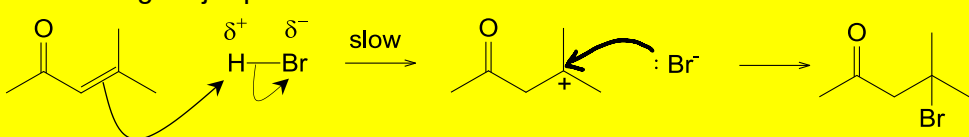
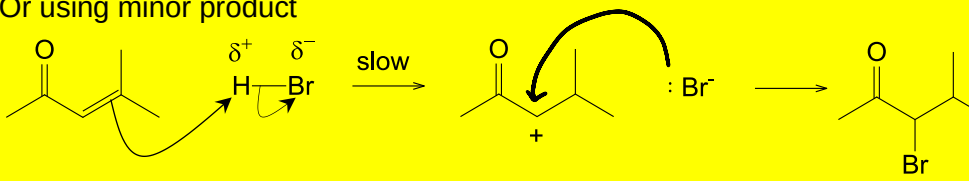
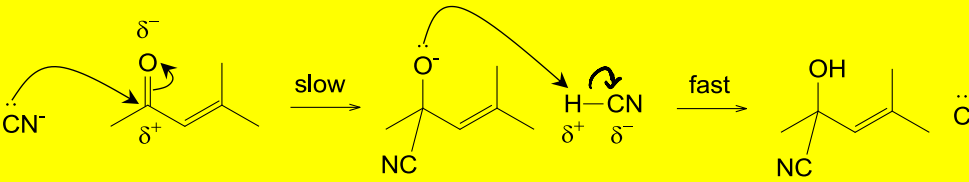
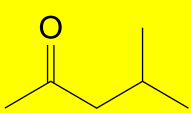
The number of marks is given in the brackets [] at the end of each question or part question.
At the end of the examination, fasten all your work securely together with the cover page provided.

SUGGESTED
SOLUTIONS

1	Sodium bisulfite (NaHSO_3) is a useful compound to treat chemical waste after organic synthesis. It reacts with methanal, converting it into a non-toxic compound which can be disposed safely. The overall equation is shown below. $\text{HSO}_3^- + \text{HCOH} \longrightarrow \text{CH}_2(\text{OH})\text{SO}_3^-$																						
(a)	Draw the dot-and-cross diagram of the bisulfite ion, HSO_3^- . [1]																						
(b)	The initial rate of this reaction can be studied by the “clock” method, using phenolphthalein as a suitable indicator. The sudden appearance of the pink colour indicates the time to stop the stopwatch. A series of experiments was carried out using different concentrations of HSO_3^- and HCOH. The following results were obtained. <table><thead><tr><th>experiment number</th><th>$[\text{HSO}_3^-]$ / mol dm^{-3}</th><th>$[\text{HCOH}]$ / mol dm^{-3}</th><th>time for the appearance of the pink colour/ s</th></tr></thead><tbody><tr><td>1</td><td>0.040</td><td>0.040</td><td>60</td></tr><tr><td>2</td><td>0.040</td><td>0.050</td><td>48</td></tr><tr><td>3</td><td>0.050</td><td>0.060</td><td>40</td></tr><tr><td>4</td><td>0.040</td><td>0.070</td><td>34</td></tr></tbody></table>			experiment number	$[\text{HSO}_3^-]$ / mol dm^{-3}	$[\text{HCOH}]$ / mol dm^{-3}	time for the appearance of the pink colour/ s	1	0.040	0.040	60	2	0.040	0.050	48	3	0.050	0.060	40	4	0.040	0.070	34
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2	0.040	0.050	48																				
3	0.050	0.060	40																				
4	0.040	0.070	34																				
(i)	What is the simple relationship between the time taken for the pink colour to appear and the initial rate of reaction? [1]																						
The shorter the time , the faster the initial rate of reaction. OR $\text{rate} \propto \frac{1}{t}$																							
(ii)	Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to the two reactants. Explain your reasoning. [2]																						
Initial rate for experiments 1: $1/60 = 0.0167 \text{ s}^{-1}$ Initial rate for experiments 2: $1/48 = 0.0208 \text{ s}^{-1}$ Initial rate for experiments 3: $1/40 = 0.0250 \text{ s}^{-1}$ Initial rate for experiments 4: $1/34 = 0.0294 \text{ s}^{-1}$ relative rate between experiments 1 and 2: $\frac{0.0208}{0.0167} = 1.25$ Using experiment 1 and 2, when the concentration of HSO_3^- remains constant and the concentration of HCOH increases 1.25 times, the rate also increases 1.25 times. Hence the order of reaction with respect to HCOH is one. Let the order of reaction for HSO_3^- be x. Using the mathematical method for experiment 2 and 3,																							

		$\frac{rate_2}{rate_3} = \frac{k[HSO_3^-]^x[HCOH]^1}{k[HSO_3^-]^x[HCOH]^1}$ $\frac{0.0208}{0.025} = \frac{k[0.04]^x[0.05]^1}{k[0.05]^x[0.06]^1}$ $\frac{0.0208}{0.025} = \left(\frac{4}{5}\right)^x \times \frac{5}{6}$ $1 = \left(\frac{4}{5}\right)^x$ $x = 0$ therefore, order of reaction with respect to HSO_3^- is zero.
	(iii)	Using your answer in (ii), write the rate equation for the reaction, stating the units of the rate constant. [2]
		rate = $k[HCOH]$ units of rate constant = $\frac{mol\ dm^{-3}\ s^{-1}}{mol\ dm^{-3}} = s^{-1}$
	(iv)	Sketch the graph of concentration against time for each reactant. [2]
	(c)	Kinetic studies suggests that the mechanism involves the following two steps: Step 1: Bisulfite reacts with water via an acid-base reaction, forming sulfite, SO_3^{2-}. Step 2: The resulting sulfite reacts with methanal to produce the non-toxic compound, $CH_2(OH)SO_3^-$ and hydroxide ion.
	(i)	Write a balanced equation each for step 1 and step 2. [2]
		Step 1: $HSO_3^- + H_2O \rightarrow SO_3^{2-} + H_3O^+$ Step 2: $H_2O + SO_3^{2-} + HCOH \rightarrow CH_2(OH)SO_3^- + OH^-$
	(ii)	Suggest why phenolphthalein is a suitable indicator to determine the completion of the reaction. [1]
		Phenolphthalein is suitable because its pH transition range lies within the region of rapid pH change in the reaction mixture.

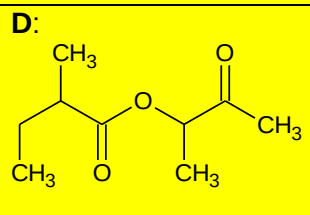
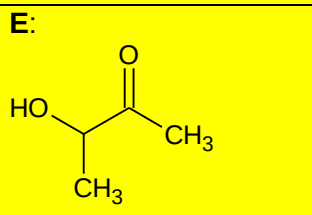
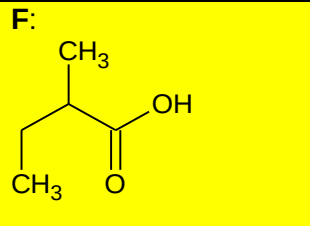
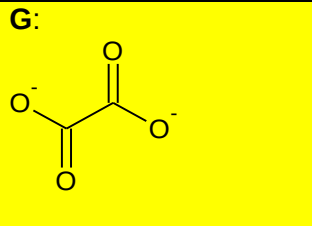
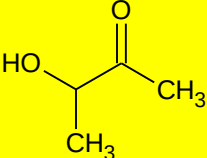
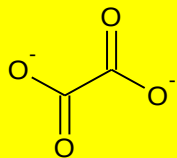
	(d)	Aldol condensations are important in organic synthesis as a good way to form carbon-carbon bonds. $ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1 - \text{C} - \text{CH}(\text{R}_2) - \text{H} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}_3 - \text{C} - \text{R}_4 \end{array} \longrightarrow \begin{array}{c} \text{O} \qquad \text{R}_3 \\ \parallel \qquad \diagup \\ \text{R}_1 - \text{C} = \text{C} - \text{R}_4 \\ \qquad \diagdown \\ \qquad \text{R}_2 \end{array} + \text{H}_2\text{O} $ (where R₁, R₂, R₃ and R₄ can be alkyl group or hydrogen atom) The following reaction sequence illustrate how MIBK, a solvent used on paints, could be synthesised from carbonyl compound B. It is known that MIBK does not undergo attack by electrophile. $ \begin{array}{ccccc} & \text{aldol} & & & \\ & \text{condensation} & & & \\ \text{Carbonyl B} & \longrightarrow & \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{CH} = \text{C}(\text{CH}_3)_2 \\ \text{intermediate C} \end{array} & \xrightarrow{\text{reduction}} & \begin{array}{c} \text{MIBK} \\ \text{C}_6\text{H}_{12}\text{O} \end{array} \end{array} $
	(i)	Using the information provided, draw the displayed formula carbonyl B. $ \begin{array}{c} \text{O} \\ \parallel \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} $
	(ii)	For each of the following reactions, describe the mechanism, showing curly arrows, dipoles and any relevant lone pairs. You are to state the condition required for reaction 2. Reaction 1: Intermediate C with dry hydrogen bromide gas. Reaction 2: Intermediate C with aqueous hydrogen cyanide. Hence, suggest with explanation if the products formed from the two reactions could rotate plane polarised light. [6]

		Reaction 1: Electrophilic addition Either using major product  Or using minor product  Reaction 2: Nucleophilic addition  Condition required for reaction 2: Presence of NaOH(aq) or NaCN, 10°C to 20°C Reaction 1: If use major product: No optical activity as there is absence of chiral carbon. If use minor product: No optical activity as there is presence of racemic mixture Reaction 2: No optical activity as there is presence of racemic mixture.
	(iii)	Deduce the structure of MIBK. [2]
		To deduce the structure of MIBK: MIBK does <u>not</u> undergo <u>electrophilic addition</u> $\Rightarrow$ <u>alkene</u> functional group absent  Thus MIBK looks like (IUPAC name is 4-methylpentan-2-one)

2(a)	Thiophenol is an organosulfur compound with the formula C_6H_5SH. The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom. Thiophenol
	(i) Suggest if the C-S-H bond angle in thiophenol will be larger than the C-O-H bond angle in phenol [1]
	<u>Oxygen is more electronegative than sulfur</u> thus the electron density around O atom will be greater. The <u>bond-pair electrons will be nearer to the nucleus resulting in more repulsion</u>. Thus the bond angle of C-O-H in phenol will be larger.
	(ii) Explain why thiophenol has a lower pK_a value than phenol. [2]
	<u>Thiophenol</u> has a lower pK_a. The sulfur atom is <u>less electronegative</u> and the lone pair of electrons on the conjugate base is able to <u>delocalise</u> into the benzene ring <u>more readily</u> as compared to phenol, thus <u>stabilising its conjugate base</u> more than the phenoxide ion.

	(iii) The reaction scheme below shows how one thiophenol derivative could be synthesised into another organic compound in four steps using inorganic reagents. Draw the structure of the intermediate compounds and state the reagents and conditions for each step 1, 2 and 3. [4]
	(b) The use of <i>Data Booklet</i> is relevant in this question. In an experiment to determine the enthalpy change of combustion of thiophenol, 2.00 cm³ of thiophenol with density of 1.08 g cm⁻³ was burnt as fuel to bring a calorimeter containing 170 cm³ of water at 30°C to boil.
	(i) Define standard enthalpy change of combustion. [1]
	Standard enthalpy change of combustion is the energy evolved when one mole of substance is completely burnt in oxygen under standard conditions.
	(ii) Calculate the enthalpy change of combustion of thiophenol, ΔH_c, given that the process is 80% efficient. [2]
	$Q' = mc\Delta T = 170 \times 4.18 \times (100 - 30) = 49742 \text{ J}$ $Q' = \frac{80}{100} Q$ $Q = \frac{100}{80} \times 49742 = 62177.5 \text{ J}$ $n_{\text{thiophenol}} = \frac{1.08 \times 2.00}{110.1} = 0.01962 \text{ mol}$ $\Delta H_c = - \frac{62177.5}{0.01962} = \underline{\underline{-3169 \text{ kJ mol}^{-1}}}$

(c)	The use of <i>Data Booklet</i> is relevant in this question. In nuclear magnetic resonance (NMR) spectroscopy, the proton chemical shift can be used to diagnose the structure of an organic molecule. Compound D has a molecular formula of $C_9H_{16}O_3$. When heated with hydrochloric acid, compound E and F are produced. Compound E has a proton chemical shift of 2.1ppm. When 1 mole of E is warmed with alkaline aqueous iodine, 2 mole of yellow precipitates are formed, along with compound G. White fumes were also observed when E is reacted with thionyl chloride. Compound F, $C_5H_{10}O_2$, rotates plane polarised light and has a proton chemical shift of 13.0ppm. Compound F, however, do not exhibit cis-trans isomerism and will not decolourise oxidising agents.
(i)	Suggest the structures of D to F, and explain the observations described above. [9]
	D undergoes <u>acidic hydrolysis</u> to form E and F. $\Rightarrow$ D is an <u>ester</u>. $\Rightarrow$ E and F are alcohol and carboxylic acid. E has a proton chemical shift of 2.1ppm. $H_3C-C(=O)-R$ $\Rightarrow$ E contains ketone with this structure. E undergoes mild <u>oxidation</u> with alkaline aqueous iodine to form 2 mol of yellow ppt and G. $\begin{array}{ccc} \begin{array}{c} O \\ \\ R-C-CH_3 \end{array} & \begin{array}{c} CH_3 \\ \\ R-C-OH \\ \\ H \end{array} & \begin{array}{c} O \\ \\ R-C-CH_3 \end{array} \\ \text{or} & & \end{array}$ $\Rightarrow$ E has $R-C(=O)CH_3$ and either $R-C(CH_3)(OH)H$ or $R-C(=O)CH_3$. $\Rightarrow$ G contains carboxylate ion. E undergoes <u>nucleophilic substitution</u> with $SOCl_2$. $\Rightarrow$ E has alcohol or carboxylic acid F is <u>chiral</u> and has a proton chemical shift of 13.0ppm. $\Rightarrow$ F has <u>4 different groups attached and is a carboxylic acid</u>. F does not contain alkene as it does not undergo oxidation

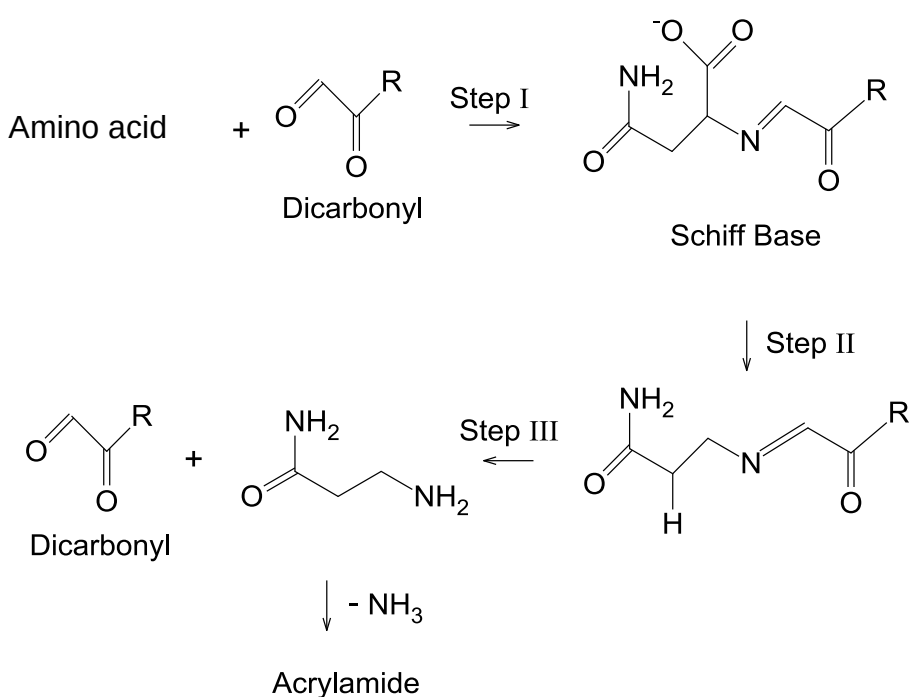
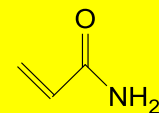
		D:  E:  F:  G: 
	(ii)	Construct a balanced chemical equation of the reaction between E and alkaline aqueous iodine. [1]
		 $+ 7\text{I}_2 + 10\text{OH}^- \rightarrow$  $+ 2\text{CHI}_3 + 8\text{I}^- + 8\text{H}_2\text{O}$

3	(a)	Haemoglobin is the iron-containing oxygen transport protein found in the red blood cells. In general, haemoglobin can be saturated with oxygen molecules (oxyhaemoglobin) or desaturated with oxygen molecules (deoxyhaemoglobin). The absorption spectra of oxyhaemoglobin and deoxyhaemoglobin differ. The oxyhaemoglobin has significantly lower absorption of the 660 nm wavelength as compared with deoxyhaemoglobin which is valued at 940 nm wavelength. This difference is used for the measurement of the amount of oxygen in a patient's blood by an instrument called a pulse oximeter.
	(i)	With reference to the haemoglobin molecule, describe and explain what is meant by the term <i>quaternary structure</i> of proteins. In your answer, you should state the type of bonding or interaction involved. [2]
		Quaternary structure consists of more than one polypeptide chain coming together to form the complete protein held together by ionic bonds, hydrogen bonds, Van der Waals' interaction and disulfide linkages between the R groups of the polypeptides. The haemoglobin molecule consists of 4 polypeptide chains: 2 α-sub-units and 2 β-sub-units, with each sub-unit being non-covalently bonded to a heme (iron) group. Each heme group consists of a central Fe^{2+} ion that can bond to one O_2 oxygen. All four components (4 sub-units and 4 haem groups) must be present to form haemoglobin.
	(ii)	Haemoglobin is typically an all alpha-protein consisting of four subunits. However, some of the connecting loops between the helices can sometimes exist in a very short beta-stranded conformation. With the aid of a diagram, describe how a polypeptide chain is held in the shape of a beta-stranded conformation. [2]
		• All peptide linkages are involved in intra-chain hydrogen bonding. • It is stabilized by hydrogen bonds between the $\text{C}=\text{O}$ group of a peptide in one strand and the $\text{N}-\text{H}$ group of another peptide in the adjacent strand. R groups (side chains) project above and below the sheet and are 90° to the plane of the pleated sheet.

		(iii)	Using the information from the question, explain if oxyhaemoglobin or deoxyhaemoglobin contain the larger energy gap, E, between its d-orbital. [2]
			<u>Wavelength</u> of light absorbed: oxyhaemoglobin (660nm) < deoxyhaemoglobin (940nm) Since E is inversely proportional to wavelength of light <u>Energy</u> required for d-d transition: oxyhaemoglobin > deoxyhaemoglobin Thus, oxyhaemoglobin has a larger energy gap E.

	(b)	Carbon monoxide mainly causes adverse effects in humans by combining with haemoglobin in the blood. Human <i>cytochrome c oxidase</i> is composed of several subunits. Some of the amino acids found in <i>cytochrome c oxidase</i> are listed below. <table><tr><th>Amino acid</th><th>Formula of side chain (R in RCH(NH₂)CO₂H)</th></tr><tr><td>valine (val)</td><td>-CH(CH₃)₂</td></tr><tr><td>aspartic acid (asp)</td><td>-CH₂COOH</td></tr><tr><td>lysine (lys)</td><td>-CH₂CH₂CH₂CH₂NH₂</td></tr><tr><td>cysteine (cys)</td><td>-CH₂SH</td></tr><tr><td>asparagine (asp)</td><td>-CH₂CONH₂</td></tr><tr><td>threonine (thr)</td><td>-CH(OH)CH₃</td></tr></table>	Amino acid	Formula of side chain (R in RCH(NH ₂)CO ₂ H)	valine (val)	-CH(CH ₃) ₂	aspartic acid (asp)	-CH ₂ COOH	lysine (lys)	-CH ₂ CH ₂ CH ₂ CH ₂ NH ₂	cysteine (cys)	-CH ₂ SH	asparagine (asp)	-CH ₂ CONH ₂	threonine (thr)	-CH(OH)CH ₃
Amino acid	Formula of side chain (R in RCH(NH ₂)CO ₂ H)															
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cysteine (cys)	-CH ₂ SH															
asparagine (asp)	-CH ₂ CONH ₂															
threonine (thr)	-CH(OH)CH ₃															
	(i)	Explain how carbon monoxide affects the normal functioning of haemoglobin. [2] <u>CO is a stronger ligand</u> than O₂ CO <u>bonds irreversibly</u> with haemoglobin forming a stable carboxyhaemoglobin complex, thus <u>preventing the haemoglobin from carrying oxygen</u>. This results in carbon monoxide poisoning due to oxygen starvation.														
	(ii)	Using the dipeptide segment of lys-thr in <i>cytochrome c oxidase</i>, give the structural formulae of the products obtained when hot hydrochloric acid is added. [2] $\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{NH}_3^+ \end{array}$ $\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ \\ \text{HO} - \text{CH} \\ \\ \text{CH}_3 \end{array}$														

		(iii) <i>Cytochrome c oxidase</i> can undergo denaturation due to various factors, resulting in loss of its biological function. Identify the site whereby the R group interactions are broken under the following conditions and explain how these interactions are affected in each cases:
		1) The addition of a reducing agent.
		Reducing agents break disulfide linkages and thus R group interaction at cysteine will be affected
		2) The addition of a base. [2]
		The base will disrupt the ionic bonds at asp or lys holding the tertiary and quaternary structures.
	(c)	In cyanide poisoning, the enzyme <i>cytochrome c oxidase</i> which aid in respiration in human are thought to be adversely affected. To treat this cases of poisoning, the United State standard cyanide antidote kit was developed and it comprises of a three step process. Step 1: Inhale small dosage of amyl nitrite. Step 2: Intravenous of sodium nitrite, NaNO_2. Step 3: Intravenous of sodium thiosulfate.
	(i)	Sodium nitrite is part of the cyanide antidote kit. It decomposes to form an acidic brown gas, a solid residue and a free radical. When the residual solid was placed in water, it forms a solution of pH 13. Using the information provided, construct a balanced chemical equation for the decomposition of sodium nitrite. [1]
		$2\text{NaNO}_2 \rightarrow \text{NO}_2 + \text{Na}_2\text{O} + \text{NO}$
	(ii)	Thiosulfate reacts differently with chlorine and iodine. Using equations only suggest an explanation for this difference. [2]
		$\text{S}_2\text{O}_3^{2-}(\text{aq}) + 4\text{Cl}_2(\text{aq}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + 10\text{H}^+(\text{aq}) + 8\text{Cl}^-(\text{aq})$ $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ Cl_2 is a stronger oxidising agent compared to iodine. Hence, it oxidises S in $\text{S}_2\text{O}_3^{2-}$ from +2 to +6 while iodine oxidises S in $\text{S}_2\text{O}_3^{2-}$ from +2 to +2.5.

		(d) The Maillard reaction is a chemical reaction between amino acid and reducing sugar that gives browned food its desirable flavour. Pan-fried dumplings, french fries and toasted marshmallows undergo this reaction when heated at high temperature.  Amino acid + Dicarbonyl $\xrightarrow{\text{Step I}}$ Schiff Base Schiff Base $\xrightarrow{\text{Step II}}$ Enamine + CO_2 Enamine + Dicarbonyl $\xrightarrow{\text{Step III}}$ Acrylamide + NH_3 Acrylamide, $\text{C}_3\text{H}_5\text{NO}$, a possible human carcinogen, can be generated as a by-product of Maillard reaction between reducing sugars and amino acid.
	(i)	Using the table from (b) , state the amino acid that is required in the synthesis of acrylamide. [1]
		Asparagine
	(ii)	Suggest the gas that was produced in Step II and propose how this gas can be identified. [1]
		CO_2 Pass the gas into $\text{Ca}(\text{OH})_2$, white ppt of CaCO_3 will be observed.
	(iii)	Suggest the structural formula of acrylamide. [1]
		
	(iv)	Propose an isomer of acrylamide which does not evolve ammonia gas on heating with aqueous sodium hydroxide. Hence, state the type of isomerism involved. [2]

			 Functional group isomerism
			[Total: 20m]

4	(a)	Limestone is mainly composed of calcite, CaCO_3 , and is usually white or transparent, shimmering crystals depending on how it is formed. It takes on a different colour when exposed to different impurities such as siderite, FeCO_3 .
	(i)	Using information from the <i>Data Booklet</i> , suggest if calcite or siderite has a lower decomposition temperature. [2]
		<u>Cationic radius: Fe^{2+} (0.076nm) < Ca^{2+} (0.099nm)</u> <u>Charge density: Fe^{2+} > Ca^{2+}</u> <u>Polarising effect</u> on the anion: <u>Fe^{2+} > Ca^{2+}</u> Or <u>Anion electron cloud distortion: Fe^{2+} > Ca^{2+}</u> <u>Less energy</u> is required to overcome the <u>C–O</u> for <u>siderite hence lower temperature</u> is required to decompose the compound.
	(ii)	Dolomitization is a process by which dolomite, $\text{CaMg}(\text{CO}_3)_2$, is formed when magnesium ions replaces calcium ions in calcite. When 1.000 g of an impure sample of dolomite was completely dissolved in excess hydrochloric acid, the carbon dioxide evolved was bubbled into aqueous calcium hydroxide where 0.80 g of white insoluble solid was isolated. Calculate the percentage purity of the dolomite. [2]
		$\text{CaMg}(\text{CO}_3)_2 + 4\text{HCl} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$ $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ Amt of ppt = $0.80 / 100.1 = 0.007992$ mol Amt of CO_2 produced = 0.007992 mol Amt of dolomite = $0.007992 \div 2 = 0.003996$ mol Mass of dolomite = $0.003996 \times 184.4 = 0.7369$ g Percentage purity = $(0.7369/1) \times 100 = 73.7\%$
	(b)	Stalagmites and stalactites in limestone caves are created when the calcite is dissolved in rain water and subsequently precipitated when the water drips off the ceiling of the cave to the cave floor. Dissolution of calcite occurs mainly via the following equilibrium:

		$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \text{ ---- (1)}$ However, it is also affected by the amount of atmospheric carbon dioxide present, and it can be represented via these four additional equilibria: $\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) \text{ ---- (2)}$ $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \text{ ---- (3)}$ $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{aq}) \text{ ---- (4)}$ $\text{CO}_2(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) \text{ ---- (5)}$								
	(i)	Calculate the enthalpy change of solution of calcite using the information given below. <table><tr><td></td><td>$\Delta H_f^\circ / \text{kJ mol}^{-1}$</td></tr><tr><td>$\text{CaCO}_3(\text{s})$</td><td>-1206.9</td></tr><tr><td>$\text{Ca}^{2+}(\text{aq})$</td><td>-542.8</td></tr><tr><td>$\text{CO}_3^{2-}(\text{aq})$</td><td>-677.1</td></tr></table> [1]		$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\text{CaCO}_3(\text{s})$	-1206.9	$\text{Ca}^{2+}(\text{aq})$	-542.8	$\text{CO}_3^{2-}(\text{aq})$	-677.1
	$\Delta H_f^\circ / \text{kJ mol}^{-1}$									
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$\text{CO}_3^{2-}(\text{aq})$	-677.1									
		$\Delta H_{\text{sol}} = -542.8 - 677.1 - (-1206.9)$ $= \underline{\underline{-13.0 \text{ kJ mol}^{-1}}}$								
	(ii)	Explain how the enthalpy change of solution of calcite would differ from siderite. [3]								
		<u>Charge of Fe^{2+} and Ca^{2+} is the same</u> <u>Radii: $\text{Ca}^{2+} > \text{Fe}^{2+}$</u> <u>$\Delta H_{\text{latt}}$) : $\text{CaCO}_3 < \text{FeCO}_3$</u> <u>and $\Delta H_{\text{hyd}}(\text{cation})$: $\text{Ca}^{2+} < \text{Fe}^{2+}$</u> Due to the <u>large anionic radius</u>, the decrease in ΔH_{latt} is <u>less significant</u> than the decrease in $\Delta H_{\text{hyd}}(\text{cation})$. ΔH_{soln} of siderite would be <u>more exothermic</u>.								
	(iii)	Given that the enthalpy change of atomisation of calcium is $178.2 \text{ kJ mol}^{-1}$, and the lattice energy of calcite is $-2804 \text{ kJ mol}^{-1}$, calculate the enthalpy change of formation of gaseous carbonate ions using an energy level diagram and other relevant information from the <i>Data Booklet</i>. [3]								

			Energy / kJ mol⁻¹ $\text{Ca}^{2+}(\text{g}) + \text{C}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) + 2\text{e}^-$ $\text{Ca}^{2+}(\text{g}) + \text{CO}_3^{2-}(\text{g})$ $\text{Ca}(\text{g}) + \text{C}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$ $\text{Ca}(\text{s}) + \text{C}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$ $\text{CaCO}_3(\text{s})$ $\Delta H_f = -1206.9$ $\Delta H_a = 178.2$ $1^{\text{st}} \text{ and } 2^{\text{nd}} \text{ I.E} = 1740$ $\text{L.E.} = -2804$ ΔH_f
			$\Delta H_f = -1740 - 178.2 + (-1206.9) - (-2804)$ $= \underline{\underline{-321.1 \text{ kJ mol}^{-1}}}$
		(iv)	With reference to the equilibria given, suggest what would happen to the calcite formations in limestone caves when the acidity of rain and river water increases due to pollutants. [3]
			The calcite formations will be <u>dissolved/destroyed</u>. By <u>LCP</u>, an <u>increase in $[\text{H}^+]$</u> would cause the <u>position of equilibria of equilibria (2) to shift right</u> to <u>reduce $[\text{H}^+]$</u>, favouring the production of HCO_3^-. This then <u>causes $[\text{CO}_3^{2-}]$ in equilibrium 2 to decrease</u> and thus by <u>LCP</u>, the <u>position of equilibrium (1) would then shift right</u> to <u>increase $[\text{CO}_3^{2-}]$</u>, <u>increasing the solubility of CaCO_3</u>.

	(c)	Limescale, which is primarily calcium carbonate is the off-white deposit that is commonly found in kettles. In addition to being unsightly and hard to clean, limescale impairs the operation of medical equipment. Ethanoic acid and glycolic acid can serve as good descaling agent and are used to remove the limescale. $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{C}-\text{CH}_2-\text{OH} \end{array}$ Glycolic acid Both organic acids can be treated using the following steps to recover a carbonyl containing compound from limescale. Step 1: Heat the limescale with the organic acid to ensure all the limescale has reacted. Step 2: Evaporate the sample and collect the salt. Step 3: Heat the salt in a test-tube and allow to cool to room temperature. Calcium carbonate will be formed together with a liquid carbonyl containing compound. Step 4: Separate the calcium carbonate residue from the liquid carbonyl containing compound using vacuum filtration.
	(i)	Propose chemical test to differentiate ethanoic acid and glycolic acid in the school laboratory. You are to state clearly the reagents and condition used and the expected observation to be made. [2]
		Test: Add KMnO_4 in dilute H_2SO_4, heat Observation: Purple KMnO_4 decolourised in glycolic acid but not ethanoic acid (Note: Glycolic acid will form CO_2 and H_2O upon reaction with acidified KMnO_4, heat.)
	(ii)	Write a balanced equation, for the reaction of limescale and ethanoic acid. Include state symbols in your answer. [1]
		$\text{CaCO}_3 (\text{s}) + 2\text{CH}_3\text{COOH} (\text{aq}) \rightarrow 2(\text{CH}_3\text{COO}^-)_2\text{Ca}^{2+} (\text{aq}) + \text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l})$
	(iii)	With reference to structure and bonding, suggest why it is possible to isolate the salt via evaporation. [1]
		Evaporation technique is appropriate as the salt has a <u>much higher boiling point</u> than the water. <i>The salt has a giant ionic structure with stronger electrostatic forces of attraction between the oppositely charged ions while water is a simple molecular structure with weaker intermolecular hydrogen bonding. Thus by heating the sample, only sufficient energy is supplied to cause the water</i>

			<i>molecule to evaporate leaving behind the salt.</i>
		(iv)	With reference to Step 3, suggest the structural formulae of the organic products formed when calcium ethanoate and calcium glycolate is heated in separate test-tubes. [2]
			From calcium ethanoate: $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array}$ From calcium glycolate: $\begin{array}{c} \text{OH} \quad \text{O} \quad \text{OH} \\ \quad \parallel \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$
			[Total: 20]

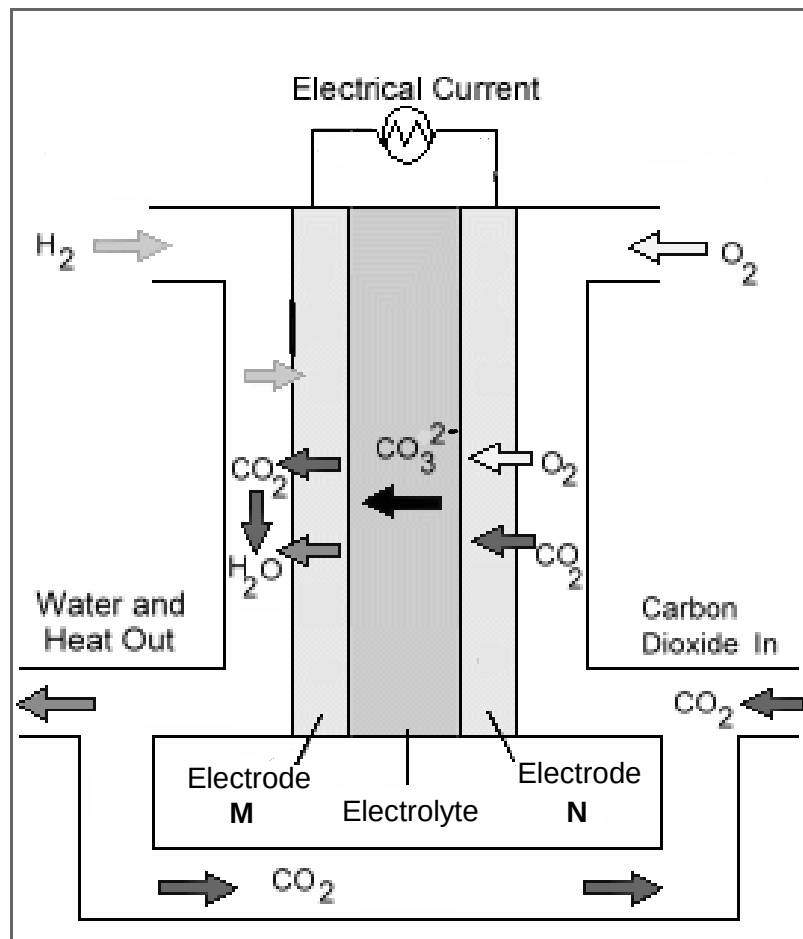
5	(a)	The following table shows some common oxidation numbers of selected metals.																														
		<table><tr><th>Metals</th><th colspan="3">Oxidation Numbers</th></tr><tr><td>Sc</td><td></td><td></td><td>+3</td></tr><tr><td>Ti</td><td></td><td></td><td>+3</td></tr><tr><td>V</td><td></td><td>+2</td><td>+3</td></tr><tr><td>Fe</td><td></td><td>+2</td><td>+3</td></tr><tr><td>Cu</td><td>+1</td><td>+2</td><td></td></tr><tr><td>Zn</td><td></td><td>+2</td><td></td></tr></table>			Metals	Oxidation Numbers			Sc			+3	Ti			+3	V		+2	+3	Fe		+2	+3	Cu	+1	+2		Zn		+2	
Metals	Oxidation Numbers																															
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Zn		+2																														
		Table 1																														
	(i)	From Table 1 , state all the ions that are colored. [1]																														
		Ti ³⁺ , V ²⁺ , V ³⁺ , Fe ²⁺ , Fe ³⁺ , Cu ²⁺																														
	(ii)	Using one of the ions stated in (a)(i) , explain why it is colored. [3]																														
		Using Cu ²⁺ as example: ▪ The d orbitals of Cu²⁺ are split into two levels by ligands. ▪ The d electron undergoes d-d transition and is promoted to a higher energy d orbital ▪ In the process, the d electron absorbs certain wavelength of light energy from the visible region of the electromagnetic spectrum and transmits the remaining wavelength which appears as the colour observed																														
	(iii)	When dilute aqueous ammonia is added to a solution that contains copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added. Give an explanation for these observations using relevant equations. [3]																														
		$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ $\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{OH})_2(\text{s}) \quad \text{Eqn (1)}$ ○ When dilute NH₃ is added gradually, [OH⁻] increases. ○ Ionic product of Cu(OH)₂ > K_{sp} of Cu(OH)₂ or ○ Pale blue precipitate of Cu(OH)₂ is formed. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \quad \text{Eqn (2)}$ deep blue ○ When excess NH₃ is added, NH₃ ligands replace H₂O ligands to form the more stable deep blue [Cu(NH₃)₄(H₂O)₂]²⁺ complex. ○ [Cu²⁺] decreases as it is used to form the complex.																														

			○ The equilibrium position in Eqn (1) shifts to the left to increase [Cu²⁺]. ○ Thus, the pale blue precipitate dissolves.
	(b)		Iron by mass, is the most common element on Earth, forming much of Earth's outer and inner core. It forms compounds mainly in the +2 and +3 oxidation states. Iron and its compounds are widely used as catalyst.
		(i)	Suggest why iron has the ability to exist in variable oxidation states. [1]
			Iron which is a transition metals possess variable oxidation states due to the <u>small energy level difference between the 3d and 4s electrons</u> . This results in different numbers of 3d and 4s electrons lost to form stable ions and compounds of different oxidation states.
		(ii)	Hydrogen peroxide decompose according to the following equation: $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ Iron(III) ions can be used to catalyse this decomposition. Using relevant data from the <i>Data Booklet</i>, suggest a mechanism for this catalysis, calculating the E⁰ values for each step. [3]
			The relevant half equations are : $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ Step 1: $\text{H}_2\text{O}_2 + 2\text{Fe}^{3+} \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{Fe}^{2+}$ $E^\ominus_{\text{cell}} = 0.77 - 0.68 = +0.09 \text{ V}$ Step II: $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}^{3+}$ $E^\ominus_{\text{cell}} = 1.77 - 0.77 = +1.00 \text{ V}$

		(iii)	The following diagram shows the reactions of some iron compounds. <pre> graph TD A[Fe²⁺(aq) green] -- "Step I Cl₂" --> B[Yellow solution] A -- "Step II" --> C[[Fe(CN)₆]⁴⁻(aq)] B -- Mg --> D[gas J] C -- Fe³⁺ --> E[Deep blue precipitate, K] </pre>
			Name the type of reaction in Step II and identify gas J and precipitate K. [3]
			Step II: ligand exchange J: H₂ K: Fe₄[Fe(CN)₆]₃ (note cation: Fe³⁺, anion: [Fe(CN)₆]⁴⁻)

- (c) Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix.

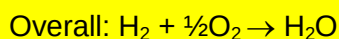
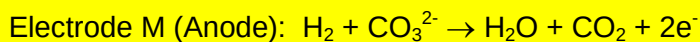
The following diagram show a MCFC:



At the electrode N, carbon dioxide is reacted with oxygen to form carbonate as the only product. The carbonate ions move towards electrode M and react with hydrogen to form carbon dioxide and water.

- (i) Write half-equations for the reactions taking place at the electrodes of the fuel cell and hence, construct the overall equation for the fuel cell reaction.

[3]



		(ii)	State the direction of the electron flow with respect to the electrode. [1]
			Electrons flow from electrode M to N .
		(iii)	Besides being high in efficiency and high operating cost, suggest one advantage and disadvantage of the molten carbonate fuel cell. [2]
			Advantage: The <u>product is clean</u> and it <u>does not generate greenhouse gas</u>. Disadvantage: <u>High temperatures</u> at which these cells operate and the <u>corrosive electrolyte</u> used accelerate component breakdown and corrosion, <u>decreasing cell life</u>.
			[Total: 20]

END



CHEMISTRY

9647/01

Paper 1 Multiple Choice

19th September 2016
1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

1. Enter your NAME (as in NRIC).

2. Enter the SUBJECT TITLE.

3. Enter the TEST NAME.

4. Enter the CLASS.

Write your **name**
and **Civics Group**

Write and shade
your CG number
followed by
last 3 digits of NRIC

WRITE	SHADE APPROPRIATE BOXES																			
INDEX NUMBER	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

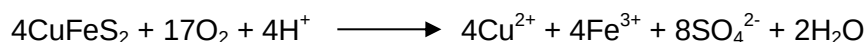
This document consists of **18** printed pages.

Section A

Part 1

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 During the bacterial leaching of low grade copper ores, acidified water is sprayed onto the ore chalcopyrite, CuFeS_2 . Bacteria then convert the insoluble ore into a solution according to the equation shown below:



No change occurs in the oxidation state of copper.

What changes in oxidation state occur for the iron and the sulfur in this reaction?

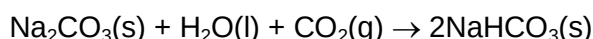
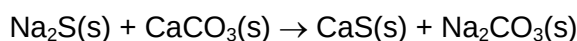
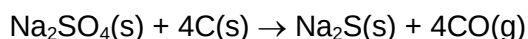
Change in oxidation state

	Fe	S
A	+1	+8
B	+1	-8
C	-1	+6
D	-1	-6

- 2 When cobalt metal is reacted with a solution containing cobalt(III) ions, only cobalt(II) ions are formed. How many moles of Co and $\text{Co}^{3+}(\text{aq})$ would result in a mixture containing both cobalt(II) and cobalt(III) ions in the mole ratio of 3:1 after the reaction had taken place?

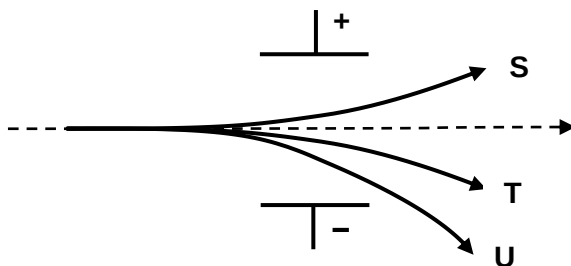
	Moles of Co	Moles of Co^{3+}
A	1	2
B	1	3
C	1	5
D	2	3

- 3 Sodium hydrogen carbonate, NaHCO_3 , can be prepared from sodium sulfate by a three-step process.



What is the mass of sodium hydrogen carbonate ($M_r = 84.0$), to the nearest kg, that could be formed from 100 kg of the sodium sulfate ($M_r = 142.1$), assuming a 90 % yield in each step?

- A** 43 **B** 86 **C** 106 **D** 118 kg



	S	T	U
A	$^{15}\text{O}^+$	$^{14}\text{C}^+$	$^{14}\text{N}^+$
B	$^{15}\text{O}^-$	$^{14}\text{C}^+$	$^{28}\text{Si}^+$
C	$^{14}\text{N}^-$	$^{16}\text{O}^{2+}$	$^{28}\text{Si}^{2+}$
D	$^{14}\text{N}^-$	$^{14}\text{C}^+$	$^{28}\text{Si}^{4+}$

- CC[N+](C)(C)COP(=O)([O-])OC[C@H](OC(=O)R)COC(=O)R

where R = long hydrophobic carbon chains

A It can form van der Waals' forces with other non-polar molecules.

B It has a low boiling point.

C It cannot rotate plane of polarised light.

D It can form hydrogen bonds between its own molecules.

- What could be the other gas in this mixture? [Density of argon = 1.78 g dm^{-3} at s.t.p.]

- A** neon
- B** oxygen
- C** fluorine
- D** carbon dioxide

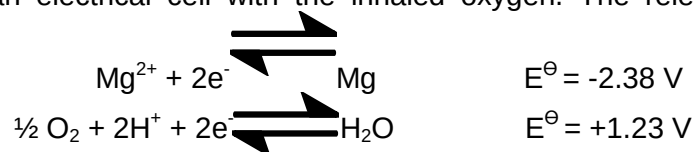
- 7 Which line in the table gives the signs of ΔH , ΔS and ΔG for the melting of ice at room temperature and pressure?

	ΔH	ΔS	ΔG
A	–	+	–
B	–	–	+
C	+	+	+
D	+	+	–

- 8 Which reaction represents standard enthalpy change at 298 K?

- A** $\text{P}_4(\text{l}) \rightarrow 4\text{P}(\text{g})$
B $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$
C $\text{HF}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaF}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
D $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

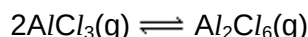
- 9 In the construction of heart ‘pacemakers’, it is possible to use a tiny magnesium electrode which creates an electrical cell with the inhaled oxygen. The relevant half-cells are as follows:



Under standard conditions, the cell e.m.f. would be +3.61 V, but in the body a potential of +3.25 V is more usual.

What is the best explanation for this lower e.m.f.?

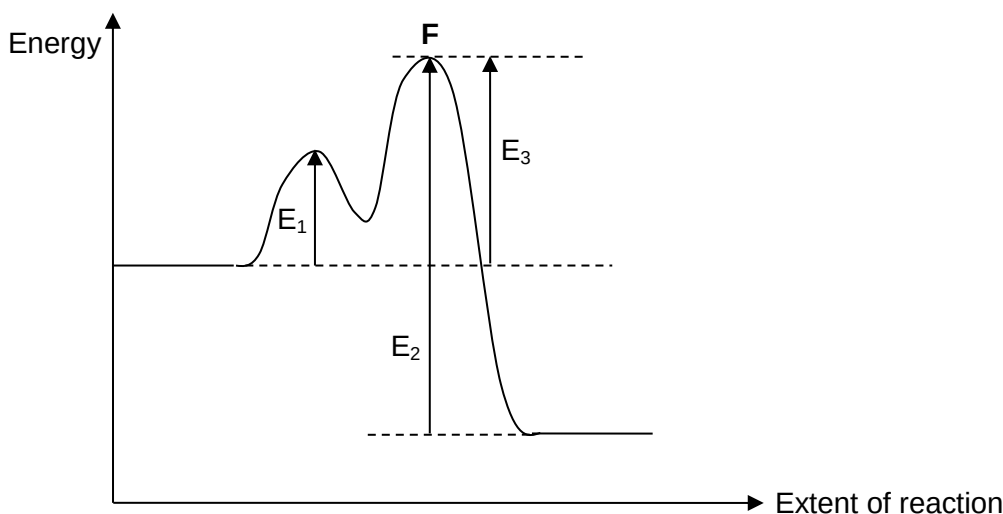
- A** the low concentration of Mg^{2+} ions surrounding the magnesium electrode
B the pH of between 7 and 8 of the body fluid surrounding the electrodes
C the high resistance of the body fluids surrounding the electrodes
D the small size of the magnesium electrode
- 10 Consider the following equilibrium system:



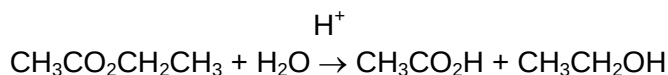
Which of the following statements will cause the position of the above equilibrium to shift to the left?

- A** decreasing the volume of the vessel
B increasing the temperature
C pumping inert gas into the vessel at constant volume
D pumping AlCl_3 gas into the vessel

- 11 Which of the following statements is true about the following energy profile for a catalysed reaction?



- A F is the intermediate formed.
 B The enthalpy change of the reaction is $E_2 - E_3$.
 C The reaction is catalysed by a heterogenous catalyst.
 D The second step of the reaction is the rate determining step.
- 12 Ethyl ethanoate undergoes a slow acid-catalysed hydrolysis in water where the concentration of acid in the solution remains constant.



The rate equation is found to be

$$\text{rate} = k[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}^+]$$

In an experiment, when 1.0 mol dm^{-3} HCl was reacted with 0.10 mol dm^{-3} ethyl ethanoate, the half-life was found to be 42 min.

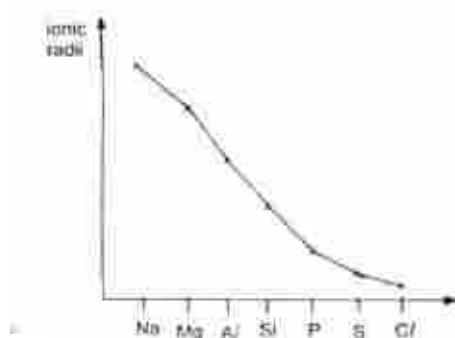
In a second experiment, 2.0 mol dm^{-3} HCl was reacted with 0.20 mol dm^{-3} ethyl ethanoate. What is the half-life of the second experiment?

- A 10.5 min B 21 min C 42 min D 63 min
- 13 Ethanol has a pK_a of 15.5 at room temperature. Sodium ethoxide can be produced by reacting ethanol with sodium metal, and Solution P is 0.1 mol dm^{-3} sodium ethoxide. Which of the following statements is **incorrect**?

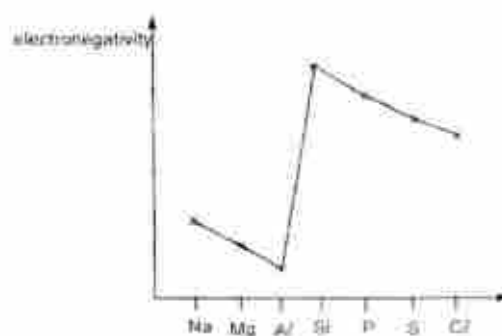
- A Ethanol is a weak acid.
 B Ethoxide is a strong base.
 C The pH of Solution P is 13.
 D The type of reaction between ethanol and sodium is acid-base

- 14 Which of the following graphs shows the correct trend in the physical property of the period 3 elements?

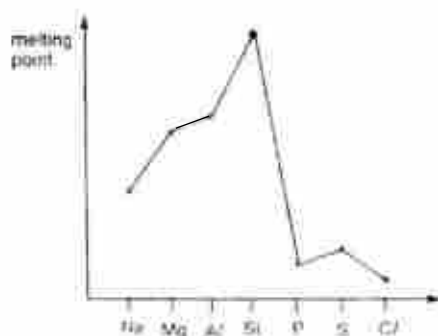
A



B



C



D



- 15 Which of the following elements has an oxide with a giant structure and a chloride which is readily hydrolysed?

A sodium

B carbon

C silicon

D phosphorus

- 16 Two experiments are carried out with anhydrous potassium chloride and observations 1 and 2 are made at the end of each experiment.

Experiment 1: Concentrated sulfuric acid is added to potassium chloride and the fumes produced are bubbled into aqueous potassium bromide solution – observation 1.

Experiment 2: Potassium chloride is dissolved in concentrated aqueous ammonia and the resulting solution is then added to aqueous silver nitrate – observation 2.

What are the observations 1 and 2?

	observation 1	observation 2
A	colourless solution	colourless solution
B	colourless solution	white precipitate
C	brown solution	colourless solution
D	brown solution	white precipitate

- 17 Which property of the Group II elements (magnesium to barium) and their compounds increases with increasing proton number?

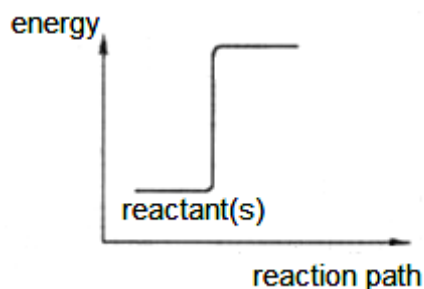
A the magnitude of the enthalpy change of hydration of the metal ion
 B the solubility of the sulfate
 C the stability of the carbonate to heat
 D the tendency to form complex ions

- 18 Letters written on paper using aqueous ammonium thiocyanate are invisible until turned blood red by brushing the paper with aqueous iron(III) chloride. If the ammonium thiocyanate is first made alkaline, the letters turned orange brown and are less clear.

Which of the following substances, when formed on the paper in these reactions, best explains these observations?

	with aqueous ammonium thiocyanate	with alkaline aqueous ammonium thiocyanate
A	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$\text{Fe}(\text{OH})_3$
B	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
C	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$\text{Fe}(\text{OH})_3$
D	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$[\text{Fe}(\text{OH})_4]^-$

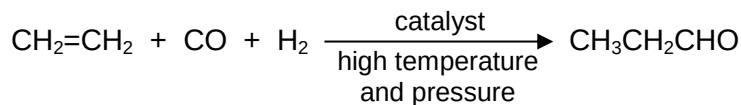
- 19 An energy profile diagram for a single reaction step is shown below.



To which of the following steps in the reaction of ethane with bromine in the presence of light does this diagram apply?

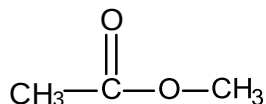
- A $\text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 B $\text{CH}_3\text{CH}_2\cdot + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{Br}\cdot$
 C $\text{CH}_3\text{CH}_2\cdot + \text{Br}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{Br}$
 D $\text{Br}_2 \rightarrow \text{Br}\cdot + \text{Br}\cdot$

- 20 The oxo reaction is an important industrial process in which an alkene combines directly with carbon monoxide and hydrogen under suitable conditions. The reaction with ethene is shown below.

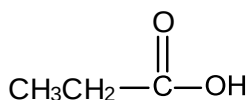


Which of the following structural formulae correctly represents the product of the oxo reaction starting with but-2-ene?

- A $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$
 B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
 C $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
 D $(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$
- 21 Compounds X and Y are isomers with the molecular formula $\text{C}_3\text{H}_6\text{O}_2$.



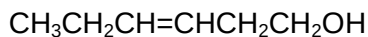
Compound X



Compound Y

Which reagent can be used to distinguish between X and Y?

- A sodium metal
 B 2,4-dinitrophenylhydrazine
 C aqueous alkaline iodine
 D aqueous sodium hydroxide
- 22 The compound hex-3-en-1-ol has a strong 'leafy' smell of newly cut grass and is used in perfumery.

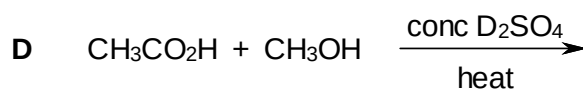
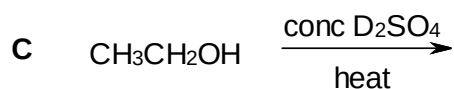
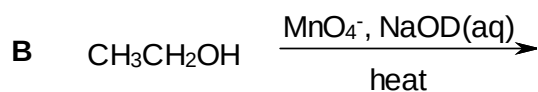
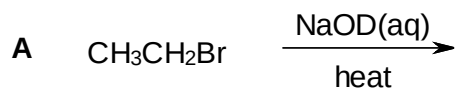


hex-3-en-1-ol

What are the organic products when hex-3-en-1-ol is treated with hot acidic $\text{K}_2\text{Cr}_2\text{O}_7$, followed by hydrogen gas in the presence of platinum?

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 B $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ and $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$
 C $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$
 D $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

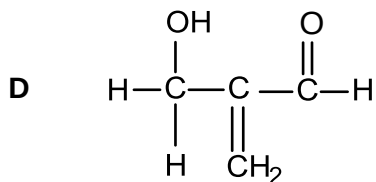
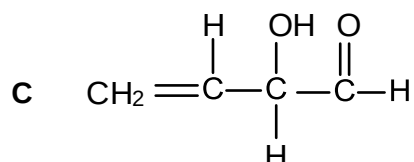
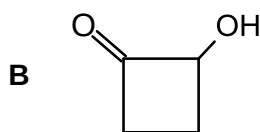
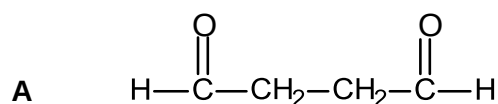
23 Which of the follow reaction produces an organic species that contains deuterium atom?



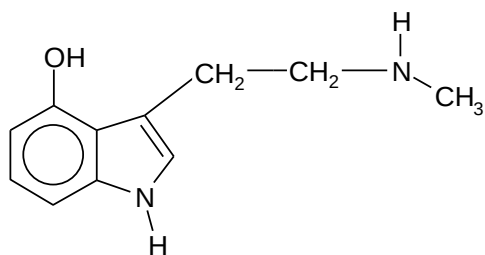
24 Compound **Z**, $\text{C}_4\text{H}_6\text{O}_2$, undergoes the following reactions.

- It gives a red precipitate with Fehling's solution.
- It gives white fumes with PCl_5 .
- Upon reaction with hydrogen gas and nickel catalyst, an optically active product is obtained.

What is compound **Z**?



- 25 Psilocin is the pharmacologically active agent in the body after ingestion of some species of psychedelic mushrooms.

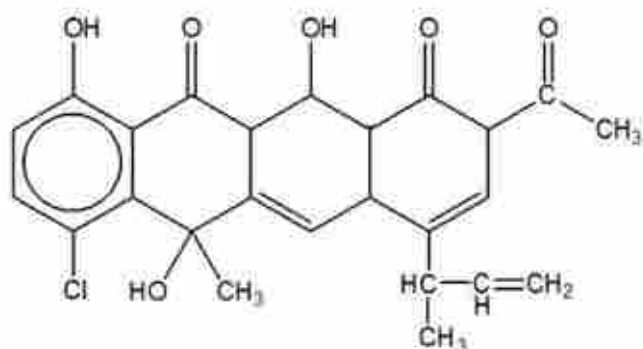


psilocin

Which σ bond formed by the following orbitals overlap is **not** present in psilocin?

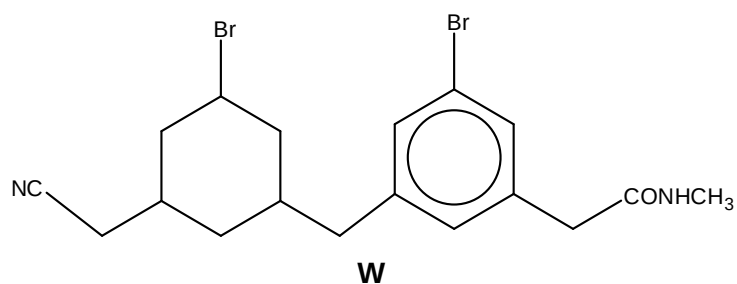
- A sp^3-sp^3 overlap between two C atoms
- B sp^2-sp^2 overlap between two C atoms
- C sp^3-sp^2 overlap between C and N atoms respectively
- D sp^3-sp^3 overlap between C and N atoms respectively

- 26 How many stereoisomers are possible for the following compound?



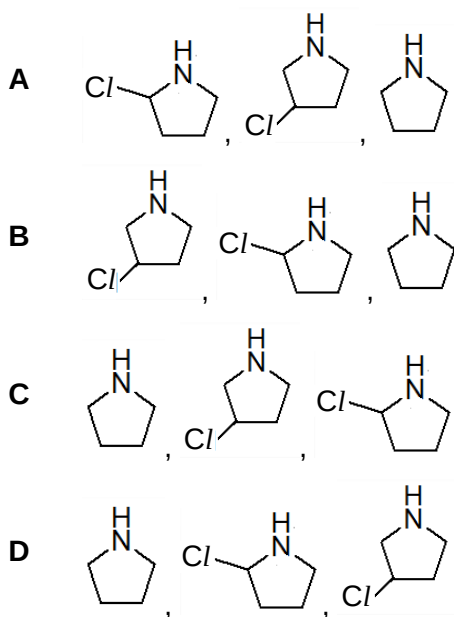
A	2^3	B	2^7
C	2^8	D	2^{10}

- 27 What is the structure of the compound formed when compound **W** was heated with aqueous sodium hydroxide, followed by acidification?



- A**
-
- B**
-
- C**
-
- D**
-

- 28 Which one of the following shows the given molecules arranged in order of decreasing pK_b values?



- 29 A polypeptide is subjected to hydrolysis.

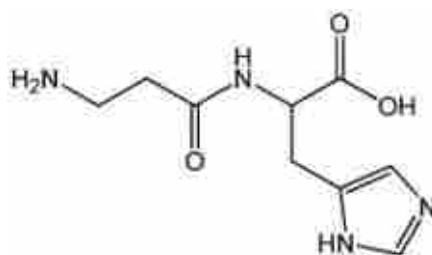
The following was found:

- The enzyme trypsin hydrolyses a peptide bond at the carboxylic end of arginine (arg) to give 2 tripeptides and gly
- The enzyme chymotrypsin hydrolyses a peptide bond at the carboxylic end of tyrosine (tyr) to give 2 dipeptides and a tripeptide
- The chemical cyanogen bromide cleaves the peptide bond at the carboxylic end of methionine (met) to give a tetrapeptide and a tripeptide

What is the primary structure of the polypeptide?

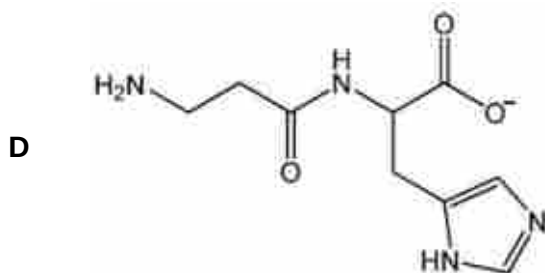
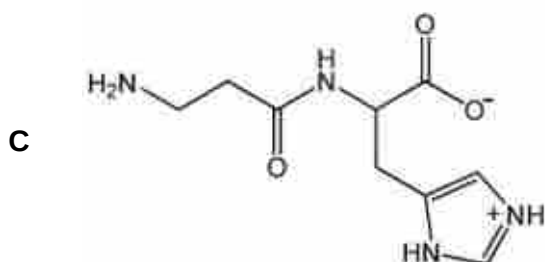
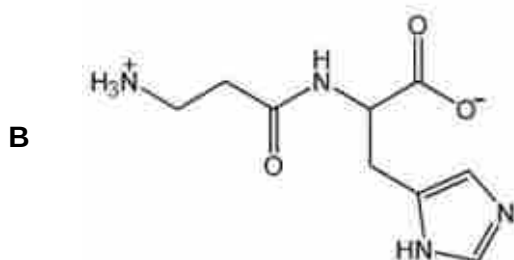
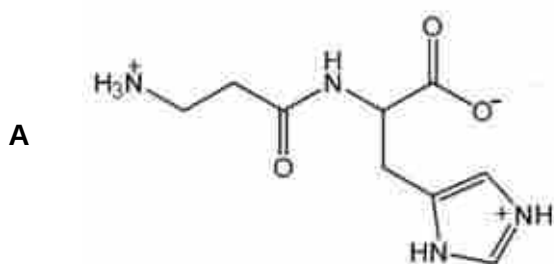
- A pro-tyr-arg-met-tyr-arg-gly
- B gly-arg-tyr-met-arg-tyr-pro
- C pro-tyr-arg-tyr-met-arg-gly
- D gly-arg-met-tyr-arg-tyr-pro

- 30 Carnosine is a dipeptide formed from β -alanine and histidine, and has been documented in recent research as having the ability to prevent many of the detrimental effects of aging.



carnosine

The isoelectric point of carnosine is 6.83. Which of the following is the predominant species present in an aqueous solution at physiological pH 7.4?



Part 2

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

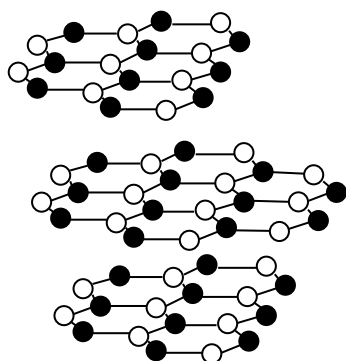
Decide whether each of the statements is or is not correct. (You may find it helpful to put a tick against the statements which you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

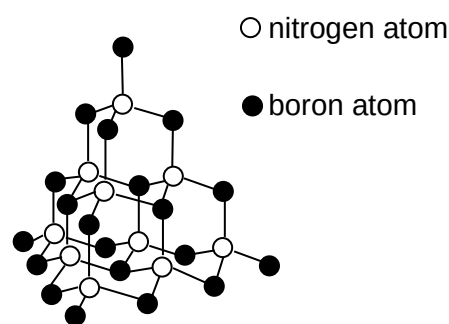
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31** Boron nitride, BN, exists in two possible forms, hexagonal boron nitride and cubic boron nitride. The structure of hexagonal boron nitride and cubic boron nitride are similar to graphite and diamond respectively.



hexagonal boron nitride



cubic boron nitride

Which of the following statements are correct?

- There is dative bonding in cubic boron nitride.
- The layers in hexagonal boron nitride are held together by van der Waals' forces.
- The boron-nitrogen bond in cubic boron nitride is shorter than that in hexagonal boron nitride.

- 32** The standard enthalpy changes of combustion of carbon are as follows:

$$\text{C(graphite)} = -393.1 \text{ kJ mol}^{-1}$$

$$\text{C(diamond)} = -395.0 \text{ kJ mol}^{-1}$$

Which of the following deductions can be made from the data above?

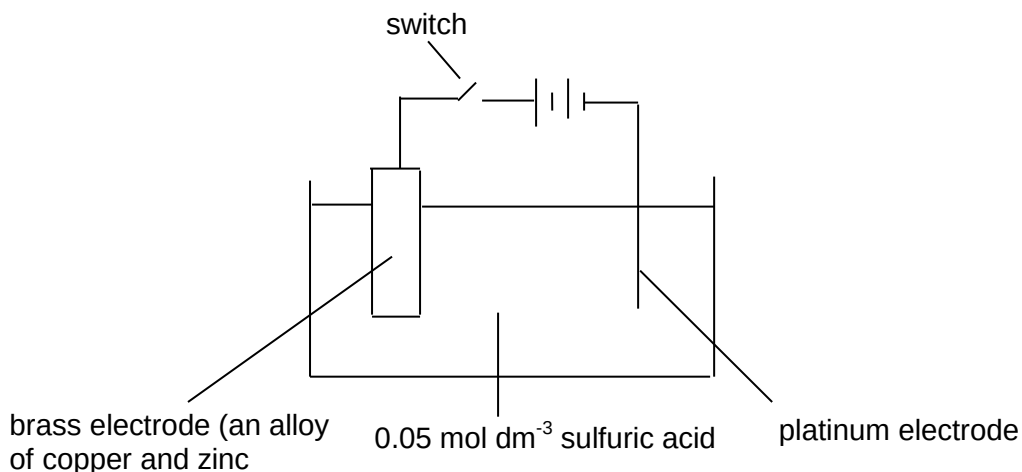
- Graphite is less stable than diamond.
- Graphite has a lower energy content than diamond.
- The conversion of diamond to graphite is exothermic.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1,2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

33 The circuit shown in the diagram was set up.

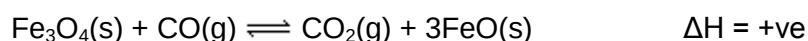


A steady current of 1.00 A was passes through the electrolyte for 10 minutes at room conditions.

Which statements regarding the electrolysis are correct?

- 1** Zinc dissolves preferentially at the anode.
- 2** Effervescence is observed at the cathode.
- 3** pH of the solution increases.

34 Consider the following equilibrium system:



Which of the following statements are correct?

- 1** Increasing the temperature causes the position of equilibrium to shift to the right.
- 2** The equilibrium constant, K_c , for this reaction has no units.
- 3** Adding FeO causes the position of equilibrium to shift to the left.

35 Which of the following shows a general decrease for Period 3 chlorides from MgCl_2 to PCl_5 ?

- 1** pH of the resulting solution when dissolve in water
- 2** maximum oxidation states of the elements in the chlorides
- 3** electrical conductivity in solid state

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

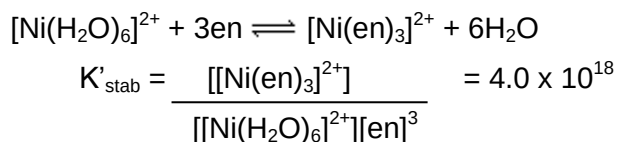
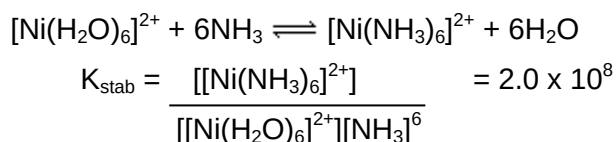
No other combination of statements is used as a correct response.

- 36** The following data refer to copper as a typical transition element and to calcium as an s-block element.

For which property are the data under the correct element?

	property	copper	calcium
1	density/g cm ⁻³	8.92	1.54
2	melting point/° C	1085	842
3	electrical conductivity/ relative units	9.6	85

- 37** Consider the following equilibria shown together with the magnitude of their respective equilibrium constants:



where en represents ethylenediamine, a bidentate ligand.

Which of the following statements are correct?

- 1** Ammonia is a stronger ligand than water.
- 2** Ethylenediamine is a stronger ligand than ammonia.
- 3** The equilibrium constant, K''_{stab} , for the following reaction is equal to $K'_{\text{stab}} / K_{\text{stab}}$:

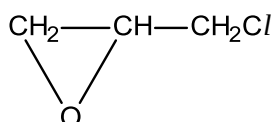
$$[\text{Ni}(\text{NH}_3)_6]^{2+} + 3\text{en} \rightleftharpoons [\text{Ni}(\text{en})_3]^{2+} + 6\text{NH}_3$$

The responses **A** to **D** should be selected on the basis of

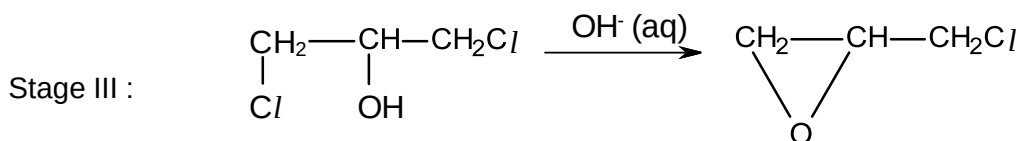
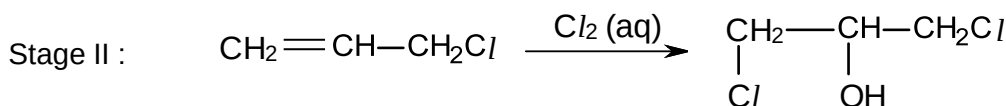
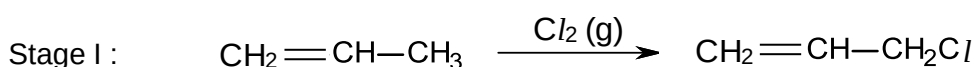
A	B	C	D
1,2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 38** Epoxy resins are polymers which are used in adhesives. One monomer used in their manufacture has the following structure:



This monomer is manufactured from propene in three stages:



Which statements are correct for the above synthesis?

- 1** Stage I involves free radical substitution.
- 2** Stage II involves electrophilic addition.
- 3** Stage III involves nucleophilic addition.

- 39** Ovalbumin is the predominant protein in egg white.

A perfect poached egg, with firm white surrounding a velvety yolk, can be made by the addition of vinegar into boiling water, before tipping the egg in and leaving it to cook for 1-2 minutes.

The addition of vinegar allows the egg white to coagulate faster around the yolk, instead of dispersing in the water. Which of the following explains this observation?

- 1** H^+ in vinegar denatures ovalbumin by protonating the R groups of amino acid residues.
- 2** H^+ in vinegar denatures ovalbumin by protonating the N atom of the peptide linkages.
- 3** H^+ in vinegar denatures ovalbumin by breaking it down to its constituent amino acids.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 40** Which of the following reagents can be used to distinguish between the two compounds shown below?



- 1** aqueous bromine
- 2** acidified KMnO_4 , reflux
- 3** CH_3Br with heating, followed by the addition of AgNO_3



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PRELIMINARY EXAMINATIONS

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CHEMISTRY
9647/02

Paper 2 Structured Questions

29th August 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	/ 12
2	/ 15
3	/ 12
4	/ 9
5	/ 24
Paper 1	/ 40
Paper 3	/ 80
Total	

This document consists of **21** printed pages.

Answer **all** the questions

1 Planning (P)

Potentiometric titration is a technique similar to direct titration of a redox reaction and can be used to determine the concentration of a reducing ion such as Fe^{2+} without the use of an indicator. It involves measurement of E_{cell} at intervals as an oxidising titrant is added. The titration is carried out on one side of a cell whose other half is a reference electrode which can be a standard hydrogen electrode or a calomel electrode.

Consider the titration of Fe^{2+} with standard Ce^{4+} , the course of which is monitored potentiometrically as shown in Figure 1 below. The reference electrode used is the calomel electrode shown in Figure 2.

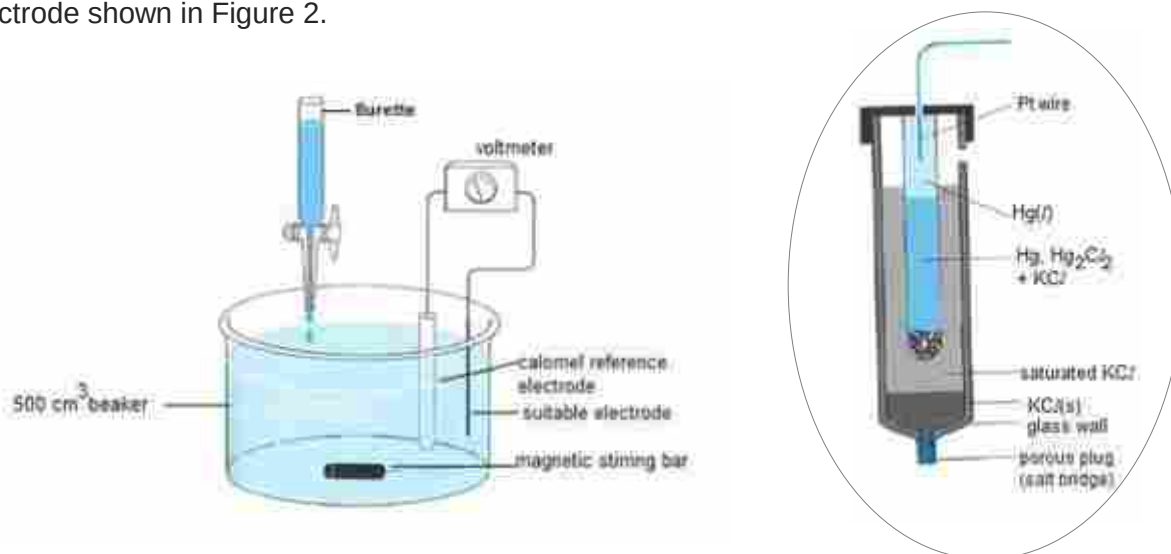


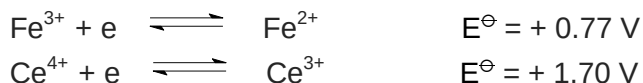
Figure 1: Set-up for potentiometric titration

Titration reaction: $\text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} +$

To follow the course of the reaction, a pair of electrodes is inserted into the reaction mixture. At the calomel reference electrode,

Reference half reaction is: $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$ $E^\ominus = +0.24 \text{ V}$

At the suitable electrode, there are two reactions that will come to equilibrium:



As the Ce^{4+} titrant is added, Fe^{2+} is oxidised to Fe^{3+} and the cell potential is controlled by the ratio of reduced and oxidised iron according to the Nernst equation which causes the potential to rise as more iron becomes oxidised.

$$E_{\text{cell}} = \left\{ E^\ominus (\text{Fe}^{3+}/\text{Fe}^{2+}) - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - 0.24 \dots\dots\dots(1)$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed, and the

potential will then be controlled by the concentration ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$. Thus beyond the end-point the potential rises rapidly to that of a $\text{Ce}^{4+}/\text{Ce}^{3+}$ cell with excess Ce^{4+} .

$$E_{\text{cell}} = \left\{ E^{\ominus}(\text{Ce}^{4+}/\text{Ce}^{3+}) - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - 0.24 \dots\dots\dots(2)$$

A graph of E_{cell} against volume of titrant added can be drawn and the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Solution **FA 1** was prepared by dissolving 0.960 g of 'iron tablets' in 100 cm^3 of 1 mol dm^{-3} HClO_4 acid. By titration method using KMnO_4 , the percentage of iron(II) ions in the iron tablets used to make **FA 1** was found to be 12.5%. A student wishes to verify the percentage of iron(II) ions present in **FA 1** by potentiometric titration using standard 0.100 mol dm^{-3} Ce^{4+} solution.

- (a) Suggest a suitable electrode for the potentiometric titration between Fe^{2+} and Ce^{4+} solution.

Suitable indicator electrode: _____

[1]

- (b) Perform a pre-calculation to estimate the end-point volume for the potentiometric titration of 100 cm^3 of **FA 1** with 0.100 mol dm^{-3} Ce^{4+} solution.

[1]

- (c) Using all the above information including the estimated end-point volume, you are required to write a plan to verify the percentage of Fe^{2+} present in **FA 1** by potentiometric titration.

You may assume that you are provided with the following:

- ◆ 100 cm³ of **FA 1** solution prepared by dissolving 0.960 g of 'iron tablets' in 1 mol dm⁻³ HClO₄ acid.
- ◆ 1.25 mol dm⁻³ Ce⁴⁺ solution
- ◆ a calomel reference electrode
- ◆ a suitable electrode
- ◆ a voltmeter
- ◆ the apparatus normally found in a school laboratory.

Your plan should include details of

- ◆ the preparation of 0.100 mol dm⁻³ Ce⁴⁺ solution
- ◆ how the electrochemical cell set-up in Figure 1 is assembled
- ◆ how you would recognize that the end-point has been reached
- ◆ a table for the recording of readings needed for the plotting of titration curve, showing suitable volumes of titrant added
- ◆ the calculation to verify the percentage of Fe²⁺ in **FA 1** in terms of the end-point volume, V_o cm³ of Ce⁴⁺

(d) Use the Nernst equation (1) and (2) to calculate the E_{cell} values when

2016 TJC H2 Chemistry Preliminary Exam

[Turn over

E_{cell} :

(ii) $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$

E_{cell} :

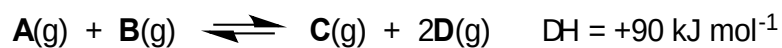
[1]

- (e) If the end-point volume is $V_o \text{ cm}^3$ of Ce^{4+} , sketch the graph you would expect to obtain. Show clearly in your sketch, the titration volumes in terms of V_o when you will be obtaining the E_{cell} values calculated in (d)(i) and (d)(ii).

[3]

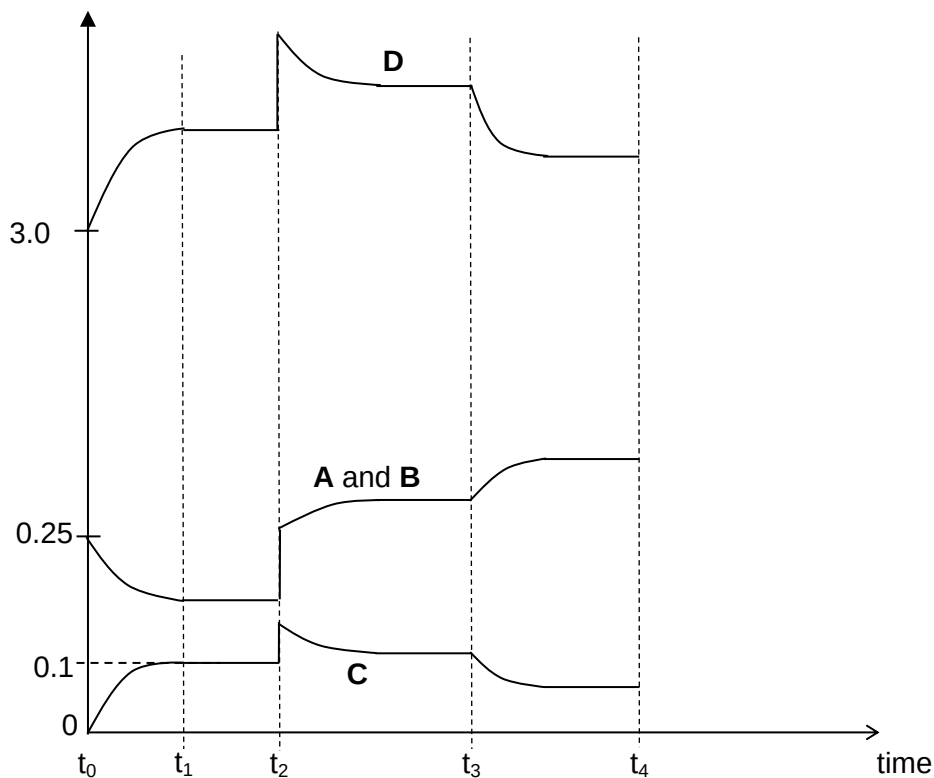
[Total:12]

- 2 Gases **A** and **B** react as shown in the equation given.



Gases **A**, **B** and **D** were injected into a vessel at 25 °C and allowed to reach dynamic equilibrium. The graph below (not drawn to scale) shows how the concentration of the four gases varies with time.

concentration / mol dm⁻³



- (a) (i) Explain what is meant by *dynamic equilibrium*.

[1]

- (ii) Write an expression for K_c for this equilibrium, stating the units.

[1]

- (iii) Calculate the value for K_c at time, t_1 .

[2]

- (b) (i) State *Le Chatelier's principle*.

[1]

At time, t_2 , the volume of the system was reduced which lead to an increase in concentration of the gases. This causes the position of the equilibrium to shift.

- (ii) Suggest and explain what happens to the system between time t_3 to t_4 .

[2]

- (iii) Sketch on the same axes how the concentration of the four gases will change when more gas **C** was introduced at time, t_4 .

[2]

- (iv) State and explain the effect of the presence of a catalyst on the equilibrium

position and the value of the equilibrium constant.

[2]

- (c) The standard Gibbs free energy change of reaction, $\Delta G^\ominus$ in J mol^{-1} , is related to the equilibrium constant by the following equation.

$$\Delta G^\ominus = -RT \ln (0.02478K_c)$$

- (i) Using your answer in (a)(iii), calculate $\Delta G^\ominus$ in kJ mol^{-1} .

[1]

- (ii) Explain the significance of the sign of your answer in (c)(i).

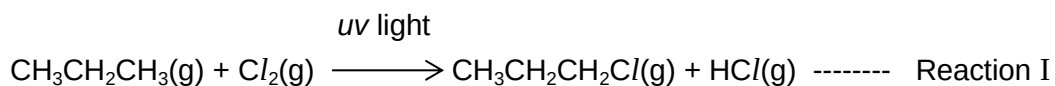
[1]

- (iii) Using your answer in (c)(i) and any other information on page 7, calculate $\Delta S^\ominus$.

[2]

[Total: 15]

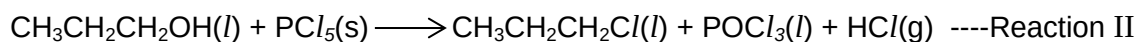
- 3 (a)** 1-chloropropane can be synthesized by the following reaction at room temperature.



With reference to the *Data Booklet*, calculate $\Delta H_r^\ominus$ of Reaction I.

[1]

- (b)** An alternate method of synthesis of 1-chloropropane is as follows:



- (i)** Suggest one reason why Reaction II is a better method to produce 1-chloropropane than Reaction I.

.....

.....

.....

[1]

- (ii)** Suggest whether the standard change in entropy of Reaction II is likely to be positive or negative, explaining your reasoning.

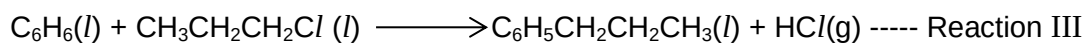
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[2]

- (c) 1-chloropropane is an important reactant in the synthesis of propylbenzene:



- (i) Define standard enthalpy change of formation.

.....

.....

.....

[1]

- (ii) Using the data listed below,

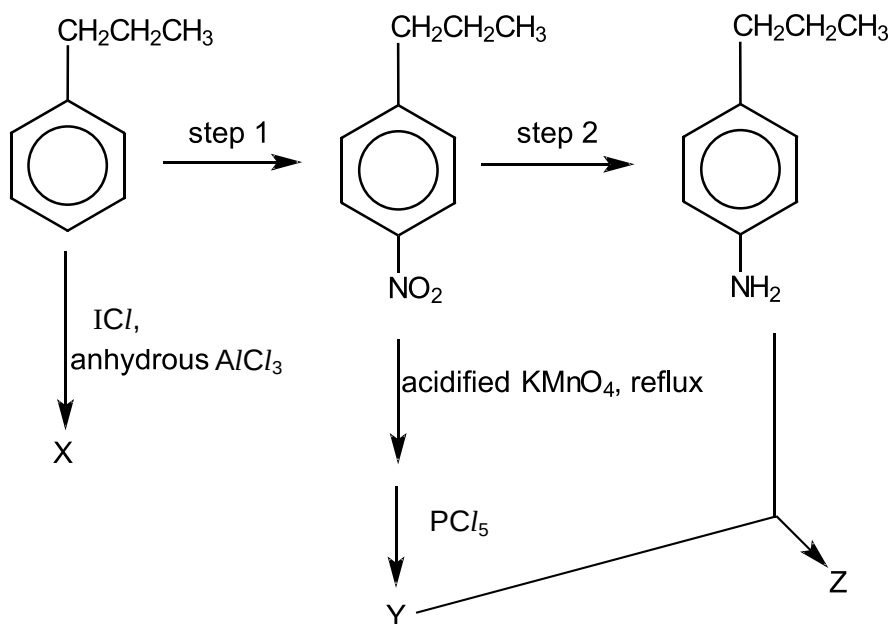
	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l)$	-161.3
$\text{HCl}(l)$	-167.2
$\text{C}_6\text{H}_6(l)$	+49.0
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3(l)$	-38.4

enthalpy change of vapourisation of HCl is $+74.9 \text{ kJ mol}^{-1}$

construct an energy cycle to calculate $\Delta H_r^\ominus$ of Reaction III.

[2]

- (d) Propylbenzene is a fuel additive and solvent. It undergoes the following chemical reactions.



- (i) State the reagents and conditions for the following steps:

Step 1 :

.....

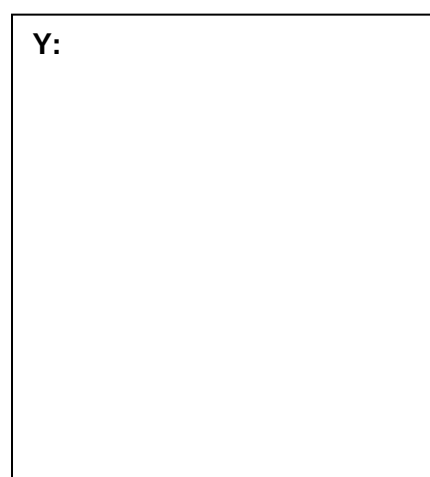
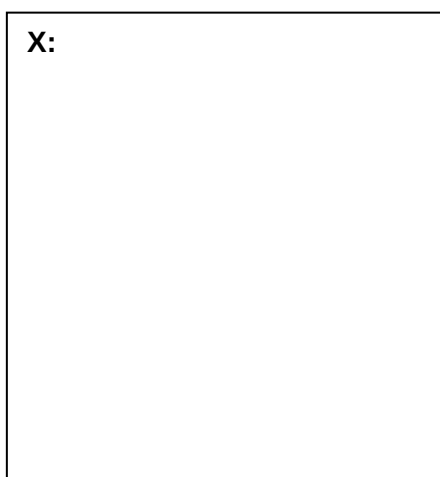
Step 2 :

.....

.....

[2]

- (ii) Draw the structural formula of the organic compounds **X**, **Y** and **Z**.



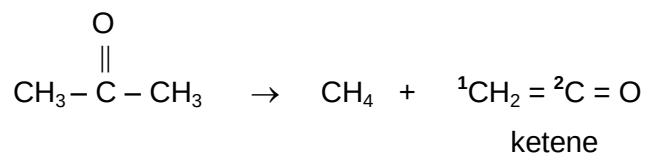
Z:



[3]

[Total:12]

- 4 When propanone vapour is passed over a heated filament, it breaks down into methane and a reactive substance called ketene.



- (a) (i) Draw the hybrid orbitals around each of the 2 carbon atoms, ${}^1\text{C}$ and ${}^2\text{C}$ in ketene molecule. State the type of hybridisation for each carbon atom.

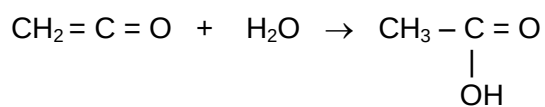
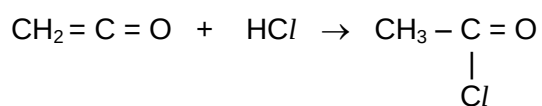
Carbon atom ${}^1\text{C}$	Carbon atom ${}^2\text{C}$
Hybridisation:	Hybridisation:

[2]

- (ii) Draw the displayed formula for the ketene molecule and on it show suggested values of the bond angles around ${}^1\text{C}$ and ${}^2\text{C}$ atoms.

[1]

Ketene is a highly reactive compound. It readily undergoes the reactions shown below.



- (b)** Name and describe the mechanism for the reaction between ketene and water, showing all charges and using curly arrows to show the movement of electron pairs.

[3]

- (c) Ketene reacts with ethanol to form a sweet smelling compound **P**, $C_4H_8O_2$, which reacts with $LiAlH_4$ to give **Q**. Identify **P** and **Q**. Name the type of reaction for the transformation of **P** to **Q**.

P	Q

Type of reaction from **P** to **Q**:

[3]

[Total: 9]

- 5 Ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, reacts with sodium hydroxide to form sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. One of the main applications of ethanedioate ions is in rust-removal, as ethanedioate ions form water-soluble derivatives with iron(III) ions.
- (a) An electrochemical cell is set up using Cu^{2+}/Cu and $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cells. The electrode in $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell is the negative electrode and the cell potential is +0.77 V.
- (i) Using relevant data from the Data Booklet, determine the electrode potential of the $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell.

[2]

- (ii) A small quantity of solid potassium iodide is added to the Cu^{2+}/Cu half-cell. Write an equation and state the observations for the reaction that will occur in this half-cell. Hence, predict and explain the effect on the e.m.f. of the electrochemical cell.

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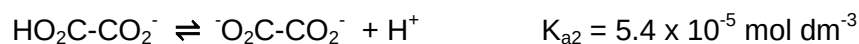
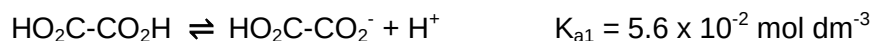
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[3]

- (b) The K_a values for the step-wise dissociation of ethanedioic acid are given below.



Calculate the pH of 0.10 mol dm^{-3} of sodium ethanedioate salt, $\text{Na}_2\text{C}_2\text{O}_4$.

[2]

- (c) Hydrated salt of magnesium ethanedioate has the formula $\text{MgC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. When 6.18 g of hydrated magnesium ethanedioate is heated strongly, a white solid **W** and three gases **X**, **Y** and **Z** are generated. Gases **X**, **Y** and **Z** are passed through anhydrous calcium chloride, followed by aqueous sodium hydroxide. The flasks containing anhydrous calcium chloride and aqueous sodium hydroxide had an increase in mass of 1.50 g and 1.83 g respectively. The residual gas **Z** occupied 1 dm^3 at room temperature and pressure. Gas **Z** is poisonous and can be heated with oxygen to give gas **Y**.

- (i) Suggest the identities of **W**, **X**, **Y** and **Z**.

W:

X:

Y:

Z:

[2]

- (ii) Hence, determine the value of n , showing your working clearly.

.....

[3]

- (iii) Ethanedioate ions form insoluble precipitates with many metal ions, one of which is calcium ethanedioate, a primary constituent of kidney stones.

Calcium ethanedioate decomposes in the same manner as magnesium ethanedioate. Using relevant data from the Data Booklet, deduce whether calcium ethanedioate would decompose at a higher or lower temperature than magnesium ethanedioate. Explain your reasoning.

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.....

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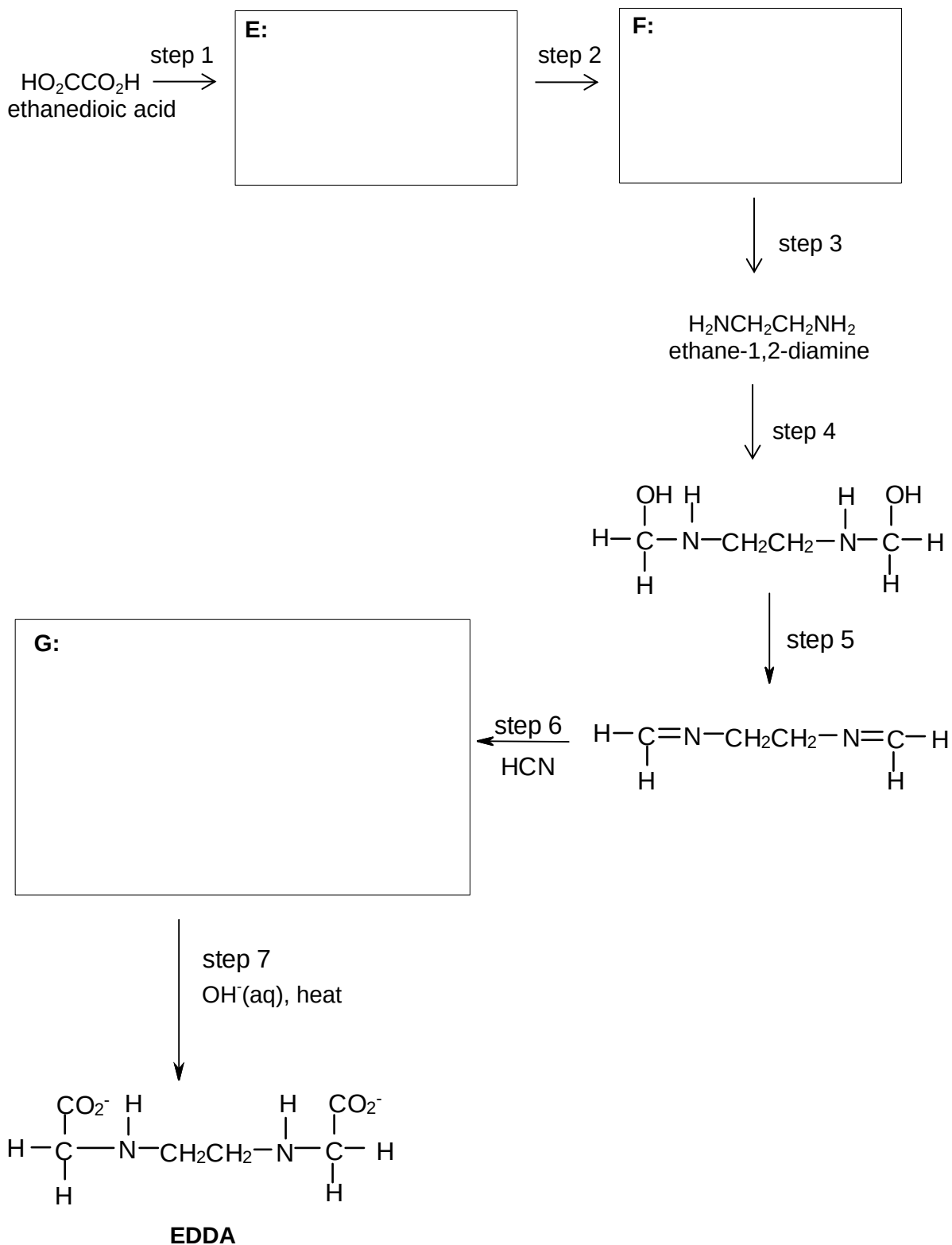
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[3]

- (d) A tetradentate ligand, ethylenediamine-N,N'-diacetate (EDDA) ion, can be synthesised from ethanedioic acid through a series of steps. Ethanedioic acid is first converted to ethane-1,2-diamine through a 3-step synthesis. Steps 4 to 7 represent the mechanism of Skrecker synthesis, which can be used to synthesise amino acids.



- (i) Propose the 3-step synthesis for the formation of ethane-1,2-diamine from ethanedioic acid, naming the reagents and conditions used in each step. Draw the structures of the intermediate compounds **E** and **F** in the spaces provided in the synthetic route.

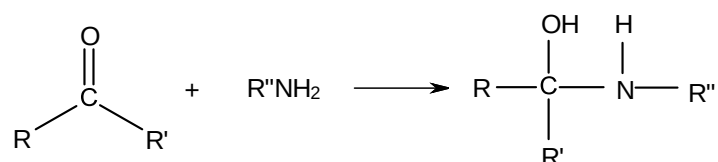
Step 1:

Step 2:

Step 3:

[5]

- (ii) Carbonyl compound and amine react in the following way.



Step 4 of the synthetic route in **(d)** involves the reaction of ethane-1,2-diamine with 2 moles of a carbonyl compound. Identify the carbonyl compound.

[1]

- (iii) Draw the structure of compound **G** in the space provided. [1]

- (iv) State the types of reaction in step 5 and step 7.

Step 5:

Step 7:

[2]

[Total: 24]



CHEMISTRY
Paper 3 Free Response

9647/03
13th September 2016
2 hours

Candidates answer on separate paper.

Additional materials: Answer paper
 Graph Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group, Centre number and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of 15 printed pages.

Answer any **four** questions

- 1** Ethanedioic acid is a substance found in many plant foods. Cabbage is among the plant foods with high ethanedioic acid content. However, its anion, $\text{C}_2\text{O}_4^{2-}$ can bind to iron to form iron(II) ethanedioate, which renders much of the iron in cabbage unusable by the body.

(a) 50.0 cm³ sample of iron(II) ethanedioate, FeC_2O_4 was extracted from 300 g of cabbage, diluted in water and the solution made up to 250 cm³. A 25.0 cm³ portion of this solution was acidified and required 26.90 cm³ of 0.0100 mol dm⁻³ potassium manganate(VII) for oxidation of iron(II) to iron(III) and ethanedioate ions to carbon dioxide.

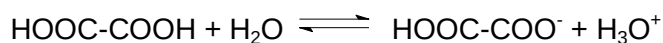
(i) State the change in oxidation number for manganese and carbon in the reaction. [1]

(ii) Write down all the relevant ion-electron half equations and hence the overall redox equation for the reaction between potassium manganate(VII) and iron(II) ethanedioate. [2]

(iii) Calculate the concentration, in mol dm⁻³, of iron(II) ethanedioate in the original sample. [2]

(iv) Calculate the number of moles of iron in each gram of cabbage. [1]

(b) Ethanedioic acid dissociates in water according to the following equation.



The table below compares the K_a values of three organic acids.

	Formula	K_a
Ethanoic acid	CH_3COOH	1.74×10^{-5}
Ethanedioic acid	$\text{HO}_2\text{CCO}_2\text{H}$	6.46×10^{-2}
Oxoethanoic acid	$(\text{CHO})\text{COOH}$	4.79×10^{-4}

With reference to the K_a values, comment on the order of acidity of the three organic acids. [2]

- (c) Compound **A**, with molecular formula C_5H_8O , decolourises aqueous bromine and reacts with PCl_5 giving off white fumes. Upon refluxing **A** with acidified potassium manganate(VII), a symmetrical product **B**, $C_5H_6O_5$, is formed. **B** does not give a red precipitate with Fehling's solution but an orange precipitate is observed with 2,4-dinitrophenylhydrazine. 1 mole of **B** also reacts with 1 mole of Na_2CO_3 with effervescence observed. **B** reacts with $NaBH_4$ to form **C**. Deduce the structures of compounds **A**, **B** and **C**, explaining the chemistry of the reactions involved. [8]
- (d) (i) Describe what you see when separate samples of sodium and sulfur are burned in excess air. Write equations for the reactions that occur. [2]
- (ii) The products resulting from the reactions in (d)(i) both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

[Total: 20]

- 2 Thallium is a Group III element discovered in 1861, and its toxicity was quickly noted. Thallium isotopes and compounds have useful applications, sometimes despite their toxic nature.

(a) Thallium forms compounds similar to aluminium, and thallium(III) chloride and thallium(III) fluoride have very different structures and bonding.

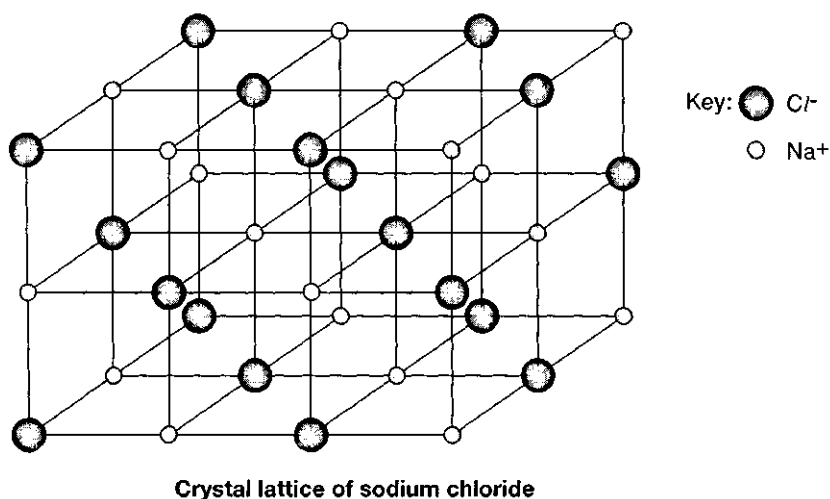
(i) Draw and state the shape of thallium(III) chloride, $TlCl_3$.
[1]

(ii) In gaseous phase, thallium(III) chloride is able to form a compound with a M_r of 621. Draw a dot-and-cross diagram of this compound, and state the $Cl-Tl-Cl$ bond angle.
[2]

(iii) Explain, in terms of structure and bonding, why thallium(III) fluoride has a high melting point of 550 °C.
[2]

(iv) Thallium is also able to form thallium(I) chloride, which is crystalline in nature.

In the crystal lattice of sodium and potassium chlorides, the co-ordination number of each ion is 6. In the crystal lattice of thallium(I) chloride, $TlCl$, the co-ordination number has a different value.



Suggest an explanation for the co-ordination number in the $TlCl$ lattice being different from those in $NaCl$ and KCl .

[1]

(b) Thallium(III) chloride, $TlCl_3$, reacts with hot water to produce thallium(III) oxide precipitate and hydrochloric acid.

(i) Write a balanced equation for the above reaction.
[1]

(ii) In an experiment, a 15 g impure sample of thallium(III) chloride ($M_r = 310.5$) was mixed with hot water, and filtered. Water was then added to the filtrate to make a standard solution in a 250 cm^3 volumetric flask. A 25.0 cm^3 aliquot was titrated against 0.5 mol dm^{-3} aqueous sodium hydroxide, requiring a titre of 22.00 cm^3 . Determine the percentage purity of the sample.

You may assume that the impurities are insoluble in water and are inert.
[2]

(c) Thallium(I) sulfate ($M_r = 504.1$) was often employed as a rodenticide and is highly poisonous. The lethal dosage is 16 ppm of the rat's mass. Assuming a typical rat has a mass of 230 g, determine the number of moles of thallium(I) sulfate needed to kill a rat.
[2]

(d) Thallium(III) ethanoate, $Tl(CH_3CO_2)_3$, is able to react with an alkene through addition. When cyclohexene reacts with thallium(III) ethanoate, a compound with the molecular formula $C_{10}H_{16}O_4$ is formed. Suggest the structural formula of this compound, and state the number of stereoisomers that this compound has.
[2]

(e) ^{201}Tl is an isotope of thallium that is often used in medical diagnostics due to its radioactive decay by electron capture with emission of gamma rays. The electronic configuration of the Tl atom is $[Xe]4f^{14}5d^{10}6s^26p^1$.

Electron capture is a process in which a proton-rich nucleus of an atom absorbs one electron from the first or second quantum shell to change one proton into a neutron.

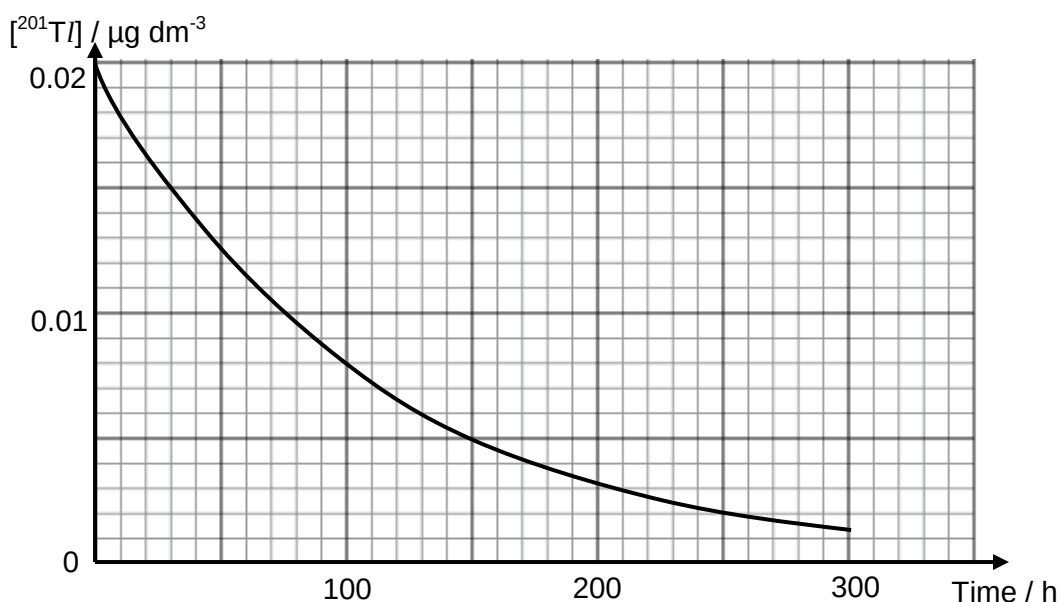
(i) Suggest the species formed, including the nucleon number, when ^{201}Tl undergoes electron capture.
[1]

(ii) The species formed immediately after electron capture is known to be in excited state, before returning to ground state by emitting gamma rays.

Name the orbital where the excited electron is most likely located in, and explain why **high energy** gamma rays are emitted when the species return to ground state.

[2]

- (iii) A patient is typically injected with $0.02 \mu\text{g}$ of thallium for heart diagnosis. The following graph shows the radioactive decay (through electron capture) of a $0.02 \mu\text{g}$ sample of ^{201}Tl dissolved in 1 dm^3 of inert solvent.



Using the graph, deduce the order of reaction for the radioactive decay of ^{201}Tl .
[2]

- (iv) Hence, write the rate equation for this reaction and determine the rate constant, stating its units.
[2]

[Total: 20 m]

- 3** The halogens and organic halides are useful laboratory reagents and have many applications.
- (a)** State and explain the difference in the reactions of chlorine and iodine with sodium thiosulfate respectively. Write balanced equations for the reactions. [3]
- (b)** Deduce which gas, fluorine or chlorine, would behave more ideally at low pressure. Explain your answer. [1]

Organic halides are a group of compounds comprising alkyl halides, ethenyl halides and aryl halides.

Alkyl halides are used as solvents for relatively non-polar compounds. They are also used as the starting materials for the synthesis of many compounds.

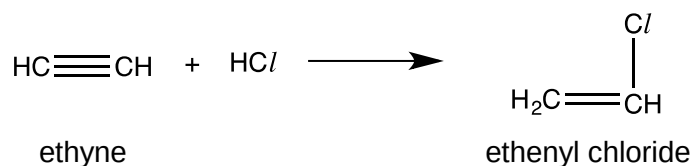
- (c)** Alcohols react with hydrogen halides to produce alkyl halides.
- (i)** Suggest the type of reaction that occur. [1]
- (ii)** 2-iodopropane is formed from propan-2-ol in the presence of sodium iodide and concentrated phosphoric acid.
- Explain, with the aid of an equation, why concentrated sulfuric acid is not used. [2]
- (d)** 2-chloro-2-methylpropane undergoes alkaline hydrolysis to form 2-methylpropan-2-ol.
- (i)** Name and describe the mechanism of the hydrolysis of 2-chloro-2-methylpropane. [3]
- (ii)** With the aid of the *Data Booklet*, explain what will happen to the rate of reaction if

2-bromo-2-methylpropane was used instead.

[2]

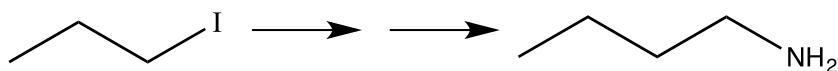
- (e) Ethenyl chloride is an important industrial chemical mainly used to produce the polymer, PVC.

Ethyne reacts with anhydrous hydrogen chloride gas over a mercuric chloride catalyst to give ethenyl chloride.



- (i) With the aid of the *Data Booklet*, determine the enthalpy change of the reaction. [2]
- (ii) Explain why ethenyl chloride does not undergo alkaline hydrolysis readily. [1]

- (f) 1-iodopropane can be converted to butylamine via a two-stage synthesis. Butylamine is then used as an ingredient in the manufacture of pesticide.



- (i) Suggest reagents and conditions for the two stages. Draw the structure of the intermediate compound. [3]
- (ii) Suggest a chemical test to distinguish between 1-iodopropane and 1-chloropropane. [2]

[Total: 20]

- 4** Co-Cr alloys are most commonly used to make artificial joints including knee and hip joints due to high wear-resistance and biocompatibility. However in 2010, faulty Co-Cr alloy hip joints manufactured by DePuy was removed from market due to leakage of toxic chromium and cobalt into the body muscles and blood stream.

(a) State the electronic configurations of

(i) an _____ atom _____ of _____ chromium,
[1]

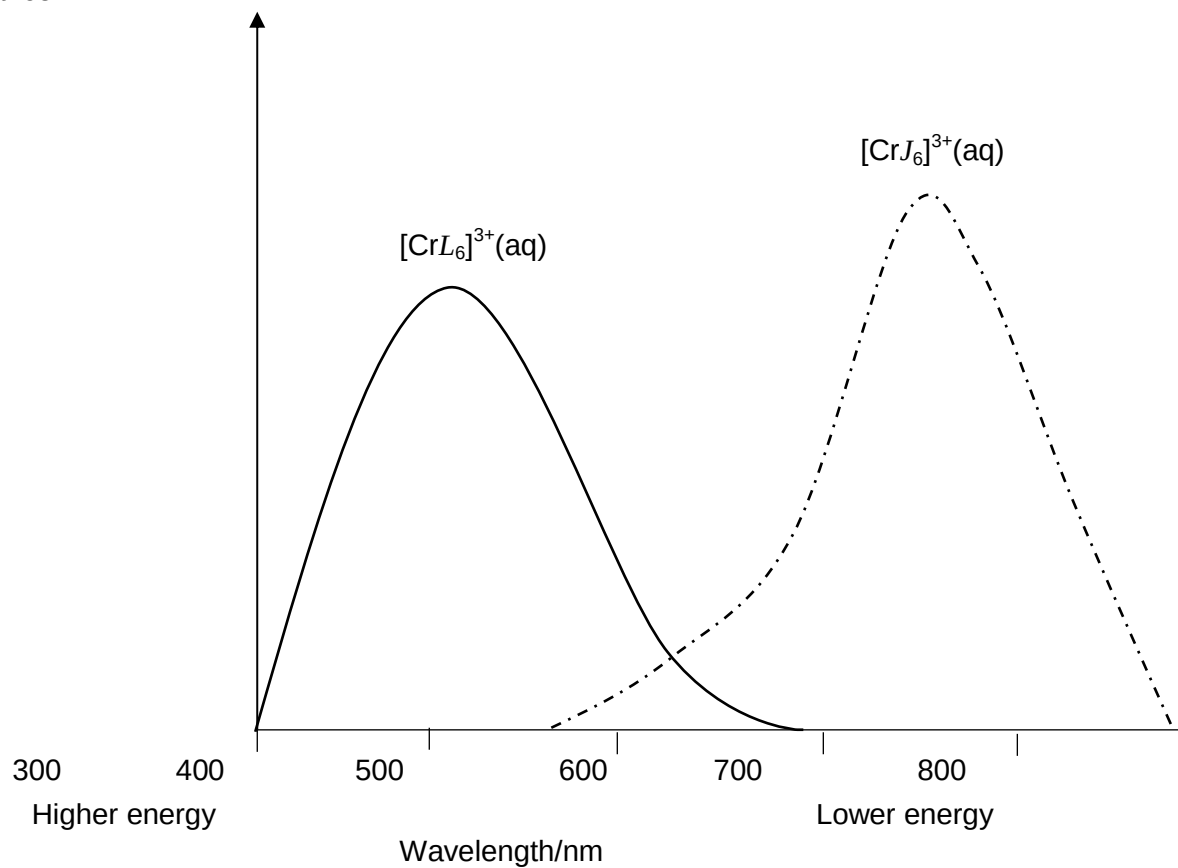
(ii) the Co^{3+} ion. [1]

(b) Why are transition metal complexes coloured? [3]

- (c) The colour of the complexes can be measured by a spectrometer. The amount of light absorbed is expressed as an absorbance value. The higher the absorbance, the more of a particular wavelength of light is being absorbed.

The spectrum below shows the major absorption peaks for $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$.

Relative
absorbance



colour	Wavelength/nm
Violet	400-430
Blue	430-490
Green	490-570
Yellow	570-590
Orange	590-620
red	620-750

- (i) What are the colours of $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$?

[2]

- (ii) What deduction can be made from the spectra about the size of the d-orbital splitting in the two complexes?
[2]

Cobalt forms many complexes with ligands such as H_2O , NH_3 and $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$. The most common oxidation states of cobalt are +2 and +3.

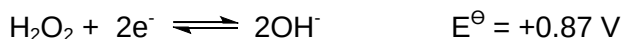
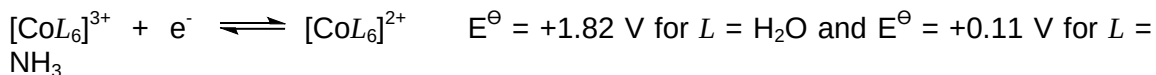
Cations containing cobalt in these two oxidation states have significantly different colours even when the ligands are the same.

- (d) When H_2O_2 is mixed with pink $\text{Co}^{2+}(\text{aq})$ solution, no significant colour change is observed.

When $\text{Co}^{2+}(\text{aq})$ is mixed with excess $\text{NH}_3(\text{aq})$ a slight colour change occurs and cation **Q** is formed.

When cation **Q** is mixed with H_2O_2 , a reddish brown solution is observed.

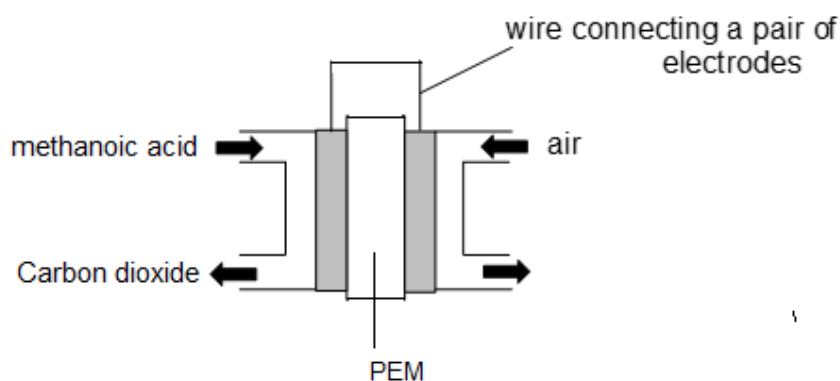
$E^\ominus$ data for the cobalt complex ions and hydrogen peroxide are given below.



Suggest an explanation for the above observations, giving equations where appropriate and identify the cation **Q**.
[5]

- (e) Explain why the neutral complex formed between a Co^{2+} ion and two $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$ ions is soluble in cyclohexane.
[1]

The direct oxidation of methanoic acid in a fuel cell, DFAFC, shown below represents potentially the most efficient method of obtaining useful energy from a renewable fuel.



- (f) The electrons pass around the external circuit to the cathode. The protons produced migrate across the proton exchange membrane, PEM, to the cathode, where they react with oxygen from air, producing water.

Write the equations for the anode and cathode reactions. Hence construct the equation for the overall reaction. [2]

- (g) One method for the construction of DFAFC, involves electroplating a layer of platinum onto the surface of the proton exchange membrane, PEM. The electrolyte for this process is a solution containing $\text{Pt}(\text{NH}_3)_4^{2+}$ and Cl^- ions. The PEM is the cathode in this electrolytic cell.

- (i) Suggest the half-equation for the cathode reaction that deposits platinum on the PEM. [1]

- (ii) In one such preparation, a PEM with a surface area of 25 cm^2 was immersed in an electrolyte bath and a current of 0.0875 A was passed for 95 minutes. Calculate the mass of platinum deposited onto the surface of PEM. [2]

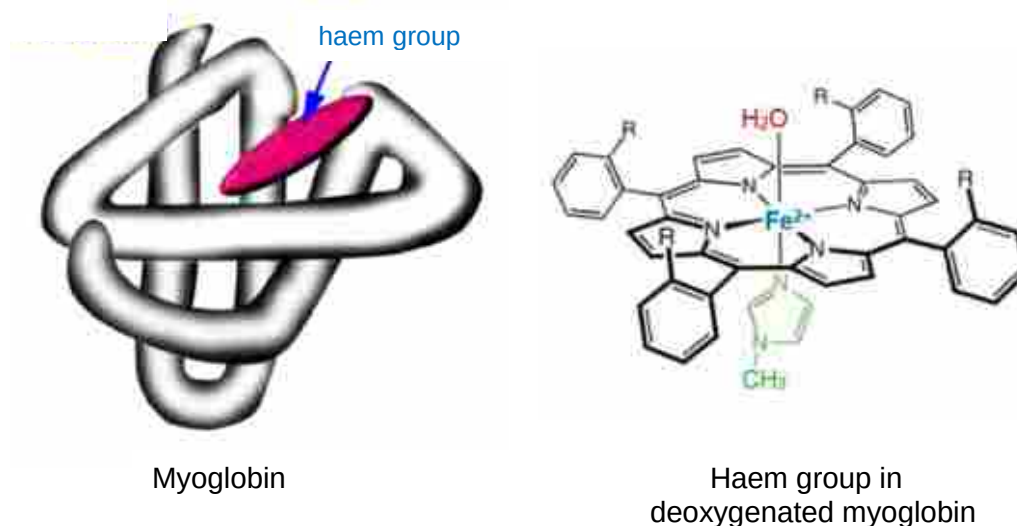
[Total: 20]

- 5 (a) Myoglobin and haemoglobin are globular proteins that serve to bind and deliver oxygen.

The former serves as an intracellular storage site for oxygen in the muscle tissues, while the latter transports oxygen in the bloodstream.

Each myoglobin molecule contains one haem group.

In deoxygenated myoglobin, a water ligand is weakly bound to the Fe^{2+} of the haem group as shown:



(i) Briefly describe how myoglobin maintains its three-dimensional shape. [2]

(ii) In the presence of the haem group, the polypeptide chain coalesces into a myoglobin molecule.

With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

and by considering the chemical interactions involved, explain why this is a spontaneous process at low temperatures. [2]

(iii) Deoxygenated myoglobin is responsible for the dull purplish red muscle colour, observed in the depth of the muscle. When meat is freshly cut, colour change occurs in two stages:

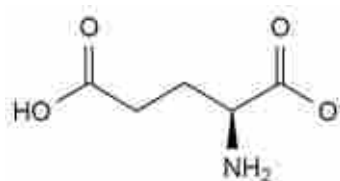
Stage 1: Bright red colour when muscle surface is exposed to air.

Stage 2: With time, the bright red colour slowly changes to an unattractive, dull brown colour associated with stale and spoiled meat.

With reference to the structure of the haem group and the reaction that occurs in each stage, explain the colour changes involved.

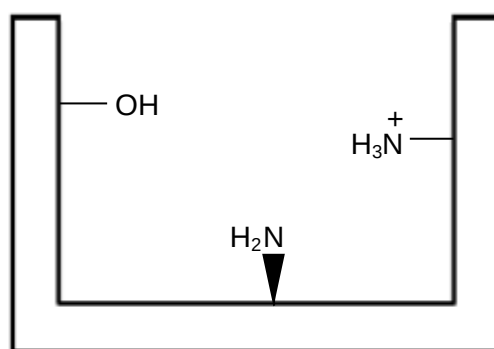
[2]

- (b) One of the isolated compounds that is primarily responsible for the umami (savory) flavor is glutamate, which is a salt formed from glutamic acid that is commonly found in meat.



glutamate

It is thought that glutamate stimulates a specific receptor site located in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below:

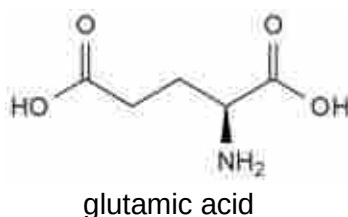


- (i) State **two** different types of interactions that can be formed between glutamate and the receptor protein. Illustrate your answer with labelled diagram(s). [2]

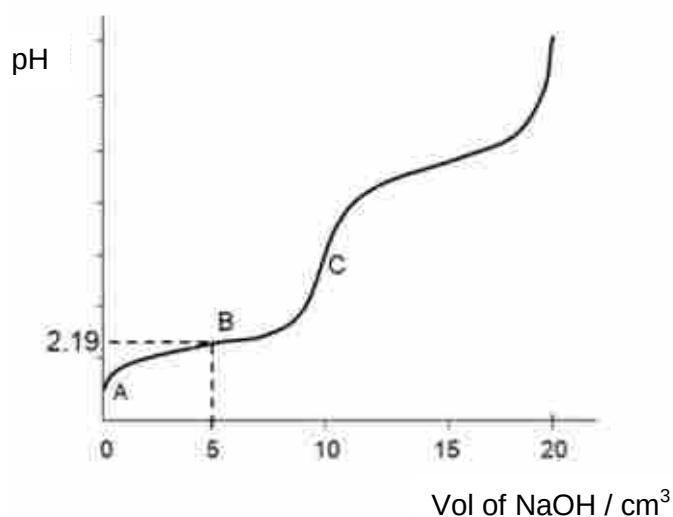
- (ii) To enhance the flavor of food, many retailers in the food industry use monosodium glutamate (MSG) as a food additive, which can be easily synthesized in the laboratory.

Given that laboratory synthesis gives a racemic mixture, explain why 50% of the glutamate synthesized in the laboratory is unable to bind precisely with the correct orientation to the receptor protein. [1]

The structure of glutamic acid is shown below:



10 cm³ of the fully protonated glutamic acid is titrated with 20 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution. Its titration curve is shown below:



(iii) Show that the concentration of glutamic acid is 1.0 mol dm⁻³ at **A**.
[1]

(iv) Hence, calculate the pH of the solution at **A**.
[1]

(v) Identify the specie(s) present at **B**.

With the help of an equation, explain how the solution at **B** can resist a change in pH when a small amount of base is added.
[2]

(vi) In a separate experiment, the solution at **B** was reacted with 10.0 cm³ of

0.05 mol dm⁻³ sodium hydroxide.

Calculate the pH of the mixture after the reaction.

You may find it useful to represent the fully protonated glutamic acid as HA.
[2]

(c) Compound **P**, C₉H₁₁NO₂, rotates the plane of polarised light and reacts with the following reagents:

- aqueous bromine to give compound **Q**, C₉H₉NO₂Br₂
- sodium carbonate to give a salt
- PCl₅ to give a 5-membered cyclic compound **R**

Deduce the structural formulae of compounds **P**, **Q** and **R**.
[5]

[Total: 20]

**2016 Preliminary Examination
H2 Chemistry MCQ Solution**

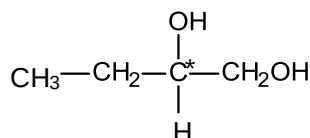
1	2	3	4	5	6	7	8	9	10
A	B	B	D	A	D	D	C	B	B
11	12	13	14	15	16	17	18	19	20
D	B	D	C	C	A	C	C	D	A
21	22	23	24	25	26	27	28	29	30
A	D	A	C	C	B	B	A	A	D
31	32	33	34	35	36	37	38	39	40
B	C	A	B	D	B	A	B	D	C

16. A Observation 1: $\text{H}_2\text{SO}_4 + \text{Cl}^- \longrightarrow \text{HCl} + \text{HSO}_4^-$ HCl bubbled into Br^-, no visible reaction is observed and solution <u>remained colourless</u>. Observation 2: Addition of Ag^+ into solution containing Cl^- and $\text{NH}_3(\text{aq})$ gives a <u>colourless solution containing $[\text{Ag}(\text{NH}_3)_2]^+$</u> as AgCl is soluble in aq NH_3	17. C A: Charge of Group II metal ions is the same but the ionic radius increases down the group. Hence, with decreasing charge density, the magnitude of ΔH_{hyd} decreases down the group. B: Solubility of Group II sulfate decreases down the group. C: Down the group as the charge density of the metal ion decreases, its polarisation power decreases, thus there is less weakening of the C - O bond resulting in greater stability. D: Tendency to form complexes should be decreasing as the charge density of the metal ion decreases down the group.
18. C Blood red seen is due to the complex formed in the following reaction: $\begin{array}{c} [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{SCN}^- \rightleftharpoons \\ \text{H}_2\text{O} + [\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+} \text{ Blood red} \end{array}$ In the presence of an alkali, red- brown precipitate of iron(III) hydroxide is formed as well thus diluting the blood red colour making the letters appear orange brown. $\begin{array}{c} [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightleftharpoons \\ 3\text{H}_2\text{O} + [\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3](\text{s}) \text{ red-brown ppt} \end{array}$	19. D Energy level diagram indicates in the single reaction step, the reactant(s) undergo bond breaking only ie reactant(s) absorb energy. There is no bond formation taking place. Hence, true for option D only. In options A and C, bond formation only occurs. In option B, there is bond breaking followed by bond formation in the reaction.
20. A Oxo reaction: $\text{CH}_2 = \text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{H} \quad \text{C} = \text{O} \\ \\ \text{H} \end{array}$ Similarly for but-2-ene, $\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{CO} + \text{H}_2 \rightarrow \begin{array}{c} \text{CH}_3\text{CH} - \text{CHCH}_3 \\ \quad \\ \text{H} \quad \text{C} = \text{O} \\ \\ \text{H} \end{array}$	21. A 2,4-DNPH and $\text{I}_2/\text{NaOH}(\text{aq})$ doesn't react with X and Y. X is an ester, not a carbonyl compound. Y reacts with $\text{NaOH}(\text{aq})$, but it doesn't give observable result. Y reacts with Na to give effervescence of H_2.
22. D $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_2\text{CH}_2\text{OH} \\ \text{Cr}_2\text{O}_7^{2-}/\text{H}^+ \downarrow \\ \text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_2\text{CO}_2\text{H} \end{array}$ which goes through hydrogenation to form $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$.	23. A Nucleophilic substitution gives $\text{CH}_3\text{CH}_2\text{OD}$. B) oxidation to give CH_3CO_2^- C) Elimination to give $\text{CH}_2 = \text{CH}_2$ D) Condensation to give $\text{CH}_3\text{CO}_2\text{CH}_3$

24. C

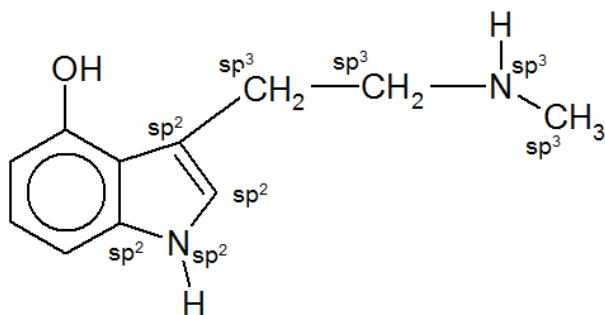
Z is an aldehyde and contains –OH group. Upon reduction by H_2 , **Z** forms a product that contains chiral carbon and no plane of symmetry.

- A) Does not contain –OH
 B) Is not an aldehyde
 C) Contains –OH and aldehyde. Product of reduction reaction is a chiral compound.



- D) Product from reduction
 $\text{CH}_2(\text{OH})\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ does not have chiral carbon.

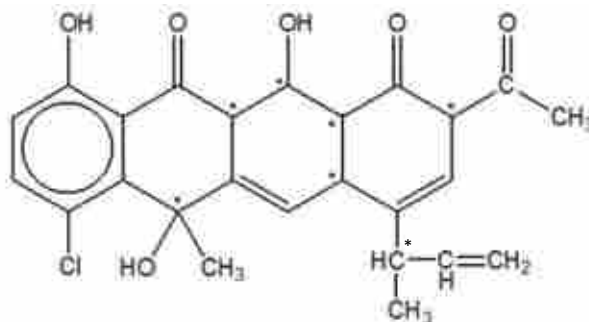
25. C



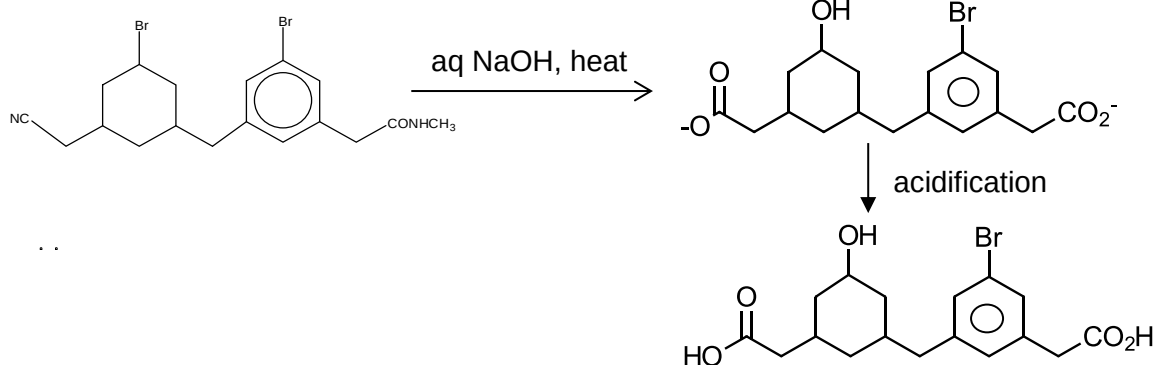
As shown in the diagram above, there is no sp^3 C atom overlapping with sp^2 N atom.

26. B

Maximum number of stereoisomers = $2^{n+m} = 2^{7+0}$
 There are 7 chiral carbons in compound. There isn't any C=C that can display cis-trans isomerism.

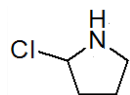


27. B



28. A

The lower the pK_b , the stronger the base. Hence, molecules should be arranged from weakest base to the strongest base.



is the least basic due to the close proximity of the electron withdrawing Cl atom, which decreases the electron density on the N atom.



is the most basic due to the presence of two electron release groups, and the absence of any electron withdrawing groups.

29. A

Trypsin treatment:

		arg			arg	gly

Chemotrypsin treatment:

	tyr	arg	tyr		arg	gly
	tyr	arg		tyr	arg	gly

Cyanogen bromide treatment:

	tyr	arg	tyr	met	arg	gly
	tyr	arg	met	tyr	arg	gly

x

Primary structure:

pro–tyr–arg–met–tyr–arg–gly

Note: A much faster way would be to analyse the options given, instead of solving in the forward direction.

30. D

General rules

Taking the neutral form of the dipeptide into account,

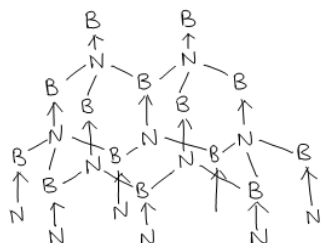
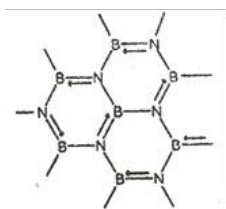
If $\text{pH} > \text{pI}$, $-\text{COOH}$ will be deprotonated, resulting in a negatively charged dipeptide

If $\text{pH} < \text{pI}$, $-\text{NH}_2$ will be protonated, resulting in a positively charged dipeptide

If $\text{pH} = \text{pI}$, the dipeptide is electrically neutral

$\text{pH } 7.4 > \text{pI of carnosine (pI} = 6.83) \rightarrow \text{deprotonation}$

31. B

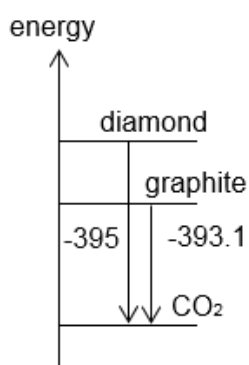


In the cubic structure, each B atom is bonded covalently to 4 N atoms in a tetrahedral manner, where one of the bonds is a dative bond (where N lone pair of electron is donated to B atom).

Like graphite, there are extensive van der Waals forces of attraction between the layers in hexagonal boron nitride.

Option 3 is incorrect. The boron-nitrogen bond in hexagonal boron nitride is shorter and stronger than that in cubic boron nitride, due to the pi bond present. Each B atom uses all its three valence electrons to form covalent bonds with three neighbouring nitrogen atoms. Each nitrogen atom still has a lone pair of electrons which it uses to form a dative pi-bond with an adjacent boron atom.

32. C



33. A

$$E^{\ominus}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V} \text{ \& } E^{\ominus}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

For anode, oxidation: select $E^{\ominus}$ that is more negative. Hence, Zn is preferentially discharged. 1 is correct.

For cathode, reduction: select $E^{\ominus}$ that is more positive.

$$E^{\ominus}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V} \text{ \& } E^{\ominus}_{\text{H}^{+}/\text{H}_2} = +0.00 \text{ V}$$

Hence, H_2 evolved.

$\text{H}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \frac{1}{2}\text{H}_2(\text{g})$, effervescence observed. 2 is correct

$[\text{H}^{+}]$ decreases, pH of solution increases. 3 is correct.

34. B

Statement 1 is correct. Increasing the temperature favours the endothermic (forward) reaction, and by Le Chatelier's principle, the position of equilibrium will shift to the right.

Statement 2 is correct. Since $\text{Fe}_3\text{O}_4(\text{s})$ and $\text{FeO}(\text{s})$ are both in solid states, they are not part of the K_c expression. $K_c = [\text{CO}_2(\text{g})] / [\text{CO}(\text{g})]$ Therefore K_c has no units.

Statement 3 is not correct. Adding a solid reactant or product does not affect the position of equilibrium.

35. D

1. pH of aqueous solution of chlorides decreases from 6.5 (MgCl_2) to 1 (PCl_5).
2. maximum oxidation states of the elements in the chlorides increases from MgCl_2 to PCl_5 .
3. All are insulators in the solid state from MgCl_2 to PCl_5 .

36. B

Option 1: Due to its greater nuclear charge, Cu has a higher atomic mass and smaller atomic volume. Hence, its density is higher than Ca.

Option 2: Metallic bond for Cu is stronger since both 3d and 4s electrons are delocalised compared to the 4s electrons only for Ca. Hence, more energy is needed during melting accounting

	for its higher m pt. Option 3: Electrical conductivity for Cu should be higher since it has a greater number of delocalised electrons (both 3d and 4s) to conduct electricity compared to the 4s electrons only for Ca.
37. A Statement 1 is correct. The magnitude of the equilibrium constant is large ($\gg 100$), which implies the position of equilibrium lies far to the right. Statement 2 is correct. Since K_2 is larger in magnitude than K_1, it implies that en has a higher tendency to replace the water ligands than ammonia. Statement 3 is correct.	$K_{\text{stab}} = \frac{[\text{Ni}(\text{NH}_3)_6]^{2+}}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+}[\text{NH}_3]^6}$ $K'_{\text{stab}} = \frac{[\text{Ni}(\text{en})_3]^{2+}}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+}[\text{en}]^3}$ $K''_{\text{stab}} = \frac{[\text{Ni}(\text{en})_3]^{2+}[\text{NH}_3]^6}{[\text{Ni}(\text{NH}_3)_6]^{2+}[\text{en}]^3}$ $= \frac{[\text{Ni}(\text{en})_3]^{2+}}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+}[\text{en}]^3} \times \frac{[\text{Ni}(\text{H}_2\text{O})_6]^{2+}[\text{NH}_3]^6}{[\text{Ni}(\text{NH}_3)_6]^{2+}}$ $= K'_{\text{stab}} / K_{\text{stab}}$
38. B Statements 1 and 2 are correct. Reactant in stage III is saturated, it cannot undergo addition reaction. Stage III is elimination.	
39. D Option 1 is correct. Protonation of R-groups of the residues in the tertiary structure disrupts existing ionic interactions and hydrogen bonds between them, which results in denaturation. Option 2 is incorrect. The amide functional group in the peptide linkages are neutral, and will not react with H^+ Option 3 is incorrect. Primary structure is only affected during hydrolysis. Complete hydrolysis will only occur when ovalbumin is heated for a prolonged period of time under highly acidic conditions, e.g. $6 \text{ mol dm}^{-3} \text{ HCl(aq)}$, heat for a few hours.	40. C Option 1 is incorrect. Both compounds react with aqueous bromine to give a white ppt. Option 2 is correct. The alkyl side chain on the benzene ring will undergo oxidation as long as there is a H atom present at the benzylic position. Purple acidified KMnO_4 will be decolourised. Option 3 is correct. The $-\text{NH}_2$ of the phenylamine will undergo nucleophilic substitution with CH_3Br. The Br^- leaving group will form a cream ppt with AgNO_3.



PRELIMINARY EXAMINATIONS

HIGHER 2

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CHEMISTRY
9647/02

Paper 2 Structured Questions

29th August 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	/ 12
2	/ 15
3	/ 12
4	/ 9
5	/ 24
Paper 1	/ 40
Paper 3	/ 80
Total	

This document consists of **21** printed pages.

Answer **all** the questions

1 Planning (P)

Potentiometric titration is a technique similar to direct titration of a redox reaction and can be used to determine the concentration of a reducing ion such as Fe^{2+} without the use of an indicator. It involves measurement of E_{cell} at intervals as an oxidising titrant is added. The titration is carried out on one side of a cell whose other half is a reference electrode which can be a standard hydrogen electrode or a calomel electrode.

Consider the titration of Fe^{2+} with standard Ce^{4+} , the course of which is monitored potentiometrically as shown in Figure 1 below. The reference electrode used is the calomel electrode shown in Figure 2.

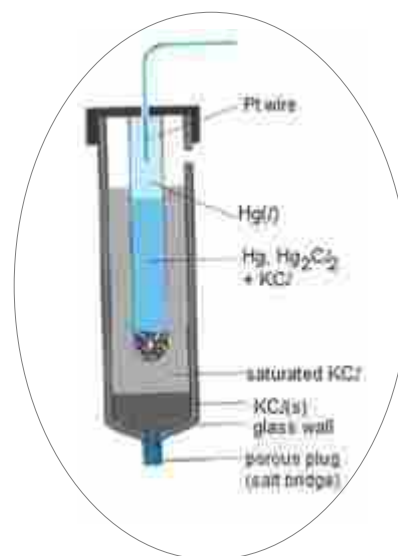
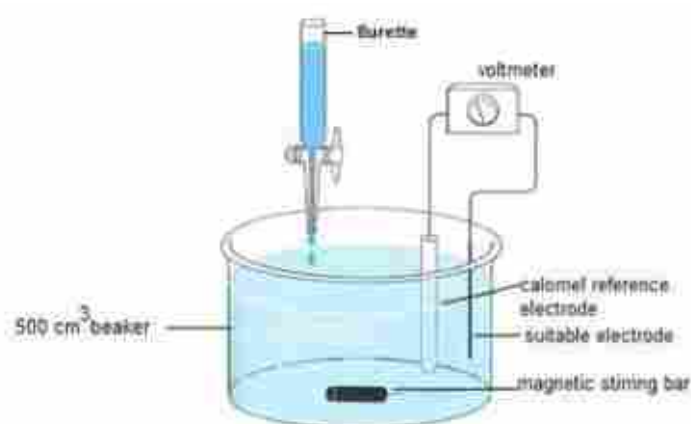
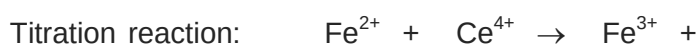


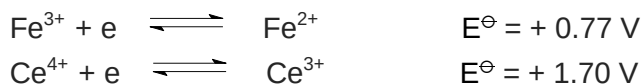
Figure 1: Set-up for potentiometric titration



To follow the course of the reaction, a pair of electrodes is inserted into the reaction mixture. At the calomel reference electrode,



At the suitable electrode, there are two reactions that will come to equilibrium:



As the Ce^{4+} titrant is added, Fe^{2+} is oxidised to Fe^{3+} and the cell potential is controlled by the ratio of reduced and oxidised iron according to the Nerst equation which causes the potential to rise as more iron becomes oxidised.

$$E_{\text{cell}} = \left\{ E^\ominus (\text{Fe}^{3+}/\text{Fe}^{2+}) - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - 0.24 \dots\dots\dots(1)$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed, and the

potential will then be controlled by the concentration ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$. Thus beyond the end-point the potential rises rapidly to that of a $\text{Ce}^{4+}/\text{Ce}^{3+}$ cell with excess Ce^{4+} .

$$E_{\text{cell}} = \left\{ E^{\ominus}(\text{Ce}^{4+}/\text{Ce}^{3+}) - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - 0.24 \dots\dots\dots(2)$$

A graph of E_{cell} against volume of titrant added can be drawn and the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Solution **FA 1** was prepared by dissolving 0.960 g of 'iron tablets' in 100 cm^3 of 1 mol dm^{-3} HClO_4 acid. By titration method using KMnO_4 , the percentage of iron(II) ions in the iron tablets used to make **FA 1** was found to be 12.5%. A student wishes to verify the percentage of iron(II) ions present in **FA 1** by potentiometric titration using standard 0.100 mol dm^{-3} Ce^{4+} solution.

- (a) Suggest a suitable electrode for the potentiometric titration between Fe^{2+} and Ce^{4+} solution.

Suitable indicator electrode: Pt
[1]

- (b) Perform a pre-calculation to estimate the end-point volume for the potentiometric titration of 100 cm^3 of **FA 1** with 0.100 mol dm^{-3} Ce^{4+} solution.

- No of moles of Fe^{2+} in 100 cm^3 of **FA 1** = $(0.125 \times 0.960) \div 55.8 = 0.00215 \text{ mol}$
 - Vol of Ce^{4+} required to reach the end-point = $(0.00215 \div 0.100) \text{ dm}^3 = 21.50 \text{ cm}^3$
- [1]

- (c) Using all the above information including the estimated end-point volume, you are required to write a plan to verify the percentage of Fe^{2+} present in **FA 1** by potentiometric titration.

You may assume that you are provided with the following:

- ◆ 100 cm^3 of **FA 1** solution prepared by dissolving 0.960 g of 'iron tablets' in 1 mol dm^{-3} HClO_4 acid.
- ◆ 1.25 mol dm^{-3} Ce^{4+} solution
- ◆ a calomel reference electrode
- ◆ a suitable electrode
- ◆ a voltmeter
- ◆ the apparatus normally found in a school laboratory.

Your plan should include details of

- ◆ the preparation of 0.100 mol dm^{-3} Ce^{4+} solution
- ◆ how the electrochemical cell set-up in Figure 1 is assembled

- ♦ how you would recognize that the end-point has been reached
- ♦ a table for the recording of readings needed for the plotting of titration curve, showing suitable volumes of titrant added
- ♦ the calculation to verify the percentage of Fe^{2+} in **FA 1** in terms of the end-point volume, $V_0 \text{ cm}^3$ of Ce^{4+}

Preparation of the standard $0.100 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution

1. Using a burette, transfer 20.00 cm^3 of $1.25 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution directly into a 250 cm^3 standard flask.
 2. Make up to the mark with distilled water. Stopper and shake well to obtain a homogeneous solution.
- 1m—correct volume for dilution using burette/pipette for measurement.*
1m- using a standard & logical procedure in the preparation

Procedure to record cell potential in the potentiometric titration

1. Transfer the given 100.0 cm^3 of FA 1 solution into a 500 ml beaker.
2. Fill a burette with the prepared $0.100 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution.
3. Assemble the apparatus as shown in Figure 1.
4. Titrate FA 1 solution with Ce^{4+} solution. Read and record the cell voltage registered on the voltmeter as each aliquot of Ce^{4+} solution is introduced from the burette. Carry out a more careful titration by adding titrant in small increments as the volume gets close to the equivalence point.
5. The end-point volume is reached when the E_{cell} value switches from cell potential based on $\text{Fe}^{3+}/\text{Fe}^{2+}$ to one based on $\text{Ce}^{4+}/\text{Ce}^{3+}$.

Table of readings

Volume of Ce^{4+} solution added / cm^3	$E_{\text{cell}} / \text{V}$
5.00	
10.00	
15.00	
17.00	
19.00	
21.00	
23.00	
25.00	
30.00	
35.00	
40.00	
45.00	

1m – Procedure on the assembly of set-up as in figure 1 and titrating carefully by adding titrant in small increments nearing the end-point

1m - how to recognize that the end-point had been passed

1m – table of readings with volume exceeding 21.50 cm^3 of Ce^{4+} solution

Calculation of % of Fe^{2+} in **FA 1** in terms of end-point volume, $V_0 \text{ cm}^3$ of Ce^{4+} solution

• No of moles of Ce^{4+} used = $0.100V_0 \div 1000 \text{ mol} = 10^{-4} V_0$

= no of moles of Fe^{2+} present in 100 cm^3 of FA 1

Mass of Fe^{2+} present in 0.960 g of iron tablets = $10^{-4} V_0 \times 55.8 = 5.58 \times 10^{-3} V_0 \text{ g}$

Hence % of Fe^{2+} in FA 1 = $(5.58 \times 10^{-3} V_0 \div 0.960) \times 100 = 0.581V_0 \%$

[6]

(d) Use the Nerst equation (1) and (2) to calculate the E_{cell} values when

(i) $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$ and

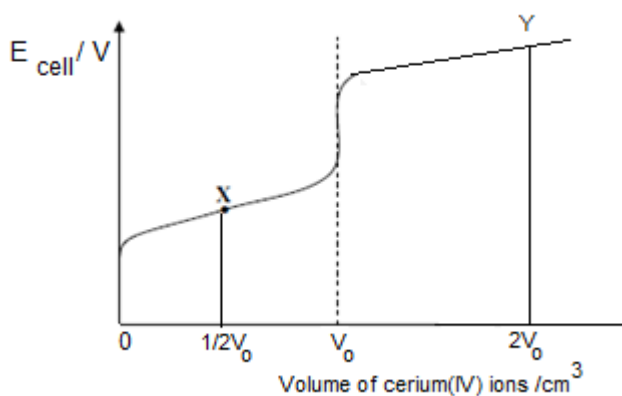
(ii) $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$.

(i) $E_{\text{cell}} = +0.53 \text{ V}$

(ii) $E_{\text{cell}} = +1.46 \text{ V}$

[1]

(e) If the end-point volume is $V_0 \text{ cm}^3$ of Ce^{4+} , sketch the graph you would expect to obtain. Show clearly in your sketch, the titration volumes in terms of V_0 when you will be obtaining the E_{cell} values calculated in (d)(i) and (d)(ii).



• Shape of titration with axes clearly labelled.

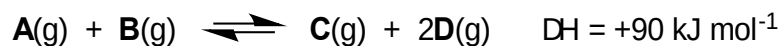
• E_{cell} at X = +0.53 V at $\frac{1}{2}V_0$ when $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$

• E_{cell} at Y = +1.46 V at $2V_0$ when $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$

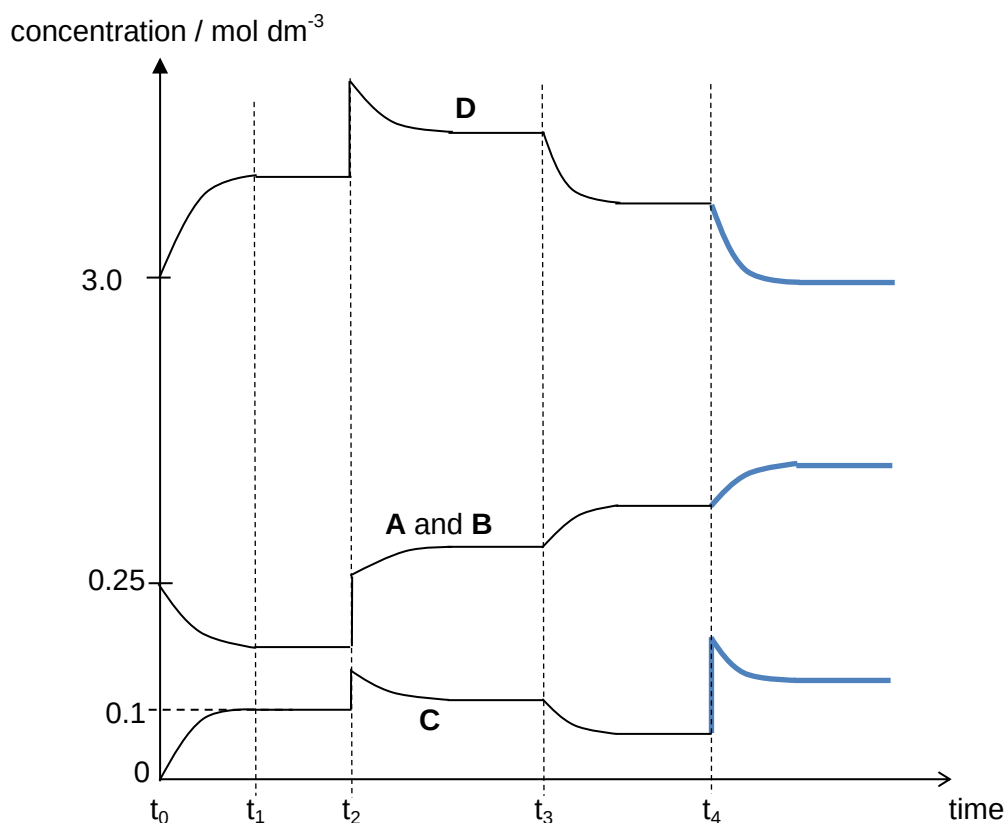
[3]

[Total:12]

2 Gases **A** and **B** react as shown in the equation given.



Gases **A**, **B** and **D** were injected into a vessel at 25 °C and allowed to reach dynamic equilibrium. The graph below (not drawn to scale) shows how the concentration of the four gases varies with time.



(a) (i) Explain what is meant by *dynamic equilibrium*.

- When a reversible reaction reaches a state of dynamic equilibrium, reaction continues to occur but the rates of the forward and backward reactions are equal such that there is no net change in the concentrations of the reactants and products.

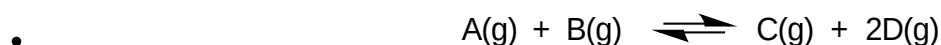
[1]

(ii) Write an expression for K_c for this equilibrium, stating the units.

- $K_c = \frac{[\text{C}][\text{D}]^2}{[\text{A}][\text{B}]} \text{ mol dm}^{-3}$

[1]

(iii) Calculate the value for K_c at time, t_1 .



Initial conc. / mol dm ⁻³	0.25	0.25	0	3.0

Change in conc. / mol dm ⁻³	- 0.1	- 0.1	+ 0.1	+ 0.2

Equil. conc. / mol dm ⁻³	0.15	0.15	0.1	3.2

$$\bullet K_c = 0.1 \times 3.2^2 / 0.15 \times 0.15 = 45.5 \text{ mol dm}^{-3}$$

[2]

(b) (i) State *Le Chatelier's principle*.

- If a system at dynamic equilibrium is subjected to a change which disturbs the equilibrium, the system will respond in such a way so as to counteract the effect of the change so as to re-establish the equilibrium.

[1]

At time, t_2 , the volume of the system was reduced which lead to an increase in concentration of the gases. This causes the position of the equilibrium to shift.

(ii) Suggest and explain what happens to the system between time t_3 to t_4 .

- Position of equilibrium shifts to the left as concentration of A and B increases gradually and concentration of C and D decreases gradually.
- Since the backward reaction is exothermic, hence the temperature of the system must have been decreased at time, t_3 .

[2]

(iii) Sketch on the same axes how the concentration of the four gases will change when more gas **C** was introduced at time, t_4 .

- Sharp increase in [C] followed by decrease in [C], decrease in [D] and increase in [A]&[B]
- Decrease in [D] is twice the increase in [A], [B] and [C]. Equilibrium [C] should not be lower than the initial [C] at t_4 .

[2]

(iv) State and explain the effect of the presence of a catalyst on the equilibrium position and the value of the equilibrium constant.

- A catalyst have no effect on the equilibrium position and the value of K_c .

- The presence of catalyst increases the rate of the forward and backward reaction to the same extent. ($K_c = k_f / k_b \Rightarrow K_c$ constant.)

[2]

- (c) The standard Gibbs free energy change of reaction, ΔG° in J mol^{-1} , is related to the equilibrium constant by the following equation.

$$\Delta G^\circ = -RT \ln (0.02478K_c)$$

- (i) Using your answer in (a)(iii), calculate ΔG° in kJ mol^{-1} .

$$\bullet \Delta G^\circ = \frac{-8.31 \times 298 \times \ln (0.02478 \times 45.5)}{1000} = -0.297 \text{ kJ mol}^{-1}$$

[1]

- (ii) Explain the significance of the sign of your answer in (c)(i).

- Since $\Delta G^\circ < 0$, the reaction is spontaneous at room temperature.

[1]

- (iii) Using your answer in (c)(i) and any other information on page 7, calculate ΔS° .

$$\bullet \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

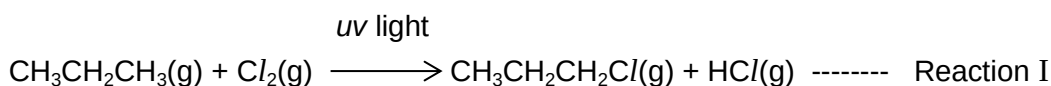
$$\bullet \Delta S^\circ = [90 - (-0.297)] / 298 = +303 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note: sign must be shown

[2]

[Total: 15]

- 3 (a) 1- chloropropane can be synthesized by the following reaction at room temperature.



With reference to the *Data Booklet*, calculate ΔH_r° of Reaction I.

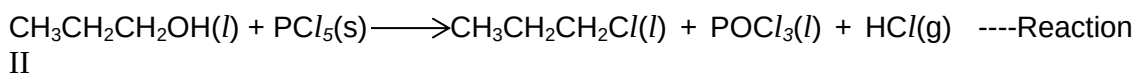
Bonds broken: 1 C-H bond, 1 Cl-Cl bond

Bonds formed: 1 C-Cl bond, 1 H-Cl bond

$$\bullet \Delta H_r^\circ = +(410+244) - (340+431) \\ = -117 \text{ kJ mol}^{-1}$$

[1]

- (b) An alternate method of synthesis of 1-chloropropane is as follows:



- (i) Suggest one reason why Reaction II is a better method to produce 1-chloropropane than Reaction I.

• Reaction I can undergo further free-radical substitution to give a mixture of halogenoalkanes thus the yield is much lower compared to Reaction II.

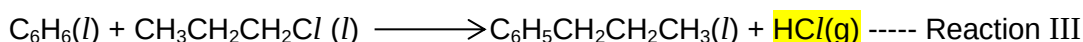
[1]

- (ii) Suggest whether the standard change in entropy of Reaction II is likely to be positive or negative, explaining your reasoning.

• ΔS° is likely to be positive.
 • This is because in the reaction, gaseous molecules are formed & highly disordered. There are more ways to arrange the molecules and distribute the energy.

[2]

- (c) 1-chloropropane is an important reactant in the synthesis of propylbenzene:



- (i) Define standard enthalpy change of formation.

The standard enthalpy change of formation of a substance, ΔH_f° , is the enthalpy change when one mole of the substance is formed from its constituent elements in their standard states at 298 K and 1 atm.

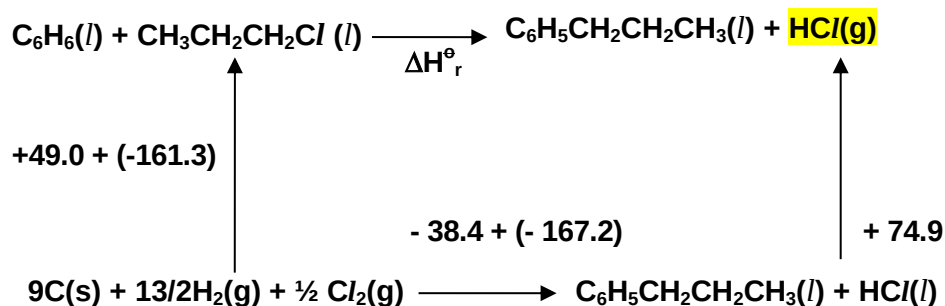
[1]

- (ii) Using the data listed below,

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l)$	-161.3
$\text{HCl}(l)$	-167.2
$\text{C}_6\text{H}_6(l)$	+49.0
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3(l)$	-38.4

enthalpy change of vapourisation of HCl is $+74.9 \text{ kJ mol}^{-1}$

construct an energy cycle to calculate ΔH_r° of Reaction III.

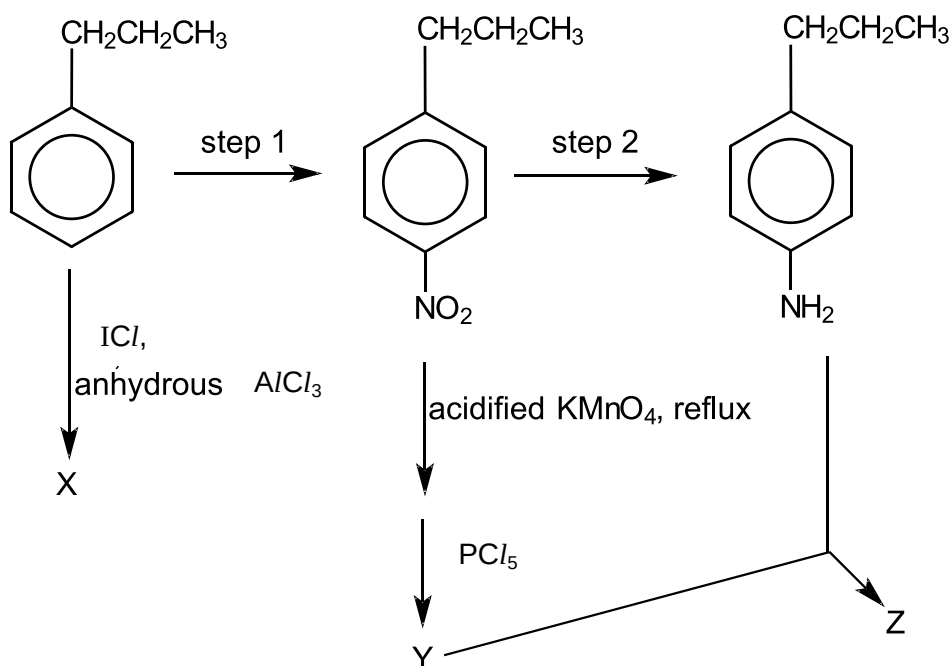


• correct energy cycle (state symbols and coefficients)

By Hess' Law, $+49.0 + (-161.3) + \Delta H_r^\ominus = -38.4 + (-167.2) + 74.9$
 $\Delta H_r^\ominus = -18.4 \text{ kJ mol}^{-1}$

[2]

- (d) Propylbenzene is a fuel additive and solvent. It undergoes the following chemical reactions.



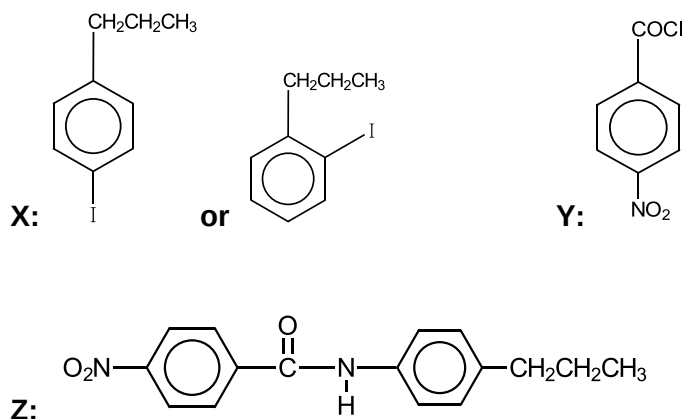
- (i) State the reagents and conditions for the following steps:

Step 1 : Concentrated H_2SO_4 , concentrated HNO_3 , reflux $\leq 60^\circ\text{C}$

Step 2 : Heat under reflux with Sn, concentrated HCl, followed by NaOH (aq)

[2]

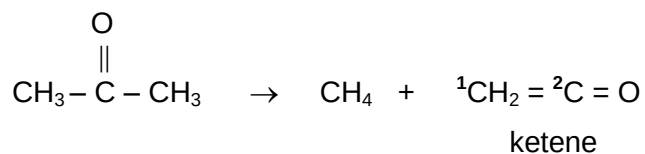
- (ii) Draw the structural formula of the organic compounds X, Y and Z.



[3]

[Total:12]

- 4 When propanone vapour is passed over a heated filament, it breaks down into methane and a reactive substance called ketene.

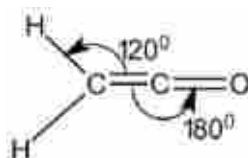


- (a) (i) Draw the hybrid orbitals around each of the 2 carbon atoms, ^1C and ^2C in ketene molecule. State the type of hybridization for each carbon atom.

Carbon atom ^1C	Carbon atom ^2C
	
Hybridisation: sp^2	Hybridisation: sp

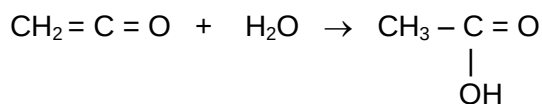
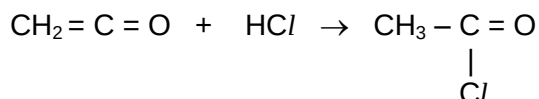
[2]

- (ii) Draw the displayed formula for the ketene molecule and on it show suggested values of the bond angles around ^1C and ^2C atoms.



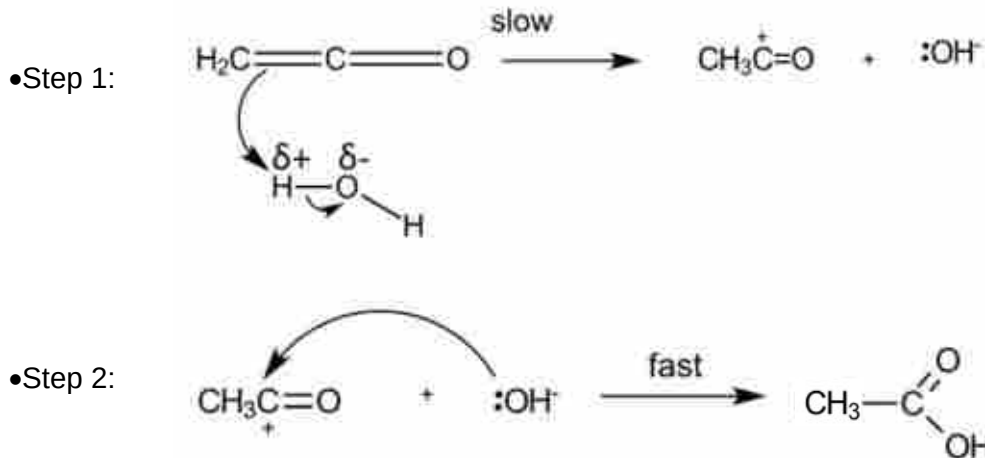
[1]

Ketene is a highly reactive compound. It readily undergoes the reactions shown below.



- (b) Name and describe the mechanism for the reaction between ketene and water, showing all charges and using curly arrows to show the movement of electron pairs.

- Name of mechanism: Electrophilic Addition



[3]

- (c) Ketene reacts with ethanol to form a sweet smelling compound **P**, $\text{C}_4\text{H}_8\text{O}_2$, which reacts with LiAlH_4 to give **Q**. Identify **P** and **Q**. Name the type of reaction for the transformation of **P** to **Q**.
-

$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C} \\ \diagdown \\ \text{OCH}_2\text{CH}_3 \end{array}$	$\text{CH}_3-\text{CH}_2\text{OH}$
P	Q

Type of reaction from **P** to **Q**: Reduction

[3]

[Total: 9]

- 5 Ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, reacts with sodium hydroxide to form sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. One of the main application of ethanedioate ions is in rust-removal, as ethanedioate forms water-soluble derivatives with iron(III) ions.

- (a) An electrochemical cell is set up using Cu^{2+}/Cu and $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cells. The electrode in $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell is the negative electrode and the cell potential is +0.77 V.

- (i) Using relevant data from the Data Booklet, determine the electrode potential of the $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell.

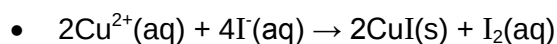
$$\begin{aligned} & \bullet \quad E_{\text{Cu}^{2+}/\text{Cu}}^\ominus = +0.34\text{V} = E_{\text{red}}^\ominus \\ & E_{\text{cell}}^\ominus = E_{\text{red}}^\ominus - E_{\text{ox}}^\ominus \end{aligned}$$

$$+0.77 = +0.34 - E_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}^\ominus$$

$$\bullet \quad E_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}^\ominus = -0.43 \text{ V}$$

[2]

- (ii) A small quantity of solid potassium iodide is added to the Cu^{2+}/Cu half-cell. Write an equation and state the observations for the reaction that will occur in this half-cell. Hence, predict and explain the effect on the e.m.f. of the electrochemical cell.

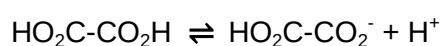


- White ppt in brown solution/ brown ppt observed in the Cu^{2+}/Cu half-cell.

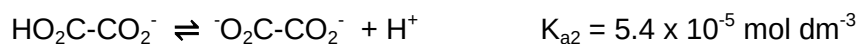
- Since CuI is formed, the $[\text{Cu}^{2+}(\text{aq})]$ will decrease. $E_{\text{Cu}^{2+}/\text{Cu}}$ (E_{red}) will become more negative and the e.m.f. of the electrochemical cell will be less positive/ decrease.

[3]

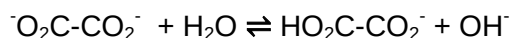
- (b) The K_a values for the step-wise dissociation of ethanedioic acid are given below.



$$K_{a1} = 5.6 \times 10^{-2} \text{ mol dm}^{-3}$$



Calculate the pH of 0.10 mol dm^{-3} of sodium ethanedioate salt, $\text{Na}_2\text{C}_2\text{O}_4$.



- $[\text{OH}^-] = \sqrt{K_{b,c}} = \sqrt{0.10 \times 10^{-14} / (5.4 \times 10^{-5})} = 4.30 \times 10^{-6} \text{ mol}$
- $\text{pH} = 14 - \lg(4.30 \times 10^{-6}) = 8.63$

[2]

- (c) Hydrated salt of magnesium ethanedioate has the formula $\text{MgC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. When 6.18 g of hydrated magnesium ethanedioate is heated strongly, a white solid **W** and three gases **X**, **Y** and **Z** are generated. Gases **X**, **Y** and **Z** are passed through anhydrous calcium chloride, followed by aqueous sodium hydroxide. The flasks containing anhydrous calcium chloride and aqueous sodium hydroxide had an increase in mass of 1.50 g and 1.83 g respectively. The residual gas **Z** occupied 1 dm^3 at room temperature and pressure. Gas **Z** is poisonous and can be heated with oxygen to give gas **Y**.

- (i) Suggest the identities of **W**, **X**, **Y** and **Z**.

- **W**: MgO , **X**: H_2O
 - **Y**: CO_2 , **Z**: CO
- Any 2 correct = 1 mark

[2]

- (ii) Hence, determine the value of n , showing your working clearly.

- No. of moles of $\text{CO} = 1/24 = 0.0417 \text{ mol}$
- Mass of $\text{CO} = 0.0417 \times (12.0 + 16.0) = 1.17 \text{ g}$
- Mass of $\text{MgO} = 6.18 - 1.50 - 1.83 - 1.17 = 1.68 \text{ g}$
- No. of moles of $\text{MgO} = 1.68 / (24.3 + 16.0) = 0.0417 \text{ mol}$
- No. of moles of $\text{H}_2\text{O} = 1.50 / 18.0 = 0.0833 \text{ mol}$
- $n = 0.0833 / 0.0417 = 2$

[3]

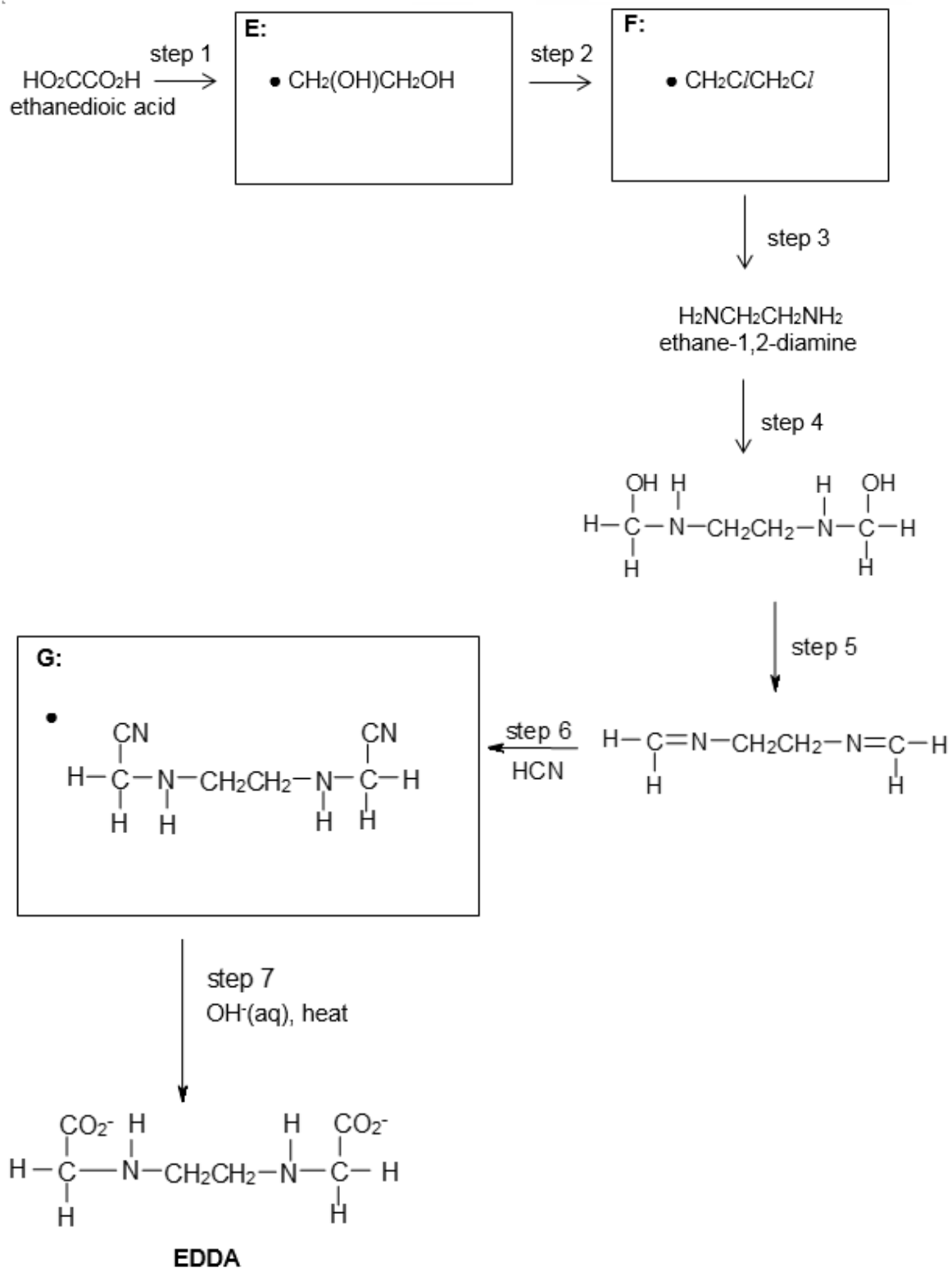
- (iii) Ethanedioate ions form insoluble precipitates with many metal ions, one of which is calcium ethanedioate, a primary constituent of kidney stones.

Calcium ethanedioate decomposes in the same manner as magnesium ethanedioate. Using relevant data from the Data Booklet, deduce whether calcium ethanedioate would decompose at a higher or lower temperature than magnesium ethanedioate. Explain your reasoning.

- Ionic radius of $\text{Ca}^{2+} = 0.099 \text{ nm}$, $\text{Mg}^{2+} = 0.065 \text{ nm}$
- Ca^{2+} is larger than Mg^{2+} , hence possesses smaller charge density / lower polarising power. Electron cloud of $\text{C}_2\text{O}_4^{2-}$ is distorted to a smaller extent and the C-O bond is weakened to a smaller extent.
- Calcium ethanedioate has a higher decomposition temperature.

[3]

- (d) A tetradentate ligand, ethylenediamine-N,N'-diacetate (EDDA) ion, can be synthesised from ethanedioic acid through a series of steps. Ethanedioic acid is first converted to ethane-1,2-diamine through a 3-step synthesis. Steps 4 to 7 represent the mechanism of Skrecker synthesis, which can be used to synthesise amino acids.



- (i) Propose the 3-step synthesis for the formation of ethane-1,2-diamine from

ethanedioic acid, naming the reagents and conditions used in each step. Draw the structures of the intermediate compounds **E** and **F** in the spaces provided in the synthetic route.

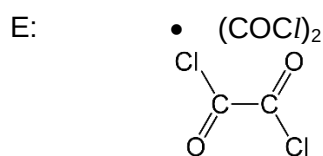
Step 1: • Anhydrous LiAlH_4 , dry ether as solvent, room temperature

Step 2: • $\text{PCl}_5(\text{s})$, cold

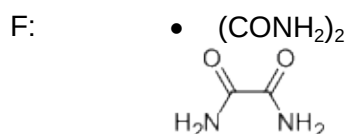
Step 3: • Excess conc NH_3 in ethanol, heat in sealed tube

Alternative Answer:

Step 1: • $\text{PCl}_5(\text{s})$, cold



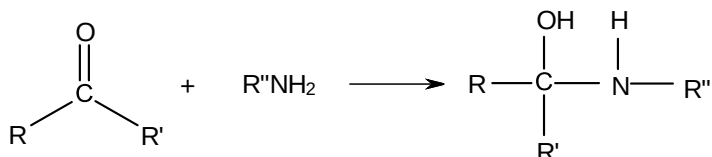
Step 2: • $\text{NH}_3(\text{g})$, room temperature



Step 3: • Anhydrous LiAlH_4 , dry ether as solvent, room temperature

[5]

(ii) Carbonyl compound and amine react in the following way.



Step 4 of the synthetic route in **(d)** involves the reaction of ethane-1,2-diamine with 2 moles of a carbonyl compound. Identify the carbonyl compound.

• CH_2O

[1]

(iii) Draw the structure of compound **G** in the space provided.

[1]

(iv) State the types of reaction in step 5 and step 7.

Step 5: • Elimination

Step 7: • Alkaline hydrolysis

[2]

[Total: 24]



CHEMISTRY
Paper 3 Free Response

9647/03
13th September 2016
2 hours

Candidates answer on separate paper.

Additional materials: Answer paper
 Graph Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group, Centre number and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of 15 printed pages.

Answer any **four** questions

- 1 Ethanedioic acid is a substance found in many plant foods. Cabbage is among the plant foods with high ethanedioic acid content. However, its anion, $\text{C}_2\text{O}_4^{2-}$ can bind to iron to form iron (II) ethanedioate, which renders much of the iron in cabbage unusable by the body.

- (a) 50.0 cm^3 sample of iron(II) ethanedioate, FeC_2O_4 was extracted from 300 g of cabbage, diluted in water and the solution made up to 250 cm^3 . A 25.0 cm^3 portion of this solution was acidified and required 26.90 cm^3 of 0.0100 mol dm^{-3} potassium manganate(VII) for oxidation of iron(II) to iron(III) and ethanedioate ions to carbon dioxide.

- (i) State the change in oxidation number for manganese and carbon in the reaction.

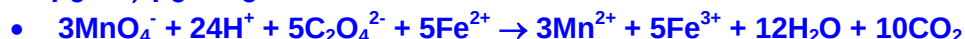
[1]

Mn: From +7 to +2 [Or decrease by 5]

C: From +3 to +4 [Or increase by 1]

- (ii) Write down all the relevant ion-electron half equations and hence the overall redox equation for the reaction between potassium manganate(VII) and iron(II) ethanedioate.

[2]



- (iii) Calculate the concentration, in mol dm^{-3} , of iron(II) ethanedioate in the original sample

[2]

$$\bullet \text{Number of moles of FeC}_2\text{O}_4 \text{ in } 25.0 \text{ cm}^3 = \frac{5}{3} \times 2.69 \times 10^{-4} \\ = 4.48 \times 10^{-4} \text{ mol}$$

$$\text{Number of moles of FeC}_2\text{O}_4 \text{ in } 250 \text{ cm}^3 = 4.48 \times 10^{-4} \times 250/25.0 \\ = 4.48 \times 10^{-3} \text{ mol}$$

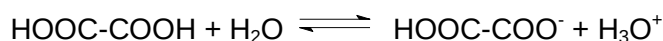
$$\bullet \text{Concentration of FeC}_2\text{O}_4 \text{ in the original sample} = \frac{4.48 \times 10^{-3}}{50 \times 10^{-3}} \\ = 0.0896 \text{ mol dm}^{-3}$$

- (iv) Calculate the number of moles of iron in each gram of cabbage.

[1]

$$\bullet \text{No. of moles of iron per gram of spinach} = \frac{4.48 \times 10^{-3}}{300} \\ = 1.49 \times 10^{-5} \text{ mol/g}$$

- (b) Ethanedioic acid dissociates in water according to the following equation.



The table below compares the K_a values of three organic acids.

	Formula	K_a
Ethanoic acid	CH_3COOH	1.74×10^{-5}
Ethanedioic acid	$\text{HO}_2\text{CCO}_2\text{H}$	6.46×10^{-2}
Oxoethanoic acid	$(\text{CHO})\text{COOH}$	4.79×10^{-4}

With reference to the K_a values, comment on the order of acidity of the three organic acids. [2]

The bigger the K_a , the stronger the acid. Acid strength is dependent on the stability of the anion formed when the acid ionises. The more stable the anion, the stronger is the acid.

Strength of acid: Ethanedioic acid > Oxoethanoic acid > Ethanoic acid

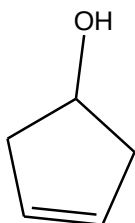
- Oxoethanoic acid is a stronger acid than ethanoic acid as -CHO group is electron withdrawing. The negative charge on the anion is dispersed, thereby stabilizing the ion compared to ethanoate ion.

- Ethanedioic acid is the strongest acid as stabilisation of the monoanion by intramolecular hydrogen bonding with the unionised -COOH group results in the highest K_a value compared with the other two acids.

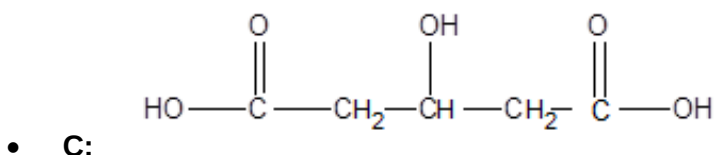
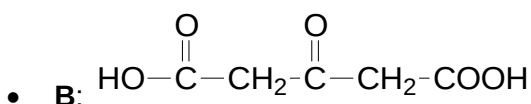
- (c) Compound **A**, with molecular formula $\text{C}_5\text{H}_8\text{O}$, decolourises aqueous bromine and reacts with PCl_5 giving off white fumes. Upon refluxing **A** with acidified potassium manganate(VII), a symmetrical product **B**, $\text{C}_5\text{H}_6\text{O}_5$, is formed. **B** does not give a red precipitate with Fehling's solution but an orange precipitate is observed with 2,4-dinitrophenylhydrazine. 1 mole of **B** also reacts with 1 mole of Na_2CO_3 with effervescence observed. **B** reacts with NaBH_4 to form **C**. Deduce the structures of compounds **A**, **B** and **C**, explaining the chemistry of the reactions involved. [8]

- **A** decolourises aqueous bromine $\Rightarrow \text{C}=\text{C}$ present
- **A** reacts with PCl_5 giving off white fumes of $\text{HCl} \Rightarrow -\text{OH}$ present
- **A** undergoes oxidation with KMnO_4 where the $-\text{OH}$ group is oxidised and $\text{C}=\text{C}$ in a ring undergoes total bond cleavage to form **B**
OR **A** undergoes oxidation with KMnO_4 to give a symmetrical product **B** with no loss in C atoms $\Rightarrow \text{C}=\text{C}$ is in a ring and **A** is a cyclic compound
- **B** does not give a red precipitate with Fehling's solution but form an orange precipitate with 2,4-dinitrophenylhydrazine $\Rightarrow \text{B}$ is a ketone and **A** is a 2° alcohol

- 1 mole of B also reacts with 1 mole of $\text{Na}_2\text{CO}_3 \Rightarrow$ B has 2 $-\text{COOH}$ groups.
- B reacts with NaBH_4 to form C $\Rightarrow$ only the carbonyl group in B is reduced but the carboxylic acid groups remain unaffected.



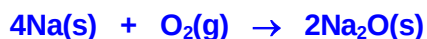
• A:



(9 marking points: Maximum 8)

- (d) (i) Describe what you see when separate samples of sodium and sulfur are burned in excess air. Write equations for the reactions that occur. [2]

Sodium burns readily with a brilliant yellow flame in air or oxygen to form white sodium oxide, Na_2O .



Sulfur burns slowly with a blue flame on heating in air or oxygen to form colourless sulfur dioxide, SO_2 . (Note: SO_3 is not formed)



- Both equations correct
- Both observations correct

- (ii) The products resulting from the reactions in (d)(i) both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

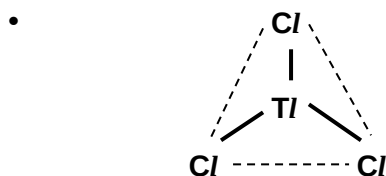
- $\text{Na}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)}$
Universal Indicator turns violet.
- $\text{SO}_2\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_3\text{(aq)}$
Universal Indicator turns red.

[Total: 20]

- 2 Thallium is a Group III element discovered in 1861, and its toxicity was quickly noted. Thallium isotopes and compounds have useful applications, sometimes despite their toxic nature.

(a) Thallium forms compounds similar to aluminium, and thallium(III) chloride and thallium(III) fluoride have very different structures and bonding.

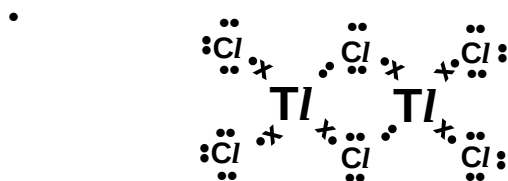
- (i) Draw and state the shape of thallium(III) chloride, $TlCl_3$.
[1]



Trigonal planar

- (ii) In gaseous phase, thallium(III) chloride is able to form a compound with a M_r of 621. Draw a dot-and-cross diagram of this compound, and state the $Cl-Tl-Cl$ bond angle.
[2]

Based on the M_r , the compound is Tl_2Cl_6 .



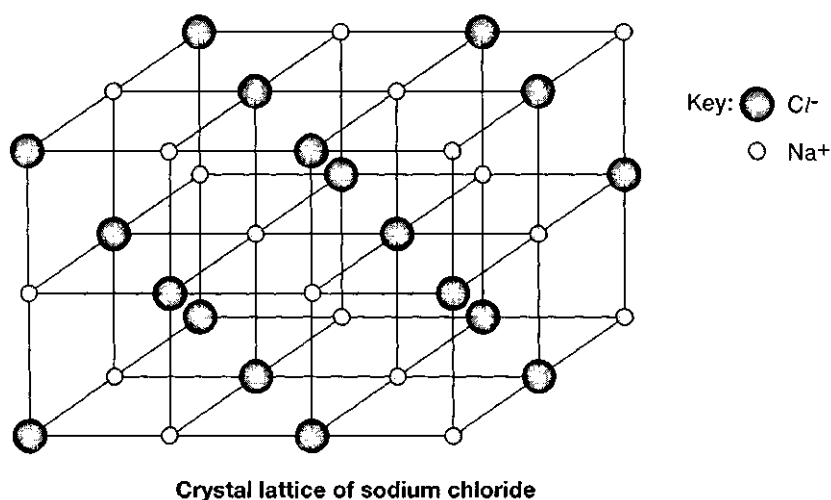
• **109.5°**

- (iii) Explain, in terms of structure and bonding, why thallium(III) fluoride has a high melting point of 550 °C.
[2]

- **Thallium(III) fluoride exists as a giant ionic lattice structure and**
- **a large amount of energy is needed to break strong ionic bonds between oppositely charged ions.**

- (iv) Thallium is also able to form thallium(I) chloride, which is crystalline in nature.

In the crystal lattice of sodium and potassium chlorides, the co-ordination number of each ion is 6. In the crystal lattice of thallium(I) chloride, $TlCl$, the co-ordination number has a different value.

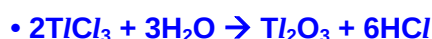


Suggest an explanation for the co-ordination number in the $TlCl$ lattice being different from those in $NaCl$ and KCl .
 [1]

- The size of the Tl^+ cations is larger than the Group I cations such as Na^+ and K^+ . More chloride ions can be packed around the larger Tl^+ cations.

- (b) Thallium(III) chloride, $TlCl_3$, reacts with hot water to produce thallium(III) oxide precipitate and hydrochloric acid.

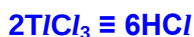
- (i) Write a balanced equation for the above reaction.
 [1]



- (ii) In an experiment, a 15 g impure sample of thallium(III) chloride ($M_r = 310.5$) was mixed with hot water, and filtered. Water was then added to the filtrate to make a standard solution in a 250 cm^3 volumetric flask. A 25.0 cm^3 aliquot was titrated against 0.5 mol dm^{-3} aqueous sodium hydroxide, requiring a titre of 22.00 cm^3 . Determine the percentage purity of the sample.

You may assume that the impurities are insoluble in water and are inert.

[2]



No of moles of NaOH = $0.022 \times 0.5 = 0.0110 \text{ mol}$

No of moles of HCl produced from the sample = $0.0110 \times 10 = 0.110 \text{ mol}$

No of moles of TlCl_3 in sample = $0.110 / 3 = 0.0367 \text{ mol}$

Mass of TlCl_3 in sample = $310.5 \times 0.0367 = 11.4 \text{ g}$

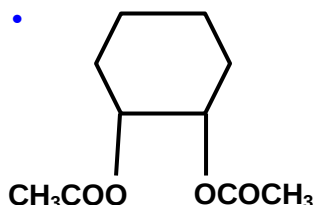
Percentage purity of TlCl_3 in sample = $11.4 / 15 \times 100\% = 76.0\%$

- (c) Thallium(I) sulfate ($M_r = 504.1$) was often employed as a rodenticide and is highly poisonous. The lethal dosage is 16 ppm of the rat's mass. Assuming a typical rat has a mass of 230 g, determine the number of moles of thallium(I) sulfate needed to kill a rat. [2]

• Mass of thallium(I) sulfate needed for lethal dosage = $230 \times 16 / 10^6 = 0.00368 \text{ g}$

• No of moles of thallium(I) sulfate needed = $0.00368 / 504.1 = 7.30 \times 10^{-6} \text{ mol}$

- (d) Thallium(III) ethanoate, $\text{Tl}(\text{CH}_3\text{CO}_2)_3$, is able to react with an alkene through addition. When cyclohexene reacts with thallium(III) ethanoate, a compound with the molecular formula $\text{C}_{10}\text{H}_{16}\text{O}_4$ is formed. Suggest the structural formula of this compound, and state the number of stereoisomers that this compound has. [2]



• This compound has a cis- and a trans-isomer, and the trans-isomer is optically active with two enantiomers. Therefore this compound will have 3 stereoisomers.

- (e) ^{201}Tl is an isotope of thallium that is often used in medical diagnostics due to its radioactive decay by electron capture with emission of gamma rays. The electronic configuration of the Tl atom is $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$.

Electron capture is a process in which a proton-rich nucleus of an atom absorbs one electron from the first or second quantum shell to change one proton into a neutron.

- (i) Suggest the species formed, including the nucleon number, when ^{201}Tl undergoes electron capture. [1]

• ^{201}Hg

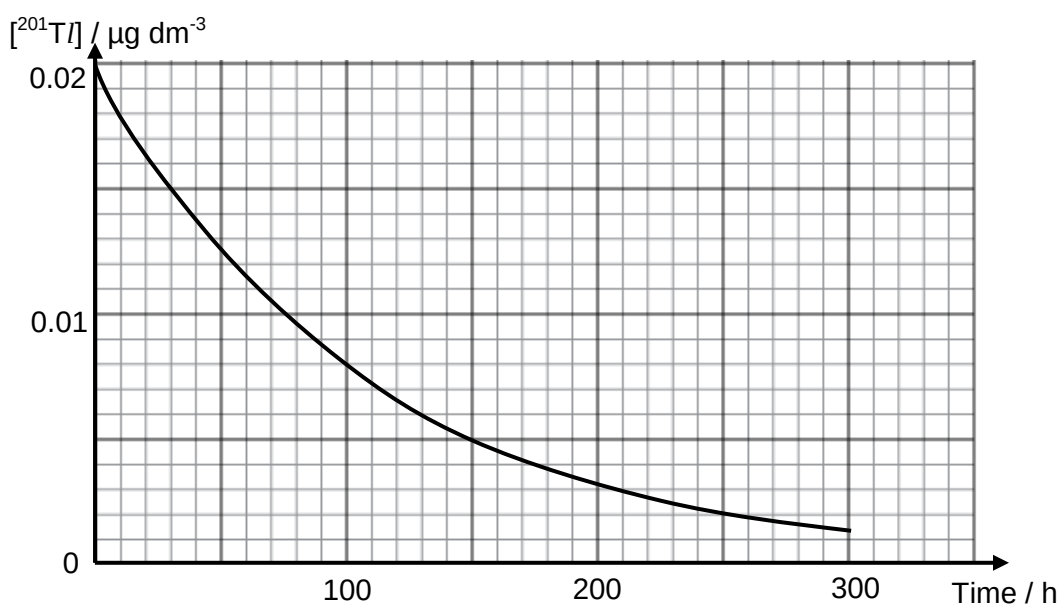
- (ii) The species formed immediately after electron capture is known to be in excited state, before returning to ground state by emitting gamma rays.

Name the orbital where the excited electron is most likely located in, and explain why **high energy** gamma rays are emitted when the species return to ground state.

[2]

- 6p. (can accept any orbital of higher energy than 6p)
- When the electron capture occurs, an inner shell (1 or 2) is now short of an electron. The 6p electron is at a high energy level, and needs to release a large amount of energy to replace the absorbed electron in shell 1 or 2 as the atom returns to ground state.

- (iii) A patient is typically injected with $0.02 \mu\text{g}$ of thallium for heart diagnosis. The following graph shows the radioactive decay (through electron capture) of a $0.02 \mu\text{g}$ sample of ^{201}Tl dissolved in 1 dm^3 of inert solvent.



Using the graph, deduce the order of reaction for the radioactive decay of ^{201}Tl .
[2]

- From the graph, $(t_{1/2})_1 = (t_{1/2})_2 = 75 \text{ h}$. Since $t_{1/2}$ is constant,
- order of reaction is 1.

- (iv) Hence, write the rate equation for this reaction and determine the rate constant, stating its units.
[2]

- rate = $k[^{201}\text{Tl}]$
- $k = \ln 2 / t_{1/2} = \ln 2 / 75 \text{ h} = 0.00924 \text{ h}^{-1}$

[Total: 20 m]

3 The halogens and organic halides are useful laboratory reagents and have many applications.

- (a) State and explain the difference in the reactions of chlorine and iodine with sodium thiosulfate respectively. Write balanced equations for the reactions. [3]



• **Oxidising power of the halogens decreases down the group as can be seen from the less positive E value, hence iodine can only oxidise thiosulfate to tetrathionate.**



- (b) Deduce which gas, fluorine or chlorine, would behave more ideally at low pressure. Explain your answer. [1]

• **Fluorine gas will behave more ideally. The electron cloud size of chlorine is larger than fluorine, hence the van der Waals forces of attraction is stronger.**

Organic halides are a group of compounds comprising alkyl halides, ethenyl halides and aryl halides.

Alkyl halides are used as solvents for relatively non-polar compounds. They are also used as the starting materials for the synthesis of many compounds.

- (c) Alcohols react with hydrogen halides to produce alkyl halides.

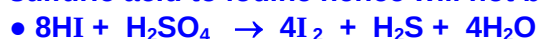
- (i) Suggest the type of reaction that occur. [1]

• **Nucleophilic substitution**

- (ii) 2-iodopropane is formed from propan-2-ol in the presence of sodium iodide and concentrated phosphoric acid.

Explain, with the aid of an equation, why concentrated sulfuric acid is not used. [2]

• **The hydrogen iodide produced will be readily oxidised by concentrated sulfuric acid to iodine hence will not be available to react with the alcohol.**

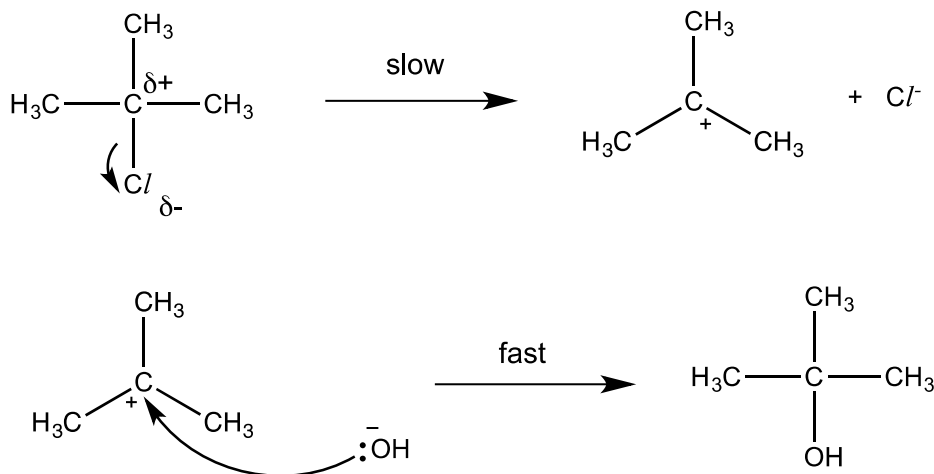


(d) 2-chloro-2-methylpropane undergoes alkaline hydrolysis to form 2-methylpropan-2-ol.

(i) Name and describe the mechanism of the hydrolysis of 2-chloro-2-methylpropane. [3]

• Nucleophilic substitution S_N1

• •



(ii) With the aid of the *Data Booklet*, explain what will happen to the rate of reaction if 2-bromo-2-methylpropane was used instead. [2]

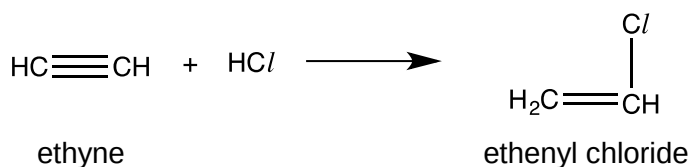
• $BE(C-Cl) = 340 \text{ kJ mol}^{-1}$

$BE(C-Br) = 280 \text{ kJ mol}^{-1}$

• Since bond energy of C-Cl is higher than that of C-Br, the bond strength of C-Cl is greater than that of C-Br. Hence the reactivity of the alkyl halides decreases in the order $RBr > RCl$. The rate of reaction will increase

(e) Ethenyl chloride is an important industrial chemical mainly used to produce the polymer, PVC.

Ethyne reacts with anhydrous hydrogen chloride gas over a mercuric chloride catalyst to give ethenyl chloride.



(i) With the aid of the *Data Booklet*, determine the enthalpy change of the reaction. [2]

• • $\Delta H_r = \text{enthalpy change for bond break} + \text{enthalpy change for bond form}$
 $= BE(H-Cl) + BE(C \equiv C) - [BE(C-Cl) + BE(C-H) + BE(C=C)]$
 $= 431 + 840 - (340 + 410 + 610) = -89 \text{ kJ mol}^{-1}$

(ii) Explain why ethenyl chloride does not undergo alkaline hydrolysis readily. [1]

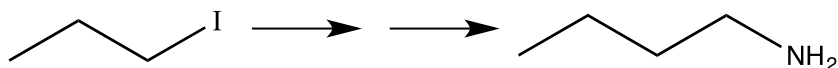
• The lone pair of electrons on chlorine delocalised across the double bond resulting in partial double bond character in C-Cl bond, hence a stronger C-Cl

bond which is harder to break.

OR

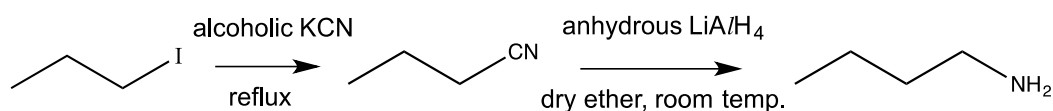
- The nucleophile is unlikely to attack the carbon-carbon double bond as it is electron rich.

- (f) 1-iodopropane can be converted to butylamine via a two-stage synthesis. Butylamine is then used as an ingredient in the manufacture of pesticide.



- (i) Suggest reagents and conditions for the two stages. Draw the structure of the intermediate compound. [3]

•••



- (ii) Suggest a chemical test to distinguish between 1-iodopropane and 1-chloropropane. [2]

• **Procedure:**

Step: (1) Boil RX with NaOH(aq).

(2) Acidify with dilute HNO₃.

(3) Add AgNO₃(aq).

OR

Boil with silver(I) ethanoate in alcohol.

• White precipitate (AgCl) observed for 1-chloropropane.

Yellow precipitate (AgI) observed for 1-iodopropane.

[Total: 20]

- 4 Co-Cr alloys are most commonly used to make artificial joints including knee and hip joints due to high wear-resistance and biocompatibility. However in 2010, faulty Co-Cr alloy hip joints manufactured by DePuy was removed from market due to leakage of toxic chromium and cobalt into the body muscles and blood stream.

(a) State the electronic configurations of

- (i) an _____ atom _____ of _____ chromium, [1]



- (ii) the Co^{3+} ion. [1]



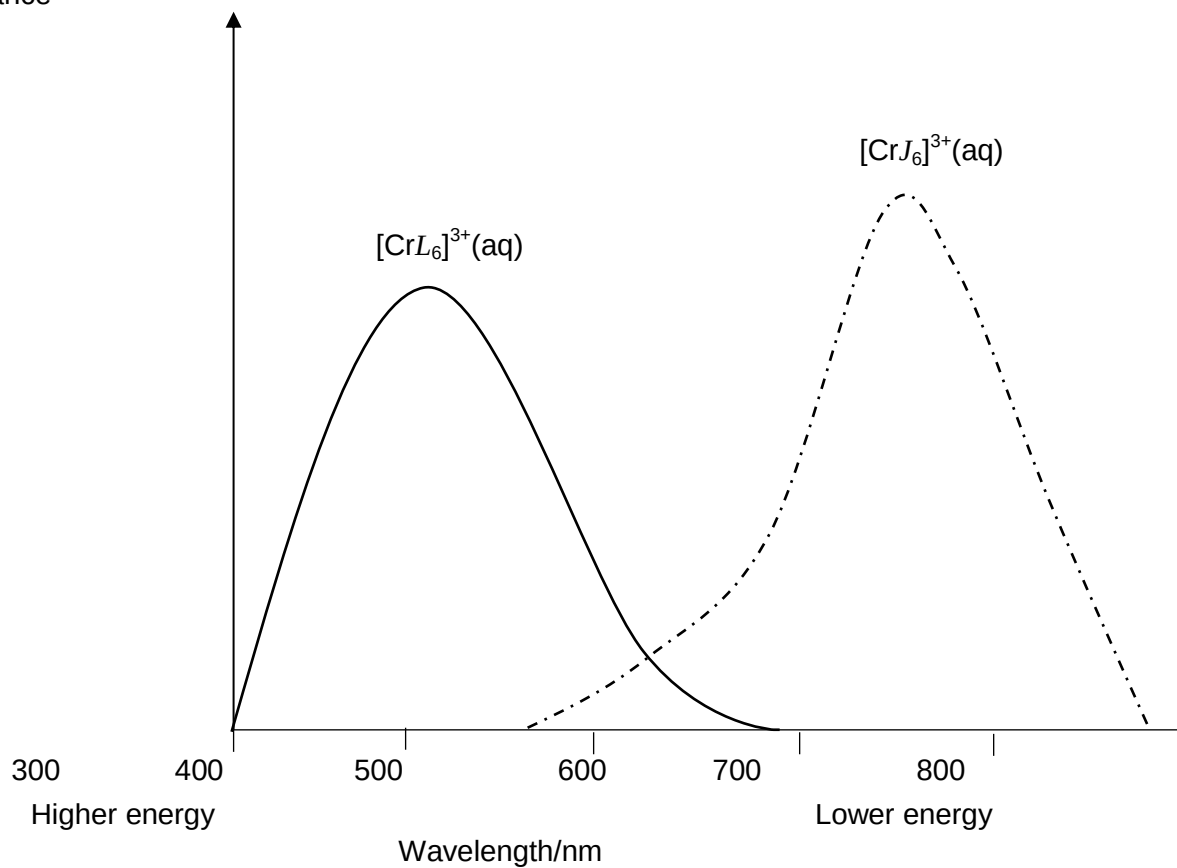
(b) Why are transition metal complexes coloured? [3]

- Transition metal complexes are often coloured due to the presence of partially filled d-orbitals in the metal ion.
- In complexes, the presence of ligands causes a splitting of the energy of d orbitals into 2 groups with an energy gap, ΔE , between them.
- When a d-electron from lower energy group is promoted to the higher energy group (d-d transition), radiation in the visible region of the electromagnetic spectrum corresponding to ΔE is absorbed.
Light energy that is not absorbed will be seen as the colour of the complex.

- (c) The colour of the complexes can be measured by a spectrometer. The amount of light absorbed is expressed as an absorbance value. The higher the absorbance, the more of a particular wavelength of light is being absorbed.

The spectrum below shows the major absorption peaks for $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$.

Relative
absorbance



The wavelengths associated with each colour of light are given below.

colour	Wavelength/nm
Violet	400-430
Blue	430-490
Green	490-570
Yellow	570-590
Orange	590-620
red	620-750

(i) What are the colours of $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$? [2]

- $[\text{CrL}_6]^{3+}(\text{aq})$: yellow/orange
- $[\text{CrJ}_6]^{3+}(\text{aq})$: green/blue

(ii) What deduction can be made from the spectra about the size of the d-orbital splitting in the two complexes? [2]

- The d-orbital splitting for $[\text{CrL}_6]^{3+}(\text{aq})$ is larger than $[\text{CrJ}_6]^{3+}(\text{aq})$
- because electrons in lower d-subshell absorbs energy in shorter wavelength and higher energy to excite to higher d-subshell, ΔE is larger.

Cobalt forms many complexes with ligands such as H_2O , NH_3 and $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$. The most common oxidation states of cobalt are +2 and +3.

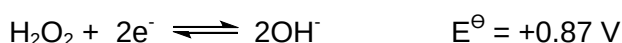
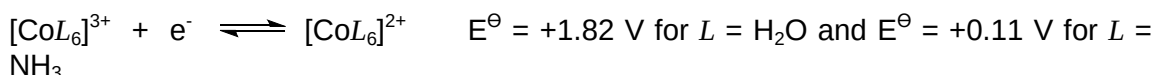
Cations containing cobalt in these two oxidation states have significantly different colours even when the ligands are the same.

(d) When H_2O_2 is mixed with pink $\text{Co}^{2+}(\text{aq})$ solution, no significant colour change is observed.

When $\text{Co}^{2+}(\text{aq})$ is mixed with excess $\text{NH}_3(\text{aq})$ a slight colour change occurs and cation **Q** is formed.

When cation **Q** is mixed with H_2O_2 , a reddish brown solution is observed.

$E^\ominus$ data for the cobalt complex ions and hydrogen peroxide are given below.



Suggest an explanation for the above observations, giving equations where appropriate and identify the cation **Q**. [5]

$$E^\ominus_{\text{Co}^{3+}/\text{Co}^{2+}} = +1.82 \text{ V}$$

$$E^\ominus_{\text{H}_2\text{O}_2/\text{OH}^-} = +0.87 \text{ V}$$

- $E^\ominus_{\text{H}_2\text{O}_2/\text{H}_2\text{O}}$ is less positive than $E^\ominus_{\text{Co}^{3+}/\text{Co}^{2+}}$, H_2O_2 is unable to oxidise $\text{Co}(\text{aq})^{2+}$ to $\text{Co}(\text{aq})^{3+}$ and there is no ligand exchange reaction taking place. Hence, no colour change.
- When excess NH_3 is added, a ligand exchange reaction occurs. NH_3 replaces H_2O ligands, resulting in a slight colour change.

$$[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$$
[explanation & equation: 1m]
- Cation **Q** is $[\text{Co}(\text{NH}_3)_6]^{2+}$.

$$E^\ominus_{[\text{Co}(\text{NH}_3)_6]^{3+} / [\text{Co}(\text{NH}_3)_6]^{2+}} = +0.11 \text{ V}$$

$$E^\ominus_{\text{H}_2\text{O}_2/\text{OH}^-} = +0.87 \text{ V}$$

$$E^\ominus_{\text{cell}} = +0.87 - (+0.11) = +0.76 \text{ V} > 0$$

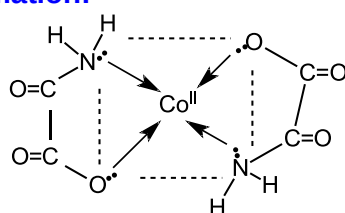
When H_2O_2 is added to Q,

- H_2O_2 oxidises Co^{2+} in $[\text{Co}(\text{NH}_3)_6]^{2+}$ to Co^{3+} in $[\text{Co}(\text{NH}_3)_6]^{3+}$, resulting in a reddish brown solution observed.
- $\text{H}_2\text{O}_2 + 2[\text{Co}(\text{NH}_3)_6]^{2+} \rightarrow 2\text{OH}^- + 2[\text{Co}(\text{NH}_3)_6]^{3+}$

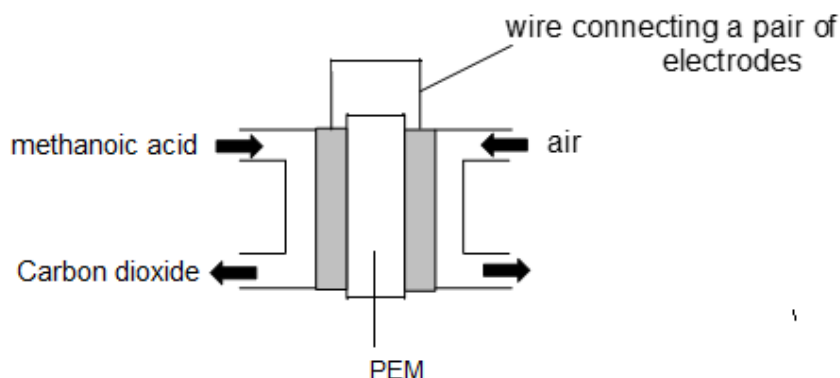
- (e) Explain why the neutral complex formed between a Co^{2+} ion and two $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$ ions is soluble in cyclohexane. [1]

It is a simple covalent molecule. The weak van der Waals' forces of attraction formed between Co-complex and cyclohexane molecules liberate sufficient energy to overcome van der Waals' forces of attraction between Co-complex molecules and those between cyclohexane molecules.

For your information:



The direct oxidation of methanoic acid in a fuel cell, DFAFC, shown below represents potentially the most efficient method of obtaining useful energy from a renewable fuel.



- (f) The electrons pass around the external circuit to the cathode. The protons produced migrate across the proton exchange membrane, PEM, to the cathode, where they react with oxygen from air, producing water.

Write the equations for the anode and cathode reactions. Hence construct the equation for the overall reaction. [2]

- $\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ [Anode]
- $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ [cathode]
- $2\text{HCO}_2\text{H} + \text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$ [overall reaction]

- (g) One method for the construction of DFAFC, involves electroplating a layer of platinum onto the surface of the proton exchange membrane, PEM. The electrolyte for this

process is a solution containing $\text{Pt}(\text{NH}_3)_4^{2+}$ and Cl^- ions. The PEM is the cathode in this electrolytic cell.

- (i) Suggest the half-equation for the cathode reaction that deposits platinum on the PEM.
[1]



- (ii) In one such preparation, a PEM with a surface area of 25 cm^2 was immersed in an electrolyte bath and a current of 0.0875 A was passed for 95 minutes.

Calculate the mass of platinum deposited onto the surface of PEM.
[2]

- $Q = It = 0.0875 \times 95 \times 60 = 498.75 \text{ C}$
 $\text{No of mol of electrons} = 498.75/96500 = 5.17 \times 10^{-3} \text{ mol}$
 $\text{No of mol of Pt deposited} = 5.17 \times 10^{-3}/2 = 2.58 \times 10^{-3} \text{ mol}$
- mass of Pt deposited = $2.58 \times 10^{-3} \times 195 = 0.504 \text{ g}$

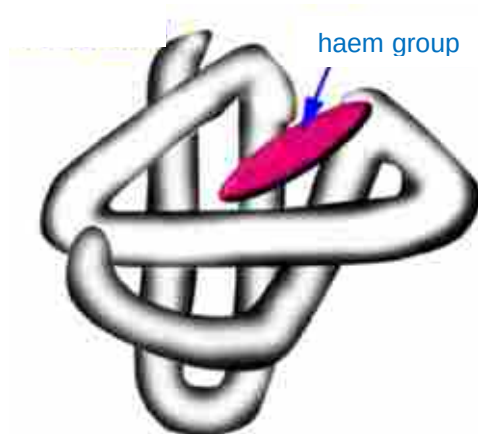
[working : 1m & answer:1m]

[Total: 20]

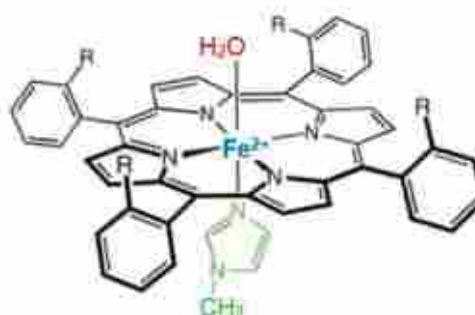
- 5 (a) Myoglobin and haemoglobin are globular proteins that serve to bind and deliver oxygen. The former serves as an intracellular storage site for oxygen in the muscle tissues, while the latter transports oxygen in the bloodstream.

Each myoglobin molecule contains one haem group.

In deoxygenated myoglobin, a water ligand is weakly bound to the Fe^{2+} of the haem group as shown:



Myoglobin



Haem group in deoxygenated myoglobin

- (i) Briefly describe how myoglobin maintains its three-dimensional shape.

[2]

• It is maintained by the interactions between the R-groups of the amino acids, such as • hydrogen bonds between polar groups ($-\text{OH}$, $-\text{NH}_2$), ionic bonds between oppositely charged groups ($-\text{CO}_2^-$ & $-\text{NH}_3^+$), van der Waals' forces of attraction between non-polar side chains (e.g: alkyl group) and disulfide linkages between $-\text{SH}$ groups.

- (ii) In the presence of the haem group, the polypeptide chain coalesces into a myoglobin molecule.

With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

and by considering the chemical interactions involved, explain why this is a spontaneous process at low temperatures.

[2]

• The bending and folding of the primary structure into a tertiary structure is exothermic (negative ΔH) due to the formation of various interactions between the R-groups of the constituent amino acids.

• The process is accompanied by a decrease in entropy (negative ΔS) as the formation of a more ordered myoglobin molecule decreases the degree of disorder because there are now fewer ways in which the molecule and energy can be distributed.

Hence ΔG is negative at low temperatures.

- (iii) Deoxygenated myoglobin is responsible for the dull purplish red muscle colour, observed in the depth of the muscle. When meat is freshly cut, colour change occurs in two stages:

Stage 1: Bright red colour when muscle surface is exposed to air.

Stage 2: With time, the bright red colour slowly changes to an unattractive, dull brown colour associated with stale and spoiled meat.

With reference to the structure of the haem group and the reaction that occurs in each stage, explain the colour changes involved.

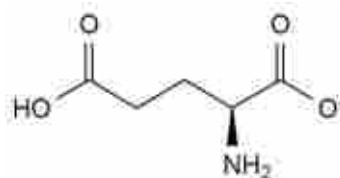
[2]

The colour of meat depends on the ligand attached to the 6th coordinate site in the haem group, and the oxidation stage of the iron centre.

• **When the meat is exposed to oxygen from the air, ligand exchange (oxygenation) occurs to form oxymyoglobin. O_2 replaces H_2O ligand and is dative bonded to the haem group, which gives the bright red colour observed.**

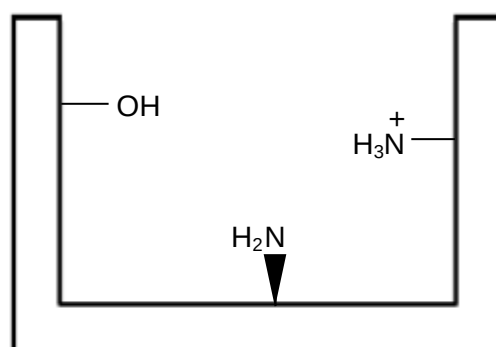
• **When meat has been stored for too long, the Fe^{2+} in the haem group undergoes oxidation to form Fe^{3+} , which gives rise to the dull brown colour.**

- (b) One of the isolated compounds that is primarily responsible for the umami (savory) flavor is glutamate, which is a salt formed from glutamic acid that is commonly found in meat.



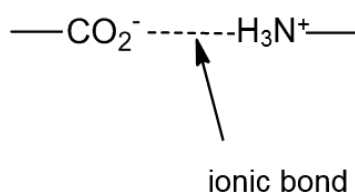
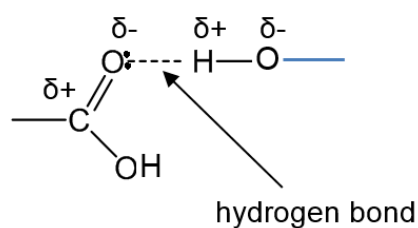
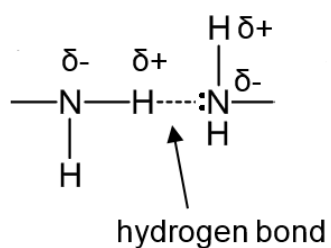
glutamate

It is thought that glutamate stimulates a specific receptor site located in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below:



- (i) State **two** different types of interactions that can be formed between glutamate and the receptor protein. Illustrate your answer with labelled diagram(s). [2]

••Any two illustrated

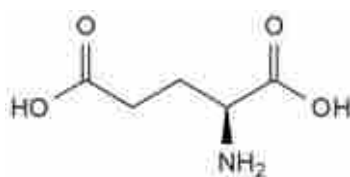


- (ii) To enhance the flavor of food, many retailers in the food industry use monosodium glutamate (MSG) as a food additive, which can be easily synthesized in the laboratory.

Given that laboratory synthesis gives a racemic mixture, explain why 50% of the glutamate synthesized in the laboratory is unable to bind precisely with the correct orientation to the receptor protein. [1]

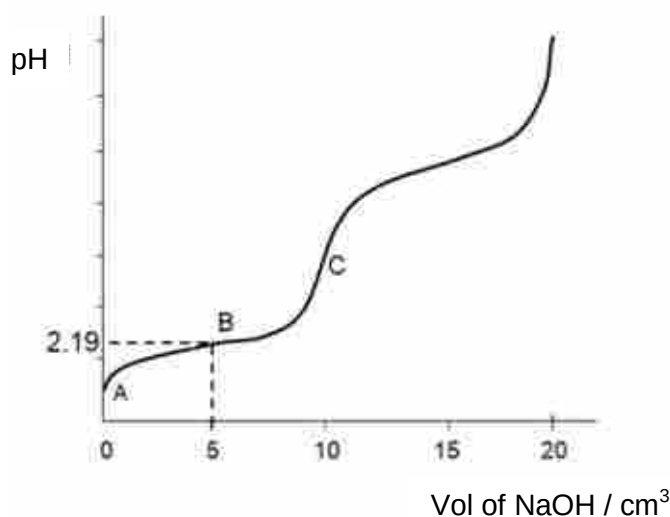
- Only one mirror image form of glutamate synthesized provides the desired biological effect as it has the correct orientation to bind to the protein receptors. The other form is inactive.

The structure of glutamic acid is shown below:



glutamic acid

10 cm³ of the fully protonated glutamic acid is titrated with 20 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution. Its titration curve is shown below:



- (iii) Show that the concentration of glutamic acid is 1.0 mol dm⁻³ at A. [1]

$$n(\text{NaOH}) \text{ used to reach 1}^{\text{st}} \text{ endpoint} = 0.010 \text{ mol}$$

$$n(\text{glutamic acid}) = 0.010 \text{ mol}$$

$$\bullet [\text{glutamic acid}] = 0.010/0.0100 = 1.0 \text{ mol dm}^{-3}$$

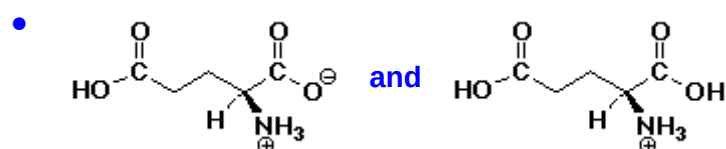
- (iv) Hence, calculate the pH of the solution at **A**.
[1]

$$[\text{H}^+] = \sqrt{K_{a1} \times c} = \sqrt{10^{-2.19} \times 1.0} = 0.0804 \text{ mol dm}^{-3}$$

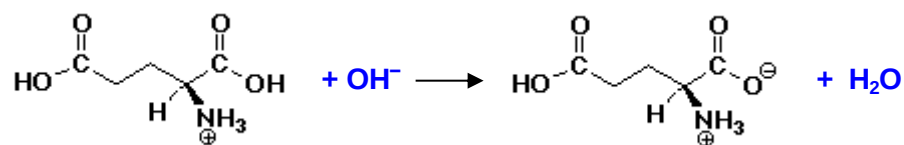
$$\bullet \text{pH at A} = -\log_{10} (0.0804) = 1.10$$

- (v) Identify the specie(s) present at **B**.

With the help of an equation, explain how the solution at **B** can resist a change in pH when a small amount of base is added. [2]



•When a small amount of alkali is added,



Negligible change in pH as OH^- ions are removed.

- (vi) In a separate experiment, the solution at **B** was reacted with 10.0 cm^3 of 0.05 mol dm^{-3} sodium hydroxide.

Calculate the pH of the mixture after the reaction.

You may find it useful to represent the fully protonated glutamic acid as HA.
[2]



$$\text{At point B, } n_{\text{HA}} = n_{\text{A}^-} = 0.010 / 2 = 0.005 \text{ mol}$$

$$\text{Number of moles NaOH added} = 0.05 \times 10/1000 = 5.00 \times 10^{-4} \text{ mol}$$

$$\text{Number of moles HA at equilibrium} = 0.005 - 5.00 \times 10^{-4} \text{ mol} = 0.0045 \text{ mol}$$

$$\text{Number of moles A}^- \text{ at equilibrium} = 0.005 + 5.00 \times 10^{-4} \text{ mol} = 0.0055 \text{ mol}$$

$$\bullet \text{pH} = \text{pK}_a + \lg [\text{salt}]/[\text{acid}]$$

$$= 2.19 + \lg \{(0.0055/0.025) / (0.0045/0.025)\} = 2.28$$

- (c) Compound **P**, $\text{C}_9\text{H}_{11}\text{NO}_2$, rotates plane polarised light and reacts with the following reagents:

- aqueous bromine to give compound **Q**, $\text{C}_9\text{H}_9\text{NO}_2\text{Br}_2$
- sodium carbonate to give a salt
- PCl_5 to give a 5-membered cyclic compound **R**

Deduce the structural formulae of compounds **P**, **Q** and **R**.

[5]

• P rotates plane polarised light → P contains a chiral carbon; has no plane of symmetry and a non-superimposable mirror image.

• P reacts with aq Br₂ to give compound Q, C₉H₉NO₂Br₂

→ P is phenylamine or phenol

→ one of the 2, 4, 6 positions relative to first substituent on benzene is occupied with another substituent

• P reacts with sodium carbonate to give a salt → P contains a –COOH group.

(Hence, P can't be phenol as molecular formula only contains 2 O atoms)

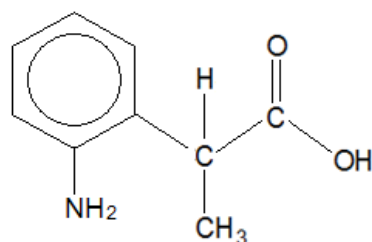
• –OH in –COOH reacts with PCl₅ to give –COCl. Formation of 5-membered ring

→ –NH₂ group in P attacks the electron deficient carbonyl C in the –COCl group.

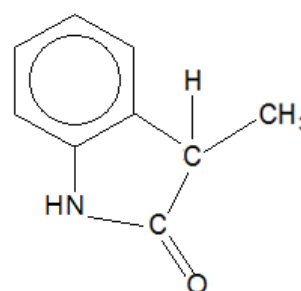
→ –NH₂ group & the other substituent on benzene ring are ortho to each other.

[4 marking points, max 2 marks]

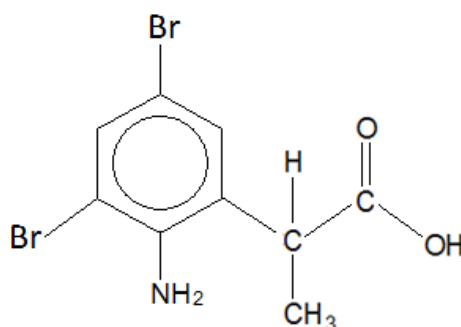
P:



R:



Q:



[1m for each structure]

[Total: 20]



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

22 September 2016

1 hour

Additional Materials: Multiple Choice Answer Sheet
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your NRIC/FIN number, name and CT group on the Answer Sheet.

There are **forty** questions. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choices in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

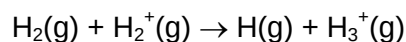
This document consists of **16** printed pages and **0** blank page.

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 *Use of the Data Booklet is relevant to this question.*

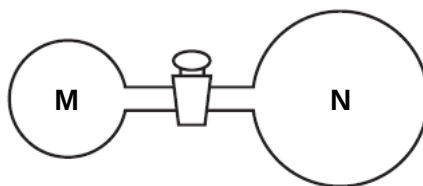
The most common ion–molecule reaction in gas clouds of the Universe is as shown.



What could be the composition of an H_3^+ ion?

	protons	neutrons	electrons
A	2	1	1
B	2	1	2
C	3	0	1
D	3	0	2

- 2 Two glass vessels **M** and **N** are connected by a closed valve.



M contains helium at 20 °C at a pressure of 1×10^5 Pa. **N** has been evacuated, and has three times the volume of **M**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to 100 °C.

What is the final pressure in the system?

- A** 3.18×10^4 Pa
B 4.24×10^4 Pa
C 1.25×10^5 Pa
D 5.09×10^5 Pa
- 3 The shell of a chicken's egg makes up 5% of the mass of an average egg. An average egg has a mass of 50 g.

Assume the egg shell is pure calcium carbonate.

How many complete chicken's egg shells would be needed to neutralise 50 cm³ of 2.0 mol dm⁻³ ethanoic acid?

- A** 1 **B** 2 **C** 3 **D** 4

- 4 Aluminium carbide, Al_4C_3 , reacts readily with aqueous sodium hydroxide. The two products of the reaction are $NaAlO_2$ and a hydrocarbon. Water molecules are also involved as reactants.

What is the formula of the hydrocarbon?

- A** CH_4 **B** C_2H_6 **C** C_3H_8 **D** C_6H_{12}

- 5 Which statement about the ammonium ion, NH_4^+ , is correct?

- A** All bond angles are 107° .
B Ammonium ions are formed when ammonia behaves as an acid.
C Ammonium ions are unreactive when heated with $NaOH(aq)$.
D The bonds are all of the same length.

- 6 2-methylpropan-1-ol and butan-1-ol are structural isomers. 2-methylpropan-1-ol has a lower boiling point.

Which statement explains why the boiling point of 2-methylpropan-1-ol is lower than that of butan-1-ol?

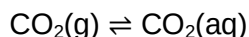
- A** 2-methylpropan-1-ol cannot form hydrogen bonds.
B 2-methylpropan-1-ol has weaker covalent bonds than butan-1-ol.
C 2-methylpropan-1-ol has weaker dispersion forces than butan-1-ol.
D 2-methylpropan-1-ol molecules have more surface area than butan-1-ol molecules.

- 7 The Gibbs free energy change, ΔG_{eq} , is related to the equilibrium constant, K_{eq} , by the following equation.

$$\Delta G_{eq} = -2.303 RT \lg K_{eq}$$

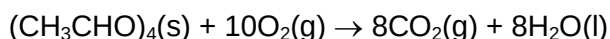
where R is the gas constant and T is the temperature in Kelvin.

Which statement about the following equilibrium is correct?



- A** Increasing the pressure at constant temperature makes ΔG_{eq} more negative.
B Adding a catalyst makes ΔG_{eq} more negative.
C The dissolution of CO_2 in water is spontaneous for all values of K_{eq} .
D At constant temperature, a shift in position of equilibrium to the right results in the same value of ΔG_{eq} .

- 8 Metaldehyde, $(\text{CH}_3\text{CHO})_4$, is used as a solid fuel for camping stoves. The equation for the complete combustion of metaldehyde is shown.



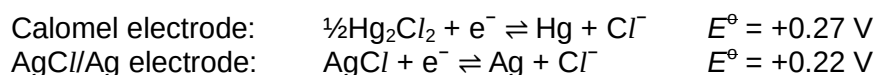
$\Delta H_c^\ominus$ = standard enthalpy change of combustion.

Which expression will give a correct value for the enthalpy change of formation of metaldehyde?

- A $\Delta H_c^\ominus$ metaldehyde – $(8\Delta H_c^\ominus$ carbon + $8\Delta H_c^\ominus$ hydrogen)
- B $\Delta H_c^\ominus$ metaldehyde – $(8\Delta H_c^\ominus$ carbon + $16\Delta H_c^\ominus$ hydrogen)
- C** $(8\Delta H_c^\ominus$ carbon + $8\Delta H_c^\ominus$ hydrogen) – $\Delta H_c^\ominus$ metaldehyde
- D $(8\Delta H_c^\ominus$ carbon + $16\Delta H_c^\ominus$ hydrogen) – $\Delta H_c^\ominus$ metaldehyde

- 9 *Use of the Data Booklet is relevant to this question.*

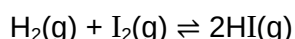
In research laboratories, the standard calomel reference electrode and the AgCl/Ag reference electrodes are often used in place of the standard hydrogen electrode (SHE). Their standard reduction potentials with respect to the SHE are shown below.



A half-cell containing Au^+/Au has a reduction potential of +1.56 V with respect to a calomel electrode.

Which of the following statements is correct?

- A** The reduction potential of the Au^+/Au half-cell with respect to the SHE is +1.83 V.
- B** The reduction potential of the Au^+/Au half-cell with respect to the AgCl/Ag electrode is +1.78 V.
- C** Ag has a higher tendency to be oxidised than H_2 .
- D** Hg_2Cl_2 has a lower tendency to be reduced than AgCl.
- 10 What is the volume of $0.100 \text{ mol dm}^{-3}$ NaOH that should be added to 20 cm^3 of $0.100 \text{ mol dm}^{-3}$ $\text{CH}_3\text{CO}_2\text{H}$ ($K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$) to form a buffer of pH 5.5?
- A** 15.0 cm^3 **B** 16.0 cm^3 **C** 17.0 cm^3 **D** 18.0 cm^3
- 11 $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ react according to the following equilibrium.



When 0.10 mol of $\text{H}_2(\text{g})$ and 0.10 mol of $\text{I}_2(\text{g})$ are heated in a sealed vessel at 600 K , 0.06 mol of HI was present at equilibrium.

What is the K_c value for the reaction at 600 K ?

- A** 0.184 **B** 0.360 **C** 0.735 **D** 1.36

- 12 After the Fukushima nuclear disaster in 2011, a radioactive isotope of iodine, ^{131}I , was detected at water purification plants in Japan. Radioactive decay is a first order reaction, and the half-life of radioactive ^{131}I is 8 days.

What is the mass of ^{131}I left after 40 days if the initial mass of ^{131}I was 15 g?

- A $\frac{15}{2 \times 5}$ g B $\frac{15}{2^5}$ g C $\frac{15}{2 \times 8}$ g D $\frac{15}{2^8}$ g

- 13 Which of the following shows the properties of a Group II element? [Ω = ohm]

	melting point / $^{\circ}\text{C}$	density / g cm^{-3}	electrical conductivity / $\Omega^{-1} \text{ m}^{-1}$
A	98	0.97	2.4×10^7
B	113	2.07	7.7×10^{-7}
C	649	1.74	2.2×10^7
D	1744	11.3	6.0×10^7

- 14 X, Y and Z are elements in the third period of the Periodic Table. The oxide of X is amphoteric, the oxide of Y is basic and the oxide of Z is acidic.

What is the order of increasing ionic radius for these three elements?

- A X, Y, Z B X, Z, Y C Y, X, Z D Y, Z, X

- 15 Sulfur is an element in the third period, Na to Ar, of the Periodic Table.

Which is the correct statement for sulfur?

- A Sulfur is the only element in this period which forms two acidic oxides.
 B Sulfur has the highest first ionisation energy of the elements in this period.
 C Sulfur is the only element in this period which can form compounds with variable oxidation states.
 D Sulfur is the only element in this period which can exist, at room temperature and pressure, as a simple molecule containing eight atoms.

- 16 Which anions containing chlorine are formed when chlorine is passed into hot aqueous potassium hydroxide?

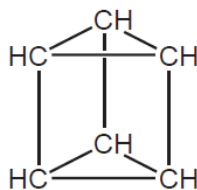
- A Cl^- and ClO^-
 B Cl^- and ClO_3^-
 C Cl^- and ClO_4^-
 D ClO^- and ClO_3^-

- 17 Four different complexes can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Different proportions of chloride are precipitated when each complex is treated with aqueous silver nitrate.

	empirical formula	colour of solid	number of moles of AgCl precipitated per mole of complex
I	$\text{CoCl}_3(\text{NH}_3)_6$	orange	3
II	$\text{CoCl}_3(\text{NH}_3)_5$	violet	2
III	$\text{CoCl}_3(\text{NH}_3)_4$	violet	1
IV	$\text{CoCl}_3(\text{NH}_3)_4$	green	1

Which of the following statements is correct regarding the four different complexes?

- A Only complexes III and IV have the coordination number of 6.
 B The cations in all four complexes have the same charge.
 C Ligands of complex I consists of both chloride and ammonia.
 D Complexes III and IV are stereoisomers.
- 18 In 1869 Ladenburg suggested a structure for benzene, C_6H_6 , in which one hydrogen atom is attached to each carbon atom.



Ladenburg structure

A compound $\text{C}_6\text{H}_4\text{Br}_2$ could be formed with the same carbon skeleton as the Ladenburg structure.

How many structural isomers would this compound have?

- A 2 B 3 C 5 D 6
- 19 Samples of the gases $\text{CH}_3\text{CH}_2\text{Cl}$ and Cl_2 are mixed together and irradiated with light.

Which of the following is **not** likely to be formed in the reaction?

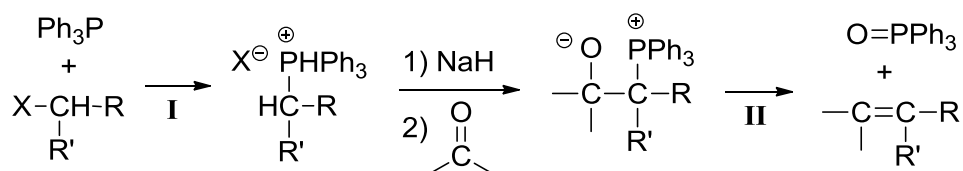
- A CH_3CHCl_2
 B $\text{CHCl}_2\text{CH}_2\text{Cl}$
 C $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 D $\text{CH}_2\text{ClCH}(\text{Cl})\text{CH}(\text{Cl})\text{CH}_3$

- 20 Compound **U** gives a positive test with Tollens' reagent and can be oxidised with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to form 3-methylbutanoic acid.

Compound **U** can be reduced by NaBH_4 to form compound **V** which reacts with ethanoyl chloride to form compound **W**.

What is the structure of compound **W**?

- A $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$
 B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_3$
 C $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OCOCH}_3$
 D $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OCOCH}_3$
- 21 The Wittig reaction offers a highly versatile method to synthesise a wide variety of alkenes. The mechanism for the reaction is summarised as follows.



(Ph denotes a phenyl group, C_6H_5^-)

Which of the following correctly represents the type of reaction occurring in stages **I** and **II**?

	stage I	stage II
A	nucleophilic substitution	elimination
B	nucleophilic substitution	condensation
C	nucleophilic addition	elimination
D	nucleophilic addition	condensation

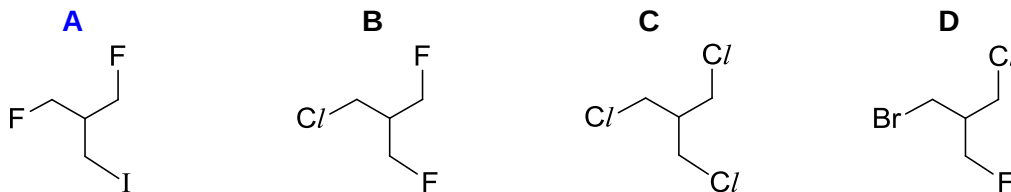
- 22 Which of the following can be used to distinguish between the two compounds?



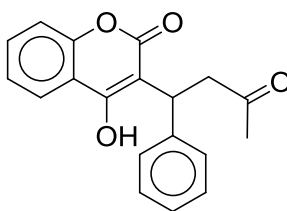
- A H_2 and Pd
 B $\text{Br}_2(\text{aq})$
 C warm Fehling's reagent
 D hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$

- 23 The presence of a halogen in an organic compound may be detected by warming the organic compound with aqueous silver nitrate.

Which compound would be the quickest to produce a precipitate?



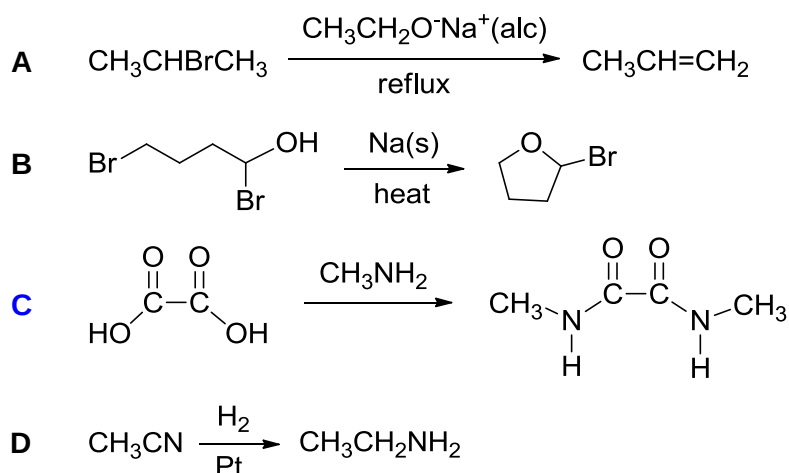
- 24 Warfarin ($M_r = 308$) is an oral anticoagulant that is used to prevent heart attacks, strokes and blood clots. The structural formula of warfarin is given below.



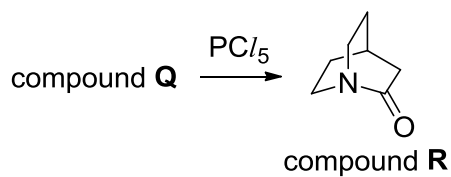
Which of the following statements about warfarin is correct?

- A** It has a total of 4 stereoisomers.
 - B** It reacts with CH_3COCl to form white fumes.
 - C** 1 mol of warfarin reacts with 1 mol of alcoholic potassium cyanide in the presence of heat.
 - D** 1 mol of warfarin reacts with 1 mol of hydrogen gas in the presence of nickel catalyst and heat.
- 25 The reaction conditions for four different transformations are given below.

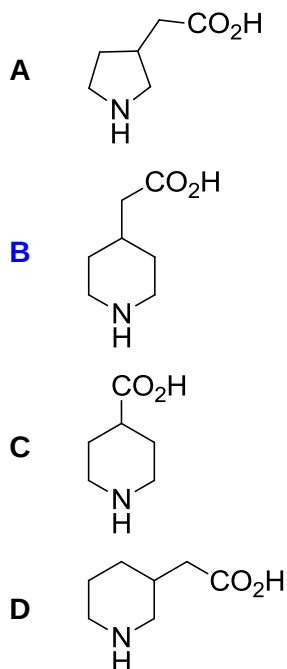
Which transformation has a set of reagents or conditions that is **not** correct?



- 26 Compound **R** is formed from compound **Q** as shown below.



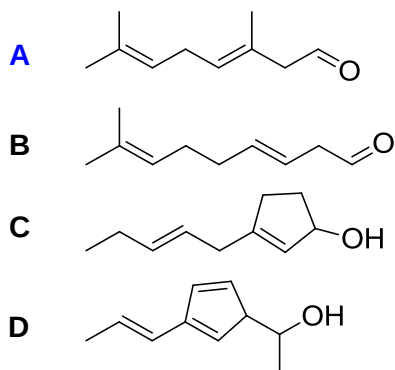
Which structure could be **Q**?



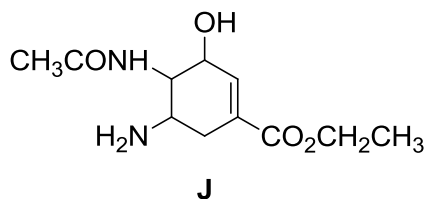
- 27 The reaction of compound **E** ($M_r = 152$) with hot acidified potassium manganate(VII) yields three products, **F**, **G** and **H**.

F can be converted to **G** with the use of alkaline aqueous iodine followed by acidification with aqueous sulfuric acid.

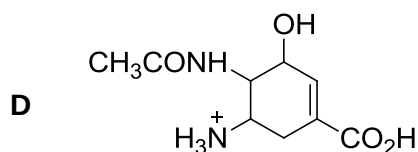
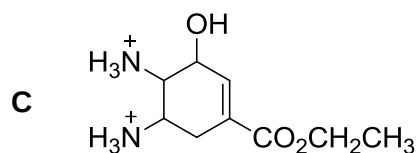
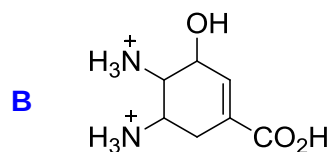
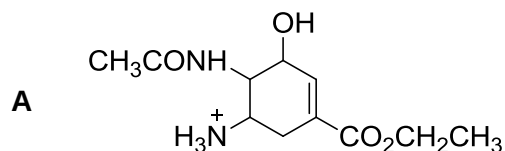
Which of the following shows the structure of compound **E**?



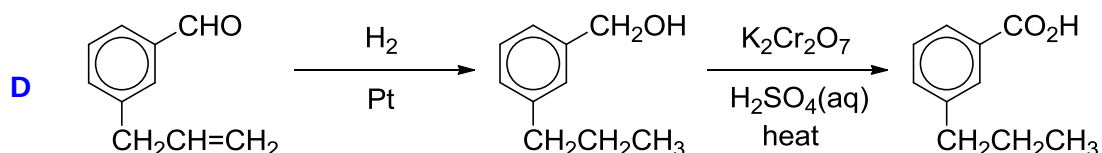
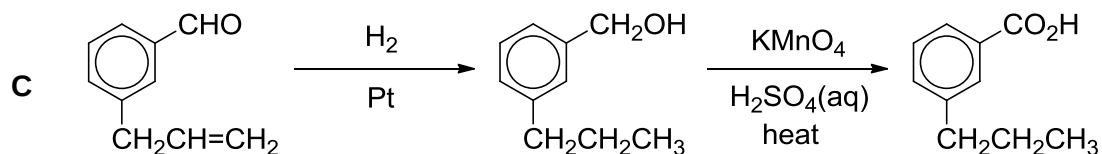
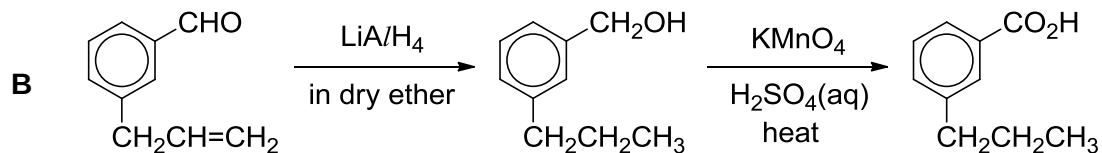
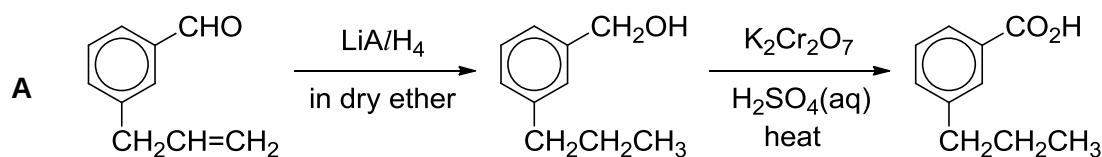
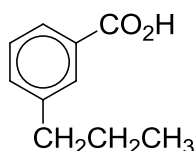
28 Compound **J** is a pharmaceutical drug.



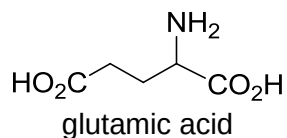
What is the species formed when compound **J** is heated with HCl(aq) ?



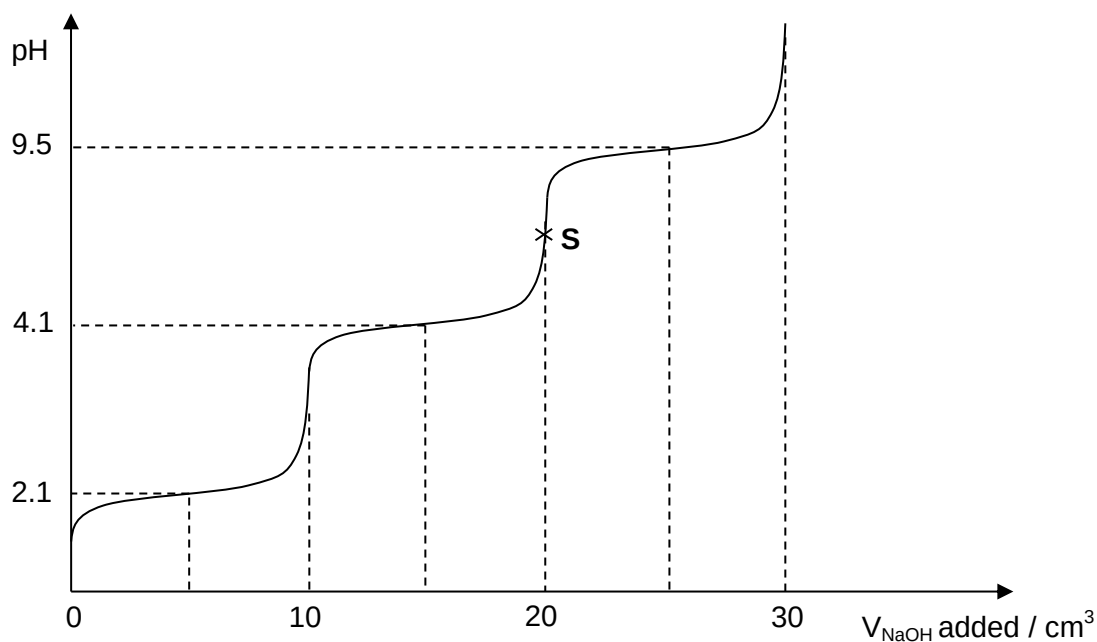
29 Which synthetic route will lead to the successful synthesis of the following product?



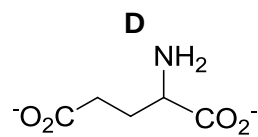
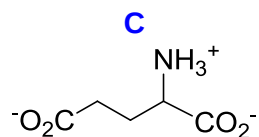
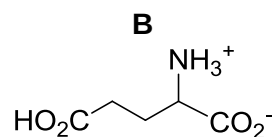
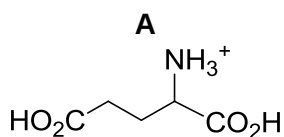
- 30 Soy sauce is produced by the fermentation of soy beans by the mould *Aspergillus oryzae*. The distinctive salty taste of the sauce is due to salts of glutamic acid formed during fermentation.



The pH–volume curve obtained when 30 cm³ of NaOH is added to 10 cm³ of the protonated form of glutamic acid of the same concentration is given below.



Which of the following is the major species present at point **S**?



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

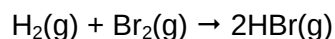
Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

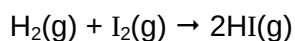
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Hydrogen reacts with gaseous bromine to form hydrogen bromide



and with gaseous iodine to form hydrogen iodide.



For the first reaction, the rate equation is

$$\text{rate} = \frac{k_1 [\text{H}_2][\text{Br}_2]^{1.5}}{[\text{Br}_2] + k_2[\text{HBr}]}$$

For the second reaction, the rate equation is

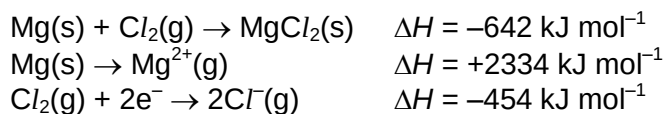
$$\text{rate} = k[\text{H}_2][\text{I}_2]$$

What can be deduced from this information only?

- 1** For the hydrogen / bromine reaction, the formation of HBr slows down the rate of the forward reaction.
- 2** Only the hydrogen / iodine reaction could be a single step reaction.
- 3** The mechanism of the hydrogen / bromine reaction involves free radicals.

32 Use of the Data Booklet is relevant to this question.

Given the enthalpy changes of the following reactions.

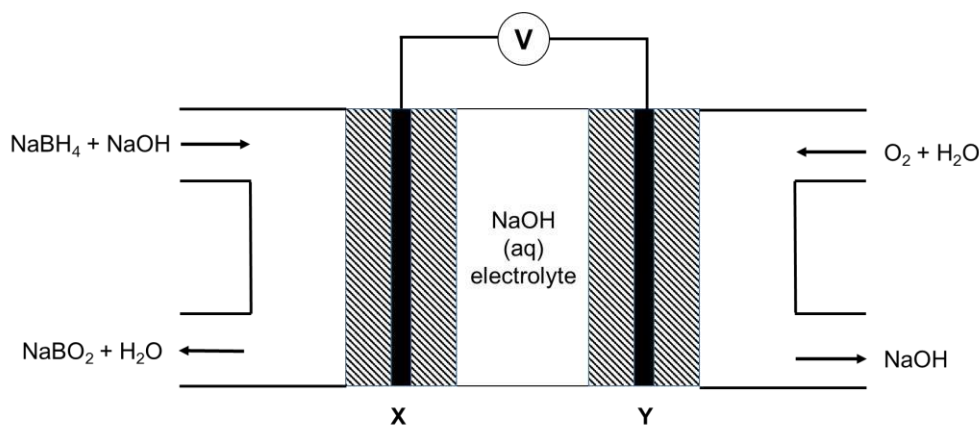


Which of the following statements are correct?

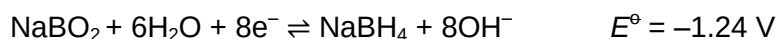
- 1 The enthalpy change of formation of $\text{MgCl}_2(\text{s})$ is -642 kJ mol^{-1} .
- 2 The enthalpy change of atomisation of Mg(s) is $+148 \text{ kJ mol}^{-1}$.
- 3 The electron affinity of Cl(g) is -698 kJ mol^{-1} .

33 Use of the Data Booklet is relevant to this question.

The Direct Borohydride Fuel Cell (DBFC) is a type of alkaline fuel cell that uses NaBH_4 as the fuel and O_2 as the oxidant. A DBFC was set up under standard conditions according to the diagram below.



The electrode potential of the $\text{NaBH}_4/\text{NaBO}_2$ half-cell is given below.



Which of the following statements regarding the DBFC are correct?

- 1 The voltmeter will register a reading of $+1.64 \text{ V}$.
- 2 Electrode **X** is the anode and electrode **Y** is the cathode in the DBFC.
- 3 The BO_2^- ion produced at electrode **X** has a bond angle of 180° .

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

34 The K_{sp} values of three metal hydroxides are given in the table below.

metal hydroxide	K_{sp}
Ca(OH)_2	$4.7 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$
Sn(OH)_2	$5.4 \times 10^{-27} \text{ mol}^3 \text{ dm}^{-9}$
Cr(OH)_3	$6.7 \times 10^{-31} \text{ mol}^4 \text{ dm}^{-12}$

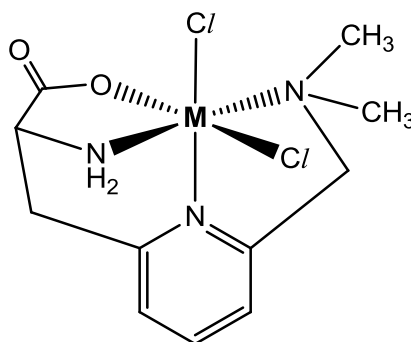
Which of the following statements are correct?

- 1** The concentration of OH^- in a saturated solution of Ca(OH)_2 is $0.021 \text{ mol dm}^{-3}$.
- 2** $\text{Ca(OH)}_2(\text{s})$ will be precipitated if equal volumes of $0.02 \text{ mol dm}^{-3} \text{ NaOH(aq)}$ and $0.02 \text{ mol dm}^{-3} \text{ Ca(NO}_3)_2(\text{aq})$ are mixed together.
- 3** Cr(OH)_3 has the lowest solubility amongst the three metal hydroxides.

35 Which of the following properties generally increase down Group II?

- 1** thermal stability of the iodate(V) salt, $\text{M(IO}_3)_2$
- 2** magnitude of the lattice energy of the oxide, MO
- 3** charge density of the M^{2+} ion

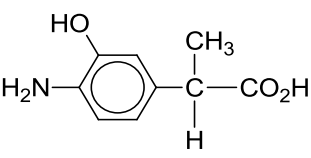
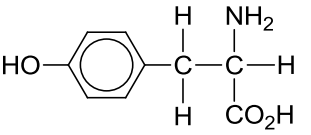
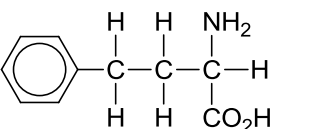
36 Which of the following statements regarding the metal complex below are correct?



- 1** The oxidation number of **M** in the complex is +3.
- 2** The coordination number of **M** in the complex is 6.
- 3** The complex contains a tetradentate ligand.

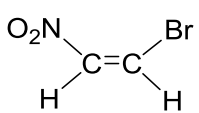
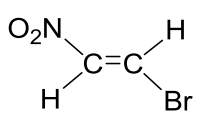
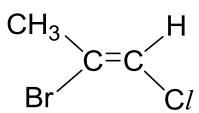
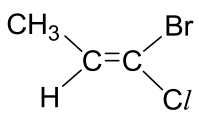
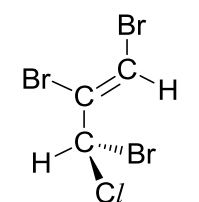
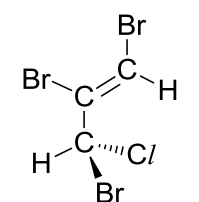
37 Compound **L** has a chiral centre and forms a zwitterion.

Which could be the structure of **L**?

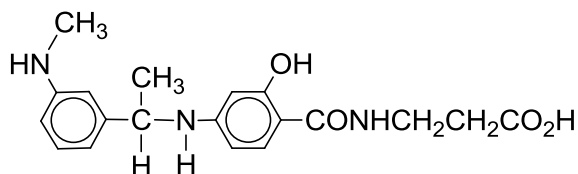
- 1 
- 2 
- 3 

38 In which of the following pairs are the members, **I** and **II**,

- stereoisomers of each other, and
- the overall dipole moment of **I** is larger than that of **II**?

	I	II
1		
2		
3		

39 Which of the following statements regarding compound **T** are correct?



compound **T**

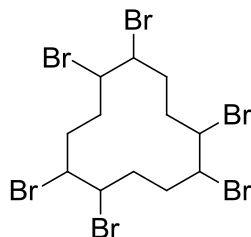
- 1 Compound **T** reacts with excess aqueous bromine to give a product with five bromine atoms.
- 2 1 mol of compound **T** reacts with 3 mol of ethanoyl chloride.
- 3 1 mol of compound **T** reacts with 3 mol of cold dilute hydrochloric acid.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

40 The diagram shows a molecule of a compound used as a flame retardant.



Which statements about this structure are correct?

- 1** Each brominated C atom is chiral.
- 2** The molecular formula is $\text{C}_{12}\text{H}_{20}\text{Br}_6$.
- 3** The C–C–C bond angles are all 120° .

Level of difficulty	Percentage	No of questions
Easy	22.5	9
Moderate	55	22
Difficult	22.5	9

MCQ Questions for H2			
Qn	Topic	Remarks	Answer
1	Atomic Structure (p, n, e)	E	D
2	Gases (calculation)	M	A
3	Atoms, Molecules, Stoichiometry (calculation)	M	B
4	Atoms, Molecules, Stoichiometry (equation)	M	A
5	Bonding (Δ , bond length) & IE I (acid–base properties)	M	D
6	Bonding (IMF)	M	C
7	Entropy	T	D
8	Enthalpy (ΔH_f , ΔH_c)	M	C
9	E° (electric cells)	T	B
10	IE I (buffer calculation)	M	C
11	Chemical Eqm (K_c calculation)	E	C
12	Kinetics I ($t_{1/2}$ calculation)	E	B
13	Group II (physical properties)	E	C
14	Periodic Table (ionic radius)	M	A
15	Periodic Table (properties of S)	M	D
16	Group VII (Cl_2 + hot OH^- reaction)	E	B
17	Transition Metals (ligand / coordination no.)	T	D
18	Organic (structural isomerism)	M	A
19	Organic (FRS mechanism)	M	C
20	Organic (RCHO, ROH reactions)	M	C
21	Organic (types of mechanism)	M	A
22	Organic (distinguishing test: RCHO, ester, phenol)	M	D
23	Organic (RX: $AgNO_3$ reaction)	E	A
24	Organic (C=C, ester, RCO, ROH reactions)	M	B
25	Organic (RX, C=C, RCO_2H reactions)	T	C
26	Organic (RX, RCO_2H , amine reactions)	T	B
27	Organic (C=C, ROH, RCO reactions)	T	A
28	Organic (hydrolysis reaction: amide, amine, ester)	M	B
29	Organic (phenol, C=C, amine reactions)	M	D
30	Organic (amino acid titration curve)	E	C
31	Kinetics II (mechanism, rate equation)	M	B
32	ΔH calculation	M	B
33	E° (fuel cell) + Bonding (bond Δ)	T	A
34	IE II (K_{sp} calculation)	T	D
35	Group II (physical/chemical properties)	E	D
36	Transition Metals (reaction)	M	A
37	Organic (amino acid)	E	A
38	Organic (stereoisomers, dipole moment)	M	D
39	Organic (phenol, RCO_2H , amine, amide reactions)	T	B
40	Organic (chiral C, MF, Δ)	M	D
Modified/New MCQ Questions for H1			
Qn No	Topic	Remarks	Answer



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE
NAME

CT GROUP

CHEMISTRY

9647/02

Paper 2 Structured

13 September 2016

Candidates answer on the Question Paper.

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

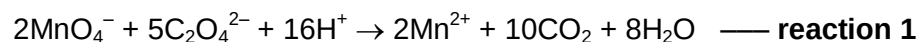
For Examiner's Use	
1	
2	
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Total	

This document consists of **16** printed pages and **0** blank page.

Answer **all** the questions in the space provided.

1 Planning (P)

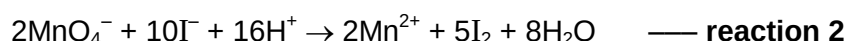
When potassium manganate(VII) reacts with sodium ethanedioate, a redox reaction occurs as shown below:



A product that is generated during the course of the reaction and helps to speed up the reaction rate is known as an autocatalyst. The autocatalyst for the above reaction is Mn^{2+} .

The kinetics of this reaction can be investigated by determining the concentration of MnO_4^- over the course of the reaction. Fixed aliquots (portions) of the reaction mixture are withdrawn at regular time intervals and added to an excess of potassium iodide.

The MnO_4^- in the aliquots reacts with excess iodide as shown below.



The amount of iodine formed can then be determined by titration with the sodium thiosulfate solution as shown below.



The volume of sodium thiosulfate used is proportional to the concentration of MnO_4^- .

- (a) In this experiment, both sodium ethanedioate and sulfuric acid are used in large excess. Explain the purpose of using a large excess of sodium ethanedioate and sulfuric acid.

.....
 [1]

- (b) Using the information given above, you are required to write a plan for the determination of the concentration of MnO_4^- at regular timing intervals.

You may assume that you are provided with the following:

- 0.0500 mol dm⁻³ potassium manganate(VII), KMnO_4
- 0.500 mol dm⁻³ sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$
- 1.00 mol dm⁻³ sulfuric acid, H_2SO_4
- 0.200 mol dm⁻³ potassium iodide, KI
- solid $\text{Na}_2\text{S}_2\text{O}_3$
- starch indicator
- stopwatch
- apparatus and chemicals normally found in a school or college laboratory.

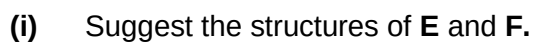
Your plan should include:

- justification for
 - the volume of each reactants to be used in **reaction 1** so as to allow a minimum of **6 aliquots** of the reaction mixture to be withdrawn and the concentration of MnO_4^- in each aliquot to be determined;
 - the intended concentration of the sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, to be used;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain.

.....

(c) The order of reaction with respect to MnO_4^- can be determined by initial rate method. Use your graph in **(b)**, suggest how the initial rate can be determined.

2 (a) Proline (pro) is one of the naturally occurring amino acids. It can be synthesised from 4-hydroxybutanal in 4 steps.



E

F

(ii) Suggest the reagents and conditions required for the following steps.

step I:

step III:

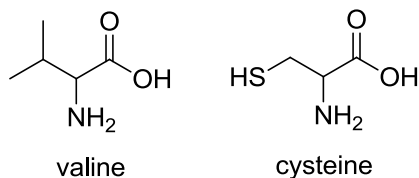
step IV:[3]

(b) The two pK_a values associated with proline are 2.0 and 10.5.

Make use of these pK_a values to suggest the major species present in the solution of proline with the following pH values.

pH 1	pH 7	pH 12

(c) The structures of amino acids, valine (val) and cys are shown below.



- (i) Draw the structure of val–pro–cys peptide.

[2]

- (ii) State the possible R group interactions that val–pro–cys may have with another val–pro–cys peptide.

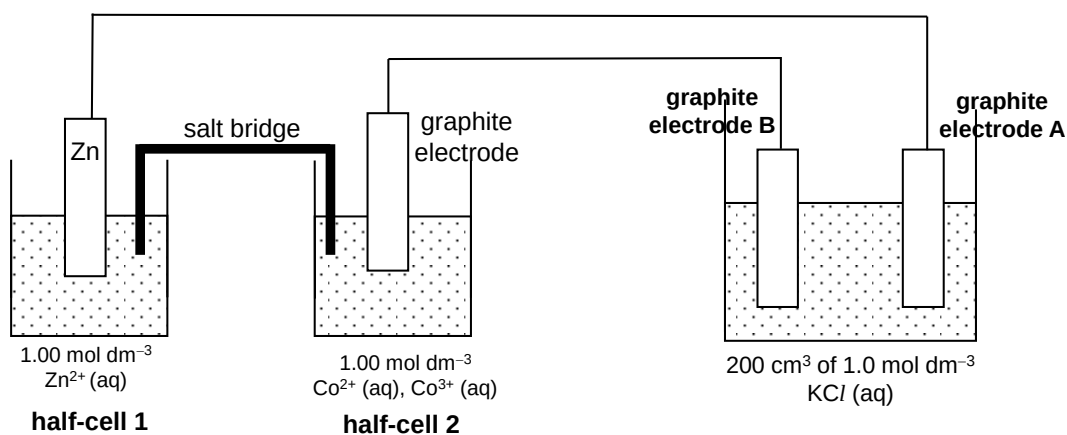
.....

.....

.....[2]

[Total: 12]

- 3 (a) A student used the following setup in an attempt to produce chlorine gas using potassium chloride solution.



- (i) Using relevant data from the *Data Booklet*, predict the type of redox reaction that occurs at each half-cell. State the polarity at the graphite electrodes **A** and **B**.

Half-cell **1**:

Half-cell **2**:

Graphite electrode **A**:

Graphite electrode **B**: [2]

- (ii) 20 cm³ of hydrogen gas was collected on one of the electrodes after 10 minutes at room temperature and pressure. Assuming 20% of the hydrogen

gas was lost during collection, calculate the current produced by the battery setup.

[2]

- (iii) With reference to relevant data from the *Data Booklet*, explain the absence of chlorine being discharged on the other electrode.

.....

.....

..... [1]

- (b) 20 cm^3 of a gas mixture containing gaseous ethanol, carbon monoxide and excess oxygen was burned completely. There was a contraction of 1 cm^3 . When the product mixture was passed through sodium hydroxide, there was a further contraction of 6 cm^3 . All gas volumes are measured at 400 K and 1 atm.

Determine the molar composition of the ethanol and carbon monoxide in this gas mixture.

[3]

[Total: 8]

- 4 Magnesium and beryllium are Group II elements but beryllium behaves differently from that of magnesium. There is said to be a 'diagonal relationship' between beryllium and

aluminium as they show similar chemical behaviour due to their similarities in electronegativity and charge density.

- (a) (i) When a few drops of water are added to solid beryllium chloride, steamy white fumes are evolved and a white solid remains, which is insoluble in water.

Write a balanced equation for this reaction.

..... [1]

- (ii) When a large amount of water is added to solid beryllium chloride, a clear, weakly acidic solution is obtained. Explain.

.....

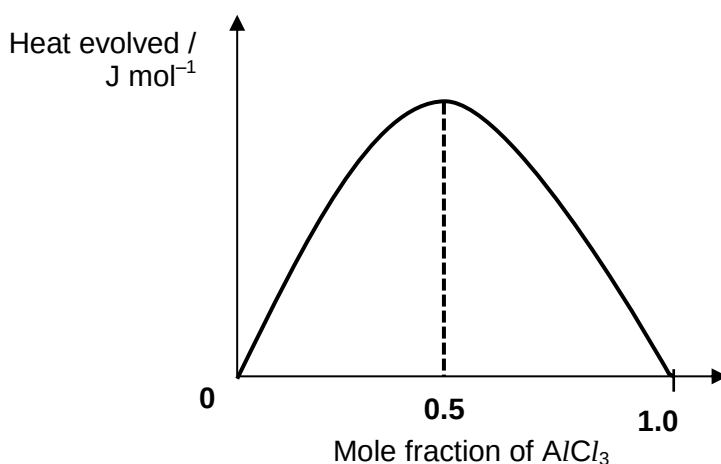
..... [1]

- (iii) At 750 °C, the relative molecular mass of gaseous beryllium chloride corresponds to the formula BeCl_2 . At 550 °C, gaseous beryllium chloride exists as a mixture of BeCl_2 and Y (relative molecular mass of Y is 160).

Determine the molar composition of gaseous beryllium chloride at 550 °C which has a relative molecular mass of 100. Draw a diagram to illustrate the nature of the bonding in Y and indicate the value of the bond angle about Be.

[2]

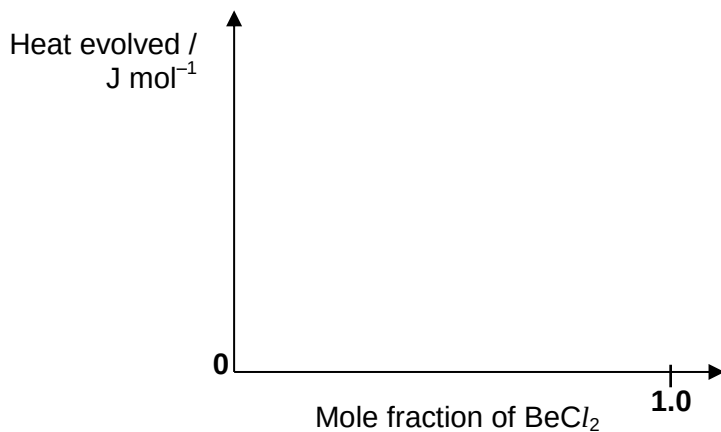
- (iv) When aluminium chloride, AlCl_3 , is mixed with ammonia, compound Z is formed and the reaction is exothermic. The diagram below shows the relationship between the heat evolved per mole of the mixture and the mole fraction of AlCl_3 .



Draw a diagram to show the bonding in a molecule of compound Z.

[1]

- (v) Sketch a labelled diagram similar to (a)(iv) that you would expect to obtain when AlCl_3 is replaced by BeCl_2 .

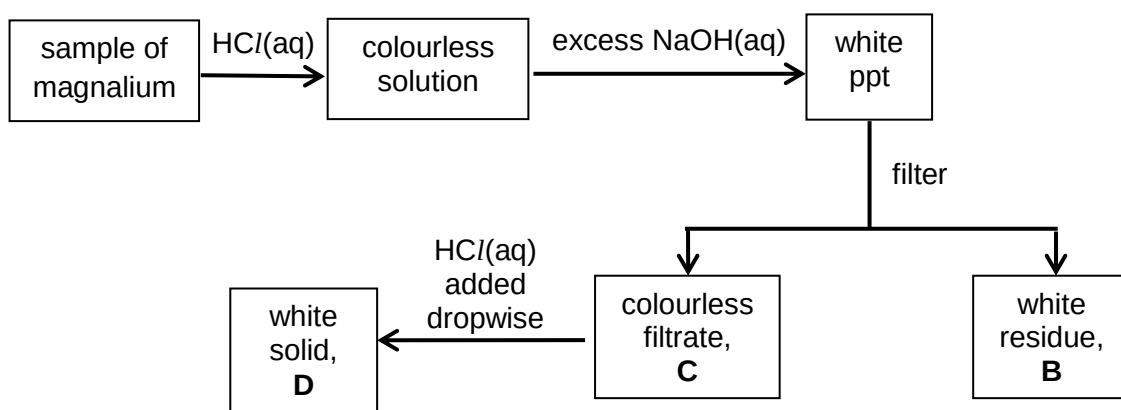


[1]

- (vi) Write a balanced equation of a chlorination reaction in Organic Chemistry that uses anhydrous BeCl_2 as a catalyst.

[1]

- (b) Magnalium is an alloy of aluminium and magnesium which is used in boat-building. The diagram below shows some reactions of magnalium.



Identify B, C and D.

B:

C:

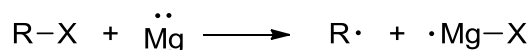
D:

[3]

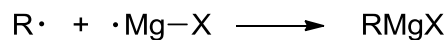
- (c) Grignard reagents, RMgX , can be prepared by the reaction of magnesium with halogenoalkane, RX , using dry ether as the solvent.

The mechanism of the reaction involves two steps.

Step 1: It involves the transfer of one electron from Mg to the halogen X followed by the homolytic fission of the carbon–halogen bond. This forms MgX, which is a radical.



Step 2: MgX radical couples with the alkyl radical formed in step 1.



(i) Draw curve arrows to show the movement of electrons in step 1 of the mechanism given above.

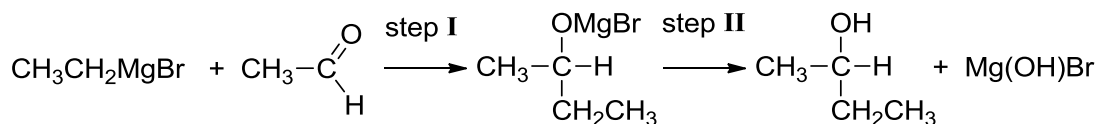
[1]

(ii) Suggest which step in the mechanism is the rate-determining step. Explain your answer.

.....

 [1]

Grignard reagents can be used to prepare alcohols from carbonyl compounds as shown by the reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with ethanal below:



(iii) What type of reaction takes place in steps I and II?

step I:

step II:[2]

(iv) The variation of the rate constant k with temperature for the reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with ethanal is given below:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where E_a denotes the activation energy in J mol^{-1} , R is the gas constant, and T is the temperature in Kelvin.

Given that at 25°C , the rate constant and activation energy of the reaction is $9.16 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and 102 kJ mol^{-1} respectively.

Explain, with calculations, the effect of temperature change on the rate of the reaction when the temperature is raised by 5°C .

.....

 [2]

- (v) Draw the structural formula of the Grignard reagent that will react with butan-2-one to form 3-methylpentan-3-ol in a similar two-step reaction.

[1]

- (vi) Suggest why $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{Br}$ and magnesium cannot be used to prepare the Grignard reagent $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{MgBr}$.

.....
 [1]

- (vii) Ethanal is oxidised to ethanoic acid by acidified potassium dichromate. Using data from the Data Booklet and the data below, calculate $E^\ominus_{\text{cell}}$ of the reaction.

$$E^\ominus(\text{CH}_3\text{CO}_2\text{H}|\text{CH}_3\text{CHO}) = +0.92 \text{ V}$$

Hence, explain why the reaction takes place only in the presence of heat.

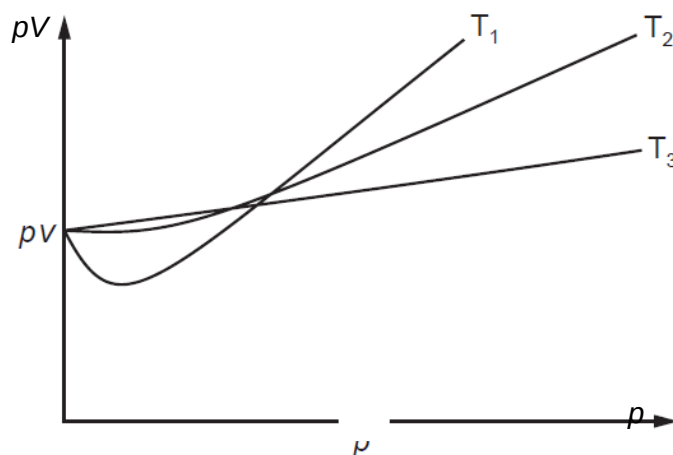
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 [2]

[Total: 20]

- 5 (a) The relationship $pV = nRT$ can be derived from the laws of mechanics by assuming ideal behaviour for gases.

The graph represents the relationship between pV and p for a real gas at three different temperatures, T_1 , T_2 and T_3 .



- (i) Draw **one** line on the graph to show what the relationship should be for the same amount of an ideal gas and state which of T_1 , T_2 or T_3 is the lowest temperature.

Lowest Temperature: [1]

- (ii) State and explain the effect of pressure on the extent to which a gas deviates from ideal behaviour.

.....

..... [1]

- (b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask. The same flask was then weighed with only gas, **Y**, filling the flask. The results, measured at 26°C and $1.00 \times 10^5 \text{ Pa}$, are shown.

Mass of flask containing air = 47.930 g
 Mass of flask containing **Y** = 47.989 g
 Density of air = $0.00118 \text{ g cm}^{-3}$

Calculate the relative molecular mass, M_r , of **Y**.

[2]

- (c) In recent years there has been worldwide interest in the possible extraction of 'shale gas' (a form of natural gas) as an important energy source.

One of the problems associated with using shale gas is its variable composition. **Table 1** shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

Table 1

source	CH ₄	C ₂ H _x	C ₃ H _y	CO ₂	N ₂
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formula above, **x** and **y** are variables.

- (i) Draw the structures of **three** possible compounds with the formula C₃H_y.

[1]

- (ii) Which source of shale gas, **J**, **K**, **L** or **M**, will provide the most energy when burned? Explain your answer.

.....

..... [1]

- (iii) Suggest one method by which carbon dioxide can be removed from shale gas.

.....

..... [1]

Table 2 shows a comparison of the relative amounts of pollutants produced when shale gas, fuel oil and coal are burned to produce **the same energy**.

Table 2

air pollutant	shale gas	fuel oil	coal
CO ₂	117	164	208
CO	0.040	0.033	0.208
NO ₂	0.092	0.548	0.457
SO ₂	0.001	1.12	2.59
particulates	0.007	0.84	2.74

- (iv) Suggest why shale gas produces the smallest amount of CO₂.

.....

..... [1]

- (v) Explain which of the three fuels, shale gas, fuel oil or coal, is the largest contributor to 'acid rain'.

.....

..... [1]

- (d) Use the following data and data from the *Data Booklet* to construct a labelled energy level diagram to determine the lattice energy of Fe_2O_3 .

enthalpy change of $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$	$-1644 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of Fe(s)	$+414 \text{ kJ mol}^{-1}$
electron affinity of the oxygen atom	-141 kJ mol^{-1}
electron affinity of the O^- ion	$+844 \text{ kJ mol}^{-1}$

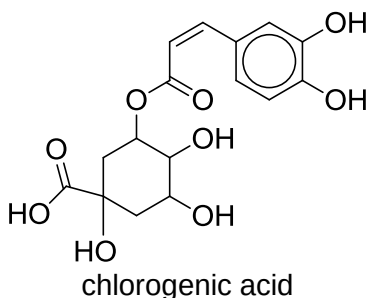
Energy



[4]

[Total: 13]

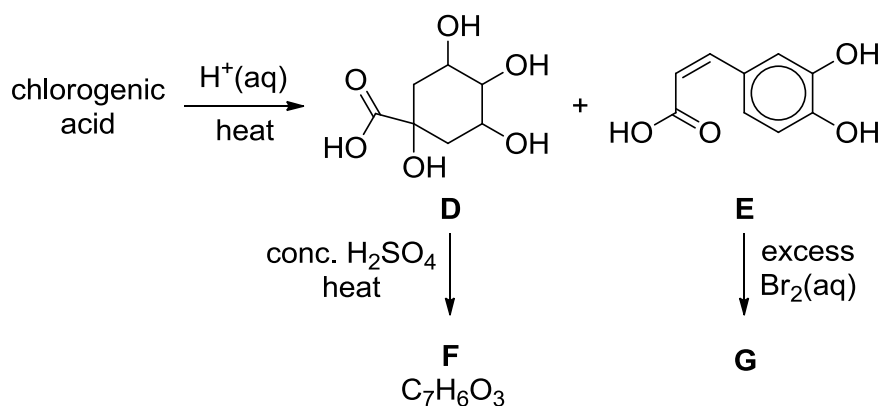
- 6 (a) Coffee beans contain chlorogenic acid.



- (i) How many moles of $\text{H}_2(\text{g})$ will be evolved when 1 mol of chlorogenic acid reacts with an excess of sodium metal?

..... [1]

On heating with dilute aqueous acid, chlorogenic acid produces two compounds **D** and **E**.



When compound **D** is heated with concentrated H_2SO_4 , compound **F**, $\text{C}_7\text{H}_6\text{O}_3$, is formed.

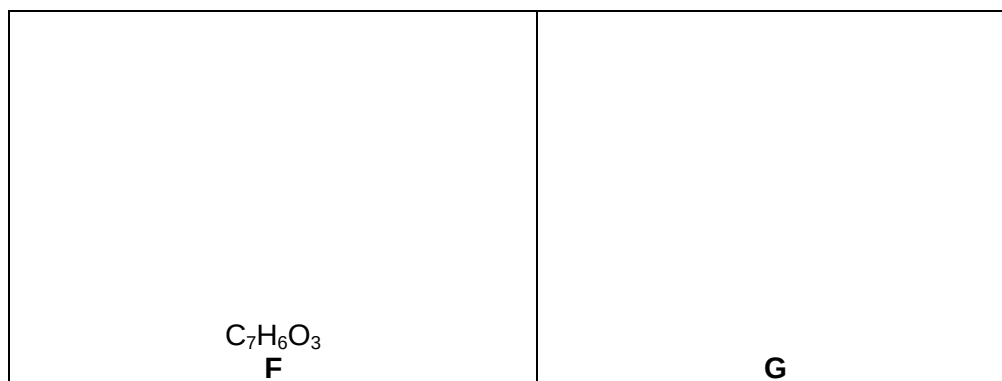
Compound **F** does not decolourise cold dilute acidified KMnO_4 but reacts with $\text{Br}_2(\text{aq})$.

When compound **E** is treated with an excess of $\text{Br}_2(\text{aq})$, compound **G** is produced.

- (ii) If the test with cold dilute acidified KMnO_4 had been positive, which functional group would this have shown to be present in **F**?

..... [1]

- (iii) Suggest the structures for compounds **F** and **G**, and draw them in the relevant boxes below.



[2]

(b) Allyl alcohol, $\text{CH}_2=\text{CHCH}_2\text{OH}$, is a colourless liquid which is soluble in water.

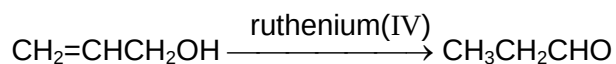
Crotyl alcohol, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$, is a colourless liquid.

- (i) Describe how you would distinguish between allyl alcohol and crotyl alcohol. The compounds may be distinguished by a preliminary chemical reaction followed by a subsequent testing of the reaction products. Include clearly the reagents, conditions and observations for each compound.

.....

 [2]

- (ii) Allyl alcohol may be converted into propanal by using a ruthenium(IV) catalyst in water.



State the type of reaction and explain your answer.

..... [1]

[Total: 7]



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

20 September 2016

Candidates answer on separate paper.

2 hours

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

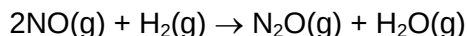
A Data Booklet is provided.

You are reminded of the need for good English and clear explanation in your answers.

The number of marks is given in brackets [] at the end of each question or part question.

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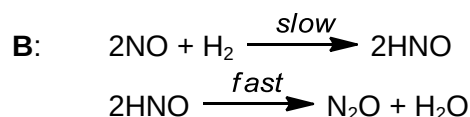
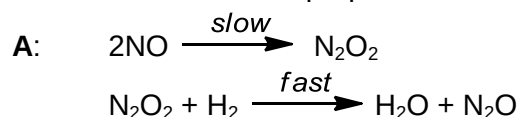
- 1 (a) At high temperatures NO reacts with H₂ to produce nitrous oxide, N₂O, a greenhouse gas.



To study the kinetics of this reaction at 820 °C, initial rates for the formation of N₂O were measured using various initial partial pressures of NO and H₂.

Experiment	Initial pressure / kPa		Initial rate of production of N ₂ O / kPa s ⁻¹
	P_{NO}	P_{H_2}	
1	16	8	1.15×10^{-2}
2	8	8	2.87×10^{-3}
3	8	24	8.60×10^{-3}

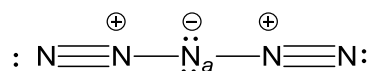
- (i) Deduce the rate equation in terms of partial pressure. [3]
- (ii) Using the rate equation and the information in the table above, calculate a value for the rate constant, giving its units. [2]
- (iii) Hence, calculate the initial rate at which NO reacts when 25 kPa of NO and 12.5 kPa of H₂ are mixed at 820 °C. [1]
- (iv) Write the rate equation for the reaction when NO is used in large excess. Hence, determine the time elapsed to reduce the partial pressure of H₂ to half of its initial value, if 100 kPa of NO and 1 kPa of H₂ are mixed at 820 °C. [3]
- (v) Two mechanisms, **A** and **B** are proposed below.



Which mechanism is consistent with the rate equation obtained in (a)(i). Explain your answer. [1]

- (b) Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amounts of energy are released from their decomposition or reactions leading to more stable products.

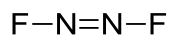
- (i) The polynitrogen species, N₅⁺ was first isolated in 1999. One of its resonance forms is shown below.



State the bond angle and molecular shape around nitrogen labelled a. [1]

- (ii) The synthesis of a white ionic solid, [N₅⁺][AsF₆⁻], was achieved by reacting [N₂F⁺][AsF₆⁻] with hydrazoic acid, HN₃, in liquid HF at -78 °C. Write a balanced equation for this reaction. [1]

- (iii) $[\text{N}_2\text{F}^+][\text{AsF}_6^-]$ was first prepared by reacting N_2F_2 with the strong Lewis acid, AsF_5 . N_2F_2 has the following structure and exhibits cis-trans isomerism.



Draw the cis-trans isomers of N_2F_2 , including all lone pairs and suggest an appropriate hybridisation for each nitrogen atom in N_2F_2 . [2]

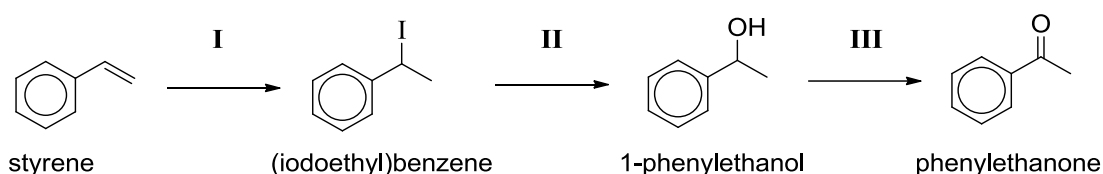
- (c) Nitrogen is found in all organisms, primarily in amino acids which made up proteins.

Isoleucine, $\text{NH}_2\text{CH}(\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$ is an α -amino acid where the amino group and carboxylic acid group are separated by one carbon. It is a constituent amino acid in many protein molecules. Isoleucine can exist as different stereoisomers.

- (i) State the reagents and conditions needed to break protein down into its constituent amino acids. [1]
- (ii) Define the term *stereoisomers*. [1]
- (iii) There are four optical isomers of isoleucine. Draw the structures of these four stereoisomers of isoleucine, indicating clearly the chiral centres. [2]
- (d) 3-amino-3-methyl-1butyne, $\text{CH}\equiv\text{CCNH}_2(\text{CH}_3)_2$ is used as the starting material to make other chemicals.
Draw a labelled diagram to show the orbitals that form $\text{C}\equiv\text{C}$ in an alkyne. [2]

[Total: 20]

- 2 (a) Styrene (phenylethene) is a useful organic intermediate used for the synthesis of many products. For instance, styrene is able to undergo the reaction shown below:



- (i) State the reagents and conditions required for reactions I, II and III. [3]
- (ii) By considering the substituent(s) attached to the carbonyl group, give two reasons for the lower reactivity of phenylethanone towards nucleophiles compared to propanone, CH_3COCH_3 . [2]
- (iii) Suggest a simple chemical test to distinguish between (iodoethyl)benzene and iodobenzene, $\text{C}_6\text{H}_5\text{I}$. State the observations for each compound. [2]
- (iv) The solubility of (iodoethyl)benzene in water was found to be 32.1 mg dm^{-3} . Explain why (iodoethyl)benzene has such a low solubility in water. [2]
- (b) (Iodoethyl)benzene exists as a pair of enantiomers **A** and **B**.
- An optically pure sample containing only isomer **A** dissolved in hexane underwent a nucleophilic substitution reaction with a solution containing radioactive iodide ions, $^{131}\text{I}^-$. After the reaction, 75% of the (iodoethyl)benzene is incorporated with radioactive iodide.
- An investigation into the kinetics of the reaction revealed that the rate of reaction was independent of the concentration of $^{131}\text{I}^-$.
- (i) Describe the mechanism for the reaction of (iodoethyl)benzene with $^{131}\text{I}^-$. In your answer, clearly label the ^{131}I , and include any relevant charges, curly arrows and dipoles or lone pairs of electrons that you consider important in this mechanism. [2]
- (ii) Calculate the percentage of (iodoethyl)benzene that exists as enantiomer **B** incorporated with ^{131}I in the product mixture. [1]
- (c) The term 'tri-iodide' refers to molecules that contain three iodine atoms in their molecular formula, such as nitrogen tri-iodide, NI_3 , and aluminium tri-iodide, AlI_3 .

AlI_3 has a simple molecular structure. In the gas phase, it dimerises readily to form the dimer Al_2I_6 . The two species are related by the equilibrium shown below.



- (i) A 10.0 g sample of Al_2I_6 was allowed to vapourise in a 2 dm^3 vessel at 400°C . Calculate the initial pressure of Al_2I_6 . [2]
- (ii) Given that the degree of dissociation (α) of Al_2I_6 was 0.35, find the K_p value for the equilibrium at 400°C . [2]

(iii) Explain the effect on the degree of dissociation of Al_2I_6 for each of the changes below.

- The reaction was carried out at 300 °C.
- A sample of $Ar(g)$ was introduced into a 1 dm³ vessel containing $AlI_3(g)$ and $Al_2I_6(g)$ at 400 °C.

[2]

(d) The table below shows the boiling points of PCl_3 and PF_5 .

Compound	Boiling Point / °C
PCl_3	76.1
PF_5	– 84.6

Explain why PCl_3 has a higher boiling point than PF_5 .

[2]

[Total: 20]

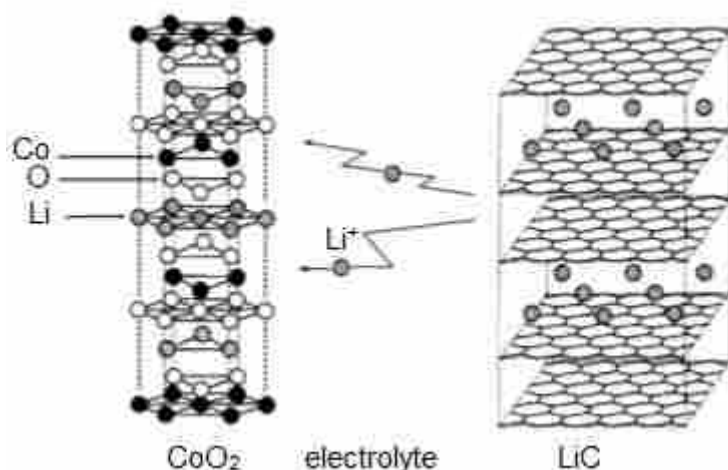
- 3 (a) Lead(II) nitrate decomposes on heating in the same way as magnesium nitrate. By using relevant data from the *Data Booklet*, predict and explain which of the two nitrates, lead(II) nitrate or magnesium nitrate, would have a higher decomposition temperature. [2]

(b) The halogens are reactive elements and are involved in many reactions.

- (i) When chlorine is bubbled through cold sodium hydroxide solution, followed by an excess of acidified silver nitrate solution, only $\frac{1}{2}$ of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide solution is hot, up to $\frac{5}{6}$ of the chlorine can be precipitated. Explain the observations with the aid of relevant equations. [3]
- (ii) When chromium is made to react with chlorine, the main product of the reaction is CrCl_3 . However, when chromium is made to separately react with other halogens such as fluorine and iodine, the main products are CrF_4 and CrI_2 . By reference to relevant $E^\ominus$ values, what can you conclude about the relative oxidising ability of the halogens? [2]

The halogens also form many interhalogen compounds in which two different halogens are combined. Interhalogen compounds like BrCl have similar properties to the halogens.

- (iii) Suggest an equation for the reaction that occurs between BrCl and aqueous KI . [1]
- (iv) BrCl reacts with alkenes faster than the pure halogens such as Cl_2 and Br_2 . Show the slow step of the reaction between BrCl and propene. [1]
- (c) A lithium-ion battery is a rechargeable battery. In a fully charged battery, lithium ions occupy the tiny spaces in graphite to form LiC . During discharge, lithium ions are produced which migrate through the electrolyte while at the same time, graphite is being regenerated. In the other electrode, lithium ions react with CoO_2 to form LiCoO_2 .



- (i) Write equations for the electrode reactions occurring at the anode and cathode during discharge. [2]
- (ii) Hence, write an equation for the overall reaction that occurs during discharge. [1]
- (iii) By determining the oxidation numbers of the relevant elements, identify the elements that have been oxidised and reduced. [1]

- (d) (i)** With reference to the *Data Booklet*, draw a fully labelled diagram showing how you could measure the standard electrode potential for the Ag^+/Ag system. Indicate the direction of electron flow. [2]

- (ii)** The electrode potential, E and the concentration of silver ions in solution under non-standard conditions are related by the following equation.

$$E = 0.80 - 0.03 \lg \frac{1}{[\text{Ag}^+(\text{aq})]^2}$$

The solubility product constant of AgCl is $K_{\text{sp}} = 1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$. Using the equation given above, calculate the electrode potential at 298 K of a half-cell formed by

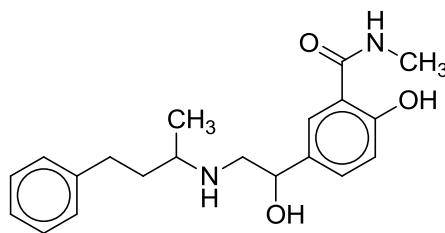
- (I) a Ag electrode immersed in a saturated solution of AgCl .
 (II) a Ag electrode immersed in a 0.5 mol dm^{-3} solution of KCl containing some AgCl precipitate.

[3]

- (iii)** A cell is made by connecting the half-cell in **(d)(i)** to a standard Cu^{2+}/Cu half-cell. By reference to relevant data from the *Data Booklet*, calculate the cell emf and write an equation (with state symbols) for the reaction that has occurred. [2]

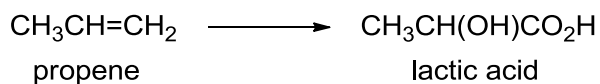
[Total: 20]

- 4 (a) Compound **G** has the structure shown.



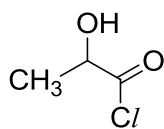
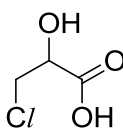
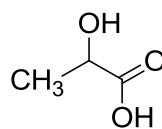
Give the structures of the organic compounds formed by compound **G** under the following conditions.

- (i) NaOH(aq), reflux [2]
- (ii) Excess CH_3COCl , room temperature [2]
- (b) Lactic acid can be used in food products as pH regulators or as a food preservative. It can also be used as a flavouring agent.
- (i) Suggest reagents and conditions needed to convert propene into 2-hydroxypropanoic acid (commonly known as lactic acid) in no more than 3 steps. Give the structures of the intermediates.



[3]

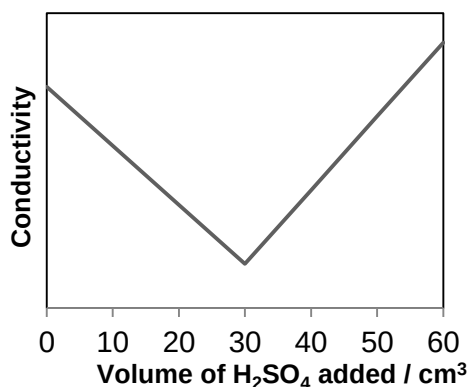
- (ii) When lactic acid is refluxed with concentrated sulfuric acid, compound **H** with the molecular formula of $\text{C}_6\text{H}_8\text{O}_4$ is formed. It does not react with sodium. Give the structural formula of **H**. [1]
- (iii) Describe and explain the relative acidity of the following three compounds.

**A****B**

lactic acid

[2]

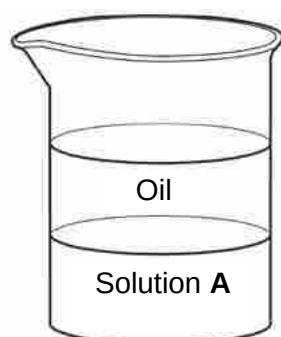
- (c) Experiment 1 is conducted in which the conductivity of 25 cm^3 of $\text{Ba}(\text{OH})_2$ solution is monitored as it is titrated with 0.10 mol dm^{-3} of aqueous H_2SO_4 . The data collected from the experiment is plotted in the graph below.



- (i) The conductivity of the $\text{Ba}(\text{OH})_2$ solution decreases as the volume of 0.10 mol dm^{-3} H_2SO_4 is added from 0 cm^3 to 30 cm^3 .

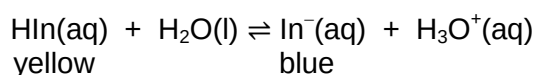
Identify the chemical species that enable the solution to conduct electricity as the first 30 cm^3 of H_2SO_4 (aq) is added. Hence explain why the conductivity decreases. [2]

- (ii) Using the information in the graph, calculate the initial concentration of $\text{Ba}(\text{OH})_2$. [1]
- (d) In Experiment 2, another 25 cm^3 sample of 0.10 mol dm^{-3} aqueous $\text{Ba}(\text{OH})_2$ is mixed with 80 cm^3 of 0.10 mol dm^{-3} of ethanoic acid to form solution **A**. Barium ethanoate, $\text{Ba}(\text{CH}_3\text{CO}_2)_2$ is the product of the reaction. The acid dissociation constant, K_a , of ethanoic acid is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the pH of the solution **A**. [3]
- (e) Half of the solution **A** formed in (d) is added to beaker **X** where there is a layer of colourless oil as shown in the figure below.



Beaker **X**

The indicator HIn is a weak acid with a $\text{p}K_a$ value of 6.0. It reacts with water as represented in the equation below.



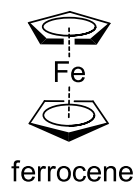
A small amount of indicator HIn is added into beaker **X**. The mixtures are stirred well and the two layers are allowed to separate.

Assume the pH of solution **A** is unaffected by the presence of colourless oil.

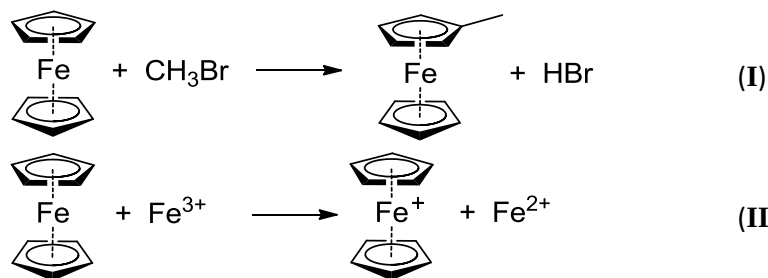
- (i) State the colour observed in the oil layer of beaker **X**. Explain the observation in terms of acid-base equilibrium and inter-molecular interactions. [2]
- (ii) A few drops of aqueous sodium hydroxide and hydrochloric acid are added to the beaker **X** successively and stirred well. Explain with the aid of equation(s) why there is no change in the colour of the oil layer after each addition. [2]

[Total: 20]

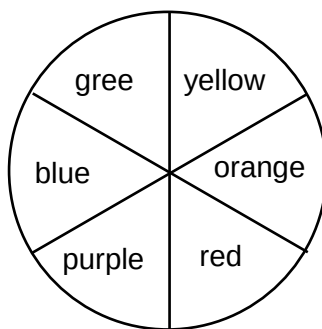
- 5 (a) Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, is an orange solid. In this complex, C_5H_5^- is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



Ferrocene can undergo a series of different reactions and some are analogues of organic reactions. Two reactions of ferrocene are shown below:



- (i) State the types of reaction for reactions I and II. [1]
- (ii) State the oxidation number of Fe in ferrocene and hence its electronic configuration. [1]
- (iii) Suggest why Ferrocene is a coloured complex. [2]
- (iv) The complementary colours are illustrated with the following colour wheel.



Aqueous Fe^{2+} ion is green in colour. Suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to C_5H_5^- . [2]

- (v) By considering reaction II, suggest if $E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ is more positive or less positive than $E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+})$. Explain your answer. [1]
- (vi) The reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- is slow in the absence of catalyst. Ferrocene can be a suitable catalyst for this reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- .

Explain with the aid of equations how it works. You may use $\text{Fe}(\text{C}_5\text{H}_5)_2$ to represent ferrocene. [2]

- (vii) By considering your answers to (v) and (vi), suggest a range of values for $E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$. [1]

- (b) Ephedrine, $C_{10}H_{15}NO$, is a drug used to prevent low blood pressure during spinal anaesthesia. It is optically active and has 2 chiral centres.

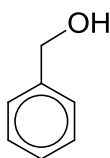
When Ephedrine is heated with acidified potassium manganate(VII), it gives benzoic acid, $C_6H_5CO_2H$ as one of the products. When it is heated with acidified potassium dichromate(VI), it gives **P**. **P** gives an orange precipitate when treated with 2,4-dinitrophenylhydrazine but it has no reaction with Tollens' reagent.

When Ephedrine is heated with equimolar CH_3Cl , it gives **Q**, $C_{11}H_{17}NO$ as the major product. When it is heated with excess CH_3Cl , it gives **R**, $C_{12}H_{20}NOCl$ as the major product.

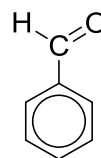
Deduce the structures of Ephedrine, **P**, **Q** and **R**. Explain your answer.

[7]

- (c) Draw a labelled diagram to show how benzaldehyde can be synthesised from phenylmethanol in a laboratory.



phenylmethanol



benzaldehyde

[3]

[Total: 20]

Victoria Junior College
2016 JC2 H2 Chemistry Prelim Paper 1
Suggested Answers

No.	Ans	No.	Ans	No.	Ans	No.	Ans
1	D	11	C	21	A	31	B
2	A	12	B	22	D	32	B
3	B	13	C	23	A	33	A
4	A	14	A	24	B	34	D
5	D	15	D	25	C	35	D
6	C	16	B	26	B	36	A
7	D	17	D	27	A	37	A
8	C	18	B	28	B	38	D
9	A	19	C	29	D	39	B
10	C	20	C	30	C	40	D

1 D

In H_3^+ ,
 $p = 3$, $n = 0$, $e = 3 - 1 = 2$ (one less e than p)

2 D

No. of moles of helium remains the same at the two temperatures. Using $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$,

$$\frac{1 \times 10^5 \times V_1}{20 + 273} = \frac{P_2 \times (V_1 + 3V_1)}{100 + 273}$$

$$P_2 = 3.18 \times 10^4 \text{ Pa}$$

3 B

Mass of CaCO_3 in one chicken's egg shell

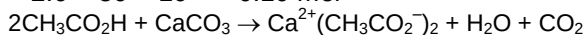
$$= 50 \times \frac{5}{100} = 2.5 \text{ g}$$

No. of moles of CaCO_3 in one chicken's egg shell

$$= 2.5 \div 100.1 = 0.025 \text{ mol}$$

No. of moles of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$ used

$$= 2.0 \times 50 \times 10^{-3} = 0.10 \text{ mol}$$



No. of moles of CaCO_3 needed

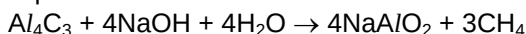
$$= 0.10 \div 2 = 0.050 \text{ mol}$$

No. of complete chicken's egg shells needed

$$= 0.050 \div 0.025 = 2$$

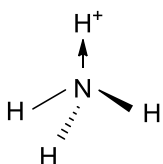
4 A

Equation:



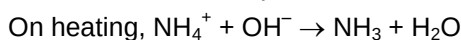
Hydrocarbon is CH_4 .

5 D

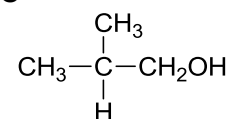


NH_4^+ is tetrahedral. The bond angles are 109° and the bonds are all of the same length.

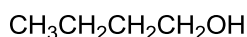
NH_4^+ ions are formed when NH_3 behaves as a base, i.e. a proton acceptor.



6 C



2-methylpropan-1-ol



butan-1-ol

Option A: Both 2-methylpropan-1-ol and butan-1-ol can form intermolecular hydrogen bonds due to the presence of $-\text{OH}$ in the molecules.

Option B: Both molecules have strong covalent bonds between their atoms.

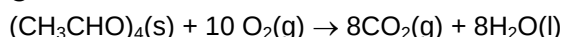
Options C and D: 2-methylpropan-1-ol has weaker dispersion forces than butan-1-ol as 2-methylpropan-1-ol is more spherical and has less (not more) surface area for electron interaction than butan-1-ol.

7 D

Options A, B and D: K_{eq} is unaffected by increasing the pressure, adding a catalyst or a shift in position of equilibrium. K_{eq} is only affected by a change in temperature. Hence ΔG_{eq} has the same value at constant temperature.

Option C: When $K_{\text{eq}} < 1$, $\lg K_{\text{eq}}$ will be negative and ΔG_{eq} will be positive according to the equation $\Delta G_{\text{eq}} = -2.303 RT \lg K_{\text{eq}}$, i.e. the dissolution of CO_2 in water is non-spontaneous when $K_{\text{eq}} < 1$.

8 C



$\Delta H_{\text{c}}^\ominus$ metaldehyde

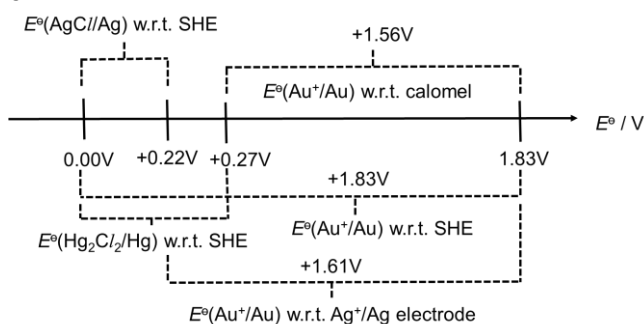
$$= (8\Delta H_{\text{f}}^\ominus \text{CO}_2 + 8\Delta H_{\text{f}}^\ominus \text{H}_2\text{O}) - \Delta H_{\text{f}}^\ominus \text{metaldehyde}$$

Hence $\Delta H_{\text{f}}^\ominus$ metaldehyde

$$= (8\Delta H_{\text{f}}^\ominus \text{CO}_2 + 8\Delta H_{\text{f}}^\ominus \text{H}_2\text{O}) - \Delta H_{\text{c}}^\ominus \text{metaldehyde}$$

$$= (8\Delta H_{\text{c}}^\ominus \text{carbon} + 8\Delta H_{\text{c}}^\ominus \text{hydrogen}) - \Delta H_{\text{c}}^\ominus \text{metaldehyde}$$

9 A



Option A: $E^\ominus(\text{Au}^+/\text{Au})$ wrt the SHE = $+1.56 + (+0.27) = +1.83 \text{ V}$ (refer to diagram above)

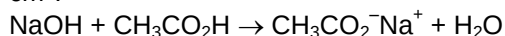
Option B: $E^\ominus(\text{Au}^+/\text{Au})$ wrt the AgCl/Ag electrode = $+1.56 + (0.27 - 0.22) = +1.61 \text{ V}$ (refer to diagram above)

Option C: The reduction potential of AgCl/Ag half-cell ($+0.22 \text{ V}$) is more positive than that of H^+/H_2 half-cell (0.00 V). Hence Ag has a lower tendency to be oxidised than H_2 .

Option D: The reduction potential of $\text{Hg}_2\text{Cl}_2/\text{Hg}$ half-cell ($+0.27 \text{ V}$) is more positive than that of AgCl/Ag half-cell ($+0.22 \text{ V}$). Hence Hg_2Cl_2 has a higher tendency to be reduced than AgCl .

10 C

Let volume of $0.100 \text{ mol dm}^{-3}$ NaOH added be $V \text{ cm}^3$.



No. of moles of NaOH added (limiting reagent)

$$= 0.100 V \div 1000 = V \times 10^{-4} \text{ mol}$$

$$= \text{no. of moles of } \text{CH}_3\text{CO}_2^-$$

No. of moles of $\text{CH}_3\text{CO}_2\text{H}$ left
 $= (0.100 \times 20 \div 1000) - (V \times 10^{-4})$
 $= (20 - V) \times 10^{-4} \text{ mol}$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

$$1.8 \times 10^{-5} = \frac{(10^{-5.5})(V \times 10^{-4})}{(20 - V) \times 10^{-4}}$$

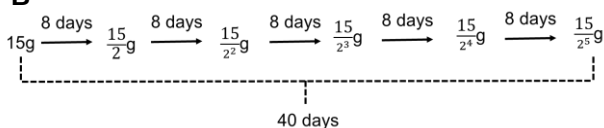
$$V = 17.0 \text{ cm}^3$$

11 C

	$\text{H}_2(\text{g})$	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
Initial / mol	0.10	0.10		0
Change / mol	-0.03	-0.03		+0.06
Eqm / mol	0.07	0.07		0.06

$$K_c = \frac{[\text{HI}]^2}{[\text{I}_2][\text{H}_2]} = \frac{(0.06)^2}{(0.07)^2} = 0.735$$

12 B



40 days is equivalent to 5 half-lives; hence the mass of ^{131}I left would be $\frac{15}{2^5} \text{ g}$.

13 C

Option A shows the properties of a Group I element.

Option B shows the properties of a non-metal with low electrical conductivity.

Option C shows the properties of a Group II element with relatively high melting point and has high electrical conductivity. Melting point is higher for Group II elements than Group I elements due to stronger metallic bonds.

Option D shows the properties of a transition metal with very high melting point $> 1000^\circ\text{C}$ and very high density.

14 A

From the acid-base nature of the oxides, it can be deduced that X is in Group III, Y is in Group I or Group II, and Z is a non-metal. Since ionic radius of metal ion decreases across the period due to increasing nuclear charge, ion of X is smaller than ion of Y. Non-metal ion of the same period has a larger ionic radius than a metal ion as it gains electrons to form an additional shell of electrons. Hence, ion of Z has the largest ionic radius.

15 D

Option A: Phosphorus also forms two acidic oxides, P_4O_6 and P_4O_{10} .

Option B: Ar has the highest 1st ionisation energy.

Option C: Phosphorus and chlorine can also form compounds with variable oxidation states, e.g. PCl_3 and PCl_5 , Cl^- and ClO^- .

Option D: Only sulfur exists as S_8 simple molecules.

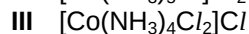
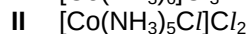
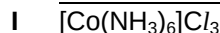
16 B

In hot $\text{KOH}(\text{aq})$, Cl_2 undergoes disproportionation reaction as shown below.



17 D

Formula of complex



Option A: All complexes, I to IV, have coordination number of 6.

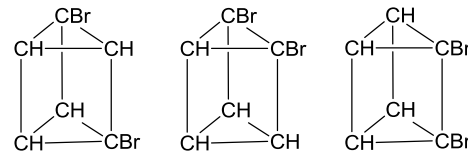
Option B: Charge of the cation depends on how many Cl^- ligand it has. Only cations in complexes III and IV have the same charge of +1. Cation in complex I has a charge of +3 and cation in complex II has a charge of +2.

Option C: Complex I only consists of ammonia ligands since all 3 moles of Cl^- are precipitated by AgNO_3 per mole of the complex.

Option D: Complexes III and IV have the same structural formula but the ligands have different arrangement in space as they have different colours.

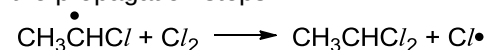
18 B

3 structural isomers are shown below.

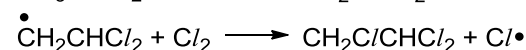
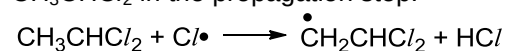


19 C

Option A: CH_3CHCl_2 can be formed from one of the propagation steps:

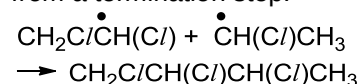


Option B: $\text{CHCl}_2\text{CH}_2\text{Cl}$ can be formed from CH_3CHCl_2 in the propagation step:



Option C: $\text{CH}_3\dot{\text{C}}\text{H}_2$ is not produced from $\text{CH}_3\text{CH}_2\text{Cl}$ as the $\text{C}-\text{Cl}$ bond is not broken. Hence $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ is not likely to be formed.

Option D: $\text{CH}_2\text{ClCH}(\text{Cl})\text{CH}(\text{Cl})\text{CH}_3$ can be formed from a termination step:

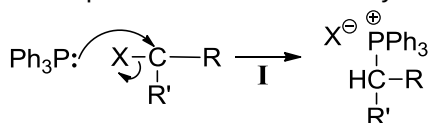


20 C

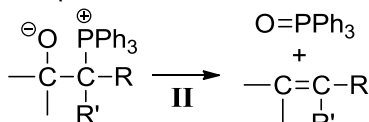
Positive test with Tollens' reagent $\Rightarrow$ U contains $-\text{CHO}$ group. Since U is oxidised by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{H}$, U is $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$. U can be reduced by NaBH_4 to form V, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$, which reacts with CH_3COCl to form an ester W, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OCOCH}_3$.

21 A

Nucleophilic substitution of $-X$ by $:PPh_3$ in stage I.



Elimination by removal of atom or groups of atoms from adjacent carbon atoms in stage II to form a multiple bond.



[In condensation reaction, two molecules react and become covalently bonded with the concurrent loss of a small molecule, e.g. H_2O , HCl .]

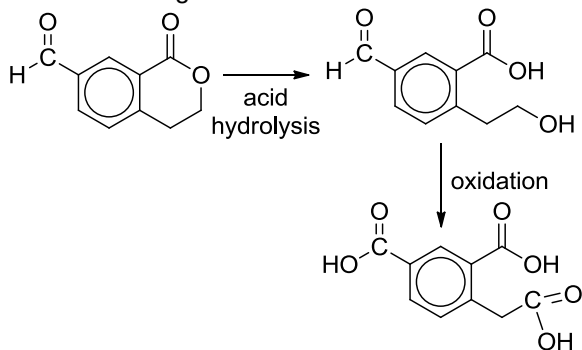
22 D

Option A: The benzaldehyde is reduced by H_2 , Pd. However, there is no visible observation to distinguish between the two compounds.

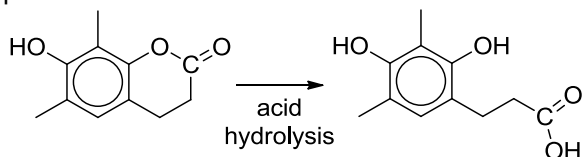
Option B: Phenol cannot react with $Br_2(aq)$ in this question as it has substituents at the 2-, 4- and 6- positions w.r.t. the phenol functional group.

Option C: The benzaldehyde cannot react with Fehling's reagent. It can only react with Tollens' reagent.

Option D: Orange acidified $K_2Cr_2O_7$ turns green for the following molecule.



Orange acidified $K_2Cr_2O_7$ remains orange for the following molecule as there is no oxidation taking place.



23 A

Size of atom: $F < Cl < Br < I$

Strength of bond: $C-F > C-Cl > C-Br > C-I$

The larger the size of the halogen atom, the longer and weaker the $C-X$ bond (where $X = F, Cl, Br, I$) which is more easily broken. Hence $C-I$ bond is most easily broken and the I^- ions formed will react with $Ag^+(aq)$ to form a yellow precipitate of AgI .

24 B

Option A: Warfarin has 2 stereoisomers as it has only one chiral centre. It has no geometric isomers as the $C=C$ bond is found in the ring structure.

Option B: The $-OH$ group reacts with CH_3COCl to form an ester and white fumes of HCl .

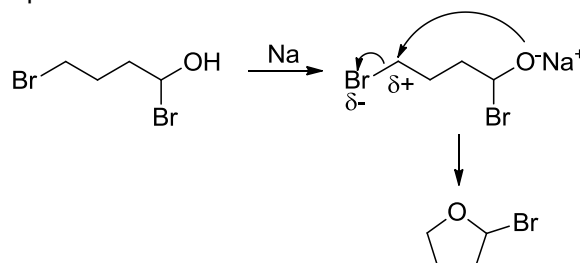
Option C: Warfarin does not react with $KCN(alc)$ in the presence of heat as there is no alkyl halide (i.e. RX) present. The ketone functional group present in Warfarin can react with HCN , $NaCN$ catalyst at room temperature, not $KCN(alc)$.

Option D: 1 mol of warfarin reacts with 2 mol of H_2 gas in the presence of nickel catalyst and heat as both the ketone and the alkene functional groups are reduced.

25 C

Option A: $CH_3CHBrCH_3$ undergoes elimination reaction with $CH_3CH_2O^-Na^+(alc)$, reflux to form $CH_3CH=CH_2$.

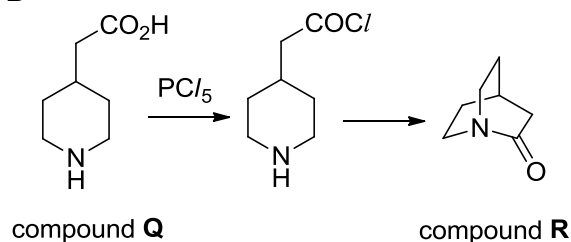
Option B:



Option C: Amine does not react with carboxylic acid to form amide. N.B. Amine reacts with acyl chloride to form amide.

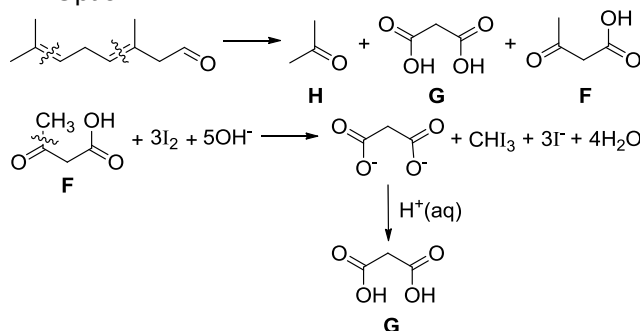
Option D: $-CN$ is reduced by H_2 , Pt to $-CH_2NH_2$.

26 B

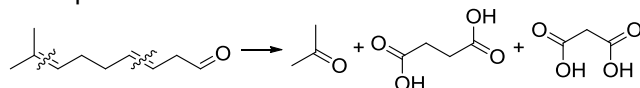


27 A

Option A:

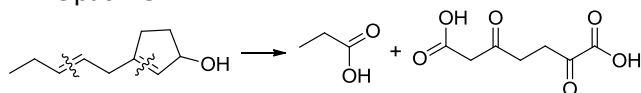


Option B:



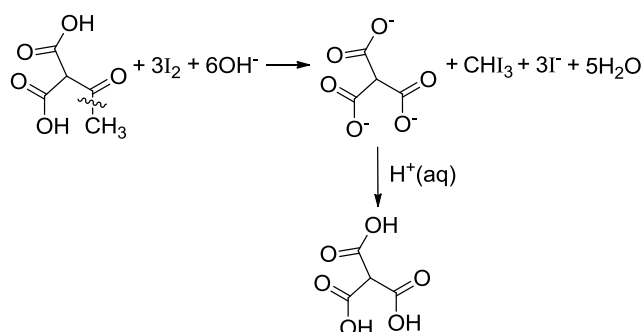
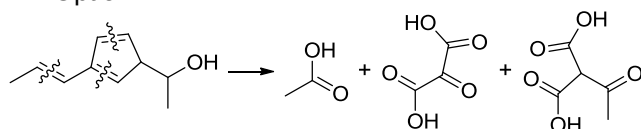
None of the products react with alkaline aqueous iodine to form any of the other product.

Option C:



Only two products are formed.

Option D:



28 B

Both the amide and ester functional groups will undergo acid hydrolysis. Amine will undergo acid-base reaction with HCl(aq) .

29 D

Options A and B: LiAlH_4 in dry ether is unable to reduce alkene.

Option C: KMnO_4 with $\text{H}_2\text{SO}_4(\text{aq})$, heat will cause both $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{CH}_3$ side chains on the benzene ring to be oxidised to $-\text{CO}_2\text{H}$ as both side chains have a benzylic hydrogen.

Option D: Both aldehyde and alkene functional groups will be reduced by H_2 , Pt. Only the primary alcohol will be oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ with $\text{H}_2\text{SO}_4(\text{aq})$, heat to form $-\text{CO}_2\text{H}$.

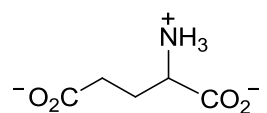
30 C

Point S corresponds to the second equivalence

point for the titration of $\text{HO}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_3^+-\text{CO}_2\text{H}$ with NaOH .

Relative acid strength: $\alpha-\text{CO}_2\text{H} > \text{alkyl}-\text{CO}_2\text{H} > \alpha-\text{NH}_3^+$.

Thus the species present at point S is



31 B (1 and 2 only are correct)

Option 1: Correct

Since $[\text{HBr}]$ is in the denominator of the rate equation, an increase in its concentration will lower the value of rate.

Option 2: Correct

For the hydrogen / iodine reaction, the given rate equation follows the molecularity of the given equation ($\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$) but this is not the case for the hydrogen / bromine reaction. Hence, the slow rate determining step involves 1 molecule of H_2 and 1 molecule of I_2 , which could be a single step reaction for the hydrogen / iodine reaction.

Option 3: Incorrect

There is no evidence from the rate equation that the mechanism of the hydrogen / bromine reaction involves free radicals.

32 B (1 and 2 only are correct)

Option 1: Correct

From $\text{Mg(s)} + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{s})$, the enthalpy change of formation of MgCl_2 is -642 kJ mol^{-1} , i.e. the energy change when 1 mol of MgCl_2 is formed from its constituent elements in their standard states, Mg(s) and $\text{Cl}_2(\text{g})$.

Option 2: Correct

From $\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{g})$,
 $+2334 = \Delta H_{\text{atom}}(\text{Mg}) + 1^{\text{st}} \text{ I.E.} + 2^{\text{nd}} \text{ I.E.}$

$\Delta H_{\text{atom}}(\text{Mg}) = +2334 - 736 - 1450 = +148 \text{ kJ mol}^{-1}$

Option 3: Incorrect

From $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{g})$,
 $-454 = \text{B.E.}(\text{Cl}-\text{Cl}) + 2(1^{\text{st}} \text{ E.A.})$

$1^{\text{st}} \text{ E.A.} = (-454 - 244) \div 2 = -349 \text{ kJ mol}^{-1}$

33 A (1, 2 and 3 are correct)

Option 1: Correct

$\text{NaBO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- \rightleftharpoons \text{NaBH}_4 + 8\text{OH}^-$ $E^\ominus = -1.24 \text{ V}$

$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$ $E^\ominus = +0.40 \text{ V}$

$E^\ominus_{\text{cell}} = 0.40 - (-1.24) = +1.64 \text{ V}$

Option 2: Correct

NaBH_4 is oxidised to NaBO_2 at the anode X while O_2 is reduced to OH^- at the cathode Y.

Option 3: Correct

$\text{O}=\text{B}=\text{O}^-$ The BO_2^- anion has 2 bond pairs and 0 lone pair around the central B atom, giving it a linear shape with a bond angle of 180° .

34 D (1 only is correct)

Option 1: Correct

$\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

Let the solubility of Ca(OH)_2 be $y \text{ mol dm}^{-3}$.

$[\text{Ca}^{2+}][\text{OH}^-]^2 = 4.7 \times 10^{-6}$

$(y)(2y)^2 = 4.7 \times 10^{-6}$

$y = 0.0106 \text{ mol dm}^{-3}$

$[\text{OH}^-] = 2y = 0.021 \text{ mol dm}^{-3}$

Option 2: Incorrect

When equal volumes of solutions are mixed together, dilution occurs and their concentrations are halved. Hence, new $[\text{Ca}^{2+}] = 0.01 \text{ mol dm}^{-3}$ and new $[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$.

Ionic product = $[\text{Ca}^{2+}][\text{OH}^-]^2 = (0.01)(0.01)^2 = 1.0 \times 10^{-6} < 4.7 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$

Since ionic product $< K_{\text{sp}}(\text{Ca(OH)}_2)$, precipitation will not occur.

Option 3: Incorrect

Sn(OH)₂ has the lowest solubility amongst the three metal hydroxides.

metal hydroxide	K_{sp}	Solubility / mol dm ⁻³
Ca(OH) ₂	4.7×10^{-6} mol ³ dm ⁻⁹	0.0106
Sn(OH) ₂	5.4×10^{-27} mol ³ dm ⁻⁹	1.11×10^{-9}
Cr(OH) ₃	6.7×10^{-31} mol ⁴ dm ⁻¹²	1.26×10^{-8}

35 D (1 only is correct)

Option 1: Correct

Down the group, cationic radius increases and charge density of M²⁺ decreases. Polarising power of M²⁺ decreases and the electron cloud of iodate(V) ion is less distorted. Thermal stability of M(IO₃)₂ increases.

Option 2: Incorrect

Since L.E. $\propto \frac{q^+q^-}{r_+ + r_-}$, magnitude of L.E. decreases

down the group with increasing cationic radius, r₊.

Option 3: Incorrect

Charge density of M²⁺ ion decreases down the group as ionic radius increases while the charge remains the same.

36 A (1, 2 and 3 are correct)

Option 1: Correct

Overall charge of complex is neutral with two Cl⁻ ligands and one RCO₂⁻ ligand. Hence the oxidation number of M is +3.

Option 2: Correct

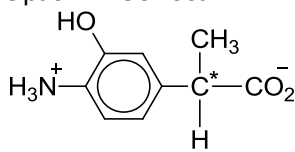
Coordination number is the number of dative bonds around M which is equal to 6 in the complex.

Option 3: Correct

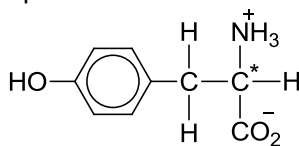
Besides the two Cl⁻ ligands, the other four dative bonds are from the same tetradentate ligand.

37 A (1, 2 and 3 are correct)

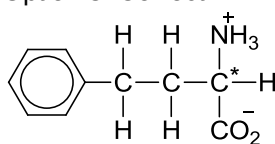
Option 1: Correct



Option 2: Correct



Option 3: Correct



38 D (1 only is correct)

Option 1: Correct

Molecule I is the cis isomer and molecule II is the trans isomer, hence they are stereoisomers. Both -NO₂ and Br are electron-withdrawing in nature.

Since these two groups are on the same side of the C=C bond in molecule I, the overall dipole moment is larger than that in molecule II.

Option 2: Incorrect

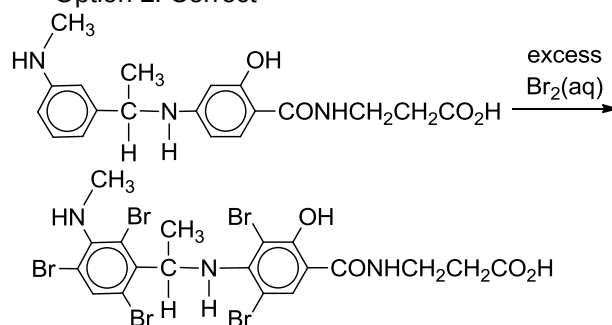
Molecules I and II are structural isomers of each other and are not stereoisomers.

Option 3: Incorrect

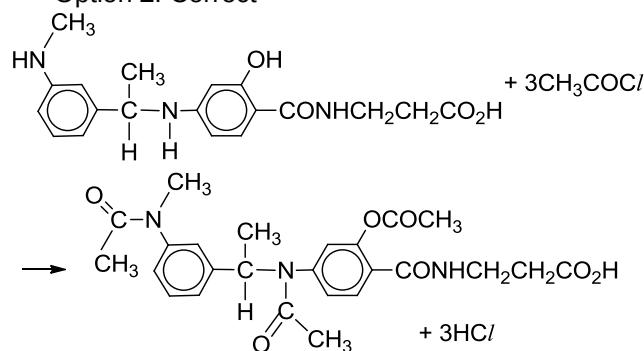
Molecules I and II are enantiomers, hence they are stereoisomers. The overall dipole moment of the two molecules are identical.

39 B (1 and 2 only are correct)

Option 1: Correct

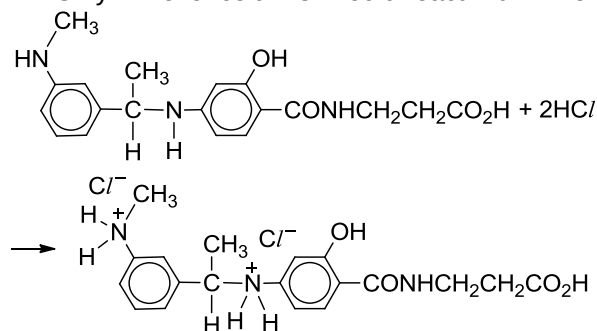


Option 2: Correct



Option 3: Incorrect

Only 2 mol of cold HCl would react with 1 mol of T.



40 D (1 only is correct)

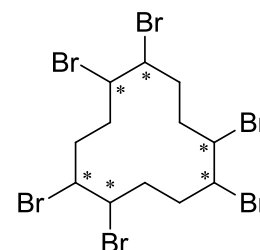
Option 1: Correct

Option 2: Incorrect

The molecular formula is C₁₂H₁₈Br₆.

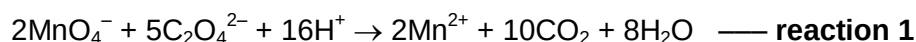
Option 3: Incorrect

The C-C-C bond angles are all 109.5° as every C atom is sp³ hybridised.



1 Planning (P)

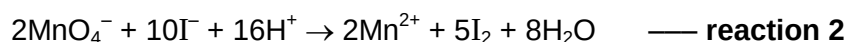
When potassium manganate(VII) reacts with sodium ethanedioate, a redox reaction occurs as shown below:



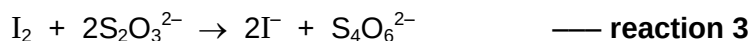
A product that is generated during the course of the reaction and helps to speed up the reaction rate is known as an autocatalyst. The autocatalyst for the above reaction is Mn^{2+} .

The kinetics of this reaction can be investigated by determining the concentration of MnO_4^- over the course of the reaction. Fixed aliquots (portions) of the reaction mixture are withdrawn at regular time intervals and added to an excess of potassium iodide.

The MnO_4^- in the aliquots reacts with excess iodide as shown below.



The amount of iodine formed can then be determined by titration with the sodium thiosulfate solution as shown below.



The volume of sodium thiosulfate used is proportional to the concentration of MnO_4^- .

- (a) In this experiment, both sodium ethanedioate and sulfuric acid are used in large excess. Explain the purpose of using a large excess of sodium ethanedioate and sulfuric acid.

This is to ensure that the concentration of sodium ethanedioate and sulfuric acid remains almost constant throughout the reaction / concentration do not affect rate. Hence, the order of reaction with respect to MnO_4^- can be determined.

- (b) Using the information given above, you are required to write a plan for the determination of the concentration of MnO_4^- at regular timing intervals.

You may assume that you are provided with the following:

- 0.0500 mol dm⁻³ potassium manganate(VII), KMnO_4
- 0.500 mol dm⁻³ sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$
- 1.00 mol dm⁻³ sulfuric acid, H_2SO_4
- 0.200 mol dm⁻³ potassium iodide, KI
- solid $\text{Na}_2\text{S}_2\text{O}_3$
- starch indicator
- stopwatch
- apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:

- justification for
 - the volume of each reactants to be used in **reaction 1** so as to allow a minimum of **6 aliquots** of the reaction mixture to be withdrawn and the concentration of MnO_4^- in each aliquot to be determined;
 - the intended concentration of the sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, to be used;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain.

[10]

Justification

Assuming 10 cm³ aliquot is withdrawn for each titration, minimum volume required for reaction 1 is 60 cm³.

Volume of MnO₄⁻ used = 25.0 cm³

Volume of Na₂C₂O₄ used = 50.0 cm³

Volume of H₂SO₄ used = 25.0 cm³

Total volume used for reaction 1 = 100 cm³
for all the volumes used.

Calculation for concentration of Na₂S₂O₃ to be used

$$\begin{aligned}\text{Amount of MnO}_4^- \text{ present in reaction 1} &= 0.0500 \times \frac{25.0}{1000} \\ &= 1.25 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of MnO}_4^- \text{ present in 10 cm}^3 \text{ aliquot} &= 1.25 \times 10^{-3} \times \frac{10.0}{100} \\ &= 1.25 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of I}_2 \text{ produced in reaction 2} &= 1.25 \times 10^{-4} \times \frac{5}{2} \\ &= 3.13 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amount of S}_2\text{O}_3^{2-} \text{ required in reaction 3} &= 3.125 \times 10^{-4} \times 2 \\ &= 6.25 \times 10^{-4} \text{ mol}\end{aligned}$$

Assuming a titre volume of 25.00 cm³ (acceptable range 10–30 cm³)

$$\begin{aligned}[\text{S}_2\text{O}_3^{2-}] \text{ used for titration} &= 6.25 \times 10^{-4} \div \frac{25.00}{1000} \\ &= 0.0250 \text{ mol dm}^{-3}\end{aligned}$$

To prepare a standard solution of 100 cm³ Na₂S₂O₃

$$\begin{aligned}\text{Mass of Na}_2\text{S}_2\text{O}_3 \text{ used} &= 0.0250 \times \frac{100}{1000} \times (158.2) \\ &= 0.396 \text{ g}\end{aligned}$$

Preparation of Na₂S₂O₃ standard solution

1. Weigh accurately about 0.315 g of Na₂S₂O₃ into a beaker.
2. Add distilled water to the beaker to dissolve Na₂S₂O₃ and transfer the solution quantitatively into a 100 ml standard flask.
3. Add distilled H₂O to the mark and shake the flask to give a homogenous solution.

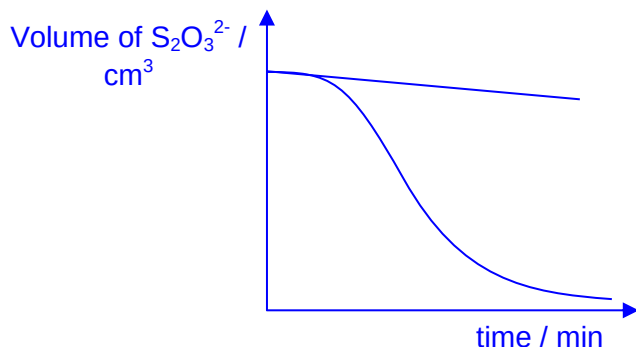
Preparation of reaction mixture

1. Using a 100 cm³ measuring cylinder, add 50.0 cm³ of Na₂C₂O₄ and 25 cm³ H₂SO₄ into a conical flask.
2. Add 25 cm³ MnO₄⁻ to a 50 cm³ measuring cylinder.
3. Pour MnO₄⁻ to the reaction mixture in the conical flask and start the stopwatch immediately.
Ensure thorough mixing by swirling the flask.
(marking point for starting stopwatch is awarded only if MnO₄⁻ is added as the last reagent.)
4. At about 1 min, pipette 10.0 cm³ of the reaction mixture into a conical flask containing 10 cm³ of KI solution. Label conical flask 1.
5. Repeat step 4 five more times at about two minute intervals, transferring the aliquots into 5 separate conical flasks. Label conical flask 2 to 6.

Titration with sodium thiosulfate

1. Fill a 50 cm³ burette with Na₂S₂O₃.
2. Titrate the iodine in conical flask 1 against Na₂S₂O₃.
3. When the colour of the solution turns pale yellow, add about 1 cm³ of starch indicator. The solution will turn blue-black.
4. Continue the titration and the end-point is reached when the blue-black colour just disappears.
3. Repeat step 2 to 4 for conical flask 2 to 6.

Shape of graph expected



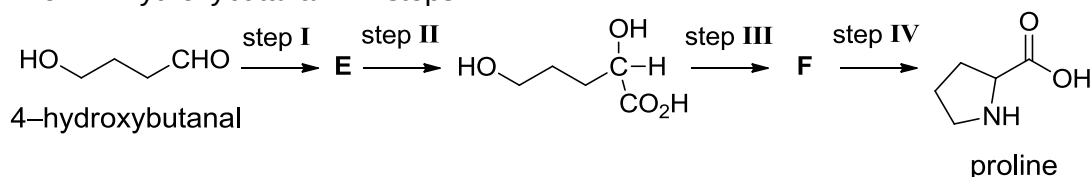
[12, max 10]

- (c) The order of reaction with respect to MnO₄⁻ can be determined by initial rate method. Use your graph, suggest how the initial rate can be determined.
As shown in the graph in (b), draw the tangent and then determine the gradient which gives the initial rate of reaction.

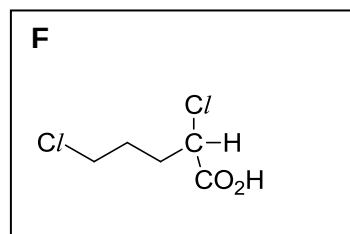
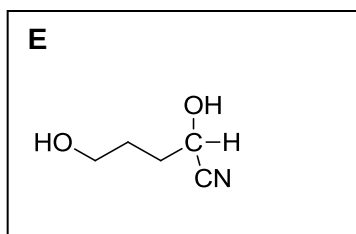
[1]

[Total: 12]

- 2 (a) Proline (pro) is one of the naturally occurring amino acids. It can be synthesised from 4-hydroxybutanal in 4 steps.



- (i) Suggest the structures of **E** and **F**.

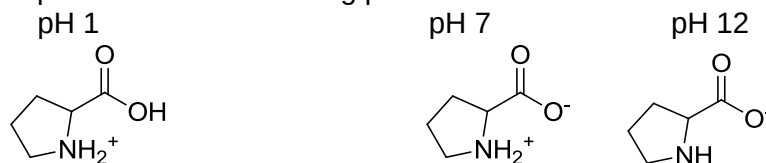


[2]

- (ii) Suggest the reagents and conditions required for the following steps.
 Step I: **HCN with KCN catalyst, room temperature**
 Step III: **conc HCl, ZnCl₂, heat,**
 Step IV: **NH₃(alc) heat in a sealed tube**

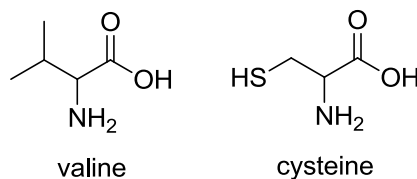
[3]

- (b) The two pK_a values associated with proline are 2.0 and 10.5. Make use of these pK_a values to suggest the major species present in the solution of proline with the following pH values.

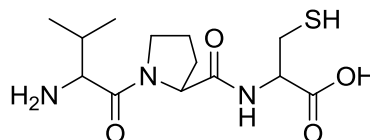


[3]

- (c) The structures of amino acids, valine (val) and cys are shown below.



- (i) Draw the structure of val-pro-cys peptide.



[2]

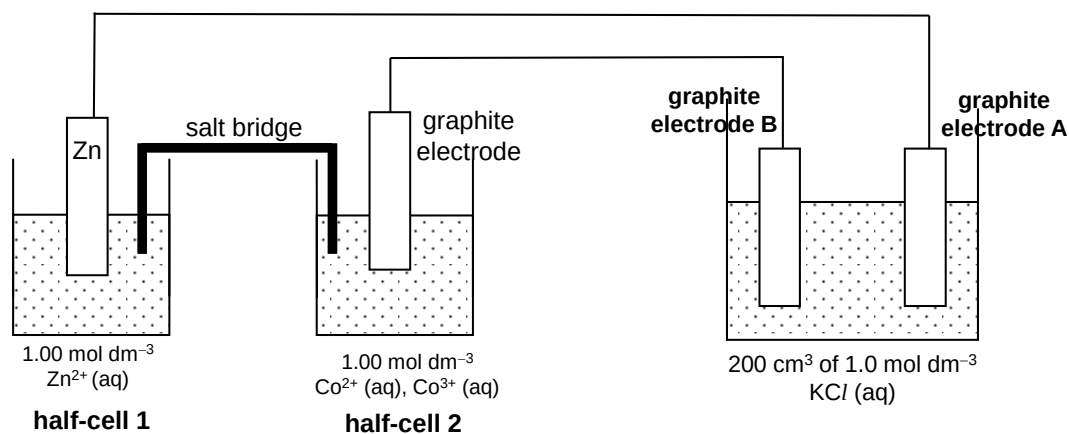
- (ii) State the possible R group interactions that val-pro-cys may have with another val-pro-cys peptide.

Disulfide bond formed between the CH_2SH in the cys groups.
van der waal's forces formed between the non-polar $\text{CH}(\text{CH}_3)_2$ groups in the valine or the non-polar $\text{CH}_2\text{CH}_2\text{CH}_2$ in the proline.

[2]

[Total: 12]

- 3 (a) A student used the following setup in an attempt to produce chlorine gas using potassium chloride solution.



- (i) Using relevant data from the *Data Booklet*, predict the type of redox reaction that occurs at each half-cell. State the polarity at the graphite electrodes **A** and **B**.

Half-cell 1: **oxidation**

Half-cell 2: **reduction**

Graphite electrode **A**: **negative (reduction occurs)**

Graphite electrode **B**: **positive (oxidation occurs)**

[2]

- (ii) 20 cm³ of hydrogen gas was collected on one of the electrodes after 10 minutes at room temperature and pressure. Assuming 20% of the hydrogen gas was lost during collection, calculate the current produced by the battery setup.

Graphite electrode A: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

Amount of hydrogen gas collected = $20 / 24000 = 8.33 \times 10^{-4}$ mol

Actual amount of hydrogen produced = $(8.33 \times 10^{-4}) \times \frac{5}{4} = 1.04 \times 10^{-3}$ mol

**Number of moles of electrons transferred = $2 \times (1.04 \times 10^{-3})$
= 2.08×10^{-3} mol**

$Q = It$

$2.08 \times 10^{-3} \times (96500) = I \times (10 \times 60)$

Current, $I = 0.335$ A

[2]

- (iii) With reference to relevant data from the *Data Booklet*, explain the absence of chlorine being discharged on the other electrode.

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^\circ = +1.23 \text{ V}$

$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^- \quad E^\circ = +1.36 \text{ V}$

At the anode, $E^\circ(\text{O}_2|\text{H}_2\text{O})$ is less positive than $E^\circ(\text{Cl}_2|\text{Cl}^-)$, so H_2O will undergo oxidation preferentially to give O_2 .

[1]

- (b) 20 cm³ of a gas mixture containing gaseous ethanol, carbon monoxide and excess oxygen was burned completely. There was a contraction of 1 cm³. When the product mixture was passed through sodium hydroxide, there was a further contraction of 6 cm³. All gas volumes are measured at 400 K and 1 atm.

Determine the molar composition of the ethanol and carbon monoxide in this gas mixture.

Let the volume of $\text{C}_2\text{H}_5\text{OH}$ and CO measured at 1 atm be x cm³ and y cm³, respectively.

$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
c/cm³ $-x$ $-3x$ $+2x$ $+3x$
Total change in volume = $2x + 3x - x - 3x = x$

$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
c/cm³ $-y$ $-1/2y$ $+y$
Total change in volume = $y - y - \frac{1}{2}y = -\frac{1}{2}y$
Hence $x - \frac{1}{2}y = -1$

The further contraction is due to the removal of CO_2 by NaOH ,

Hence, $2x + y = 6$

$x = 1, y = 4$

Molar composition of ethanol = $1/20 \times 100\% = 5\%$

Molar composition of $\text{CO} = 4/20 \times 100\% = 20\%$

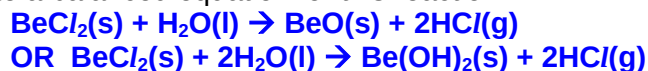
[3]

[Total: 8]

- 4 Magnesium and beryllium are Group II elements but beryllium behaves differently from that of magnesium. There is said to be a 'diagonal relationship' between beryllium and aluminium as they show similar chemical behaviour due to their similarities in electronegativity and charge density.

- (a) (i) When a few drops of water are added to solid beryllium chloride, steamy white fumes are evolved and a white solid remains, which is insoluble in water.

Write a balanced equation for this reaction.



[1]

- (ii) When a large amount of water is added to solid beryllium chloride, a clear, weakly acidic solution is obtained. Explain.

Due to the high charge density of Be^{2+} , BeCl_2 undergoes hydration and hydrolysis/ $\text{Be}^{2+}(\text{aq})$ pulls electrons away from one of the surrounding water molecules, hence weakening the O–H bond which results in the release of a proton and give rise to an acidic solution.

[1]

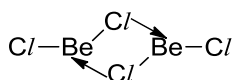
- (iii) At 750°C , the relative molecular mass of gaseous beryllium chloride corresponds to the formula BeCl_2 . At 550°C , gaseous beryllium chloride exists as a mixture of BeCl_2 and Y (relative molecular mass of Y is 160).

Determine the molar composition of gaseous beryllium chloride at 550°C which has a relative molecular mass of 100. Draw a diagram to illustrate the nature of the bonding in Y and indicate the value of the bond angle about Be.

$$100 = 80x + 160(1-x)$$

$$x = 0.75 \text{ and } 1-x = 0.25$$

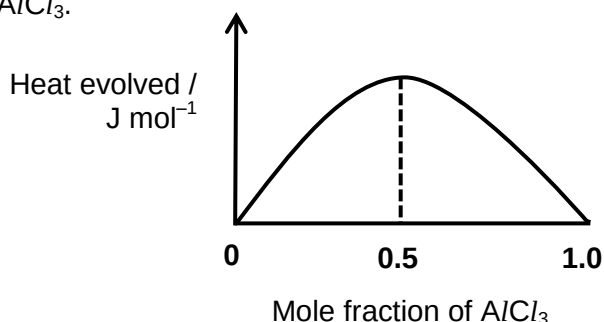
Composition is 75% BeCl_2 and 25% Y



Trigonal planar with respect to Be, hence bond angle is 120°

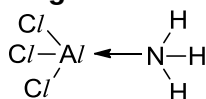
[2]

- (iv) When aluminium chloride, AlCl_3 , is mixed with ammonia, compound Z is formed and the reaction is exothermic. The diagram below shows the relationship between the heat evolved per mole of the mixture and the mole fraction of AlCl_3 .



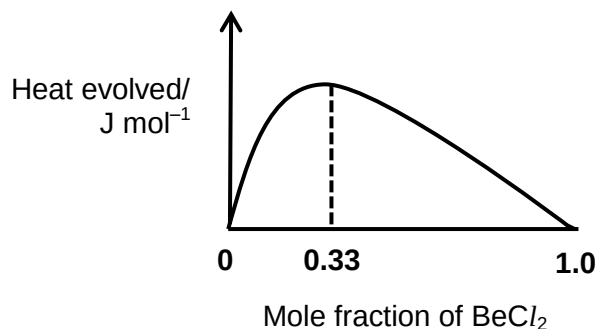
Draw a diagram to show the bonding in a molecule of compound Z.

Diagram of Compound Z :



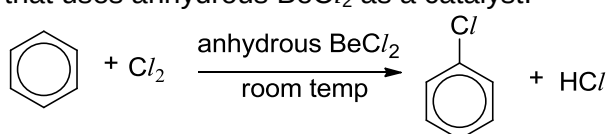
[1]

- (v) Sketch a labelled diagram similar to (a)(iv) that you would expect to obtain when $AlCl_3$ is replaced by $BeCl_2$.



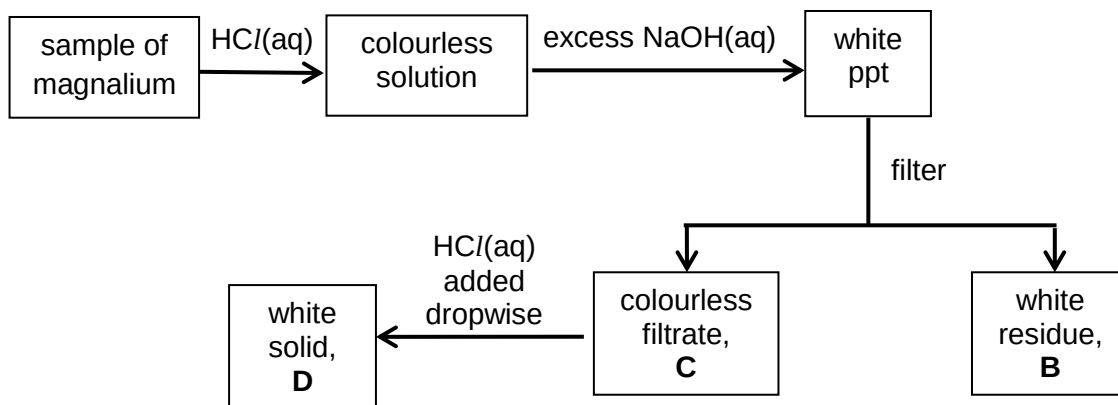
[1]

- (vi) Write a balanced equation of a chlorination reaction in Organic Chemistry that uses anhydrous $BeCl_2$ as a catalyst.



[1]

- (b) Magnalium is an alloy of aluminium and magnesium which is used in boat-building. The diagram below shows some reactions of magnalium.



Identify **B**, **C** and **D**.

B : $Mg(OH)_2$

C : $Al(OH)_4^-$

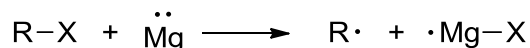
D : $Al(OH)_3$

[3]

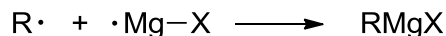
- (c) Grignard reagents, RMgX , can be prepared by the reaction of magnesium with halogenoalkane, RX , using dry ether as the solvent.

The mechanism of the reaction involves two steps.

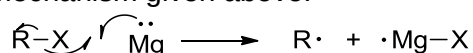
Step 1: It involves the transfer of one electron from Mg to the halogen X followed by the homolytic fission of the carbon–halogen bond. This forms MgX , which is a radical.



Step 2: MgX radical couples with the alkyl radical formed in step 1.



- (i) Draw curve arrows to show the movement of electrons in step 1 of the mechanism given above.



[1]

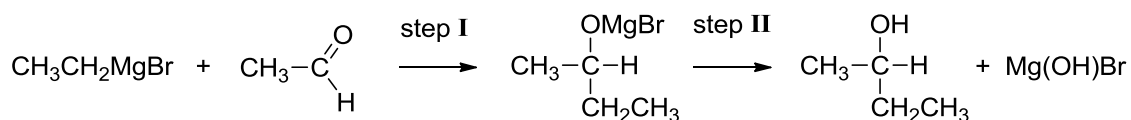
- (ii) Suggest which step in the mechanism is the rate-determining step. Explain your answer.

Step 1 is the rate-determining step

Step 1 has higher activation energy as it involves breaking of covalent bond.

[1]

Grignard reagents can be used to prepare alcohols from carbonyl compounds as shown by the reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with ethanal below:



- (iii) What type of reaction takes place in steps I and II?

step I : Nucleophilic addition

step II : Hydrolysis or Acid–base reaction

[2]

- (iv) The variation of the rate constant k with temperature for the reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with ethanal is given below:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where E_a denotes the activation energy in J mol^{-1} , R is the gas constant, and T is the temperature in Kelvin.

Given that at 25°C , the rate constant and activation energy of the reaction is $9.16 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and 102 kJ mol^{-1} respectively.

Explain, with calculations, the effect of temperature change on the rate of the reaction when the temperature is raised by 5°C .

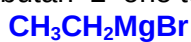
$$\ln \frac{k_2}{9.16 \times 10^{-3}} = -\frac{102000}{8.31} \left(\frac{1}{303} - \frac{1}{298} \right)$$

$$k_2 = 1.81 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

A rise in temperature results in a larger rate constant. Since the concentrations of the reactants are kept constant, a larger rate constant indicates a faster reaction. (or rate constant doubles, hence rate doubles)

[2]

- (v) Draw the structural formula of the Grignard reagent that will react with butan-2-one to form 3-methylpentan-3-ol in a similar two-step reaction.



[1]

- (vi) Suggest why $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{Br}$ and magnesium cannot be used to prepare the Grignard reagent $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{MgBr}$.

$\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_2\text{MgBr}$ cannot be prepared as it will react further with the ketone group in the same molecule.

[1]

- (vii) Ethanal is oxidised to ethanoic acid by acidified potassium dichromate. Using data from the Data Booklet and the data below, calculate E°_{cell} of the reaction.

$$E^\circ(\text{CH}_3\text{CO}_2\text{H}|\text{CH}_3\text{CHO}) = +0.92 \text{ V}$$

Hence, explain why the reaction takes place only in the presence of heat.

$$\begin{aligned} E^\circ_{\text{cell}} &= 1.33 - 0.92 \\ &= 0.41 \text{ V} \end{aligned}$$

$E^\circ_{\text{cell}} > 0$, hence reaction is thermodynamically feasible.

Heat is needed to overcome the high activation energy needed to break strong covalent bonds.

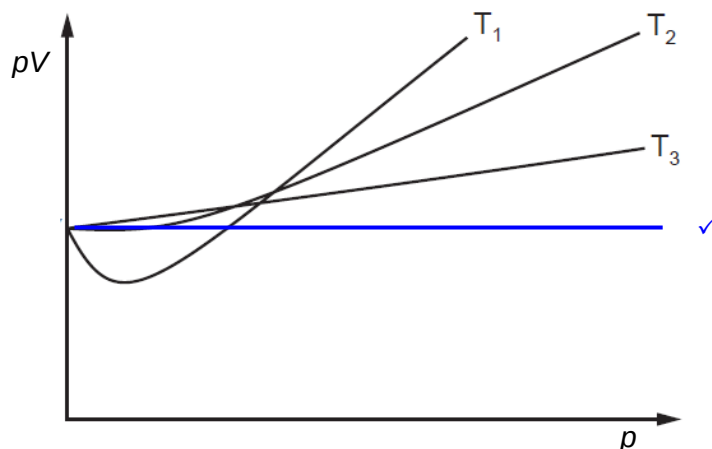
(or reaction is kinetically not feasible in the absence of heat as it involves breaking of strong covalent bonds)

[2]

[Total: 20]

- 5 (a) The relationship $pV = nRT$ can be derived from the laws of mechanics by assuming ideal behaviour for gases.

The graph represents the relationship between pV and p for a real gas at three different temperatures, T_1 , T_2 and T_3 .



- (i) Draw **one** line on the graph to show what the relationship should be for the same amount of an ideal gas and state which of T_1 , T_2 or T_3 is the lowest temperature.
 T_1 is the lowest temperature.

[1]

- (ii) State and explain the effect of pressure on the extent to which a gas deviates from ideal behaviour.
A gas deviates from ideal behaviour at high pressure as the molecular volume is significant / no longer negligible OR the intermolecular forces of attraction are significant.

[1]

- (b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask. The same flask was then weighed with only gas, **Y**, filling the flask. The results, measured at 26°C and $1.00 \times 10^5 \text{ Pa}$, are shown.

Mass of flask containing air = 47.930 g
 Mass of flask containing **Y** = 47.989 g
 Density of air = $0.00118 \text{ g cm}^{-3}$

Calculate the relative molecular mass, M_r , of **Y**.

$$\begin{aligned} \text{Mass of air} &= 0.00118 \times 100 = 0.118 \text{ g} \\ \text{Mass of flask} &= 47.930 - 0.118 = 47.812 \text{ g} \\ \text{Mass of Y} &= 47.989 - 47.812 = 0.177 \text{ g} \\ 1.00 \times 10^5 \times 100 \times 10^{-6} &= \frac{0.177}{M_r} \times 8.31 \times (26 + 273) \end{aligned}$$

$$M_r \text{ of Y} = 44.0$$

[2]

- (c) In recent years there has been worldwide interest in the possible extraction of 'shale gas' (a form of natural gas) as an important energy source.

One of the problems associated with using shale gas is its variable composition. **Table 1** shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

Table 1

source	CH ₄	C ₂ H _x	C ₃ H _y	CO ₂	N ₂
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formula above, **x** and **y** are variables.

- (i) Draw the structures of **three** possible compounds with the formula C₃H_y.

CH₃CH₂CH₃, CH₃CH=CH₂, CH₃C≡CH and CH₂CCH₂ [Any 3 of 4.]

[1]

- (ii) Which source of shale gas, **J**, **K**, **L** or **M**, will provide the most energy when burned? Explain your answer.

Source K

Source K has the highest percentage composition of hydrocarbons which will provide the most energy when burned.

[1]

- (iii) Suggest one method by which carbon dioxide can be removed from shale gas.

Carbon dioxide can be removed from shale gas by passing it through aqueous sodium hydroxide.

[1]

Table 2 shows a comparison of the relative amounts of pollutants produced when shale gas, fuel oil and coal are burned to produce **the same amount of energy**.

Table 2

air pollutant	shale gas	fuel oil	coal
CO ₂	117	164	208
CO	0.040	0.033	0.208
NO ₂	0.092	0.548	0.457
SO ₂	0.001	1.12	2.59
particulates	0.007	0.84	2.74

- (iv) Suggest why shale gas produces the smallest amount of CO₂.
Shale gas contains small hydrocarbon molecules with low C:H ratio unlike fuel oil and coal which contain more carbon atoms, and thus produces the smallest amount of CO₂.

[1]

- (v) Explain which of the three fuels, shale gas, fuel oil or coal, is the largest contributor to 'acid rain'.

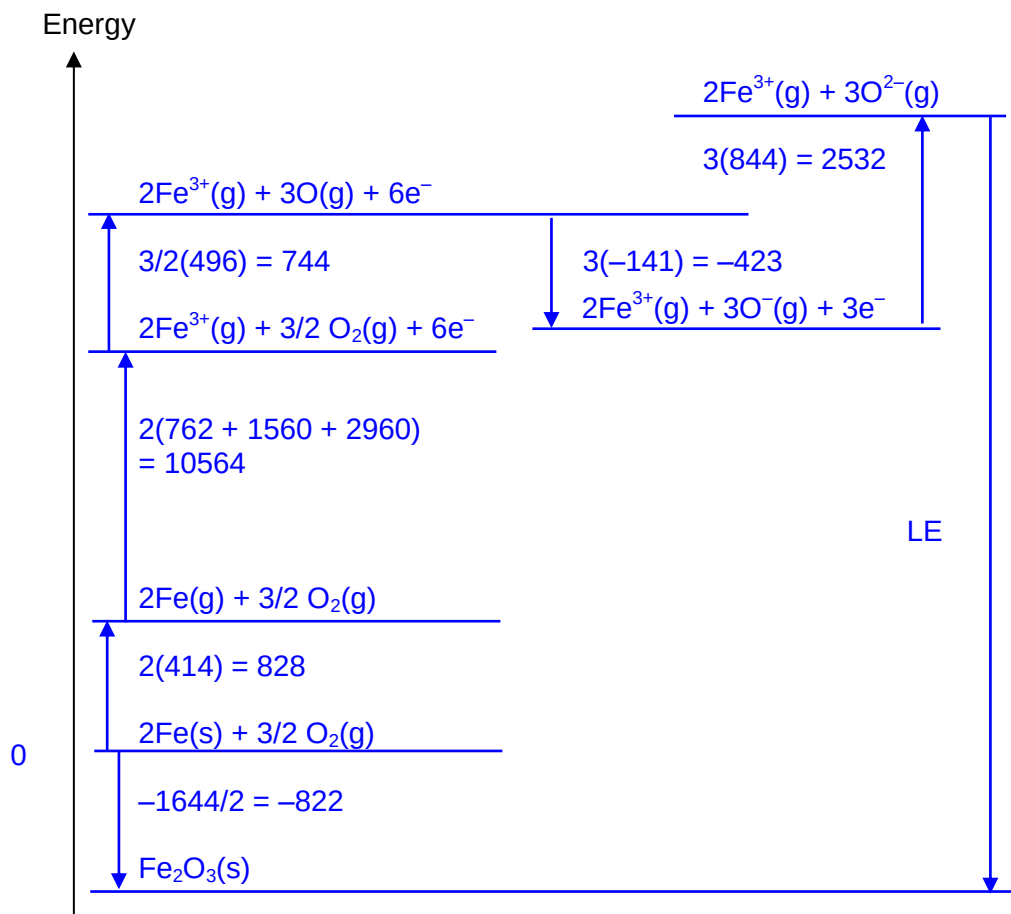
coal

Coal produced the largest relative amounts of CO₂, NO₂ and SO₂ when burned to produce the same amount of energy.

[1]

- (d) Use the following data and data from the *Data Booklet* to construct a labelled energy level diagram to determine the lattice energy of Fe_2O_3 .

enthalpy change of $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$	$-1644 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of Fe(s)	$+414 \text{ kJ mol}^{-1}$
electron affinity of the oxygen atom	-141 kJ mol^{-1}
electron affinity of the O^- ion	$+844 \text{ kJ mol}^{-1}$



By Hess' law,

$$-822 = 828 + 10564 + 744 - 423 + 2532 + \text{LE (ecf)}$$

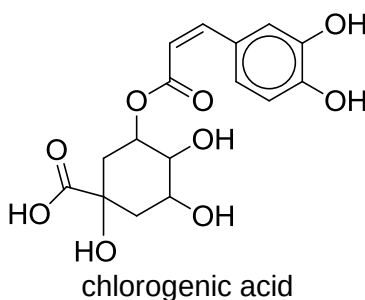
$$\text{LE} = -15067 \approx -1.51 \times 10^4 \text{ kJ mol}^{-1}$$

[5, max 4]

[4]

[Total: 13]

- 6 (a) Coffee beans contain chlorogenic acid.

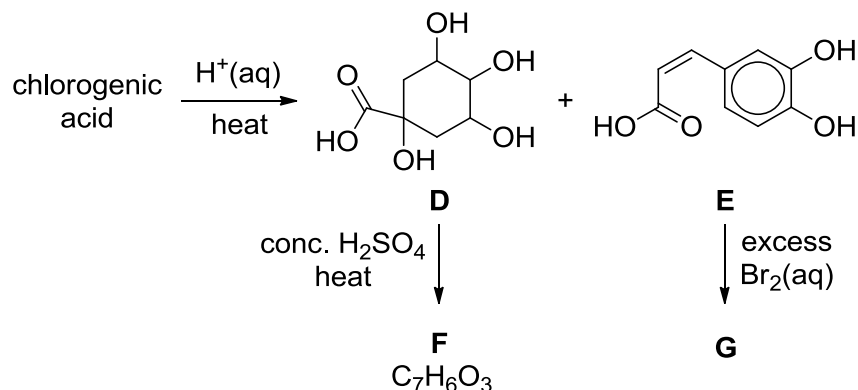


- (i) How many moles of $\text{H}_2\text{(g)}$ will be evolved when 1 mol of chlorogenic acid reacts with an excess of sodium metal?

3 mol

[1]

On heating with dilute aqueous acid, chlorogenic acid produces two compounds **D** and **E**.



When compound **D** is heated with concentrated H_2SO_4 , compound **F**, $\text{C}_7\text{H}_6\text{O}_3$, is formed.

Compound **F** does not decolourise cold dilute acidified KMnO_4 but reacts with $\text{Br}_2(\text{aq})$.

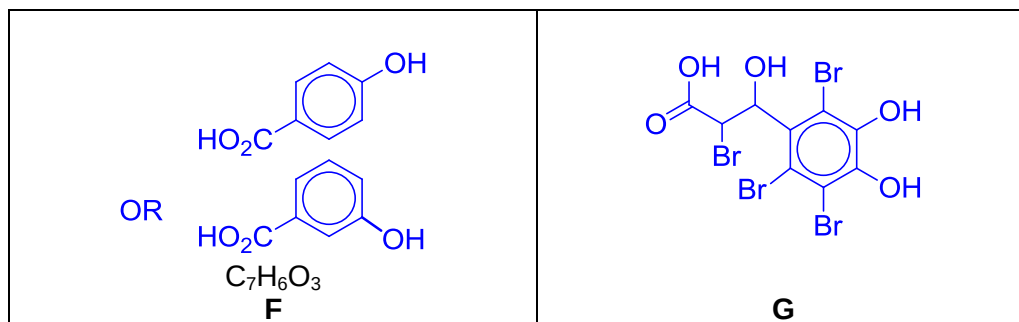
When compound **E** is treated with an excess of $\text{Br}_2(\text{aq})$, compound **G** is produced.

- (ii) If the test with cold dilute acidified KMnO_4 had been positive, which functional group would this have shown to be present in **F**?

C=C bond OR alkene functional group

[1]

- (iii) Suggest the structures for compounds **F** and **G**, and draw them in the relevant boxes below.



[2]

- (b) Allyl alcohol, $\text{CH}_2=\text{CHCH}_2\text{OH}$, is a colourless liquid which is soluble in water.

Crotyl alcohol, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$, is a colourless liquid which is used as a solvent.

- (i) Describe how you would distinguish between allyl alcohol and crotyl alcohol. The compounds may be distinguished by a preliminary chemical reaction followed by a subsequent testing of the reaction products. Include clearly the reagents, conditions and observations for each compound.

Step I: KMnO_4 , $\text{NaOH}(\text{aq})$, cold

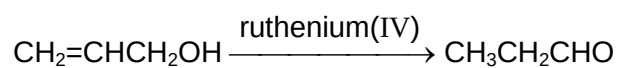
Step II: I_2 , $\text{NaOH}(\text{aq})$, warm

Crotyl alcohol gives yellow ppt.

Allyl alcohol does not give yellow ppt.

[2]

- (ii) Allyl alcohol may be converted into propanal by using a ruthenium(IV) catalyst in water.



State the type of reaction and explain your answer.

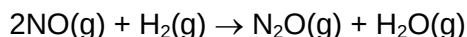
It is a disproportionation reaction where the C=C bond is reduced and the primary alcohol is oxidised.

[1]

[Total: 7]

VJC 2016 H2 Chemistry Prelim Exam Paper 3 Suggested Answers

- 1 (a) At high temperatures NO reacts with H₂ to produce nitrous oxide, N₂O, a greenhouse gas.



To study the kinetics of this reaction at 820 °C, initial rates for the formation of N₂O were measured using various initial partial pressures of NO and H₂.

Experiment	Initial pressure / kPa		Initial rate of production of N ₂ O / kPa s ⁻¹
	P_{NO}	P_{H_2}	
1	16	8	1.15×10^{-2}
2	8	8	2.87×10^{-3}
3	8	24	8.60×10^{-3}

- (i) Deduce the rate equation in terms of partial pressure. [3]

Comparing expts 2 and 3,
Rate increases by 3 times when the P_{H_2} increases by 3 times.
Order of reaction with respect to H₂ is 1.
Comparing expts 1 and 2,
Rate increases by 4 times when P_{NO} increases by 2 times.
Order of reaction with respect to NO is 2.
Hence rate = $k (P_{\text{NO}})^2 P_{\text{H}_2}$

- (ii) Using the rate equation and the information in the table above, calculate a value for the rate constant, giving its units. [2]

Using data from expt 1:
 $1.15 \times 10^{-2} = k (16)^2 (8)$
 $k = 5.62 \times 10^{-6}$
unit = (kPa)⁻² s⁻¹

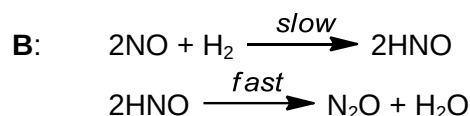
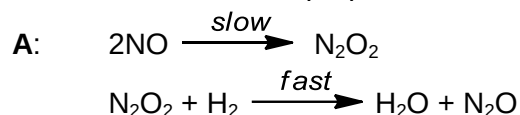
- (iii) Hence, calculate the initial rate at which NO reacts when 25 kPa of NO and 12.5 kPa of H₂ are mixed at 820 °C. [1]

rate = $5.62 \times 10^{-6} \times 25^2 \times 12.5 = 4.39 \times 10^{-2} \text{ kPa s}^{-1}$ (ecf)
rate of disappearance of NO = $2 \times 4.39 \times 10^{-2} = 8.78 \times 10^{-2} \text{ kPa s}^{-1}$

- (iv) Write the rate equation for the reaction when NO is used in large excess. Hence, determine the time elapsed to reduce the partial pressure of H₂ to half of its initial value, if 100 kPa of NO and 1 kPa of H₂ are mixed at 820 °C. [3]

Rate = $k' P_{\text{H}_2}$
Since $P_{\text{NO}} \gg P_{\text{H}_2}$,
 $k' = k (P_{\text{NO}})^2$
 $= 5.62 \times 10^{-6} \times (100)^2$ (ecf)
 $= 5.62 \times 10^{-2}$
 $t_{1/2} = \ln 2 / k'$
 $= 12.3 \text{ s}$

(v) Two mechanisms, **A** and **B** are proposed below.



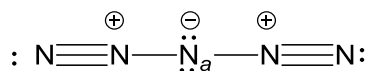
Which mechanism is consistent with the rate equation obtained in (a)(i). Explain your answer. [1]

B

The molecularity of the reactants in the slow step is 2 with respect to NO and 1 with respect to H₂. It is consistent with the experimentally-determined order of reaction with respect to each reactant.

(b) Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amounts of energy are released from their decomposition or reactions leading to more stable products.

(i) The polynitrogen species, N₅⁺ was first isolated in 1999. One of its resonance forms is shown below.



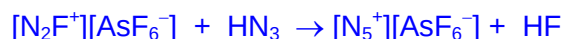
State the bond angle and molecular shape around nitrogen labelled a. [1]

Bond angle: any value between 105° and 109°

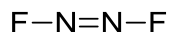
Shape: bent

(ii) The synthesis of a white ionic solid, [N₅⁺][AsF₆⁻], was achieved by reacting [N₂F⁺][AsF₆⁻] with hydrazoic acid, HN₃, in liquid HF at -78 °C.

Write a balanced equation for this reaction. [1]

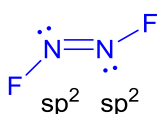


(iii) [N₂F⁺][AsF₆⁻] was first prepared by reacting N₂F₂ with the strong Lewis acid, AsF₅. N₂F₂ has the following structure and exhibits cis-trans isomerism.

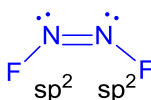


Draw the cis-trans isomers of N₂F₂, including all lone pairs and suggest an appropriate hybridisation for each nitrogen atom in N₂F₂.

[2]



trans



cis

All lone pairs shown

All sp² correctly labelled

- (c) Nitrogen is found in all organisms, primarily in amino acids which made up proteins.

Isoleucine, $\text{NH}_2\text{CH}(\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$ is an α -amino acid where the amino group and carboxylic acid group are separated by one carbon. It is a constituent amino acid in many protein molecules. Isoleucine can exist as different stereoisomers.

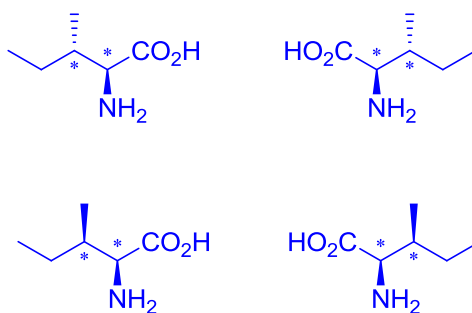
- (i) State the reagents and conditions needed to break protein down into its constituent amino acids. [1]

$\text{H}_2\text{SO}_4(\text{aq})$ or $\text{NaOH}(\text{aq})$
Heat

- (ii) Define the term *stereoisomers*. [1]

Molecules with same structural formula but different arrangement of atoms in space.

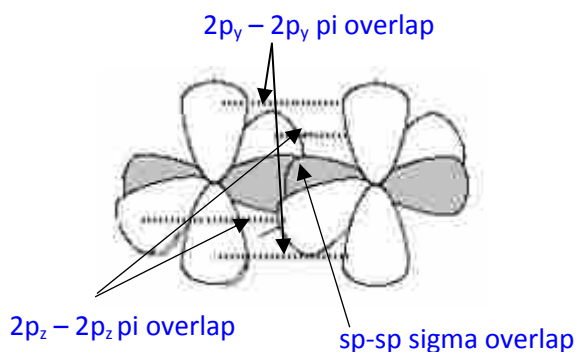
- (iii) There are four optical isomers of isoleucine. Draw the structures of these four stereoisomers of isoleucine, indicating clearly the chiral centres. [2]



Two chiral centres correctly labelled in one structure

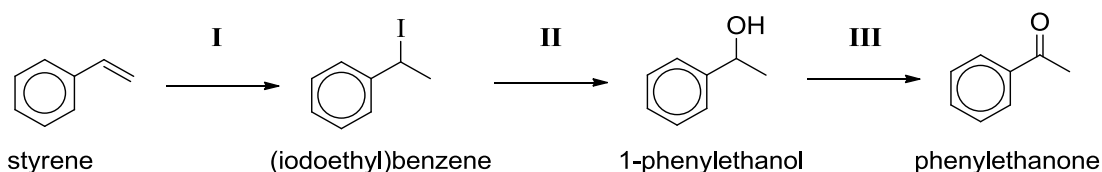
- (d) 3-amino-3-methyl-1butyne, $\text{CH}\equiv\text{CCNH}_2(\text{CH}_3)_2$ is used as the starting material to make other chemicals.

Draw a labelled diagram to show the orbitals that form $\text{C}\equiv\text{C}$ in an alkyne. [2]



[Total: 20]

- 2 (a) Styrene (phenylethene) is a useful organic intermediate used for the synthesis of many products. For instance, styrene is able to undergo the reaction shown below:



- (i) State the reagents and conditions required for reactions I, II and III. [3]

I: HI(g) , room temperature
(ignore state symbol unless it's given as aqueous state)

II: NaOH(aq) , heat

III: $\text{K}_2\text{Cr}_2\text{O}_7\text{(aq)}$, $\text{H}_2\text{SO}_4\text{(aq)}$, heat

- (ii) By considering the substituent(s) attached to the carbonyl group, give two reasons for the lower reactivity of phenylethanone towards nucleophiles compared to propanone, CH_3COCH_3 . [2]

Steric hindrance of the bulky phenyl group makes it harder for the nucleophile to approach.

The p-orbitals of the carbonyl carbon overlap with the π orbitals of the benzene ring OR Electrons from the benzene ring delocalise to the carbonyl carbon, making it less electron-deficient and hence less susceptible to nucleophilic attack.

- (iii) Suggest a simple chemical test to distinguish between (iodoethyl)benzene and iodobenzene, $\text{C}_6\text{H}_5\text{I}$. State the observations for each compound. [2]

NaOH(aq) , heat,
followed by excess $\text{HNO}_3\text{(aq)}$ and $\text{AgNO}_3\text{(aq)}$
(iodoethyl)benzene forms yellow precipitate
iodobenzene does not form yellow precipitate

- (iv) The solubility of (iodoethyl)benzene in water was found to be 32.1 mg dm^{-3} . Explain why (iodoethyl)benzene has such a low solubility in water. [2]

The predominant interactions between (iodoethyl)benzene molecules are dispersion forces.

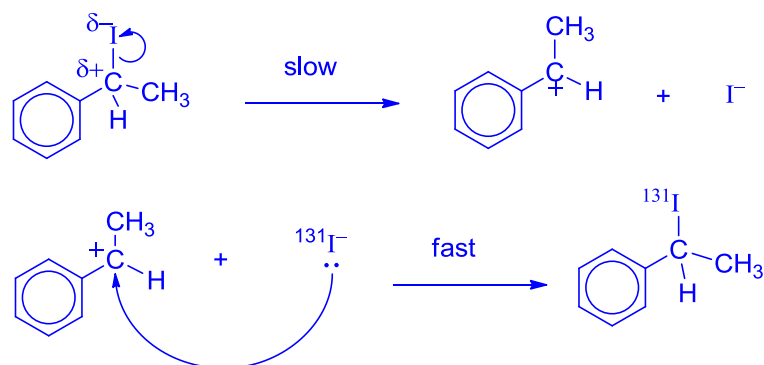
Weak dipole-induced dipole interactions formed between (iodoethyl)benzene and water release insufficient energy to overcome the strong hydrogen bonding in water.

- (b) (Iodoethyl)benzene exists as a pair of enantiomers **A** and **B**.

An optically pure sample containing only isomer **A** dissolved in hexane underwent a nucleophilic substitution reaction with a solution containing radioactive iodide ions, $^{131}\text{I}^-$. After the reaction, 75% of the (iodoethyl)benzene is incorporated with radioactive iodide.

An investigation into the kinetics of the reaction revealed that the rate of reaction was independent of the concentration of $^{131}\text{I}^-$.

- (i) Describe the mechanism for the reaction of (iodoethyl)benzene with $^{131}\text{I}^-$. In your answer, clearly label the ^{131}I , and include any relevant charges, curly arrows and dipoles or lone pairs of electrons that you consider important in this mechanism. [2]

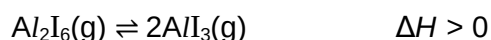


- (ii) Calculate the percentage of (iodoethyl)benzene that exists as enantiomer **B** incorporated with ^{131}I in the product mixture. [1]

Since 75% of **A** reacted, 25% of **A** remained unreacted.
percentage of enantiomer **B** = $75 / 2$
= 37.5%

- (c) The term 'tri-iodide' refers to molecules that contain three iodine atoms in their molecular formula, such as nitrogen tri-iodide, NI_3 , and aluminium tri-iodide, AlI_3 .

AlI_3 has a simple molecular structure. In the gas phase, it dimerises readily to form the dimer Al_2I_6 . The two species are related by the equilibrium shown below.



- (i) A 10.0 g sample of Al_2I_6 was allowed to vapourise in a 2 dm^3 vessel at 400°C . Calculate the initial pressure of Al_2I_6 . [2]

$$\begin{aligned} P_{\text{Al}_2\text{I}_6} &= \frac{nRT}{V} \\ &= \frac{\left(\frac{10.0}{816}\right)(8.31)(673)}{2 \times 10^{-3}} \\ &= 34300 \text{ Pa} \end{aligned}$$

- (ii) Given that the degree of dissociation (α) of Al_2I_6 was 0.35, find the K_p value for the equilibrium at 400°C . [2]

$$\begin{aligned} P_{\text{Al}_2\text{I}_6} \text{ (after dissociation)} &= 0.65 \times 34300 \text{ (ecf)} \\ &= 22300 \text{ Pa} \\ P_{\text{AlI}_3} &= 2 \times 0.35 \times 34300 \text{ (ecf)} \\ &= 24000 \text{ Pa} \\ K_p &= \frac{(P_{\text{AlI}_3})^2}{P_{\text{Al}_2\text{I}_6}} = \frac{24000^2}{22300} \\ &= 25800 \text{ Pa} \end{aligned}$$

- (iii) Explain the effect on the degree of dissociation of Al_2I_6 for each of the changes below.

- The reaction was carried out at 300°C .
- A sample of $\text{Ar}(\text{g})$ was introduced into a 1 dm^3 vessel containing $\text{AlI}_3(\text{g})$ and $\text{Al}_2\text{I}_6(\text{g})$ at 400°C . [2]

When the temperature is decreased, the backward exothermic reaction is favoured. Hence, the position of equilibrium will shift to the left and degree of dissociation decreases.

While total pressure in the vessel increases as number of moles of gases increases with injection of inert Ar(g), mole fraction and partial pressure of the $AlI_3(g)$ and $Al_2I_6(g)$ remain constant. Hence there is no shift in the position of equilibrium and no change in the degree of dissociation.

(d) The table below shows the boiling points of PCl_3 and PF_5 .

Compound	Boiling Point / °C
PCl_3	76.1
PF_5	– 84.6

Explain why PCl_3 has a higher boiling point than PF_5 .

[2]

PCl_3 molecules are held by dipole-dipole interactions, PF_5 molecules are held by dispersion forces. Hence more energy is needed to overcome the stronger dipole-dipole interactions in PCl_3 .

[Total: 20]

- 3 (a) Lead(II) nitrate decomposes on heating in the same way as magnesium nitrate. By using relevant data from the *Data Booklet*, predict and explain which of the two nitrates, lead(II) nitrate or magnesium nitrate, would have a higher decomposition temperature. [2]

$Pb(NO_3)_2$ has the higher decomposition temperature.
Both Mg^{2+} and Pb^{2+} have the same ionic charge (2+) but ionic radius of Pb^{2+} is larger than that of Mg^{2+}
Charge density of Pb^{2+} is lower (or polarising power of Pb^{2+} is lower)
Electron cloud of NO_3^- is distorted to a smaller extent by Pb^{2+}
 $\Rightarrow Pb(NO_3)_2$ has a higher thermal stability and thus a higher decomposition temperature.

(b) The halogens are reactive elements and are involved in many reactions.

- (i) When chlorine is bubbled through cold sodium hydroxide solution, followed by an excess of acidified silver nitrate solution, only $\frac{1}{2}$ of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide solution is hot, up to $\frac{5}{6}$ of the chlorine can be precipitated. Explain the observations with the aid of relevant equations. [3]

Precipitation: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

With cold NaOH(aq):

$Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$

Molar ratio of $Cl^- : ClO^- = 1:1$

$\frac{1}{2}$ of the chlorine is precipitated as $AgCl$.

With hot NaOH(aq):



Molar ratio of $\text{Cl}^- : \text{ClO}_3^- = 5:1$

$\frac{5}{6}$ of the chlorine is precipitated as AgCl.

- (ii) When chromium is made to react with chlorine, the main product of the reaction is CrCl_3 . However, when chromium is made to separately react with other halogens such as fluorine and iodine, the main products are CrF_4 and CrI_2 . By reference to relevant E° values, what can you conclude about the relative oxidising ability of the halogens? [2]

Correct E° data for F_2 , Cl_2 and I_2



Oxidising power: $\text{F}_2 > \text{Cl}_2 > \text{I}_2$ as $E^\circ(\text{X}_2/\text{X}^-)$ is less positive down the group.

Correct O.N. of Cr in all three compounds

F_2 is the strongest oxidising agent and oxidises Cr to CrF_4 , where the oxidation state of Cr in CrF_4 is +4.

Cl_2 is less oxidising than F_2 and oxidises Cr to CrCl_3 , where the oxidation state of Cr in CrCl_3 is +3.

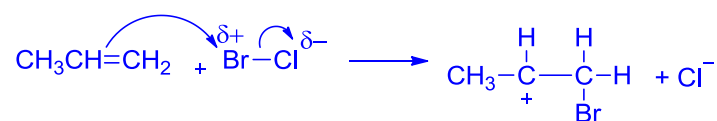
Iodine is the weakest oxidising agent and oxidises Cr to CrI_2 , where the oxidation state of Cr in CrI_2 is +2.

The halogens also form many interhalogen compounds in which two different halogens are combined. Interhalogen compounds like BrCl have similar properties to the halogens.

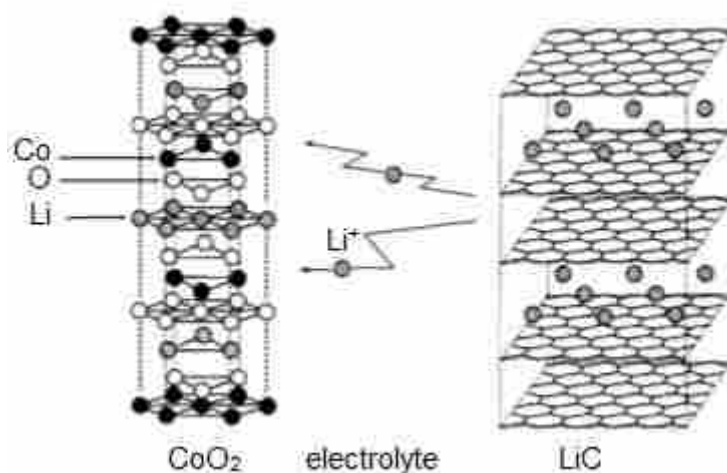
- (iii) Suggest an equation for the reaction that occurs between BrCl and aqueous KI. [1]



- (iv) BrCl reacts with alkenes faster than the pure halogens such as Cl_2 and Br_2 . Show the slow step of the reaction between BrCl and propene. [1]



- (c) A lithium-ion battery is a rechargeable battery. In a fully charged battery, lithium ions occupy the tiny spaces in graphite to form LiC . During discharge, lithium ions are produced which migrate through the electrolyte while at the same time, graphite is being regenerated. In the other electrode, lithium ions react with CoO_2 to form LiCoO_2 .



- (i) Write equations for the electrode reactions occurring at the anode and cathode during discharge. [2]



- (ii) Hence, write an equation for the overall reaction that occurs during discharge. [1]

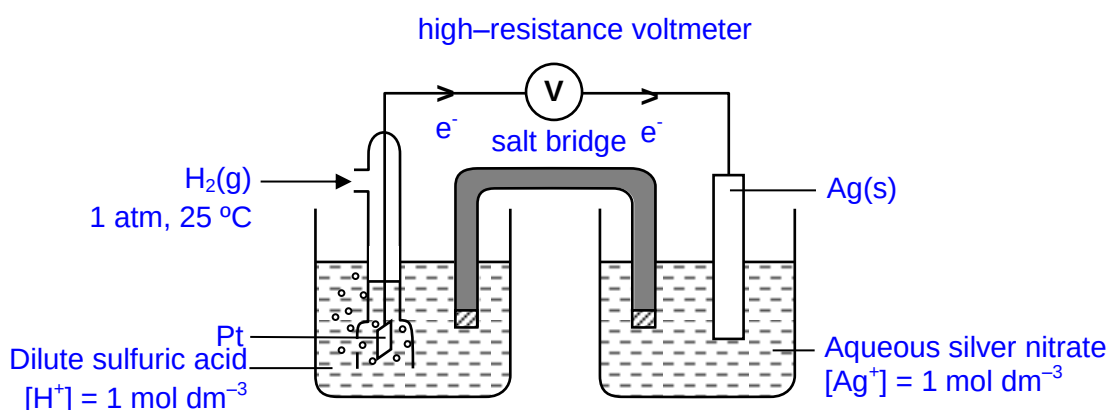


- (iii) By determining the oxidation numbers of the relevant elements, identify the elements that have been oxidised and reduced. [1]

C is oxidised as O.N. increased from -1 in LiC to 0 in C.

Co is reduced as O.N. decreased from +4 in CoO_2 to +3 in LiCoO_2 .

- (d) (i) With reference to the *Data Booklet*, draw a fully labelled diagram showing how you could measure the standard electrode potential for the Ag^+/Ag system. Indicate the direction of electron flow. [2]



- (ii) The electrode potential, E and the concentration of silver ions in solution under non-standard conditions are related by the following equation.

$$E = 0.80 - 0.03 \lg \frac{1}{[\text{Ag}^+(\text{aq})]^2}$$

The solubility product constant of AgCl is $K_{\text{sp}} = 1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$. Using the equation given above, calculate the electrode potential at 298 K of a half-cell formed by

- (I) a Ag electrode immersed in a saturated solution of AgCl .

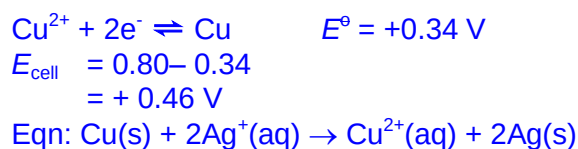
$$\begin{aligned} [\text{Ag}^+] &= \sqrt{1.8 \times 10^{-10}} \\ &= 1.3 \times 10^{-5} \text{ mol dm}^{-3} \\ E &= 0.80 - 0.03 \lg \frac{1}{(1.3 \times 10^{-5})^2} \\ &= +0.51 \text{ V} \end{aligned}$$

- (II) a Ag electrode immersed in a 0.5 mol dm^{-3} solution of KCl containing some AgCl precipitate.

$$\begin{aligned} [\text{Ag}^+] &= \frac{1.8 \times 10^{-10}}{0.5} \\ &= 3.6 \times 10^{-10} \text{ mol dm}^{-3} \\ E &= 0.80 - 0.03 \lg \frac{1}{(3.6 \times 10^{-10})^2} \\ &= +0.23 \text{ V} \end{aligned}$$

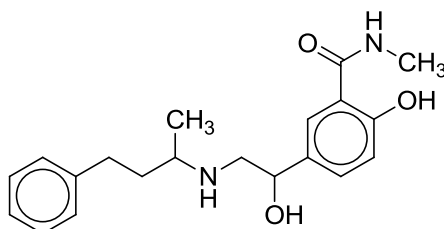
[3]

- (iii) A cell is made by connecting the half-cell in (d)(i) to a standard Cu^{2+}/Cu half-cell. By reference to relevant data from the Data Booklet, calculate the cell emf and write an equation (with state symbols) for the reaction that has occurred. [2]



[Total: 20]

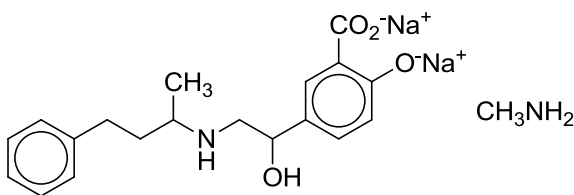
- 4 (a) Compound **G** has the structure shown.



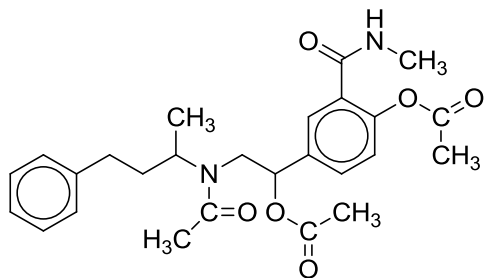
Give the structures of the organic compounds formed by compound **G** under the following conditions.

(i) NaOH(aq), reflux

[2]

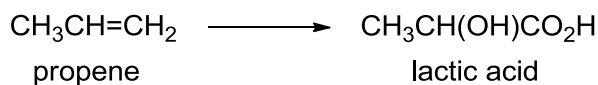
(ii) Excess CH_3COCl , room temperature

[2]



(b) Lactic acid can be used in food products as pH regulators or as a food preservative. It can also be used as a flavouring agent.

(i) Suggest reagents and conditions needed to convert propene into 2-hydroxypropanoic acid (commonly known as lactic acid) in no more than 3 steps. Give the structures of the intermediates.

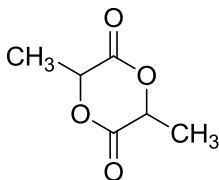


[3]

Step I: Cold KMnO_4 / NaOH(aq)Step II: $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 (aq), refluxStep III: NaBH_4 (alc), reflux

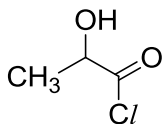
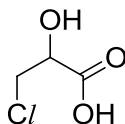
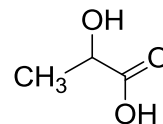
(ii) When lactic acid is refluxed with concentrated sulfuric acid, compound **H** with the molecular formula of $\text{C}_6\text{H}_8\text{O}_4$ is formed. It does not react with sodium. Give the structural formula of **H**.

[1]



(iii) Describe and explain the relative acidity of the following three compounds.

[2]

**A****B**

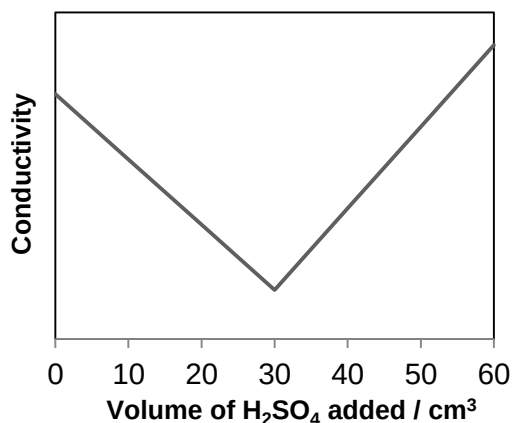
lactic acid

Compound **A** is the most acidic and lactic acid is the least acidic.

A contains the acyl chloride which hydrolyses readily in water to produce a strong acid HCl.

Presence of Cl atom in **B** exerts an electron-withdrawing inductive effect which produces a more stable anion than the anion formed from lactic acid.

- (c) Experiment 1 is conducted in which the conductivity of 25 cm³ of Ba(OH)₂ solution is monitored as it is titrated with 0.10 mol dm⁻³ of aqueous H₂SO₄. The data collected from the experiment is plotted in the graph below.



- (i) The conductivity of the Ba(OH)₂ solution decreases as the volume of 0.10 mol dm⁻³ H₂SO₄ is added from 0 cm³ to 30 cm³.

Identify the chemical species that enable the solution to conduct electricity as the first 30 cm³ of H₂SO₄ (aq) is added. Hence explain why the conductivity decreases. [2]

Species: Ba²⁺(aq) and OH⁻(aq)

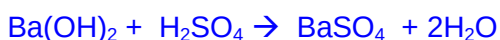
As the titration proceeds before the equivalence point,

OH⁻(aq) is removed by neutralisation to form H₂O(l).

Ba²⁺(aq) is removed by precipitation to form BaSO₄(s).

Thus there are less mobile charge carriers, and conductivity decreases.

- (ii) Using the information in the graph, calculate the initial concentration of Ba(OH)₂. [1]



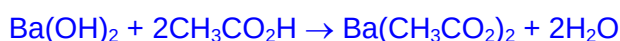
$$n_{\text{Ba(OH)}_2} = n_{\text{H}_2\text{SO}_4}$$

$$\begin{aligned} \text{No. of moles of Ba(OH)}_2 &= 30/1000 \times 0.10 \\ &= 0.003 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Concentration of Ba(OH)}_2 &= 0.003 / 0.025 \\ &= 0.12 \text{ mol dm}^{-3} \end{aligned}$$

- (d) In Experiment 2, another 25 cm³ sample of 0.10 mol dm⁻³ aqueous Ba(OH)₂ is mixed with 80 cm³ of 0.10 mol dm⁻³ of ethanoic acid to form solution **A**. Barium ethanoate, Ba(CH₃CO₂)₂ is the product of the reaction. The acid dissociation constant, K_a, of ethanoic acid is 1.7 × 10⁻⁵ mol dm⁻³. Calculate the pH of the solution **A**. [3]

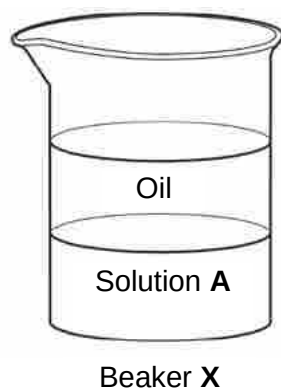
$$K_a = [\text{H}^+][\text{CH}_3\text{CO}_2^-] / [\text{CH}_3\text{CO}_2\text{H}]$$



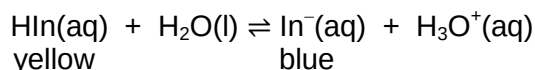
$$\text{New } [\text{CH}_3\text{CO}_2\text{H}] = (80 - 50)/1000 \times 0.10 / 0.105$$

$$\begin{aligned}
 &= 0.0286 \text{ mol dm}^{-3} \\
 \text{New } [\text{CH}_3\text{CO}_2^-] &= 2 \times 25/1000 \times 0.10 / 0.105 \\
 &= 0.0476 \text{ mol dm}^{-3} \\
 0.0476[\text{H}^+]/0.0286 &= 1.7 \times 10^{-5} \\
 [\text{H}^+] &= 1.02 \times 10^{-5} \text{ mol dm}^{-3} \\
 \text{pH} &= -\lg(1.02 \times 10^{-5}) \\
 &= 4.99
 \end{aligned}$$

- (e) Half of the solution **A** formed in (d) is added to beaker **X** where there is a layer of colourless oil as shown in the figure below.



The indicator HIn is a weak acid with a $\text{p}K_{\text{a}}$ value of 6.0. It reacts with water as represented in the equation below.



A small amount of indicator HIn is added into beaker **X**. The mixtures are stirred well and the two layers are allowed to separate.

Assume the pH of solution **A** is unaffected by the presence of colourless oil.

- (i) State the colour observed in the oil layer of beaker **X**. Explain the observation in terms of acid-base equilibrium and inter-molecular interactions.

[2]

The oil layer is yellow in colour.

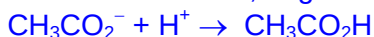
Solution **A** is of pH 4.99, acid form of indicator HIn(aq) predominates since $\text{pH} < \text{p}K_{\text{a}}$. Since HIn is a neutral (uncharged) molecule, some of it can dissolve better in the oil layer because of dispersion forces (or dipole-induced dipole or dipole-dipole interactions) with the oil molecules

- (ii) A few drops of aqueous sodium hydroxide and hydrochloric acid are added to the beaker **X** successively and stirred well. Explain with the aid of equation(s) why there is no change in the colour of the oil layer after each addition. [2]

On addition of NaOH, large reservoir of $\text{CH}_3\text{CO}_2\text{H}$ removes the OH^- added.



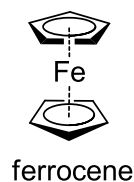
On addition of HCl, large reservoir of CH_3CO_2^- removes the H^+ added.



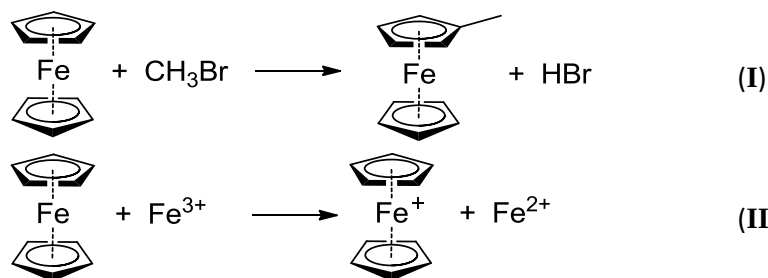
$[\text{H}^+]$ remains unchanged, the HIn form still predominates and is soluble in the oil layer

[Total: 20]

- 5 (a) Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, is an orange solid. In this complex, C_5H_5^- is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



Ferrocene can undergo a series of different reactions and some are analogues of organic reactions. Two reactions of ferrocene are shown below:



- (i) State the types of reaction for reactions I and II. [1]

I: electrophilic substitution

II: redox

- (ii) State the oxidation number of Fe in ferrocene and hence its electronic configuration. [1]

Oxidation Number of Fe: +2

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

- (iii) Suggest why Ferrocene is a coloured complex. [2]

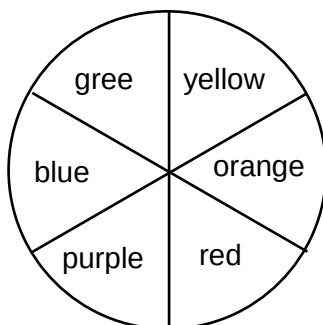
In the presence of ligands, 3d orbitals of iron are split into 2 groups with slightly different energy (d–d splitting).

A 3d electron from the lower energy group is promoted to the higher energy group (d–d transition)

by absorbing energy from the visible region of the electromagnetic spectrum.

Colour observed is complementary to the colour absorbed.

- (iv) The complementary colours are illustrated with the following colour wheel.



Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to C_5H_5^- . [2]

C_5H_5^- causes a larger 3d orbital split.

With water as the ligand, electromagnetic waves with energy corresponding to red is absorbed which has a lower energy than blue, which is absorbed when C_5H_5^- is the ligand.

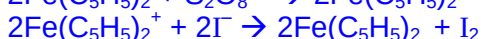
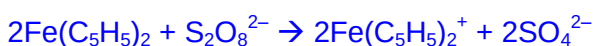
- (v) By considering reaction II, suggest if $E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ is more positive or less positive than $E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+})$. Explain your answer. [1]

$E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ is less positive than $E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+})$.

In reaction II ferrocene has been oxidised by Fe^{3+} , thus $E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$ has a less positive E° value than $E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+})$ since $E^\circ_{\text{cell}} = E^\circ_{\text{reduced}} - E^\circ_{\text{oxidised}} > 0$.

- (vi) The reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- is slow in the absence of catalyst. Ferrocene can be a suitable catalyst for this reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- .

Explain with the aid of equations how it works. You may use $\text{Fe}(\text{C}_5\text{H}_5)_2$ to represent ferrocene. [2]



Without the catalyst, the reaction has a high activation energy due to collisions between ions of the same charge.

In the presence of catalyst, collisions between ions of the same charge are avoided hence it lowers the activation energy.

- (vii) By considering your answers to (v) and (vi), suggest a range of values for $E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2)$. [1]

$$+0.54\text{V} < E^\circ(\text{Fe}(\text{C}_5\text{H}_5)_2^+|\text{Fe}(\text{C}_5\text{H}_5)_2) < +0.77\text{V}$$

- (b) Ephedrine, $\text{C}_{10}\text{H}_{15}\text{NO}$, is a drug used to prevent low blood pressure during spinal anaesthesia. It is optically active and has 2 chiral centres.

When Ephedrine is heated with acidified potassium manganate(VII), it gives benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ as one of the products. When it is heated with acidified potassium dichromate(VI), it gives **P**. **P** gives an orange precipitate when treated with 2,4-dinitrophenylhydrazine but it has no reaction with Tollens' reagent.

When Ephedrine is heated with equimolar CH_3Cl , it gives **Q**, $\text{C}_{11}\text{H}_{17}\text{NO}$ as the major product. When it is heated with excess CH_3Cl , it gives **R**, $\text{C}_{12}\text{H}_{20}\text{NOCl}$ as the major product.

Deduce the structures of Ephedrine, **P**, **Q** and **R**. Explain your answer. [7]

Ephedrine has 2 chiral centres, it has two carbon atoms attached to four different groups.

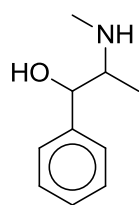
Ephedrine undergoes side-chain oxidation of benzene with hot acidified potassium manganate to give benzoic acid, it contains mono-substituted benzene with a benzylic hydrogen.

P undergoes condensation with 2,4-dinitrophenylhydrazine, it suggests it contains either aldehyde or ketone functional groups. Since it does not react with Tollens' reagent, it must be a ketone.

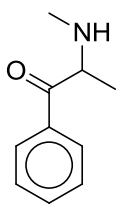
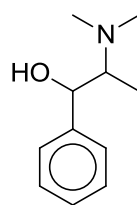
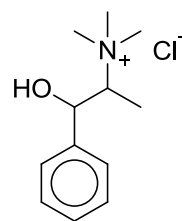
Hence, Ephedrine contains a secondary alcohol since it can be oxidised by dichromate to form a ketone.

Ephedrine undergoes nucleophilic substitution with CH_3Cl to form **Q**. It contains an amine group.

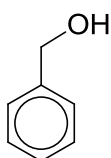
When Ephedrine is reacted with excess CH_3Cl , two methyl groups have been incorporated in **R** as confirmed by the change in the molecular formula, hence it contains secondary amine group.



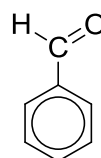
Ephedrine

**P****Q****R**

(c) Draw a labelled diagram to show how benzaldehyde can be synthesised from phenylmethanol in a laboratory.

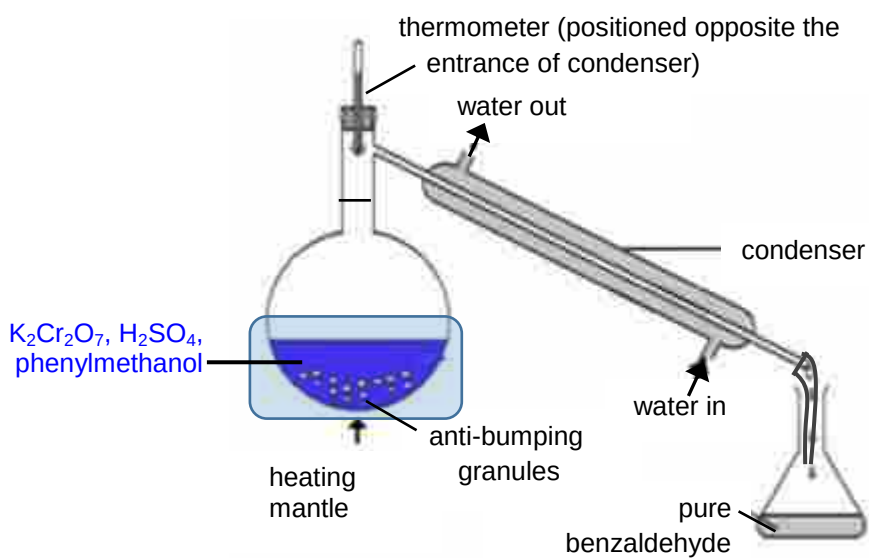


phenylmethanol



benzaldehyde

[3]



[Total: 20]

YJC Chemistry H2 P1 Prelim 2016

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct and shade your choice on the answer sheet provided.

- 1** For indoor air quality safety standards, the maximum safe tolerance level of carbon monoxide gas is $6 \times 10^{-4} \text{ m}^3$ of carbon monoxide in 1 m^3 of air. Given that a typical room measures 4 m by 4 m by 3 m, calculate the number of molecules of carbon monoxide present in the room at this tolerance level at room temperature and pressure?

- A** 1.13×10^{24}
B 7.22×10^{23}
C 1.51×10^{22}
D 7.22×10^{20}

- 2** Soluble mercury compounds such as mercury(II) nitrate are highly toxic. One removal method involves the treatment of wastewater contaminated with mercury(II) nitrate with sodium sulfide to produce solid mercury(II) sulfide and sodium nitrate solutions.

Calculate the mass of mercury(II) sulfide formed when 0.020 dm^3 of $0.100 \text{ mol dm}^{-3}$ sodium sulfide reacts with 0.050 dm^3 of $0.010 \text{ mol dm}^{-3}$ mercury(II) nitrate?

- A** 0.117 g **B** 0.133 g **C** 0.280 g **D** 0.466 g

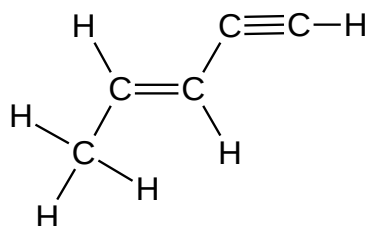
- 3** Gaseous particle **X** has a proton number n , and a charge of +1.
Gaseous particle **Y** has a proton number $(n+1)$, and is isoelectronic with **X**.

Which statement about **X** and **Y** is correct?

- A** When placed in an electric field, the angle of deflection for **X** is the same as that of **Y**.
B **X** requires more energy than **Y** when a further electron is removed from each particle.
C **X** releases more energy than **Y** when an electron is added to particle.
D **X** has a larger radius than **Y**.

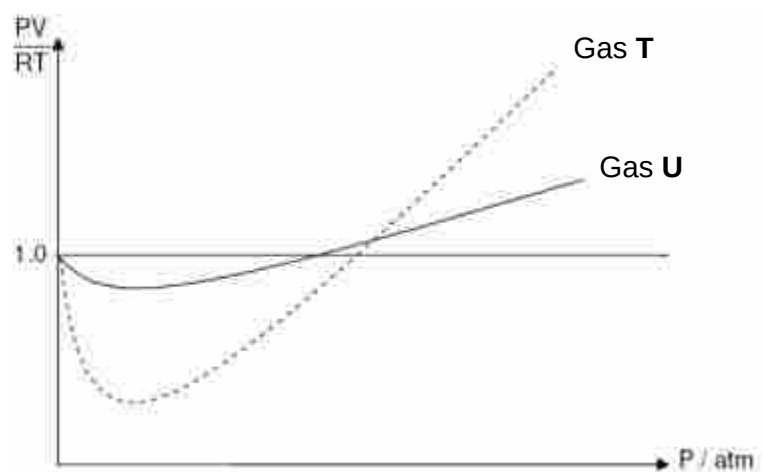
- 4 Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is not present in the molecule shown below?



- A σ bond formed by $2sp^3 - 2sp^2$ overlap.
- B σ bond formed by $2sp^3 - 2sp$ overlap.
- C σ bond formed by $1s - 2sp$ overlap.
- D π bond formed by $2p - 2p$ overlap.
- 5 Which statement about graphite is **not** correct?
- A The carbon-carbon bonds in graphite are shorter than those in diamond.
- B It can act as a good lubricant due to the weak forces of attraction between the layers of atoms.
- C Carbon to carbon distances between the planes of hexagonal rings are smaller than those within the planes.
- D It acts as a good conductor of electricity in the direction parallel to the planes containing hexagonal rings of carbon.

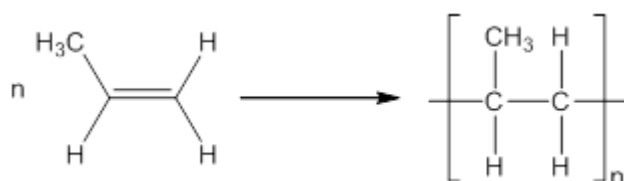
6



Which of the following could be the identities of the gases?

	Gas T	Gas U
A	H ₂ (g) at 298 K	CO ₂ (g) at 298 K
B	CH ₄ (g) at 298 K	NH ₃ (g) at 298 K
C	O ₂ (g) at 500 K	O ₂ (g) at 298 K
D	N ₂ (g) at 298 K	N ₂ (g) at 500 K

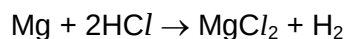
7 The polymerisation of propene to form polypropene occurs readily at room temperatures.



What will be the signs of ΔG , ΔH and ΔS for the polymerisation reaction at room temperature?

	ΔG	ΔH	ΔS
A	+	–	–
B	+	+	–
C	–	+	–
D	–	–	–

- 8 The rate of the redox reaction between hydrochloric acid and Mg



can be followed by measuring the time taken for the same volume of hydrogen to be produced from a range of hydrochloric acid concentrations.

To find the order with respect to hydrochloric acid, which would be the most suitable graph to plot using the data?

- A [HCl] against time
- B [HCl] against $\frac{1}{\text{time}}$
- C Volume H_2 against time
- D Volume H_2 against $\frac{1}{\text{time}}$
- 9 The numerical value of the solubility product of nickel(II) carbonate is 6.6×10^{-9} while that of silver carbonate is 2.1×10^{-11} at 25°C .

Which of the following statements is true?

- A Addition of silver nitrate increases the solubility of silver carbonate.
- B The solubility of silver carbonate is higher than the solubility of nickel(II) carbonate.
- C Addition of nitric acid to a solution containing nickel(II) carbonate increases the solubility product of nickel(II) carbonate.
- D Nickel(II) carbonate precipitates first when sodium carbonate is added to a solution containing equal concentrations of nickel(II) and silver ions.
- 10 What is the pH of 10 cm^3 of 0.05 mol dm^{-3} sodium benzoate?

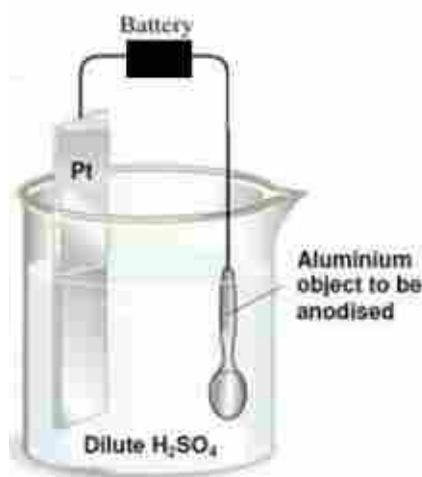
[K_a of benzoic acid = $6 \times 10^{-5}\text{ mol dm}^{-3}$]

- A 6.46
- B 7.46
- C 8.46
- D 9.46

- 11** A sample of 20.0 cm^3 of 0.20 mol dm^{-3} iron(II) sulfate is titrated against 0.05 mol dm^{-3} potassium manganate(VII) in the presence of excess fluoride ions. It is found that 20.0 cm^3 of the manganate(VII) solution is required to reach the end-point.

What is the oxidation number of manganese at end-point?

- A** +3
B +4
C +5
D +6
- 12** Anodisation is a process to increase corrosion resistance and surface hardness in aluminium objects.
- A possible set up for the process is shown as below:



- Which of the following statements about the anodisation of aluminium is true?
- A** Aluminium dissolves at the anode.
B Hydrogen gas is liberated at the anode.
C Water is oxidised at the anode to form oxygen gas.
D Replacing the electrolyte with NaOH(aq) will cause the reaction to cease.
- 13** Which of the following elements forms an oxide with a giant structure and a chloride which is readily hydrolysed?
- A** Silicon
B Barium
C Sodium
D Phosphorus

14 An element in Period 3 has the following properties:

- Its first ionisation energy is larger than both the elements before and after it across the period.
- It conducts electricity.
- It reacts slowly with cold water but react readily with steam to give a gas.

Which statement about this element is **not** correct?

- A It has a high melting and boiling point.
- B It forms an oxide that produces a solution that is acidic when added to water.
- C It forms a chloride that produces a solution that is slightly acidic when added to water.
- D Its oxidation state in compounds usually follows the group number it belongs to in the Periodic Table.

15 The following report appeared in a newspaper article.

Drums of bromine broke open after a vehicle crash on the motorway. Traffic was diverted as purple gaseous bromine drifted over the road (it is denser than air), causing irritation to drivers' eyes. Firemen sprayed water over the scene of the accident, dissolving the bromine and washing it away.

What is wrong with the report?

- A Bromine does not dissolve in water.
- B Bromine does not vapourise readily.
- C Bromine is less dense than air.
- D Bromine is not purple.

16 When crystalline potassium chromate(VI) was dissolved in water, a yellow solution **Q** was formed. Addition of dilute sulfuric acid to **Q** gave an orange solution **R**. When hydrogen sulfide was bubbled through solution **R**, there was a color change in the solution and yellow sulfur was produced.

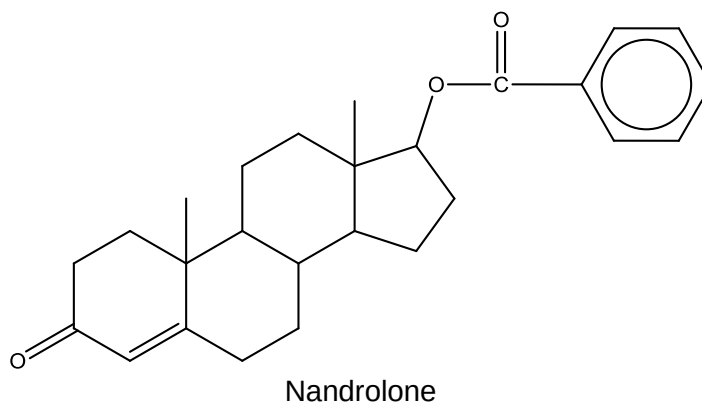
Which process **did not** occur in the above experiment?

- A Ligand exchange
- B Redox reaction
- C Precipitation
- D Acid-base

- 17 Chlorine compounds show oxidation states ranging from -1 to $+7$.

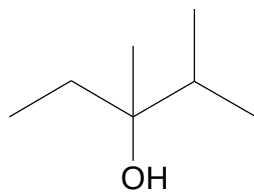
What are the reagents and conditions necessary for the oxidation of chlorine gas into a compound containing chlorine in the $+5$ oxidation state?

- A Cold dilute NaOH
B Hot concentrated NaOH
C Concentrated H_2SO_4 at room temperature
D $\text{AgNO}_3(\text{aq})$ followed by $\text{NH}_3(\text{aq})$ at room temperature
- 18 Which statement correctly **defines** a transition element?
- A Transition elements form many coloured compounds.
B Transition elements or their compounds are widely used as catalysts.
C Transition elements form one or more stable ions with partially filled d-orbitals.
D Transition elements exhibit more than one oxidation state in their compounds.
- 19 How many stereoisomers does a molecule of Nandrolone has?



- A 8 B 16 C 32 D 64

- 20 The structure of compound **Z** is as seen below:

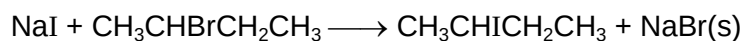


Compound **Z**

It is completely reacted with hot concentrated H_2SO_4 to form compound **Y**. What is the total number of isomers of **Y**?

- A** 2 **B** 3 **C** 4 **D** 5
- 21 2-methylpropanoic acid can be synthesised from 1-chloropropane through a series of reactions.
- Which set of reagents, used in sequential order, would be the most suitable for this synthesis?
- A** PCl_5 , acidified KMnO_4
- B** ethanolic KCN , dilute HCl
- C** aqueous KOH , HCl , ethanolic KCN , dilute HCl
- D** ethanolic KOH , HBr , ethanolic KCN , dilute H_2SO_4
- 22 Which statement about ethanal and propanone is **not** correct?
- A** Both give a positive tri-iodomethane test.
- B** Both react with 2,4-dinitrophenylhydrazine reagent.
- C** Both may be prepared by the oxidation of an alcohol.
- D** Both react with hot acidified sodium dichromate(VI).

- 23** When sodium iodide in propanone is added to an optically active sample of 2-bromobutane, a sodium bromide precipitate is formed after 13 minutes upon heating.

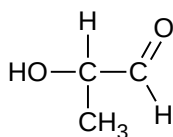


The experiment was repeated several times and the rate equation was found to be

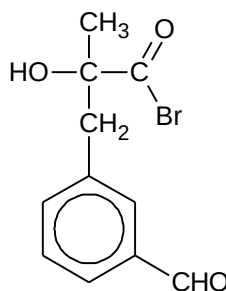
$$\text{Rate} = k[\text{CH}_3\text{CHBrCH}_2\text{CH}_3][\text{NaI}]$$

Which of the following statements is **not** correct?

- A** The mechanism involves a reactive intermediate.
 - B** The organic product sample obtained rotates the plane of polarised light.
 - C** A similar experiment, using 1-bromobutane, will produce a precipitate in less than 13 minutes.
 - D** A similar experiment, using 2-chlorobutane, will take more than 13 minutes to produce a precipitate.
- 24** Which reagent can be used to distinguish between compounds **R** and **S** under suitable conditions?



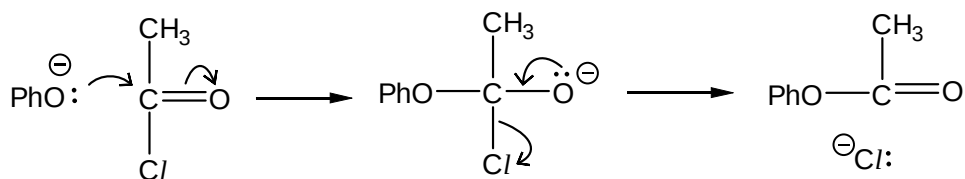
R



S

- A** Acidified potassium dichromate (VI)
- B** Alkaline copper(II) solution
- C** Sodium metal
- D** Phosphorus pentachloride

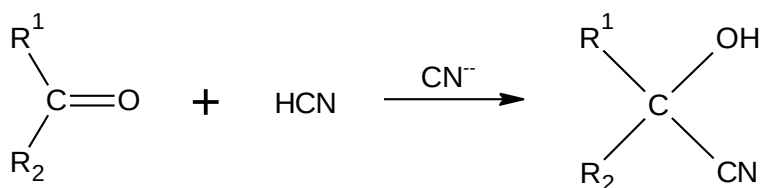
- 25 The two-stage reaction sequence given shows a possible mechanism for the reaction between phenoxide ion and ethanoyl chloride.



where Ph = phenyl

How should the *overall* reaction be classified?

- A Electrophilic addition
 - B Nucleophilic addition
 - C Electrophilic substitution
 - D Nucleophilic substitution
- 26 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.

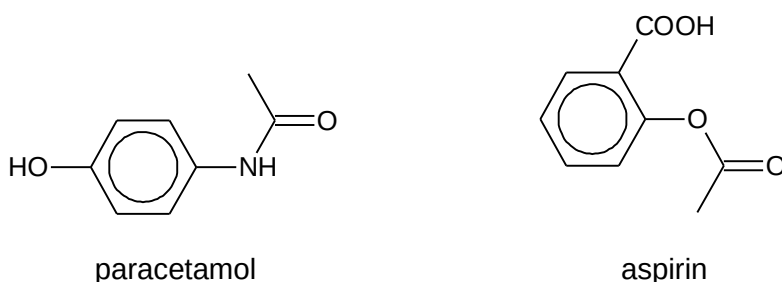


In a similar reaction, $^-\text{CH}_2\text{COOCH}_3$ ions are generated from $\text{CH}_3\text{COOCH}_3$ by strong bases.

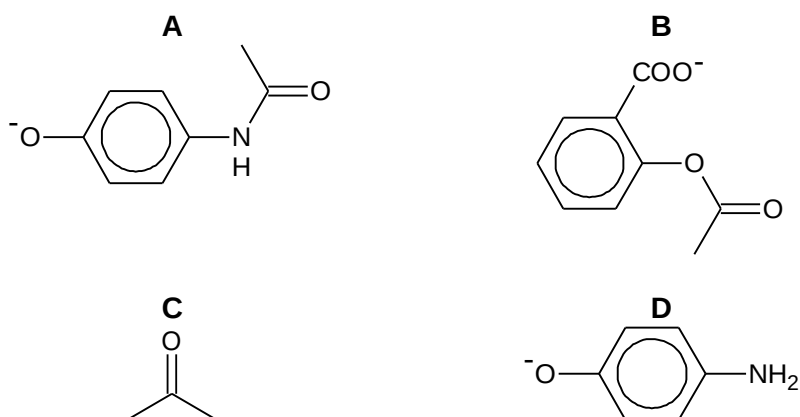
Which compound can be made from an aldehyde and $\text{CH}_3\text{COOCH}_3$?

- A $\text{CH}_3\text{CH}(\text{OH})\text{COOCH}_3$
- B $\text{CH}_3\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_3$
- C $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{COOCH}_3$
- D $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COOCH}_3$

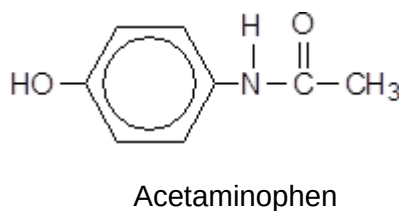
- 27 Two common drugs administered when a patient experiences headache or fever are paracetamol and aspirin.



A solution of the two drugs was hydrolysed using hot aqueous sodium hydroxide. Which organic product would be produced?



- 28 Acetaminophen is a drug used in headache remedies. It has the following structure:



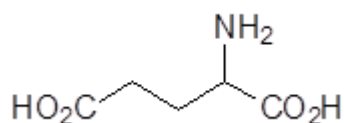
Which of the following reagents reacts with Acetaminophen?

- A** Sodium carbonate
- B** Cold sodium hydroxide
- C** Alkaline aqueous iodine
- D** 2,4-dinitrophenylhydrazine

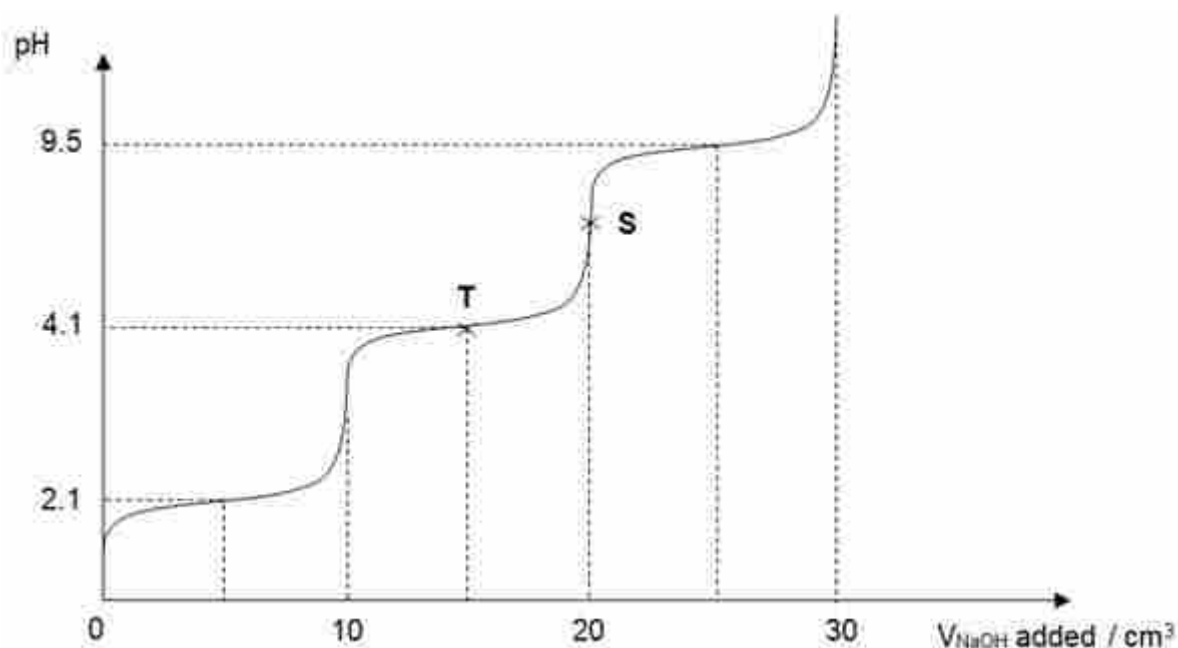
29 Which sequence shows the correct order of increasing pK_b in an aqueous solution of equal concentration?

- A $C_2H_5CONH_2 < C_6H_5NH_2 < C_2H_5NH_2 < C_2H_5NH_3^+$
 B $C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5NH_3^+ < C_2H_5CONH_2$
 C $C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5CONH_2 < C_2H_5NH_3^+$
 D $C_2H_5NH_3^+ < C_2H_5CONH_2 < C_2H_5NH_2 < C_6H_5NH_2$

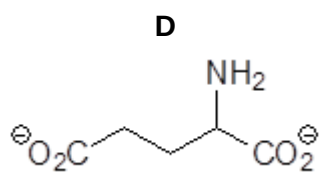
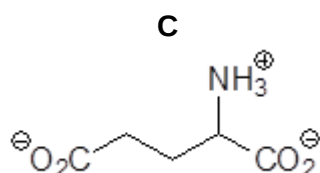
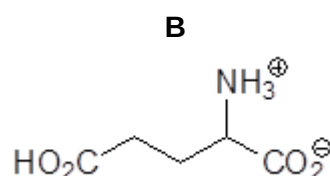
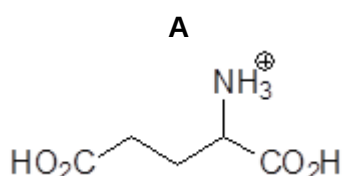
30 There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.



The pH-volume curve obtained when 30 cm³ of NaOH is added to 10 cm³ of the protonated form of glutamic acid of the same concentration is given below.



Which of the following is the major species present at point S?



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to pick a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

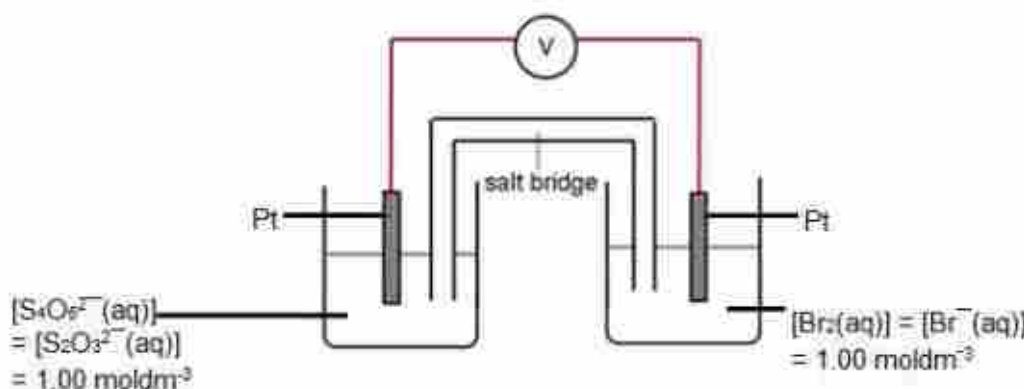
No other combination of statements is used as a correct response.

- 31** The radius and charge of each of the six ions are shown below.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. Which of the following statements are correct?

- 1** The melting point increases in the order $LY < JX < MZ$.
 - 2** The numerical value of hydration energy of X^- is smaller than that of Z^{2-} .
 - 3** The solution containing M^{2+} ions is more acidic than the solution containing J^+ ions.
- 32** Use of the *Data Booklet* is relevant to this question.



Which of the following will increase the cell potential?

- 1** Adding iodine crystals into the anodic half cell.
- 2** Adding solid silver nitrate into the cathodic half cell.
- 3** Increasing the concentration of $Br_2(aq)$ in the $Br_2(aq)/Br^-(aq)$ half cell.

- 33** From the position of the elements present in the Periodic Table and the physical properties of the compounds, which compounds are covalent?

1	$(\text{CH}_3)_2\text{SiCl}_2$	b.p. 70°C
2	GeCl_4	b.p. 86°C
3	AlBr_3	b.p. 265°C

- 34** *Use of the Data Booklet is relevant to this question.*

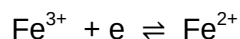
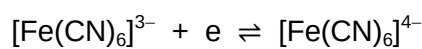
The oxides of titanium, iron and nickel are used as catalysts in the industries.

Which properties are titanium, iron and nickel likely to have in common?

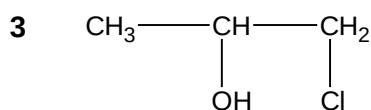
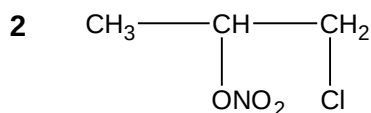
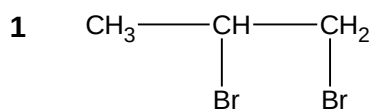
- 1** similar ionic radii
- 2** high melting points
- 3** variable oxidation states

- 35** *Use of the Data Booklet is relevant to this question.*

With reference to the two half equations below, which statements are correct?



- 1** $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than Fe^{3+}
 - 2** $[\text{Fe}(\text{CN})_6]^{4-}$ is a stronger reducing agent than Fe^{2+}
 - 3** Both $[\text{Fe}(\text{CN})_6]^{3-}$ and Fe^{3+} can oxidize MnO_4^{2-} to MnO_4^-
- 36** Propene is found to react with chlorine in the presence of aqueous sodium bromide and sodium nitrate. Which of the following are not possible products of the reaction?

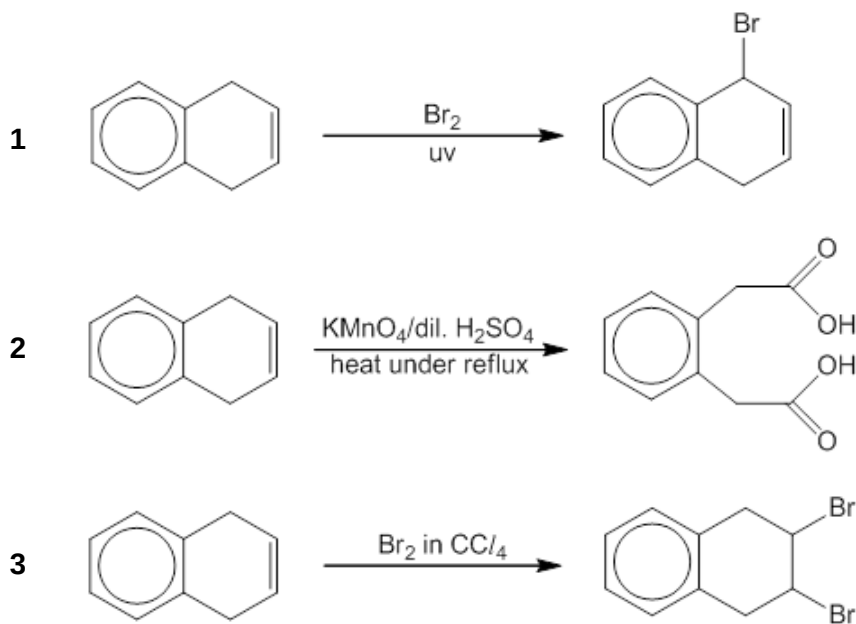


The responses **A** to **D** should be selected on the basis of

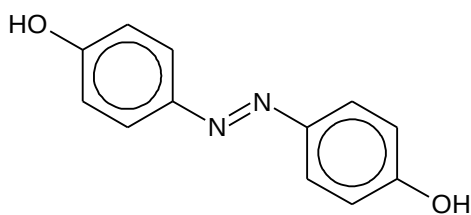
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

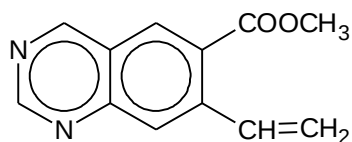
37 Which of the following reactions will not give a good yield of the desired product?



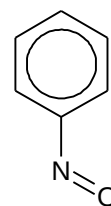
38 The three compounds **E**, **F** and **G** have the following structures?



E



F

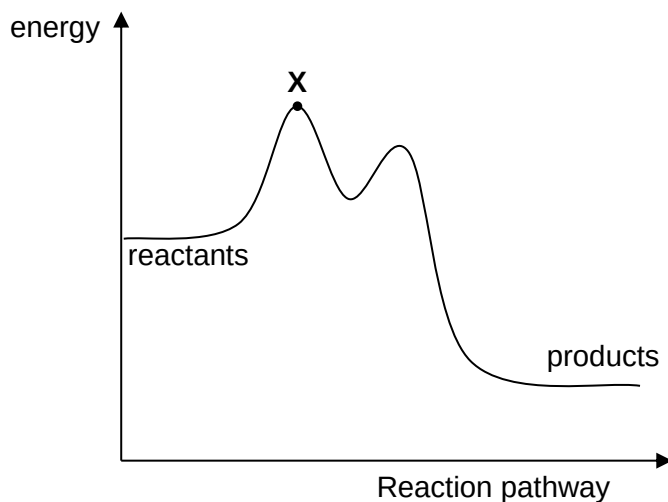
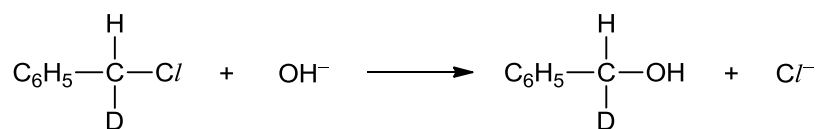


G

Which statements about **E**, **F** and **G** are correct?

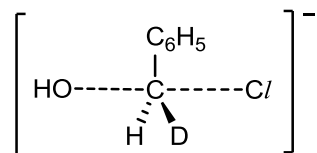
- 1** **E** and **G** have the same empirical formula.
- 2** **E** and **F** are isomers
- 3** The Mr of **F** is exactly twice that of **G**

- 39 The energy profile for the following reaction is shown below. [D = ^2H]

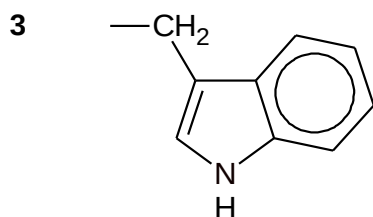
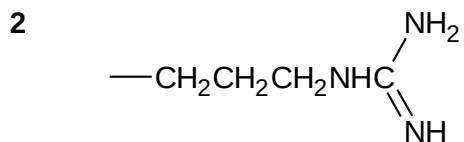
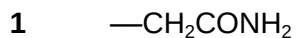


Which conclusions can be drawn?

- 1 The product has no effect on the rotation of plane polarised light.
- 2 The rate of reaction can be increased by increasing concentration of OH^- .
- 3 The structure of the transition state at point X is



- 40 Which groups within an amino acid are able to form a cross-chain link to stabilise the tertiary structure of a protein?



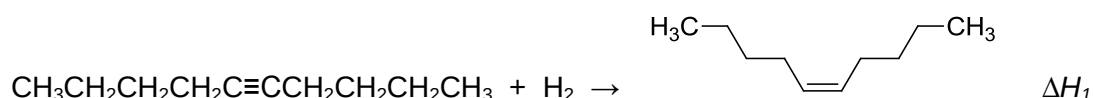
~ END OF PAPER ~

Answer **all** the questions.

1 Planning (P)

The selective partial hydrogenation of alkynes, which contain $\text{C}\equiv\text{C}$ triple bonds, to cis-alkenes represents an importance class of chemical transformations that have found extensive uses such as in bioactive molecules, in lubricants as well as in the syntheses of organic intermediates.

The partial hydrogenation of 5-decyne forms cis-dec-5-ene and the reaction is as shown :



The enthalpy change for hydrogenation of 5-decyne, ΔH_1 cannot be measured directly in the laboratory. You are required to plan an experiment to find the enthalpy change for hydrogenation of 5-decyne, ΔH_1 via Hess's Law.

The enthalpy change for the combustion of hydrogen is -286 kJ mol^{-1} . 5-decyne and cis-dec-5-ene are both liquids at standard conditions.

- (a) Based on the given information and the equation above, state **two** enthalpy changes that are necessary to calculate ΔH_1 .

.....
[1]

- (b) Using the information given above and your answer in (a), you are required to write a plan to determine a value for the enthalpy change for hydrogenation of 5-decyne, ΔH_1 .

You may assume that you are provided with

- liquid 5-decyne
- liquid cis-dec-5-ene
- copper calorimeter
- two spirit lamps with a 5 cm-wick each
- deionised water
- a lighter
- thermometer
- apparatus normally found in a school or college laboratory

Your plan should contain the following:

- a diagram of the experimental set-up

- appropriate quantities of chemicals and solutions
- all essential experimental details

Diagram of the experimental set-up

For
Examiner's
Use

Procedure:

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[7]

- You may assume the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and density of water is 1 g cm^{-3} .

Tables used to tabulate and record experimental data:

Treatment of results:

[4]

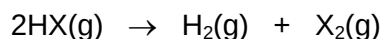
[Total: 12]

- 2 Eighty-five percent of all pharmaceutical agents and vitamins involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective.

Data about the halides are given below.

Halide (X)	pK _a (HX)	Percentage of HX decomposed at 2000°C	Boiling point of HX / °C	Dipole moment of C–X / D	K _a (HOX) at 298K
F	+3	6×10^{-5}	19.5	1.82	
Cl	–7	4×10^{-1}	–84.2	1.08	2.9×10^{-8}
Br	–9	4	–67.1	0.82	2.4×10^{-9}
I	–10	30	–35.1	0.44	

- (a) Hydrogen halides decompose at high temperature according to the equation:



Use relevant data from the *Data Booklet*, explain the trend indicated by percentage decomposition of HX.

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..... [3]

- (b) The boiling point of HF is higher than the rest of the hydrogen halides despite it being the smallest molecule. By means of a diagram, indicate the interaction between two molecules of HF that leads to this significant difference.

[2]

- (c) When dissolved in water, the hydrogen halides show different pK_a values. Write balanced equations to represent the extent of ionisation of HF and HI in water.

HF :

HI :

[2]

- (d) (i) Draw a diagram to illustrate the shape of oxoacid, HOCl , indicating clearly the bond angle.

[2]

- (ii) Using the information from the table, state which of the two acids, HOCl or HOBr is stronger?

..... [1]

- (iii) Hypoiodous acid has the formula HOI . Predict and explain whether HOI is a stronger or weaker acid than the acid you identified in (d)(ii).

.....
.....
.....

-[2]
- (iv) Some solid NaOCl solution is dissolved in a solution of HOCl at 298 K. The pH of this mixture is determined to be 6.48. Calculate the ratio of OCl^- to HOCl in this mixture.

[2]

- (e) The halides can react with concentrated sulfuric acid.

- (i) When concentrated sulfuric acid was warmed with sodium chloride, white fumes of hydrogen chloride was evolved. Write a balanced equation for the reaction.

.....[1]

- (ii) The method described in **e(i)** cannot be used to prepare hydrogen iodide. Describe what you would observe when sodium iodide is heated with concentrated sulfuric acid. Explain the chemistry behind it, and give any relevant equations.

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.....[5]

[Total: 20]

- 3 (a)** AlCl_3 is a compound of interest to scientists due to its industrial applications. For example, AlCl_3 can react with molten aluminium to form AlCl(g) . This is a useful procedure as the AlCl formed can be used to recover useful metalloids from their compounds.

Typically, the reaction has to be carried out in the presence of argon instead of air.

- (i)** The reaction has to be carried out in an atmosphere of argon. Suggest a reason for the need of argon.

.....[1]

Consider the reaction between $\text{AlCl}_3(\text{g})$ and molten aluminium that was carried out at 1573 K :



In the reaction vessel, 0.200 mol of $\text{AlCl}_3(\text{g})$ was reacted with 0.400 mol of molten Al . When the reaction system achieved equilibrium with a total pressure of 1.50 atm, it was determined that 0.200 mol of molten Al remained in the vessel.

- (ii)** Write an expression for the equilibrium constant, K_p for reaction **1** and hence calculate its value at 1573 K.

[3]

The same reaction vessel was heated to 1700 K rapidly in a way such that no reaction took place during the short interval of heating. The reaction system was allowed to re-establish equilibrium. It was found that the partial pressure of $\text{AlCl}_3(\text{g})$ was 0.390 atm when the equilibrium was re-established.

- (iii) Using the information from **a(ii)**, determine the partial pressures of $\text{AlCl}_3(\text{g})$ and $\text{AlCl}(\text{g})$ at the instant when the reaction was heated to 1700 K, before the equilibrium was re-established. You can assume that the gases behave ideally and the volume of vessel is unchanged.

[2]

- (iv) Using the calculated values from **a(iii)**, calculate K_p of the reaction at 1700 K. Hence, explain whether reaction **1** is endothermic or exothermic.

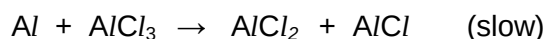
[4]

- (v) The rate equation for reaction between Al and $AlCl_3$ is shown below.

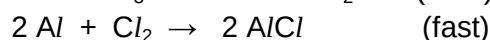
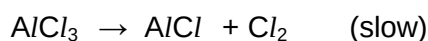
$$\text{rate} = k[AlCl_3][Al]$$

Suggest which of the two mechanisms shown is a possible mechanism for the reaction.

Mechanism 1:



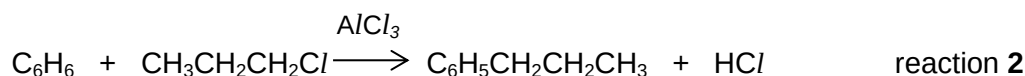
Mechanism 2:



.....

.....[1]

- (b) Anhydrous $AlCl_3$ is often used as a catalyst in the Friedel-Crafts alkylation of benzene.



- (i) Explain why $AlCl_3$ can act as a catalyst in Friedel-Crafts alkylation.

.....

.....[1]

- (ii) With the aid of an equation, explain the need to have anhydrous condition when $AlCl_3$ is used for reaction 2.

.....

.....

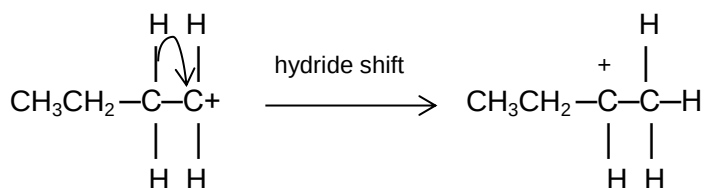
.....[2]

- (iii) Use information from the *Data Booklet*, calculate the enthalpy change of reaction for reaction 2.

- (iv) Describe the mechanism for the formation of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ in reaction 2, showing clearly the movement of electrons and partial charges. [2]

[3]

One key limitation of the alkylation reaction is that a mixture of products tends to form despite using only one type of halogenoalkane. For primary halogenoalkane, this is due to the occurrence of a process known as hydride shift which results in rearrangement of primary carbocation intermediates as shown :



- (v) Explain why hydride shift occurs for primary halogenoalkane.

.....

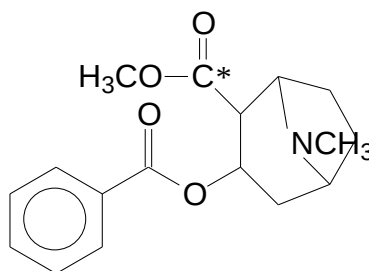
.....

.....

.....[3]

[Total: 22]

- 4 (a) Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant. Its structure is as shown:



cocaine

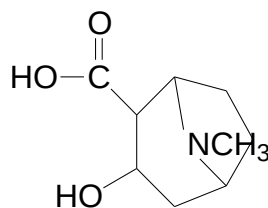
- (i) State the functional groups, other than phenyl ring, present in cocaine.

.....[1]

- (ii) State the hybridisation of the carbon atom labelled with the asterisk (*).

.....[1]

- (b) Student X was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound A.



compound A

Student X suggested the following steps:

Step 1	Methylbenzene is oxidised with hot, acidified $KMnO_4$ to give benzoic acid.
Step 2	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step 1 with phosphorus pentachloride.
Step 3	Benzoyl chloride is reacted with compound A at room temperature.
Step 4	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid at room conditions.

Explain why steps **2** and **4** of the synthetic route will not work.

.....

.....

.....

.....

.....

.....[2]

- (c)** Cocaine is sold in its protonated hydrochloride salt, known as cocaine hydrochloride. Suggest a possible reason for this.

.....[1]

- (d)** Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is converted back to cocaine before smoking.

- (i)** Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine.

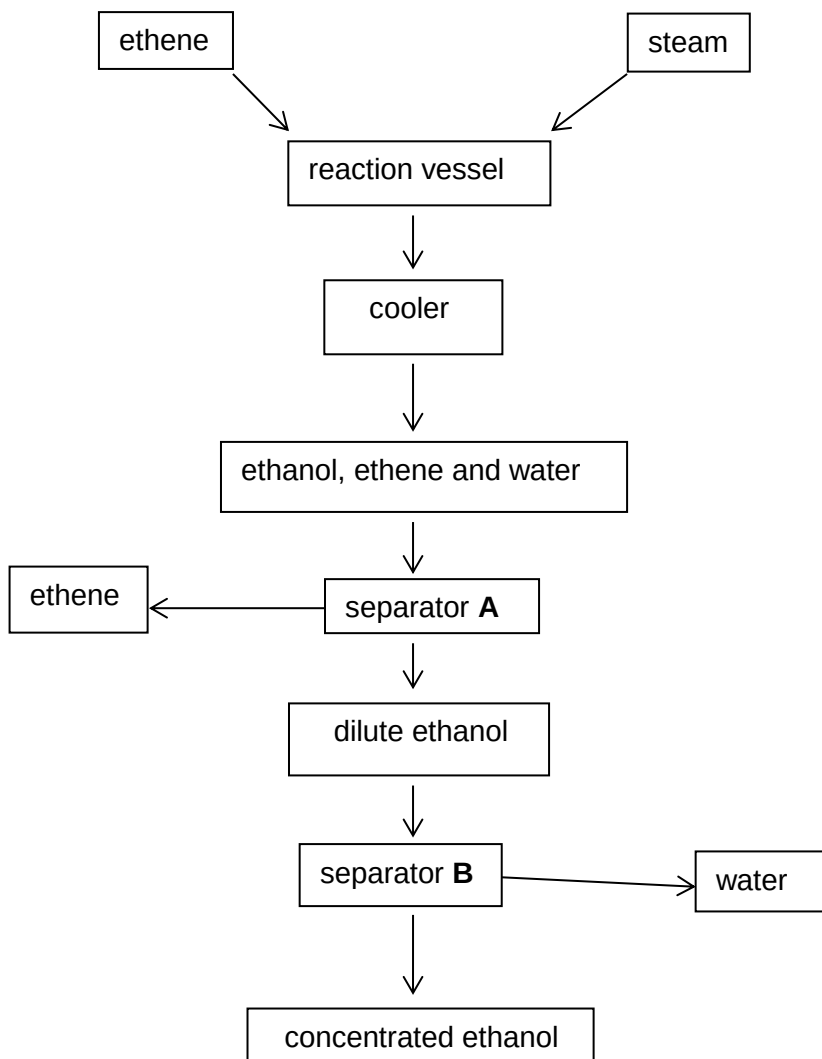
.....[1]

- (ii)** Suggest a suitable solvent to extract cocaine and separate it from its salt.

.....[1]

[Total: 7]

- 5 An industrial method for the production of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is outlined in the following flow diagram.



- (a) (i) Unreacted ethene is removed in separator A. Suggest how the separated ethene could be used to increase the efficiency of the overall process of the manufacture of ethanol.

.....
.....[1]

- (ii) Name the process that takes place in separator B.

.....[1]

- (b) In the reaction vessel, ethanol is produced in an exothermic reaction.

- (i) State the reagents and conditions for the industrial preparation of ethanol from

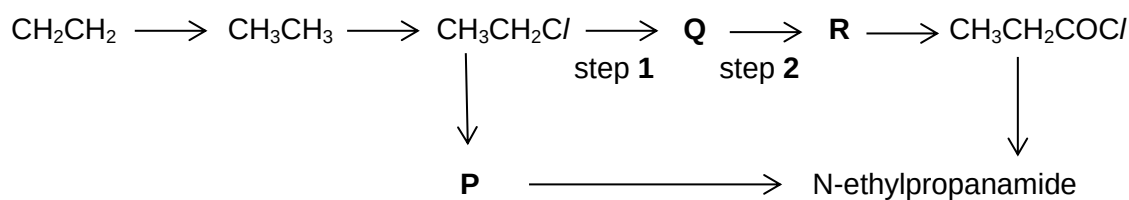
ethene.

..... [2]

- (ii) If 1.64 kg of ethanol is produced from 10.0 kg of ethene, calculate the percentage yield of ethanol.

[2]

- (c) Ethene is used to synthesise N-ethylpropanamide as shown in the following reaction scheme:



- (i) Give the structural formulae of compounds **P**, **Q** and **R**.

Compound **P**:

Compound **Q**:

Compound **R**:

[3]

- (ii) State the reagents and conditions for steps **1** and **2**.

Step **1** :

Step **2** :

[2]

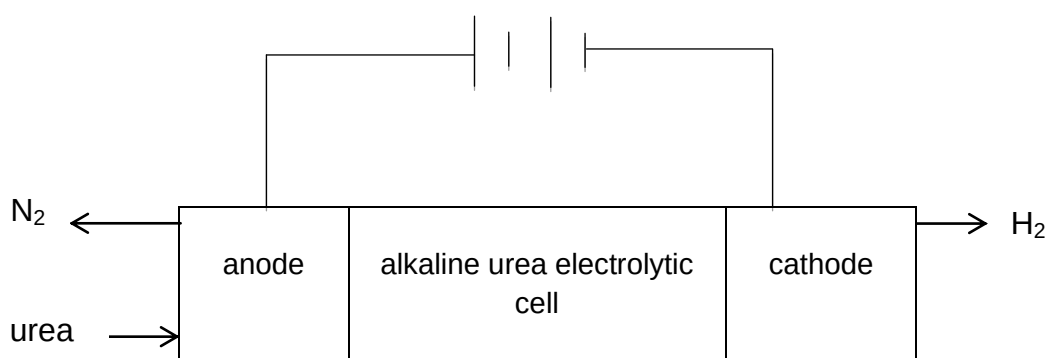
[Total: 11]

End of Paper

For
Examiner's
Use

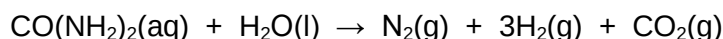
Answer any **four** questions

- 1** Phosphorus was first discovered by the German alchemist, Hennig Brandt's experiment with human waste, urine. Phosphorus occurs in different allotropic forms with the two common ones being white phosphorus and red phosphorus.
- (a)** Depending if oxygen is in excess, phosphorus reacts with oxygen to form two different oxides, phosphorus(III) oxide and phosphorus(V) oxide.
- (i)** Write the equations for the reactions of phosphorus(III) oxide and phosphorus(V) oxide with water separately, including state symbols. [2]
- (ii)** Describe the observation when the resulting solutions from **(i)** are added to solid aluminium oxide. [1]
- (b)** Nitrogen, which is in the same group as phosphorus, forms an important molecule ammonia, NH_3 . NH_3 is used to make fertilisers as well as explosives.
- (i)** When aqueous ammonia is gradually added to an aqueous solution containing $\text{Cu}^{2+}(\text{aq})$, several observations are seen. Describe and explain these observations and write equations where appropriate. [3]
- (ii)** When black copper(II) oxide is stirred with liquid ammonia, it dissolves to give a coloured solution. During this reaction the oxide ion is acting as a Bronsted-Lowry base. Suggest an equation for this reaction, and suggest the colour of the solution. [1]
- (c)** A group of researchers have recently developed an efficient way of producing hydrogen from urine, a nitrogen containing compound as shown in the diagram below.



Urea, $\text{CO}(\text{NH}_2)_2$, in aqueous KOH , which acts as the electrolyte, is oxidized at the anode to form nitrogen and carbon dioxide. At the cathode, water is reduced to hydrogen gas.

The overall equation for the urea electrolyte cell is :



- (i) Write the half equation, with state symbols, occurring at each electrode in this urea electrolytic cell. [2]
- (ii) By considering why CO_2 is not liberated at the anode, deduce the by-product produced at the anode. [1]
- (d) Nitrogen is also commonly found in organic compounds. **D**, $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$, is a neutral compound with a benzene ring. Upon reaction with hot sodium hydroxide, **E** and **F** are formed. On acidification, **E** forms $\text{C}_2\text{H}_4\text{O}_2$ which gives effervescence with sodium carbonate.

One mole of **F**, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$, reacts with one mole of aqueous sulfuric acid at room temperature. One mole of **F** is also able to decolourise three moles of aqueous bromine and gives a white ppt, **G**.

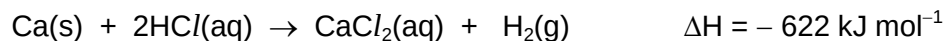
When acidified orange potassium dichromate(VI) is added to **F**, compound **H**, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$ is formed and the solution turns green. A yellow ppt is also formed when **F** and **H** is reacted with alkaline aqueous iodine separately.

Suggest the structures for compounds **D**, **E**, **F**, **G** and **H** and explain the observations described above. You do not need to consider the positions of the substituents on the benzene ring. [10]

[Total :20]

- 2 (a) With the aid of an equation, define the term *standard enthalpy change of formation* of calcium carbonate, CaCO_3 . [2]

- (b) The enthalpy change of the reaction, ΔH for the reaction shown below is determined to be -622 kJ mol^{-1} .



In a similar experiment, solid calcium carbonate reacted with an excess of hydrochloric acid and the enthalpy change of reaction was found to be -95.0 kJ per mole of calcium carbonate.



The values of enthalpy change of formation of water and enthalpy change of combustion of carbon are provided.

$$\Delta H_f^\circ(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ(\text{C}) = -394 \text{ kJ mol}^{-1}$$

Using the information given, calculate the standard enthalpy change of formation of calcium carbonate. [3]

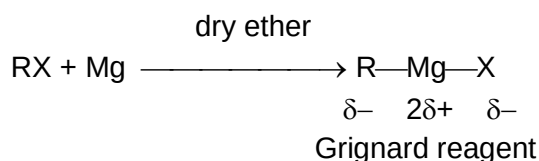
- (c) Magnesium carbonate decomposes on heating according to the equation shown below. The values of the standard enthalpy change and standard entropy change of the decomposition are provided.



$$\Delta H^\circ = +117 \text{ kJ mol}^{-1} ; \Delta S^\circ = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

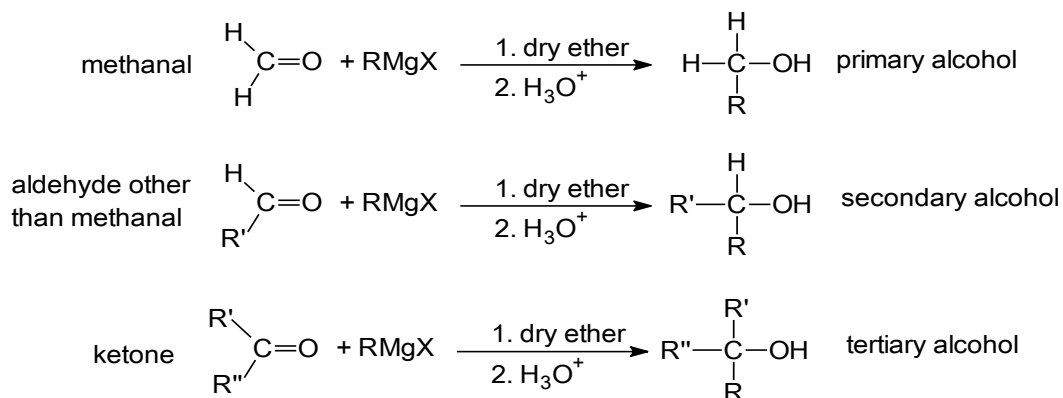
- (i) Why does the entropy increase when magnesium carbonate decomposes? [1]
- (ii) Calculate the standard Gibbs free energy change, ΔG° , for the decomposition of magnesium carbonate. Hence, comment on the spontaneity of the decomposition of magnesium carbonate at room temperature. [2]
- (iii) Compare the ease of thermal decomposition of magnesium carbonate with barium carbonate. [3]
- (d) Describe the reaction of Mg and Ca with water, giving appropriate equations with state symbols. [2]

- (e) Mg reacts with halogenoalkanes, RX in dry ether, forming Grignard reagents which are important intermediates used to produce many organic compounds.

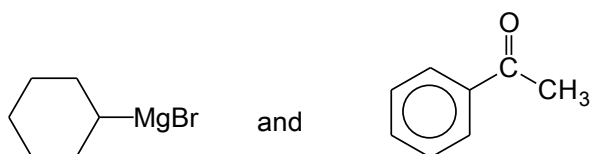


RMgX is called an organometallic compound, where R is an alkyl group and X is chlorine, bromine or iodine. R in RMgX behaves like an anion R^- , and is strongly basic and nucleophilic.

On reaction with carbonyl compounds, RMgX forms various classes of alcohols:



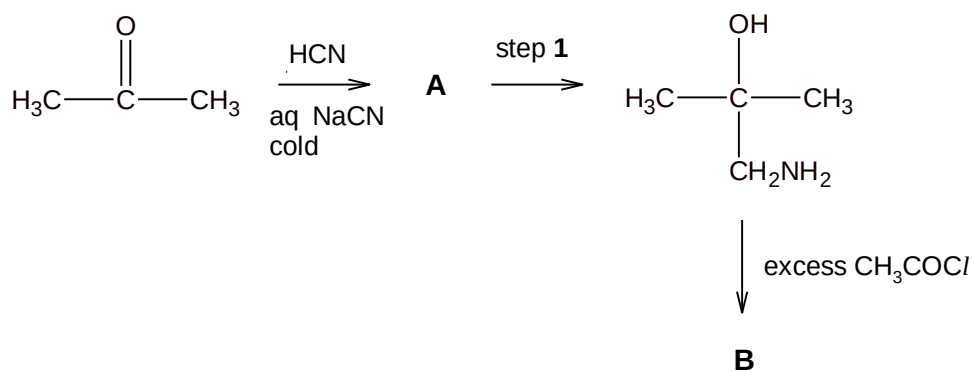
- (i) Draw the structure of the organic products formed when the following compounds are reacted:



[1]

- (ii) Give the displayed formula of the bromoalkane which can be used to form a Grignard reagent that would react with butanal to give 2-methylhexan-3-ol. [1]
- (iii) When RMgBr is reacted with ethanoyl bromide, 2 moles of RMgBr are required per mole of ethanoyl bromide and the product formed is $\text{CH}_3\text{CR}_2\text{OH}$. Explain why one mole of ethanoyl bromide reacts with two moles of RMgBr while one mole of aldehyde or ketone reacts with one mole of RMgBr. [2]

- (f) Ketones and aldehydes react with HCN via nucleophilic addition mechanism similar to the reaction with Grignard reagents. The reaction scheme below is one such example.



- (i) Draw the structures of compounds **A** and **B**. [2]
- (ii) State the reagent and condition for step 1. [1]

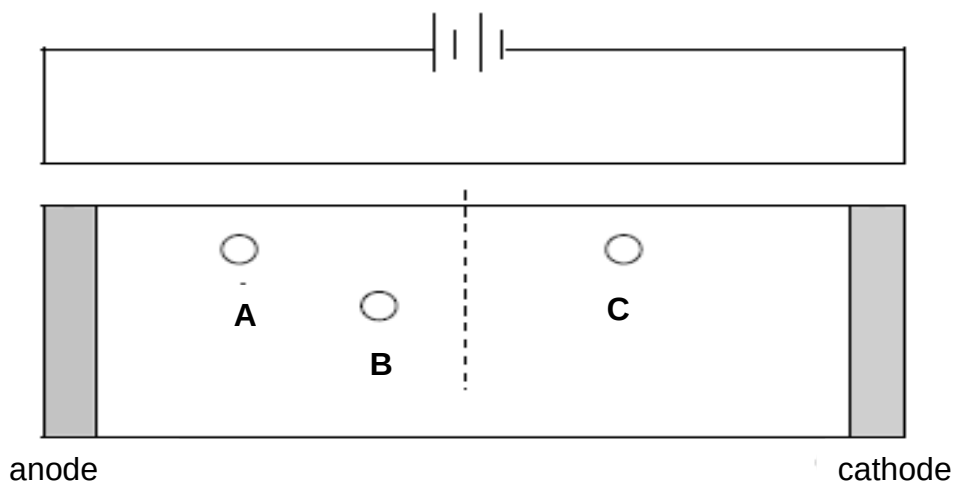
[Total :20]

- 3 Transport proteins serve the function of moving other materials within an organism. They are vital to the growth and life of all living things. Haemoglobin is an iron-containing oxygen-transport protein found in the red blood cells of all vertebrates.

- (a) State the type of bonding or interactions involved in the *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins like haemoglobin. [2]
- (b) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

Amino Acids	Formula of side chain (R' in R'CH(NH ₂)CO ₂ H)	Isoelectric Point
Lysine	-(CH ₂) ₄ NH ₂	9.74
Glutamic acid	-CH ₂ CH ₂ COOH	3.15
Aspartic acid	-CH ₂ COOH	2.77

An electrophoresis experiment is ran on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.

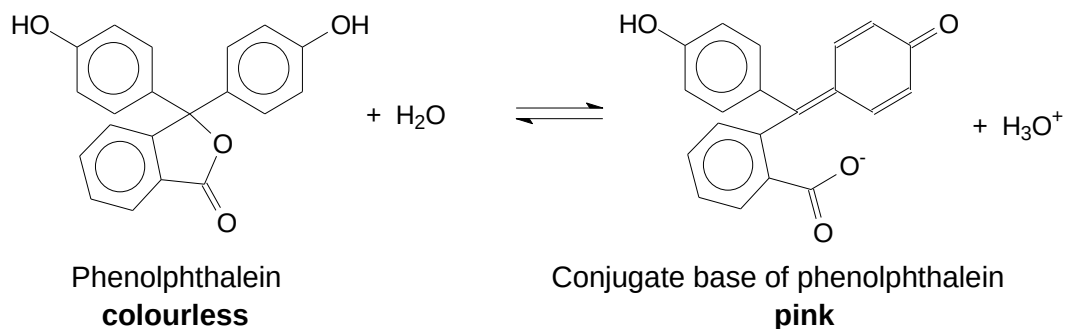


Suggest the identities of amino acids **A**, **B** and **C**.

[1]

- (c) Haemoglobin is able to exhibit peroxidase-like activity to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base. This reaction is often used to test for the presence of blood at a crime scene.

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:

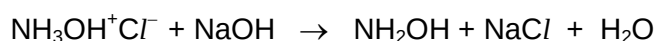


The K_a of phenolphthalein is $3.00 \times 10^{-10} \text{ mol dm}^{-3}$.

Distinct colour change for phenolphthalein occurs when half of the indicator is phenolphthalein and the other half is its conjugate base.

- (i) Calculate the pH at which phenolphthalein shows distinct colour change. [1]
- (ii) The change of colour for phenolphthalein occurs over a limited range of pH and falls within ± 1.00 of the pK_a value.

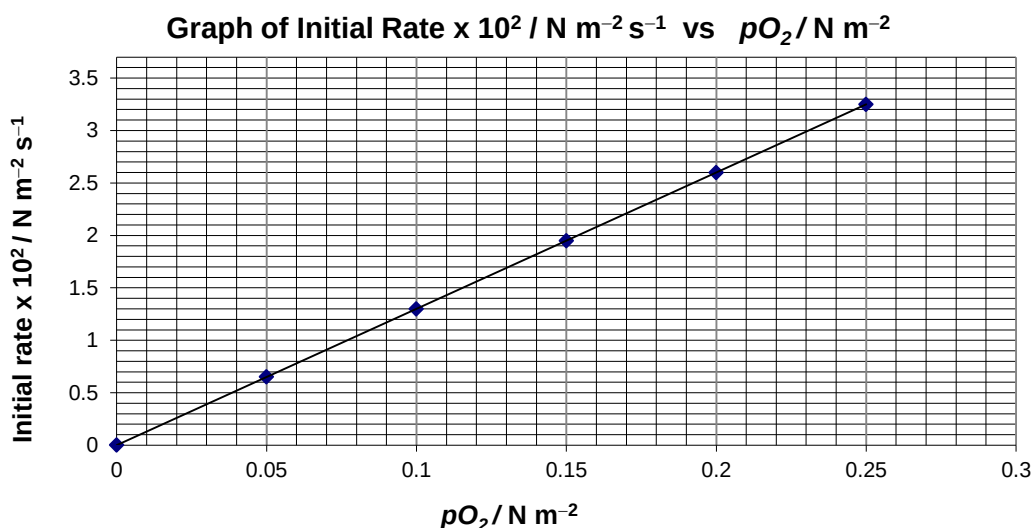
In an experiment, a solution of a weak acid hydroxylammonium chloride, $\text{NH}_3\text{OH}^+\text{Cl}^-$, was titrated against a solution of sodium hydroxide as shown by the equation below:



With the aid of an equation and your answer in (i), explain if phenolphthalein is a suitable indicator for this titration. [2]

- (d) The reaction kinetics of oxygen binding to haemoglobin in human red blood cell suspension is studied. This is done by measuring the rates of uptake of oxygen by haemoglobin at different partial pressures of oxygen.

The graph of initial rate against partial pressure of oxygen was plotted below.



- (i) Using the graph above, state the order of reaction with respect to oxygen. [1]

- (ii) The concentration of haemoglobin was halved and a new series of experiments was conducted at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the above graph.

Deduce the order of reaction with respect to haemoglobin? Explain your answer. [2]

- (iii) Using your answers to (i) and (ii), construct the rate equation for the reaction between haemoglobin and oxygen. [1]

- (iv) Oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at $1.6 \times 10^{-6} \text{ mol dm}^{-3}$ by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to $8.0 \times 10^{-6} \text{ mol dm}^{-3}$.

Calculate the rate constant, including the unit, given that the rate of oxyhaemoglobin formation is $2.68 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 37°C . [1]

- (e) Another type of protein that transports oxygen throughout the bodies of invertebrates is *haemocyanin*, which contains two copper atoms that reversibly bind a single oxygen molecule.

- (i) *Haemocyanin* exhibits catalytic activity to catalyse the hydroxylation of monophenols to diphenols.

Using an appropriate sketch of the Maxwell-Boltzmann distribution curve, explain how the presence of *haemocyanin* increases the rate of hydroxylation of monophenols. [3]

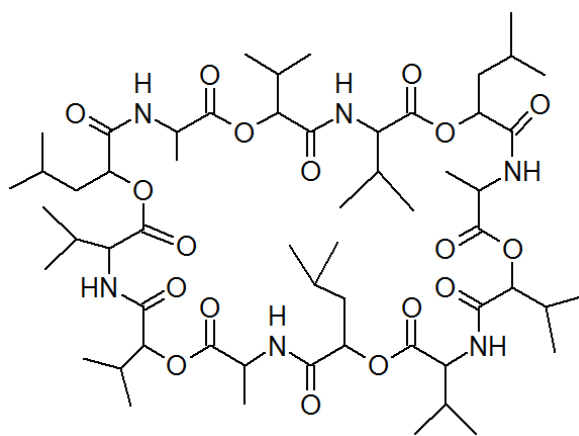
- (ii) Partial *denaturation* actually improves *haemocyanin*'s catalytic ability by providing greater access to the active site.

1 What is meant by the term *denaturation*?

2 Suggest how a weak acid might interact with *haemocyanin* to bring about denaturation.

[3]

- (f) *Cereulide* is another example of a transport protein. As a natural dodecadepsipeptide ionophore, *cereulide* acts as potassium transporters, where potassium, K^+ , plays a vital role in bacterial physiology.



Cereulide

- (i) Apart from the peptide group, name another functional group that is present in the molecule? [1]

When treated with a peptidase enzyme, the peptide bonds in the ring are hydrolysed. Only two different products are formed.

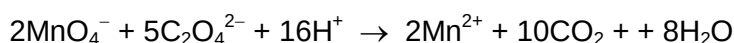
- (ii) Out of the products formed, two of the amino acid residues are present **more than once** in the protein. Draw the structural formula of these two amino acid residues. [2]

[Total :20]

- 4 (a) Manganese is a transition element that can exist in several oxidation states.

Manganese species	Mn^{2+}	MnO_4^{2-}	MnO_4^-
Colour (in aqueous medium)	pale pink	green	purple

- (i) Write the full electronic configurations of Mn in Mn^{2+} and MnO_4^- , and explain why Mn can exhibit variable oxidation states. [2]
- (ii) Explain why transition elements form compounds that are coloured. [3]
- (b) A student wanted to investigate the rate of reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ ions in an acidic medium. The reaction is shown in the equation below.



The rate of reaction was followed by mixing the following two solutions, and measuring the concentration of remaining MnO_4^- ions at fixed time intervals.

Solution A: 100 cm³ of 0.20 mol dm⁻³ ethanedioic acid, 5 cm³ of 2 mol dm⁻³ sulfuric acid, 15 cm³ of 0.20 mol dm⁻³ copper(II) sulfate and 80 cm³ of water

Solution B: 50 cm³ of 0.020 mol dm⁻³ potassium manganate(VII)

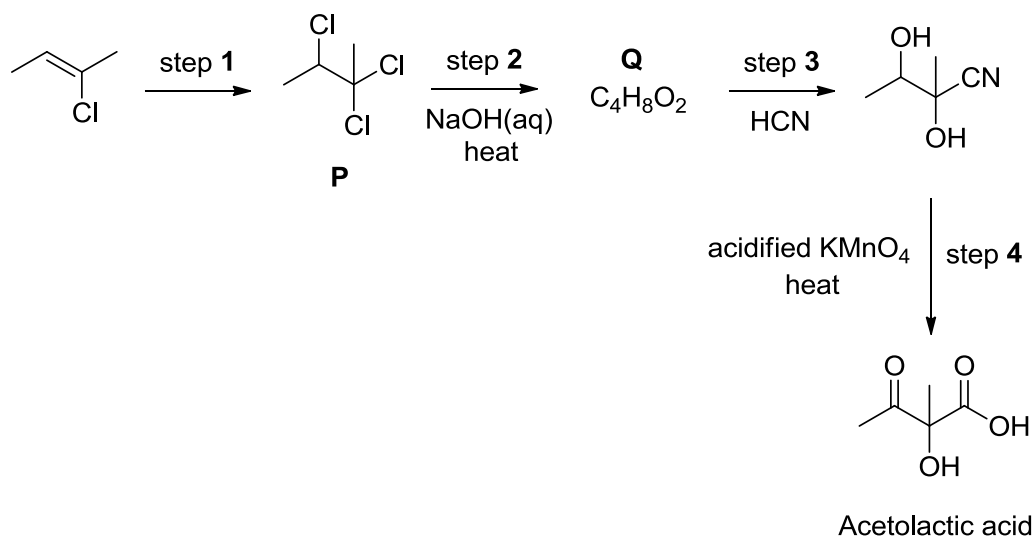
The following results were obtained.

Time/s	$[\text{MnO}_4^-] / \text{mol dm}^{-3}$
0	0.0040
10	0.0026
20	0.0016
30	0.00096
50	0.00040
75	0.00016

- (i) By means of a graphical method, determine the rate equation under the conditions whereby the reaction was conducted. [3]
- (ii) The rate of consumption of $\text{MnO}_4^-(\text{aq})$ at a particular time is $1.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. Using the equation for the reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$, calculate the rate of consumption of ethanedioate ions at that particular time? [1]
- (iii) What is the role of copper(II) sulfate in the reaction? [1]

(c) Potassium manganate(VII) is commonly used as an oxidising agent in organic chemistry.

Acetolactic acid, $C_5H_8O_4$, is a precursor in the biosynthesis of the branched chain amino acids, valine and leucine. Acetolactic acid can be synthesised from 2-chlorobut-2-ene by the following reactions.



- (i) State the reagent and conditions used in step 1 and outline the mechanism for this reaction. In your answer, you should include curly arrows showing the movement of electrons and any relevant charges and dipoles. [4]
- (ii) Compound **P** obtained from step 1 does not rotate the plane of polarised light despite it containing a chiral carbon. Use the mechanism which you have proposed in (i), to explain this observation. [3]
- (iii) Suggest the structure of compound **Q**. [1]
- (iv) Draw the organic products formed when acetolactic acid is warmed with iodine in the presence of aqueous potassium hydroxide. [2]

[Total :20]

- 5 (a) New applications such as hybrid electric vehicles and power backup require rechargeable batteries that combine high energy density with high charge and discharge rate capability. One such current battery electrode material in used is LiCoO_2 .

The following cell diagram notation is a simplified illustration of the electrochemical cell.

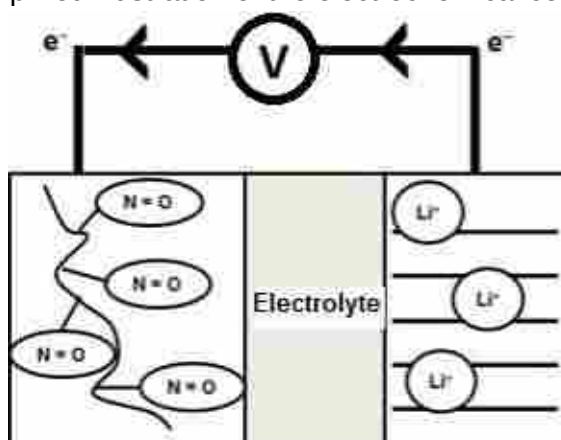


In this cell, Li is oxidised to Li^+ while CoO_2 is reduced to LiCoO_2 . State the oxidation state of Co in LiCoO_2 and hence write the electronic configuration of Co in LiCoO_2 . [2]

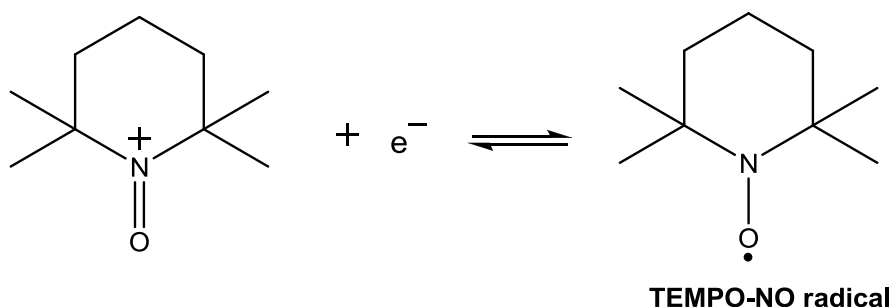
- (b) In recent years, organic radical polymers have been developed as alternatives to inorganic materials because of their light weight, flexibility and their environmentally-friendly features. With the increase in demand for thinner mobile phones and tablet computers, there is a surge to invent film-like organic-derived electrode-active battery materials to power such devices.

One such material is **TEMPO-NO radical** which is capable of repeated stable oxidation-reduction between **N=O** radicals and **N=O** cations. Its voltage when paired with a Li/Li^+ half-cell is able to reach +3.60 V which is comparable to a common lithium-ion battery.

The following is a simplified illustration of the electrochemical cell set-up.



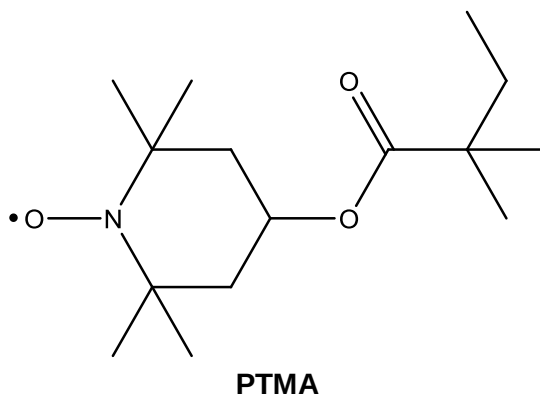
- (i) The following half-equation represents the reaction which occurs at the organic derived electrode.



With the use of the *Data Booklet* and the information above, write the overall

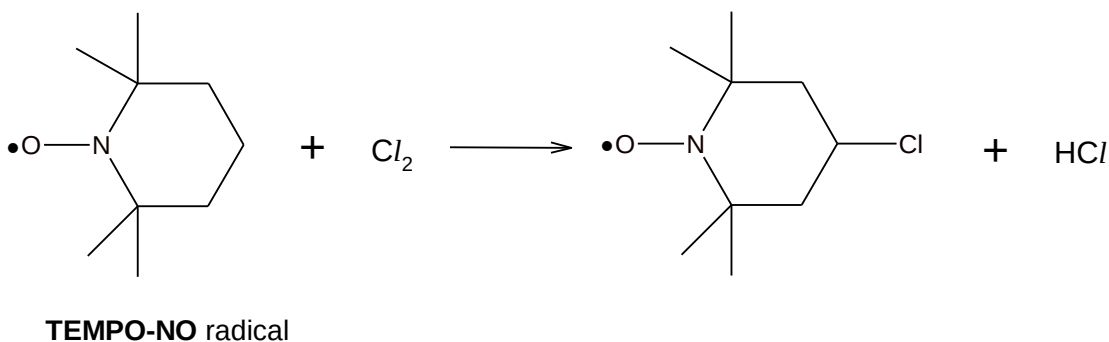
balanced equation for the electrochemical reaction and calculate the standard electrode potential for **TEMPO-NO** radical half cell. [3]

- (ii) In order for the radical polymer to be used as an electrode, it must not be soluble in the electrolyte. To improve the usability of **TEMPO-NO** radical, the material can be converted to **PTMA** which has the following structure:



Explain how the structure of **PTMA** will help to reduce its solubility in polar solvents like water. [3]

- (iii) Water cannot be used as the solvent for $\text{Li}^+ | \text{Li}$ half cell. Write an equation to illustrate the reaction when an aqueous medium is used at the $\text{Li}^+ | \text{Li}$ half cell which hinders the working of the battery. [1]
- (iv) The synthesis of **PTMA** required the mono-substitution of the **TEMPO-NO** radical with chlorine as shown in the reaction below.



Outline the mechanism for this reaction. [4]

- (v) Suggest the synthesis route for the formation of **PTMA** from **TEMPO-NO** radical. [4]
- (c) When the organic radical battery is recharged, lithium ion is being converted back to lithium metal. Given that the charging process is 87% efficient, how many hours does it take to restore 1.25 g of lithium metal using a current of 3 A? [3]

[Total :20]

End of Paper

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct and shade your choice on the answer sheet provided.

- 1** For indoor air quality safety standards, the maximum safe tolerance level of carbon monoxide gas is $6 \times 10^{-4} \text{ m}^3$ of carbon monoxide in 1 m^3 of air. Given that a typical room measures 4 m by 4 m by 3 m, calculate the number of molecules of carbon monoxide present in the room at this tolerance level at room temperature and pressure?

- A** 1.13×10^{24}
B 7.22×10^{23}
C 1.51×10^{22}
D 7.22×10^{20}

Answer: B

For 1 m^3 of air, 6×10^{-4} of CO is allowed
 For $4 \times 4 \times 3 = 48 \text{ m}^3$ of air, volume of CO = $48 \times 6 \times 10^{-4} = 0.0288 \text{ m}^3 = 28.8 \text{ dm}^3$
 Number of moles of CO = $28.8 / 24 = 1.20 \text{ mol}$
 Number of molecules
 = $1.20 \times (6.02 \times 10^{23})$
 = 7.22×10^{23}

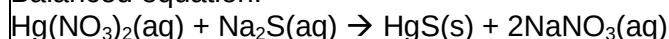
- 2** Soluble mercury compounds such as mercury(II) nitrate are highly toxic. One removal method involves the treatment of wastewater contaminated with mercury(II) nitrate with sodium sulfide to produce solid mercury(II) sulfide and sodium nitrate solutions.

Calculate the mass of mercury(II) sulfide formed when 0.020 dm^3 of $0.100 \text{ mol dm}^{-3}$ sodium sulfide reacts with 0.050 dm^3 of $0.010 \text{ mol dm}^{-3}$ mercury(II) nitrate?

- A** 0.117 g **B** 0.133 g **C** 0.280 g **D** 0.466 g

Answer: A

Balanced equation:



No. of moles of Na_2S

$$= 0.020 \times 0.100 = 2.00 \times 10^{-3} \text{ mol}$$

No. of moles of $\text{Hg}(\text{NO}_3)_2$

$$= 0.050 \times 0.010 = 5.00 \times 10^{-4} \text{ mol}$$

$2.00 \times 10^{-3} \text{ mol}$ of Na_2S will require $2.00 \times 10^{-3} \text{ mol}$ of $\text{Hg}(\text{NO}_3)_2$ for complete reaction.

Since $5.00 \times 10^{-4} \text{ mol}$ of $\text{Hg}(\text{NO}_3)_2$ is used (lesser than 2.00×10^{-3} needed), thus $\text{Hg}(\text{NO}_3)_2$ is limiting.

No. of moles of $\text{HgS} = 5.00 \times 10^{-4} \text{ mol}$

Mass of HgS

$$= (5.00 \times 10^{-4}) \times (201 + 32.1) = 0.11655 \text{ g}$$

$= 0.117 \text{ g}$

- 3 Gaseous particle **X** has a proton number n , and a charge of $+1$.
Gaseous particle **Y** has a proton number $(n+1)$, and is isoelectronic with **X**.

Which statement about **X** and **Y** is correct?

- A** When placed in an electric field, the angle of deflection for **X** is the same as that of **Y**.
B **X** requires more energy than **Y** when a further electron is removed from each particle.
C **X** releases more energy than **Y** when an electron is added to particle.
D **X** has a larger radius than **Y**.

Answer: D

Particle **X**

Number of protons	n
Number of electrons	$n-1$

Thus **X** has a charge of $+1$

Particle **Y**

Number of protons	$n+1$
Number of electrons	$n-1$

Thus **Y** has a charge of -2

A is incorrect.

Angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

Y has double the charge of **X** (-2 as compared to $+1$), however, the atomic mass of **Y** is not double that of **X** (**X** and **Y** are consecutive elements as deduced from their proton numbers). Thus their charge/mass ratios will not be the same.

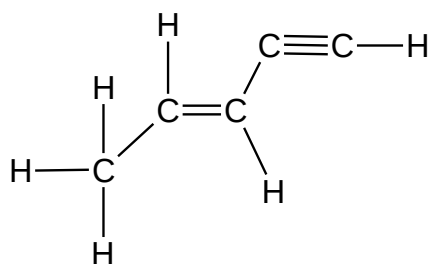
B is incorrect. As **X** has one less proton than **Y**, it has a smaller nuclear charge. As both particles are isoelectronic (same number of inner shell electrons), shielding effect will be the similar. Effective nuclear of **X** will be smaller. The valence electrons of **X** will be less strongly attracted to the nucleus. Thus less energy is needed to remove the outermost electron.

C is incorrect. **X** releases lesser energy than **Y** when an electron is added. The attractive force between the incoming electron and the nucleus is weaker than that for **Y** as **X** has smaller effective nuclear charge.

D is correct. Same explanation as Option **B**. **X** has a smaller nuclear charge (fewer protons than **Y**) and the same shielding effect as **Y** (same number of inner shell electrons). Effective nuclear of **X** will be smaller. The valence electrons of **X** will be less strongly attracted to the nucleus. Thus the radius of **X** is larger than that of **Y**.

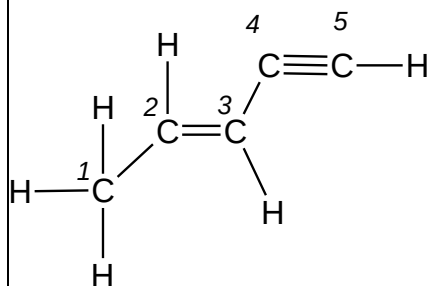
- 4 Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is not present in the molecule shown below?



- A σ bond formed by $2sp^3 - 2sp^2$ overlap.
 B σ bond formed by $2sp^3 - 2sp$ overlap.
 C σ bond formed by $1s - 2sp$ overlap.
 D π bond formed by $2p - 2p$ overlap.

Answer: B



A is correct. There is a σ bond formed by $2sp^3 - 2sp^2$ overlap present between C1-C2.

B is incorrect. There isn't any σ bond formed by $2sp^3 - 2sp$ overlap present.

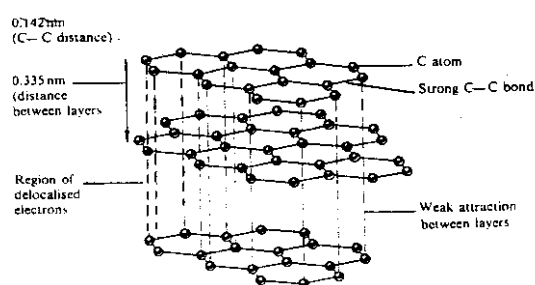
C is correct. There is a σ bond formed by $1s - 2sp$ overlap present between hydrogen atom and C5.

D is correct. There is a π bond formed by $2p - 2p$ overlap present between C2-C3 and C4-C5.

5 Which statement about graphite is **not** correct?

- A The carbon-carbon bonds in graphite are shorter than those in diamond.
- B It can act as a good lubricant due to the weak forces of attraction between the layers of atoms.
- C Carbon to carbon distances between the planes of hexagonal rings are smaller than those within the planes.
- D It acts as a good conductor of electricity in the direction parallel to the planes containing hexagonal rings of carbon.

Answer: C



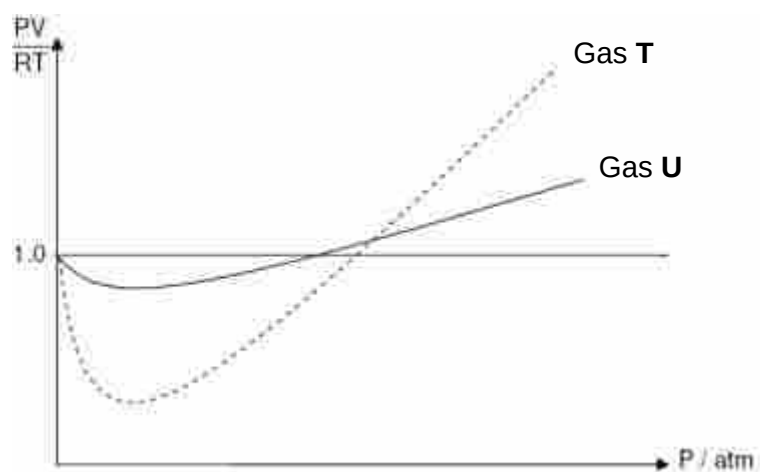
A is true. The carbon-carbon bonds in graphite are formed by sp^2 - sp^2 overlap whereas carbon-carbon bonds in diamond are formed by sp^3 - sp^3 overlap. sp^2 - sp^2 overlap is more effective than sp^3 - sp^3 overlap due to the greater s-character, thus the C-C bond length in graphite is shorter.

B is true. The weak id-id forces between the layers allow the layers to slide past one another, thus graphite is a good lubricant.

C is false. Carbon to carbon distances between the planes of hexagonal rings (weak id-id interactions) are longer than those within the planes (strong C-C covalent bonds).

D is true. Within each layer, each carbon atom is covalently bonded to three other carbon atoms using 3 of the 4 valence electrons. The presence of delocalised electrons between the layers accounts for graphite being a good conductor when a potential difference is applied along the layer. It does not conduct across the layer.

6



Which of the following could be the identities of the gases?

	Gas T	Gas U
A	H ₂ (g) at 298 K	CO ₂ (g) at 298 K
B	CH ₄ (g) at 298 K	NH ₃ (g) at 298 K
C	O ₂ (g) at 500 K	O ₂ (g) at 298 K
D	N ₂ (g) at 298 K	N ₂ (g) at 500 K

Answer: D

From graph, Gas T deviates more from ideality than Gas U.

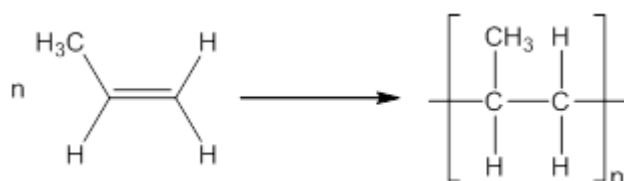
A is incorrect. Deviation of CO₂ from ideal gas behaviour is larger than that of H₂. CO₂ has a greater number of electrons than O₂, thus the electron cloud is more polarisable, resulting in stronger instantaneous dipole-induced dipole interactions between CO₂ molecules.

B is incorrect. Deviation of NH₃ from ideal gas behaviour is larger than that of CH₄. There is stronger hydrogen bonding between NH₃ molecules than instantaneous dipole-induced dipole interactions between CH₄ molecules.

C is incorrect. Deviation of O₂(g) at 298 K from ideal gas behaviour is larger than that at 500 K. At higher temperatures, particles in a gas possess large kinetic energy and are able to overcome intermolecular forces of attraction such that these attractions can be considered to be insignificant and negligible.

D is correct. Deviation of N₂(g) at 500 K from ideal gas behaviour is smaller than that at 298 K. At higher temperatures, particles in a gas possess large kinetic energy and are able to overcome intermolecular forces of attraction such that these attractions can be considered to be insignificant and negligible.

- 7 The polymerisation of propene to form polypropene occurs readily at room temperatures.



What will be the signs of ΔG , ΔH and ΔS for the polymerisation reaction at room temperature?

	ΔG	ΔH	ΔS
A	+	–	–
B	+	+	–
C	–	+	–
D	–	–	–

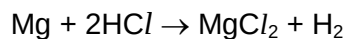
Answer: D

Question states that the reaction is spontaneous at room temperature, thus ΔG is negative.

The overall reaction involves the breaking of a C-C π bond and the formation of C-C σ bond. Since the σ bond is stronger than the π bond, the energy released from the formation of the σ bond is greater than the energy absorbed for the breaking of the π bond. Thus ΔH is negative.

The sign for ΔS is negative as there is a decrease in the number of molecules, thus there are fewer ways of arranging the molecules, level of disorderliness decreases.

- 8 The rate of the redox reaction between hydrochloric acid and Mg



can be followed by measuring the time taken for the same volume of hydrogen to be produced from a range of hydrochloric acid concentrations.

To find the order with respect to hydrochloric acid, which would be the most suitable graph to plot using the data?

- A [HCl] against time
- B [HCl] against $\frac{1}{\text{time}}$
- C Volume H₂ against time
- D Volume H₂ against $\frac{1}{\text{time}}$

Answer: B

A is incorrect. Using graph of [HCl] against time, the order of reaction with respect to hydrochloric acid cannot be found but only the instantaneous rate of reaction can be found by finding drawing tangent and calculate the gradient to the tangent at different time.

B is correct. The rate equation proposed is $\text{Rate} = k[\text{HCl}]^n$. Since question has mentioned that time taken for the same volume of hydrogen to be produced, $1/\text{time}$ will thus be deemed as rate. If order of reaction with respect to hydrochloric acid is 1 ($n=1$), the appropriate graph, $\text{rate} = [\text{HCl}]$ against $1/\text{time}$ (also deemed as rate) will be a straight line with positive gradient and the gradient = k .

C is incorrect. As the question mentioned that the data collected is time taken to produce the same volume when different concentrations of hydrochloric acid, the graph of volume of hydrogen against time will be the same even different concentrations of hydrochloric acid is used.

D is incorrect. As the question mentioned that the data collected is time taken to produce the same volume when different concentrations of hydrochloric acid, the graph of volume of hydrogen against $1/\text{time}$ will be the same despite that different concentrations of hydrochloric acid are used.

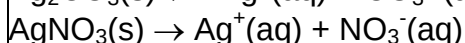
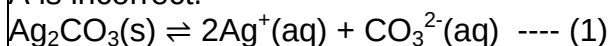
- 9 The numerical value of the solubility product of nickel(II) carbonate is 6.6×10^{-9} while that of silver carbonate is 2.1×10^{-11} at 25 °C.

Which of the following statements is true?

- A Addition of silver nitrate increases the solubility of silver carbonate.
- B The solubility of silver carbonate is higher than the solubility of nickel(II) carbonate.
- C Addition of nitric acid to a solution containing nickel(II) carbonate increases the solubility product of nickel(II) carbonate.
- D Nickel(II) carbonate precipitates first when sodium carbonate is added to a solution containing equal concentrations of nickel(II) and silver ions.

Answer: B

A is incorrect.



Addition of silver nitrate increases $[\text{Ag}^+]$ in eqm 1, the position of eqm 1 shifts LHS, the solubility should decrease.

B is correct

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = 2.1 \times 10^{-11}$$

$$K_{\text{sp}} = (2s)^2(s)$$

$$s = \sqrt[3]{\frac{2.1 \times 10^{-11}}{4}} = 1.73 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{CO}_3^{2-}] = 6.6 \times 10^{-9}$$

$$s = \sqrt{6.6 \times 10^{-9}} = 8.14 \times 10^{-5} \text{ mol dm}^{-3}$$

From the above calculation it is seen that the solubility of silver carbonate is higher than that of nickel(II) carbonate.

C is incorrect. Solubility product is only affected by temperature. Therefore addition of nitric acid cannot change the magnitude of solubility product.

D is incorrect.

$$\text{Assuming } [\text{Ni}^{2+}] = [\text{Ag}^+] = 0.100 \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{CO}_3^{2-}] = 6.6 \times 10^{-9}$$

$$[\text{CO}_3^{2-}] = \frac{6.6 \times 10^{-9}}{0.100} = 6.6 \times 10^{-8} \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = 2.1 \times 10^{-11}$$

$$[\text{CO}_3^{2-}] = \frac{2.1 \times 10^{-11}}{0.100^2} = 2.1 \times 10^{-9} \text{ mol dm}^{-3}$$

Since lower $[\text{CO}_3^{2-}]$ needed to see first trace of silver carbonate is lower than that of nickel (II) carbonate, silver carbonate should be precipitated out first.

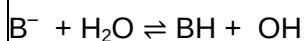
- 10 What is the pH of 10 cm³ of 0.05 mol dm⁻³ sodium benzoate?

$$[K_{\text{a}} \text{ of benzoic acid} = 6 \times 10^{-5} \text{ mol dm}^{-3}]$$

- A 6.46
B 7.46
C 8.46
D 9.46

Answer: C

Let the salt B⁻ be the benzoate salt.



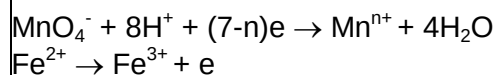
$$\begin{aligned}
 K_b &= \frac{K_w}{K_a} \\
 &= \frac{1 \times 10^{-14}}{6 \times 10^{-6}} \\
 &= 1.6667 \times 10^{-10} \text{ mol dm}^{-3} \\
 K_b &= \frac{[\text{OH}^-][\text{BH}]}{[\text{B}^-]} = 1.6667 \times 10^{-10} \\
 \frac{[\text{OH}^-]^2}{[\text{B}^-]} &= 1.6667 \times 10^{-10} \\
 [\text{OH}^-] &= \sqrt{1.6667 \times 10^{-10} \times 0.05} \\
 &= 2.8868 \times 10^{-6} \text{ mol dm}^{-3} \\
 \text{pOH} &= -\log(2.8868 \times 10^{-6}) = 5.5395 \\
 \text{pH} &= 14 - 5.5395 = 8.46
 \end{aligned}$$

- 11** A sample of 20.0 cm³ of 0.20 mol dm⁻³ iron(II) sulfate is titrated against 0.05 mol dm⁻³ potassium manganate(VII) in the presence of excess fluoride ions. It is found that 20.0 cm³ of the manganate(VII) solution is required to reach the end-point.

What is the oxidation number of manganese at end-point?

- A** +3
B +4
C +5
D +6

Answer: A



$$\text{no of mol of electrons gained by Mn} = (7 - n) \times \frac{20}{1000} \times 0.05 = 0.00100 \text{ mol}$$

$$\text{no of mol of electrons lost by Fe} = \frac{20}{1000} \times 0.20 = 0.00400 \text{ mol}$$

$$\text{no of mol of electrons lost by Fe} = \text{no of mol of electrons gained by Mn}$$

$$(7 - n) = 4$$

$$n = 3$$

Thus the new oxidation state of Mn is +3.

Alternative method:

0.00400 mol of Fe²⁺ lost 0.00400 mol of electron to Mn

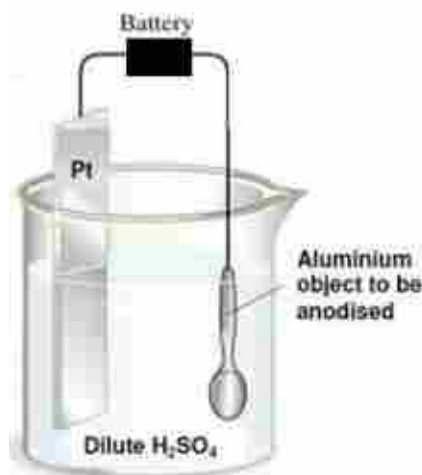
0.00100 mol of MnO₄⁻ gained 0.00400 mol of electron from Fe²⁺

1 mol of MnO₄⁻ gained 0.004/0.001 = 4 mol of electron from Fe²⁺

The original oxidation state of Mn in MnO₄⁻ is +7 and the Mn gained 4 electrons, thus the new oxidation state is +3.

- 12** Anodisation is a process to increase corrosion resistance and surface hardness in aluminium objects.

A possible set up for the process is shown as below:



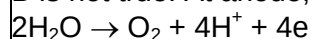
Which of the following statements about the anodisation of aluminium is true?

- A** Aluminium dissolves at the anode.
- B** Hydrogen gas is liberated at the anode.
- C** Water is oxidised at the anode to form oxygen gas.
- D** Replacing the electrolyte with NaOH(aq) will cause the reaction to cease.

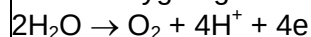
Answer: C

A is not true. In this electrolytic process, water is oxidised in preference to aluminium. Therefore, aluminium is not oxidised hence it is not dissolved.

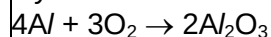
B is not true. At anode, water from electrolyte is oxidised to oxygen gas.



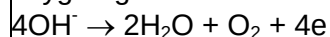
C is true. The purpose of the process is to allow water from the electrolyte to be oxidised to form oxygen gas.



Oxygen liberated then reacts with the aluminium object at the anode to form the protective layer of aluminium oxide.



D is not true. During the process, hydroxide ions from electrolyte can be oxidised to form oxygen gas at the anode. Therefore, the process does not stop.



- 13** Which of the following elements forms an oxide with a giant structure and a chloride which is readily hydrolysed?

- A** Silicon
- B** Barium
- C** Sodium

D Phosphorus

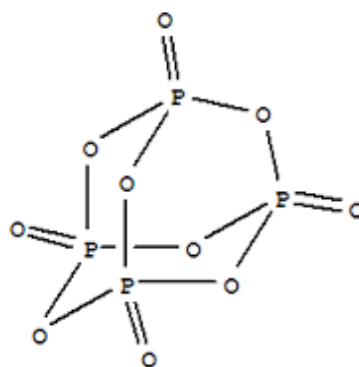
Answer: A

A is correct. The oxide of silicon, SiO_2 , exists as a giant covalent structure while the chloride of silicon, SiCl_4 , hydrolyses in water to form SiO_2 and HCl .

B is incorrect. Barium oxide has a giant ionic lattice structure and barium chloride does not undergo hydrolysis.

C is incorrect. Similar explanation to B.

D is incorrect. Phosphorus pentoxide has a simple molecular structure although phosphorus pentachloride undergoes hydrolysis readily.



Structure of P_4O_{10}

14 An element in Period 3 has the following properties:

- Its first ionisation energy is larger than both the elements before and after it across the period.
- It conducts electricity.
- It reacts slowly with cold water but react readily with steam to give a gas.

Which statement about this element is **not** correct?

- A** It has a high melting and boiling point.
- B** It forms an oxide that produces a solution that is acidic when added to water.
- C** It forms a chloride that produces a solution that is slightly acidic when added to water.
- D** Its oxidation state in compounds usually follows the group number it belongs to in the Periodic Table.

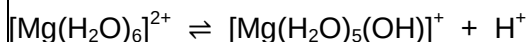
Answer: B

The element is magnesium.

A is correct. The strong metallic bonding in magnesium results in its high melting and boiling point.

B is incorrect. Magnesium oxide is basic in nature and does not produce H^+ .

C is correct. When dissolved in water, hydrated Mg^{2+} is formed. Due to its relatively high charge density, Mg^{2+} partially hydrolyses in water.



D is correct. It has an oxidation state of +2.

- 15 The following report appeared in a newspaper article.

Drums of bromine broke open after a vehicle crash on the motorway. Traffic was diverted as purple gaseous bromine drifted over the road (it is denser than air), causing irritation to drivers' eyes. Firemen sprayed water over the scene of the accident, dissolving the bromine and washing it away.

What is wrong with the report?

- A Bromine does not dissolve in water.
- B Bromine does not vapourise readily.
- C Bromine is less dense than air.
- D Bromine is not purple.

Answer: D

A is correct. Bromine dissolves in water to form an orange solution.

B is correct. Bromine has a relatively high boiling point due to its big and polarisable electron cloud and hence stronger instantaneous dipole–induced dipole forces.

C is correct. Bromine has a molecular weight of 160 grams per mole, which is denser than air, which has a molecular weight of 28 grams per mole (mainly nitrogen gas).

D is incorrect. Bromine exists as a red-brown gas.

- 16 When crystalline potassium chromate(VI) was dissolved in water, a yellow solution **Q** was formed. Addition of dilute sulfuric acid to **Q** gave an orange solution **R**. When hydrogen sulfide was bubbled through solution **R**, there was a color change in the solution and yellow sulfur was produced.

Which process **did not** occur in the above experiment?

- A Ligand exchange

- B Redox reaction
- C Precipitation
- D Acid-base

Answer: A

K_2CrO_4 dissolves in water to give **Q**, CrO_4^{2-} .

Q undergoes acid-base reaction to give **R**, $Cr_2O_7^{2-}$. **R** undergoes redox reaction with H_2S where sulfur was precipitated.

- 17 Chlorine compounds show oxidation states ranging from -1 to $+7$.

What are the reagents and conditions necessary for the oxidation of chlorine gas into a compound containing chlorine in the $+5$ oxidation state?

- A Cold dilute NaOH
- B Hot concentrated NaOH
- C Concentrated H_2SO_4 at room temperature
- D $AgNO_3(aq)$ followed by $NH_3(aq)$ at room temperature

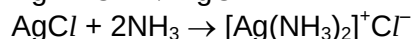
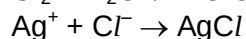
Answer: B

A is incorrect. The compound formed is $NaOCl$ and the oxidation state of chlorine in the compound is $+1$.

B is correct. The compound formed is $NaClO_3$ and the oxidation state of chlorine in the compound is $+5$.

C is incorrect. No reaction occurs between chlorine gas and sulfuric acid.

D is incorrect. $Cl_2 + H_2O \rightleftharpoons HClO + HCl$



Cl in product does not have oxidation state of $+5$.

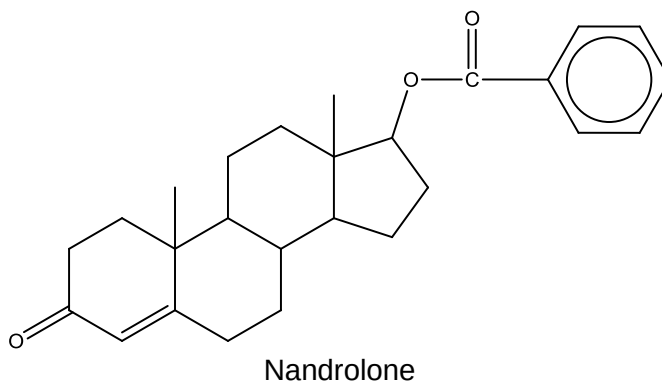
- 18 Which statement correctly **defines** a transition element?

- A Transition elements form many coloured compounds.
- B Transition elements or their compounds are widely used as catalysts.
- C Transition elements form one or more stable ions with partially filled d-orbitals.
- D Transition elements exhibit more than one oxidation state in their compounds.

Answer: C

A transition element is defined as a d-block element which forms one or more stable ions with partially filled d-orbitals.

19 How many stereoisomers does a molecule of Nandrolone has?



A 8

B 16

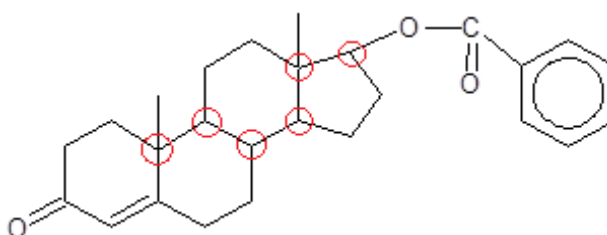
C 32

D 64

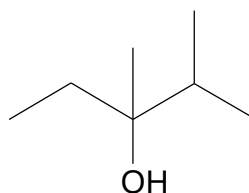
Answer: D

A chiral carbon has four different groups attached to it. Nandrolone has 6 chiral carbons. Double bond within a ring cannot exhibit cis-trans isomerism.

Total number of stereoisomers = $2^6 = 64$



20 The structure of compound **Z** is as seen below:



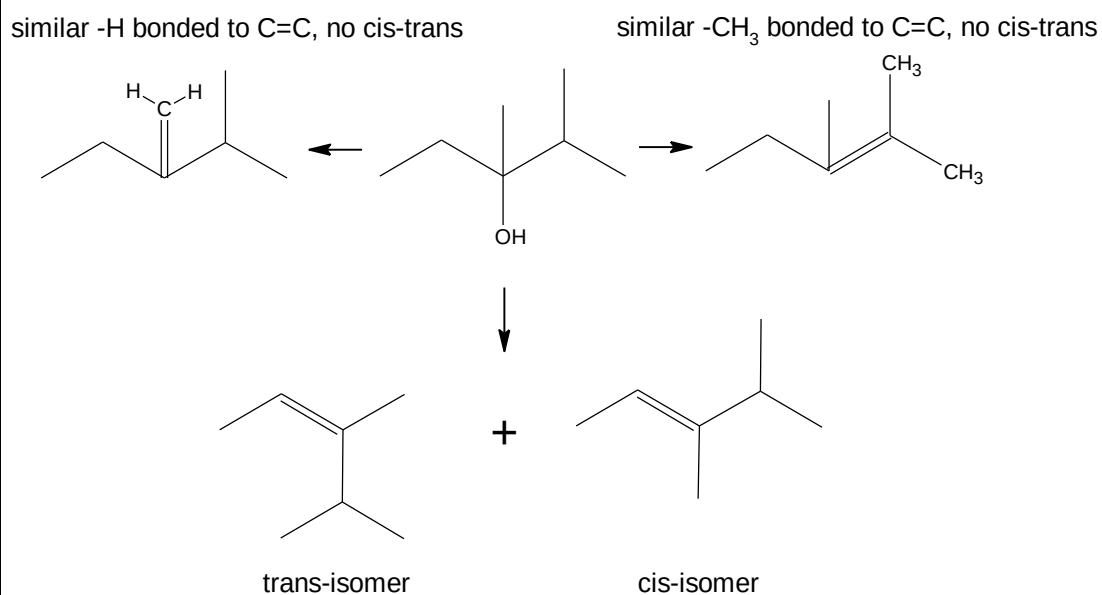
Compound Z

It is completely reacted with hot concentrated H_2SO_4 to form compound Y. What is the total number of isomers of Y?

- A** 2 **B** 3 **C** 4 **D** 5

Answer: C

This is an elimination reaction. The $-\text{OH}$ group and a H atom on a adjacent C atom are removed to form an alkene.

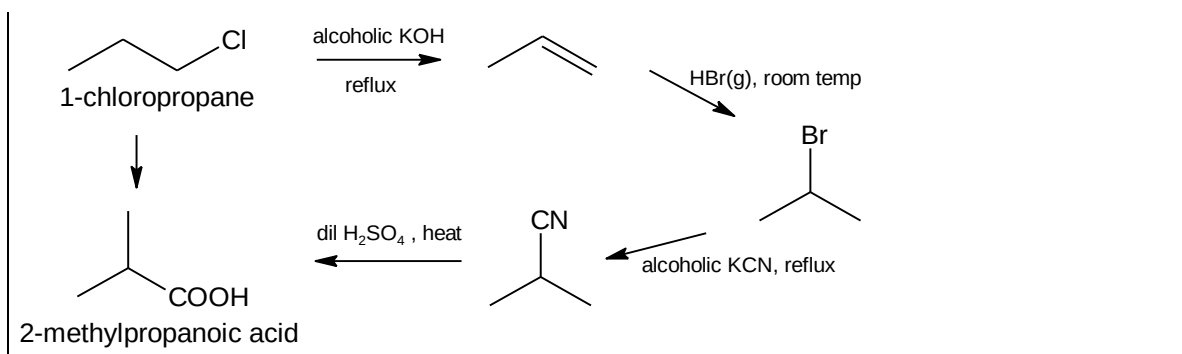


- 21** 2-methylpropanoic acid can be synthesised from 1-chloropropane through a series of reactions.

Which set of reagents, used in sequential order, would be the most suitable for this synthesis?

- A** PCl_5 , acidified KMnO_4
B ethanolic KCN , dilute HCl
C aqueous KOH , HCl , ethanolic KCN , dilute HCl
D ethanolic KOH , HBr , ethanolic KCN , dilute H_2SO_4

Answer: D



22 Which statement about ethanal and propanone is **not** correct?

- A Both give a positive tri-iodomethane test.
- B Both react with 2,4-dinitrophenylhydrazine reagent.
- C Both may be prepared by the oxidation of an alcohol.
- D Both react with hot acidified sodium dichromate(VI).

Answer: D

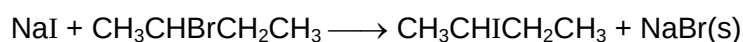
A is correct. Both compounds contain $\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$ structure and will produce a yellow ppt, CHI₃ with aqueous alkaline iodine.

B is correct. Both compounds contain $\text{—}\overset{\text{O}}{\parallel}\text{C—}$ functional group and will produce an orange ppt with 2,4-DNPH.

C is correct. Ethanal is an aldehyde that can be prepared by the oxidation of a primary alcohol. Propanone is a ketone that can be prepared by the oxidation of a secondary alcohol.

D is incorrect. Cr₂O₇²⁻ can only oxidise ethanal but not propanone. Aldehydes can be further oxidised to carboxylic acids but ketones cannot be further oxidised.

23 When sodium iodide in propanone is added to an optically active sample of 2-bromobutane, a sodium bromide precipitate is formed after 13 minutes upon heating.



The experiment was repeated several times and the rate equation was found to be

$$\text{Rate} = k[\text{CH}_3\text{CHBrCH}_2\text{CH}_3][\text{NaI}]$$

Which of the following statements is **not** correct?

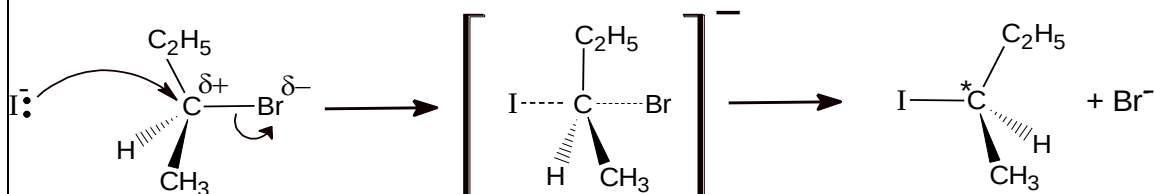
- A The mechanism involves a reactive intermediate.
- B The organic product sample obtained rotates the plane of polarised light.
- C A similar experiment, using 1-bromobutane, will produce a precipitate in less than 13 minutes.
- D A similar experiment, using 2-chlorobutane, will take more than 13 minutes to produce a precipitate.

Answer: A

A is incorrect. The rate equation shows that both reactants are involved in the rate-determining step. Hence, it is S_N2 mechanism where no intermediate is formed.

B is correct. The reactant is chiral and all its molecules undergo an inversion of configuration to remain as a chiral compound. The product will display optical activity.

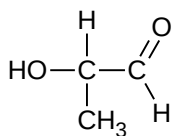
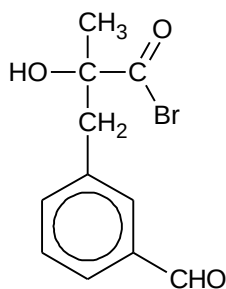
For example, the starting optically active sample contains 40% (+) and 60% (-) isomers. After S_N2 reaction, the product sample obtained will contain 60% (+) and 40% (-) isomers which is still optically active and rotate the plane of polarised light.



C is correct. 1-bromobutane is a primary halogenoalkane while 2-bromobutane is a secondary halogenoalkane. With a primary halogenoalkane, the attacking nucleophile experiences less steric hindrance when attacking the $C^{\delta+}$ and reacts more readily and the precipitate is produced faster.

D is correct. The $C-Cl$ bond is shorter than the $C-Br$ bond and has higher bond energy. More energy is needed to break the bond and the rate of reaction of 2-chlorobutane will be slower than that of 2-bromobutane.

- 24 Which reagent can be used to distinguish between compounds **R** and **S** under suitable conditions?

**R****S**

- A** Acidified potassium dichromate (VI)
- B** Alkaline copper(II) solution
- C** Sodium metal
- D** Phosphorus pentachloride

Answer: B

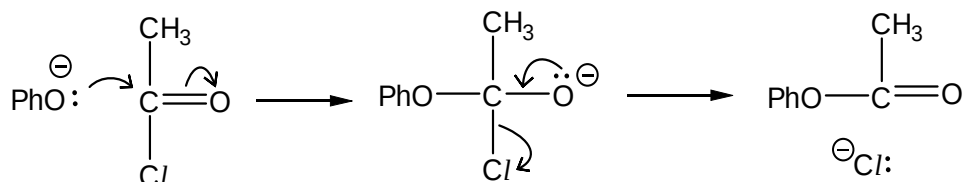
A cannot be used for the distinguishing test as it will oxidise the secondary alcohol and aldehyde in **R** as well as the aldehyde in **S**. Orange acidified $\text{K}_2\text{Cr}_2\text{O}_7$ will turn green.

B can be used for the distinguishing test. **R** is an aliphatic aldehyde and reacts to form a brick red precipitate of Cu_2O . **S** is an aromatic aldehyde and will not be able to reduce alkaline copper(II) solution.

C cannot be used for the distinguishing test. Na will react with -OH groups in both **R** and **S** and give off H_2 gas.

D cannot be used for the distinguishing test. PCl_5 will react with -OH groups in both **R** and **S** to produce white fume of HCl.

- 25** The two-stage reaction sequence given shows a possible mechanism for the reaction between phenoxide ion and ethanoyl chloride.



where Ph = phenyl

How should the *overall* reaction be classified?

- A** Electrophilic addition
- B** Nucleophilic addition
- C** Electrophilic substitution

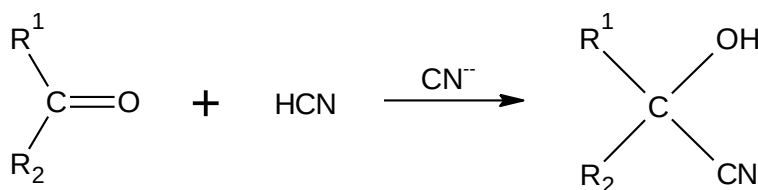
D Nucleophilic substitution

Answer: D

In the first step, PhO^- behaves as a nucleophile by attacking the $\text{C}^{\delta+}$ that is attached to O and Cl atoms.

At the end of the reaction, the Cl^- has left the molecule after being substituted.

- 26** Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-\text{CH}_2\text{COOCH}_3$ ions are generated from $\text{CH}_3\text{COOCH}_3$ by strong bases.

Which compound can be made from an aldehyde and $\text{CH}_3\text{COOCH}_3$?

- A** $\text{CH}_3\text{CH}(\text{OH})\text{COOCH}_3$
B $\text{CH}_3\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_3$
C $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{COOCH}_3$
D $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COOCH}_3$

Answer: C

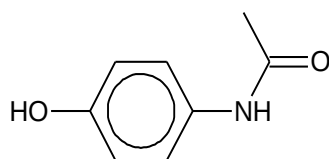
A is incorrect. The nucleophile used is $^-\text{COOCH}_3$.

B is incorrect. The nucleophile used is $\text{CH}_3\text{COOCH}_2^-$.

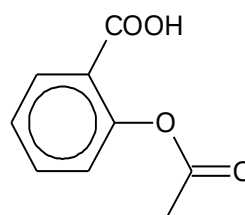
C is correct. The nucleophile used is $^-\text{CH}_2\text{COOCH}_3$ and it reacts with an aldehyde $\text{CH}_3\text{CH}_2\text{CHO}$.

D is incorrect. The nucleophile used is $^-\text{CH}_2\text{COOCH}_3$ but it reacts with a ketone CH_3COCH_3 .

- 27** Two common drugs administered when a patient experiences headache or fever are paracetamol and aspirin.

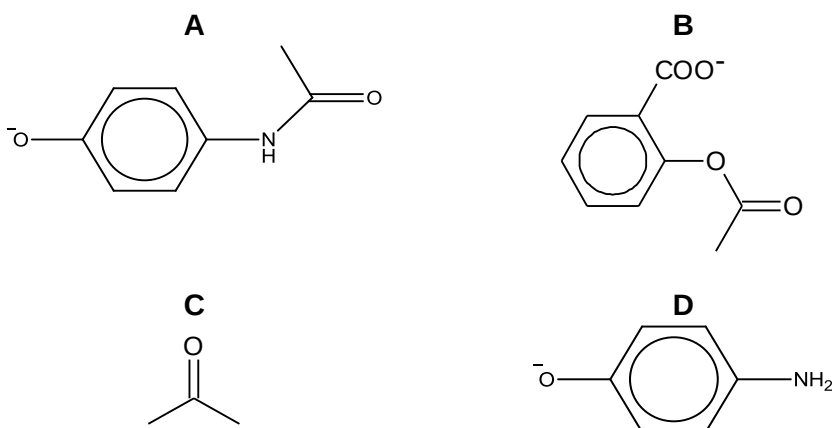


paracetamol



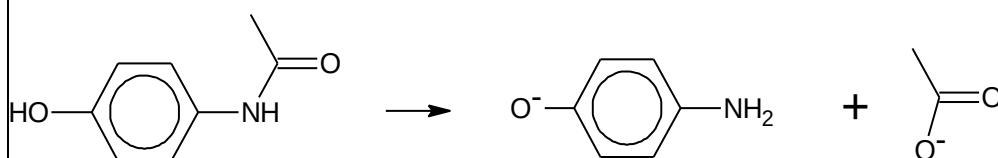
aspirin

A solution of the two drugs was hydrolysed using hot aqueous sodium hydroxide. Which organic product would be produced?

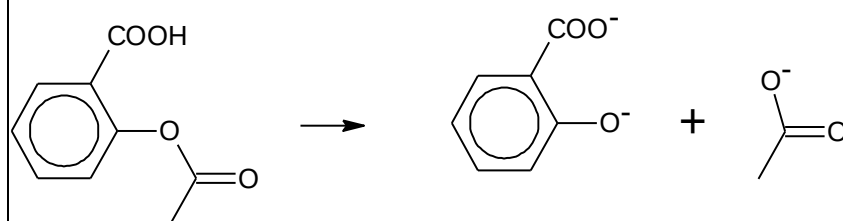


Answer: D

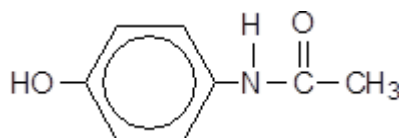
Alkaline hydrolysis of the amide bond in paracetamol produces the following:



Alkaline hydrolysis of the ester bond in aspirin produces the following:



- 28** Acetaminophen is a drug used in headache remedies. It has the following structure:



Acetaminophen

Which of the following reagents reacts with Acetaminophen?

- A** Sodium carbonate
B Cold sodium hydroxide

- C** Alkaline aqueous iodine
- D** 2,4-dinitrophenylhydrazine

Answer: B

A has no reaction. There is no -COOH present to react with the sodium carbonate.

B will react with the acidic phenol group in acetaminophen in a neutralisation reaction.

C has no reaction. The $\begin{array}{c} \text{O} \\ || \\ \text{-C-CH}_3 \end{array}$ structure is present but no C or H is directly bonded to C=O for the reaction to occur.

D has no reaction. The aldehyde and ketone functional groups are not present.

- 29** Which sequence shows the correct order of increasing pK_b in an aqueous solution of equal concentration?

- A** $\text{C}_2\text{H}_5\text{CONH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_3^+$
- B** $\text{C}_2\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_3^+ < \text{C}_2\text{H}_5\text{CONH}_2$
- C** $\text{C}_2\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{CONH}_2 < \text{C}_2\text{H}_5\text{NH}_3^+$
- D** $\text{C}_2\text{H}_5\text{NH}_3^+ < \text{C}_2\text{H}_5\text{CONH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2$

Answer: C

Increasing pK_b means becoming less basic.

The electron donating C_2H_5 group in $\text{C}_2\text{H}_5\text{NH}_2$ makes the lone pair of electrons on N atom most available for donation to a proton and therefore the strongest base.

In $\text{C}_6\text{H}_5\text{NH}_2$, the lone pair of electrons on N atom is delocalised into the benzene ring, making it less available for donation to a proton. Phenylamine is therefore a weaker base than aliphatic amines.

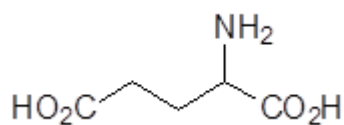
In $\text{C}_2\text{H}_5\text{CONH}_2$, the lone pair of electrons on N atom is delocalised over the carbonyl C=O and hence not available for donation to a proton.

In $\text{C}_2\text{H}_5\text{NH}_3^+$, there are no lone pair of electrons on the N atom for donation to a proton.

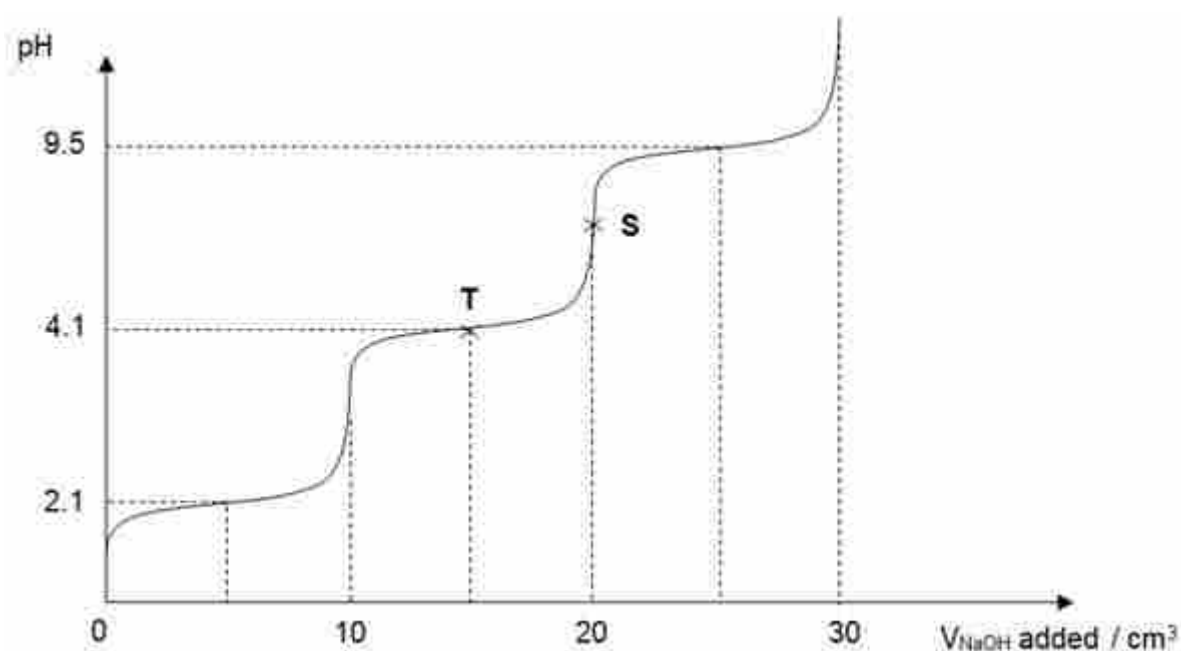
-NH_3^+ is an acidic group with a proton for donation.

30

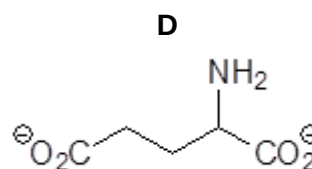
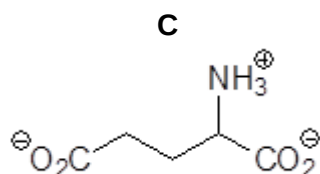
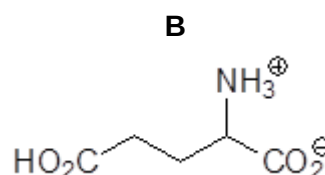
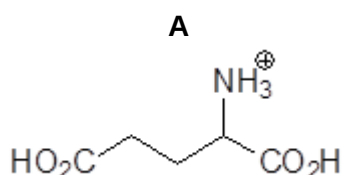
There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.



The pH-volume curve obtained when 30 cm^3 of NaOH is added to 10 cm^3 of the protonated form of glutamic acid of the same concentration is given below.

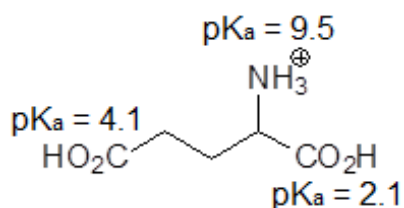


Which of the following is the major species present at point **S**?



Answer: C

The protonated form of glutamic acid and its associated pK_a values are:



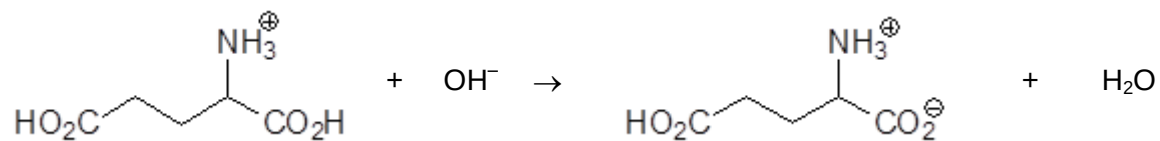
-COOH with pK_a of 2.1 is the most acidic. $-NH_3^+$ is an electron withdrawing group and disperses the negative charge of $-COO^-$ of its conjugate base and stabilises it. $-NH_3^+$ is closer to -COOH with pK_a of 2.1 than -COOH with pK_a of 4.1. Hence, the dissociation of the carboxylic acid with pK_a of 2.1 occurs to a larger extent.

Carboxylic acid is more acidic than protonated amine ($-NH_3^+$) as the conjugate base of the carboxylic acid ($-COO^-$) is resonance stabilised. Hence, the dissociation of the carboxylic acid occurs to a larger extent than $-NH_3^+$.

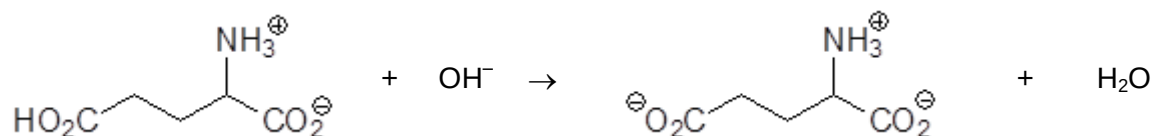
Adding NaOH would result in three equivalence points being obtained as shown in the

graph.

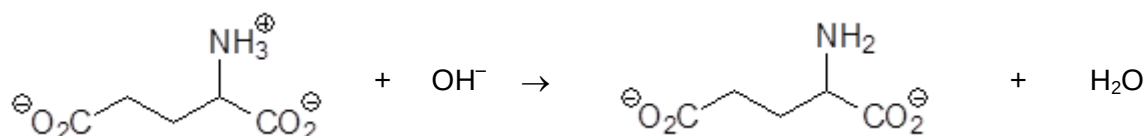
The 1st equivalence point is achieved when 10 cm³ of NaOH was added:



At point S, the 2nd equivalence point is achieved when 20 cm³ of NaOH was added:



The 3rd equivalence point is achieved when 30 cm³ of NaOH was added:



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to pick a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31** The radius and charge of each of the six ions are shown below.

ion	J ⁺	L ⁺	M ²⁺	X ⁻	Y ⁻	Z ²⁻
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. Which of the following statements are correct?

- The melting point increases in the order LY < JX < MZ.
- The numerical value of hydration energy of X⁻ is smaller than that of Z²⁻.
- The solution containing M²⁺ ions is more acidic than the solution containing J⁺ ions.

Answer: A

Option 1 is correct. JX, LY and MZ are ionic solids, thus their melting points are determined by the strength of electrostatic forces of attraction between the oppositely charged ions. The larger the magnitude of the lattice energy, the higher the melting point.

$$\text{Lattice energy} \propto \left| \frac{q^+ \times q^-}{r^+ + r^-} \right|$$

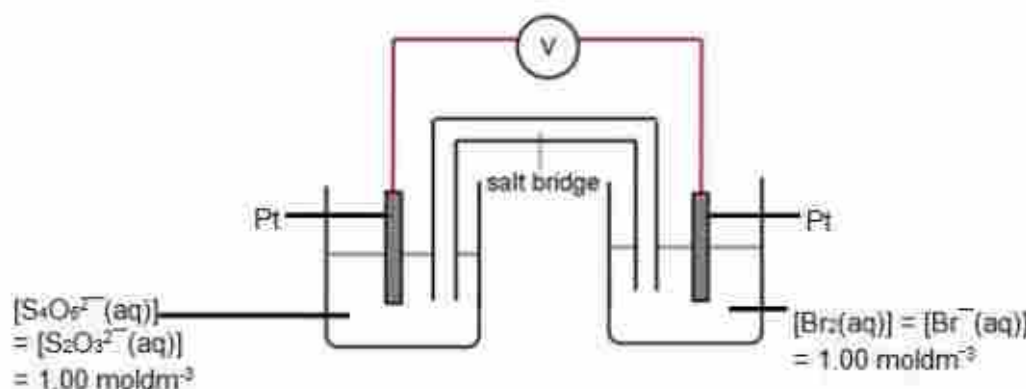
Lattice energy for JX, LY and MZ are: 3.57, 2.78 and 13.3 respectively. Thus melting point increases in the order LY < JX < MZ.

Option 2 is correct. Numerical value of hydration energy is dependent on the charge density of the ion $\left(\frac{q}{r}\right)$. Charge density of X⁻ is $1 / 0.14 = 7.14$ while that of Z²⁻ is $2 / 0.15 = 13.3$.

Thus the numerical value of hydration energy of X⁻ is smaller than that of Z²⁻.

Option 3 is correct. Charge density of M²⁺ is $2 / 0.15 = 13.3$ while that of J⁺ is $1 / 0.14 = 7.14$. Hence, M²⁺ has a higher charge density and thus a higher polarising power. M²⁺ draws electron density from the datively bonded water molecule towards itself more and weaken the O-H bond to a greater extent. This gives rise to a more acidic solution.

32 Use of the *Data Booklet* is relevant to this question.

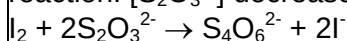


Which of the following will increase the cell potential?

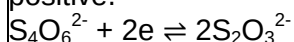
- 1 Adding iodine crystals into the anodic half cell.
- 2 Adding solid silver nitrate into the cathodic half cell.
- 3 Increasing the concentration of $\text{Br}_2(\text{aq})$ in the $\text{Br}_2(\text{aq})/\text{Br}^-(\text{aq})$ half cell.

Answer: C

Option 1 is incorrect. Adding iodine crystals remove thiosulfate ions through redox reaction. $[\text{S}_2\text{O}_3^{2-}]$ decreases while $[\text{S}_4\text{O}_6^{2-}]$ will increase at the anode.



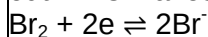
The equilibrium at anode will be disturbed. According to Le Chatelier's principle, the position of equilibrium shift right to replenish the $\text{S}_2\text{O}_3^{2-}$ ions lost and to use up the $\text{S}_4\text{O}_6^{2-}$ ions which were added from the above redox reaction. This makes $E^\circ_{\text{oxd (anode)}}$ to be more positive.



E°_{cell} becomes less positive as the $E^\circ_{\text{red (cathode)}}$ of same magnitude subtracts a larger positive $E^\circ_{\text{oxd (anode)}}$.

Option 2 is correct. Solid silver nitrate removes Br^- ions in the cathode. This reduces $[\text{Br}^-]$.
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$

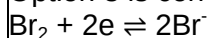
The equilibrium at cathode will be disturbed. According to Le Chatelier's principle, the position of equilibrium will shift to right to replenish bromide ions which are precipitated out. This makes $E^\circ_{\text{red (cathode)}}$ to be more positive.



$$E^\circ_{\text{cell}} = E^\circ_{\text{red (cathode)}} - E^\circ_{\text{oxd (anode)}}$$

E°_{cell} becomes more positive as the more positive $E^\circ_{\text{red (cathode)}}$ subtracts positive $E^\circ_{\text{oxd (anode)}}$ which has the same magnitude.

Option 3 is correct. At the cathode,



Increasing $[\text{Br}_2]$ shifts the equilibrium at cathode towards right. Le Chatelier's principle predicts that position of equilibrium shifts to the right to use up the bromine added. This makes $E^\circ_{\text{red (cathode)}}$ to be more positive.

$$E^\circ_{\text{cell}} = E^\circ_{\text{red (cathode)}} - E^\circ_{\text{oxd (anode)}}$$

E°_{cell} becomes more positive as the more positive $E^\circ_{\text{red (cathode)}}$ subtracts positive $E^\circ_{\text{oxd (anode)}}$ which has the same magnitude.

- 33** From the position of the elements present in the Periodic Table and the physical properties of the compounds, which compounds are covalent?

1	$(\text{CH}_3)_2\text{SiCl}_2$	b.p. 70°C
2	GeCl_4	b.p. 86°C
3	AlBr_3	b.p. 265°C

Answer: A

$(\text{CH}_3)_2\text{SiCl}_2$ is covalent. This can be inferred from its low boiling point and that it resembles $(\text{CH}_3)_2\text{CCl}_2$ since both Si and C are in the same group.

GeCl_4 is covalent. Similar reasoning as above since both Ge and Si are in the same group.

AlBr_3 is covalent as its boiling point is relatively low. Al^{3+} has a high charge density and polarises the electron cloud of Cl^- such that AlCl_3 is covalent. Since Br^- is more polarisable due to larger electron cloud than Cl^- , AlBr_3 is likely to be covalent.

- 34** Use of the Data Booklet is relevant to this question.

The oxides of titanium, iron and nickel are used as catalysts in the industries.

Which properties are titanium, iron and nickel likely to have in common?

1	similar ionic radii
2	high melting points
3	variable oxidation states

Answer: A

Titanium, iron and nickel belong to the first row of the d-block transition elements.

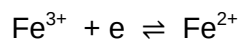
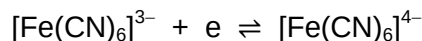
They have similar ionic radii due to the increase in shielding effect which is largely cancelled out by the increase in nuclear charge. The effective nuclear charge remains relatively constant across the first row of the d-block elements.

They have high melting points due to the strong metallic bonding, as both their 4s and 3d electrons have similar energy and can be delocalised.

They have variable oxidation states as both the 3d and 4s orbitals are similar in energy. The 4s and some (or all) of the 3d electrons can be removed without requiring too much energy.

35 Use of the Data Booklet is relevant to this question.

With reference to the two half equations below, which statements are correct?



- 1** $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than Fe^{3+}
- 2** $[\text{Fe}(\text{CN})_6]^{4-}$ is a stronger reducing agent than Fe^{2+}
- 3** Both $[\text{Fe}(\text{CN})_6]^{3-}$ and Fe^{3+} can oxidize MnO_4^{2-} to MnO_4^-

Answer: B

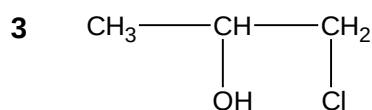
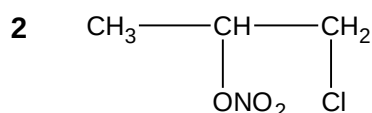
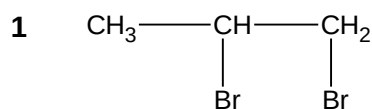


Option 1 is correct. From the reduction potential values, it can be inferred that CN^- stabilises the higher oxidation state of Fe (Fe^{3+}) to a greater extent than H_2O .

Option 2 is correct. The reduction potential of $[\text{Fe}(\text{CN})_6]^{3-}$ is less positive than that of Fe^{3+} , hence $[\text{Fe}(\text{CN})_6]^{3-}$ is a weaker oxidising agent than Fe^{3+} . Thus $[\text{Fe}(\text{CN})_6]^{4-}$ is a stronger reducing agent than Fe^{2+} .

Option 3 is incorrect. Reduction potential of $\text{MnO}_4^-/\text{MnO}_4^{2-}$ is +0.56 V, hence the cell potential for the reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ and MnO_4^- is -0.20 V. Since the cell potential is negative, the reaction is non-spontaneous.

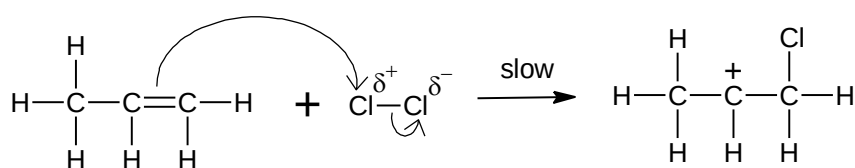
36 Propene is found to react with chlorine in the presence of aqueous sodium bromide and sodium nitrate. Which of the following are not possible products of the reaction?



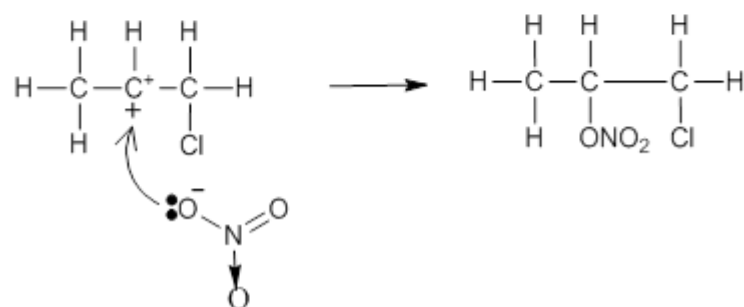
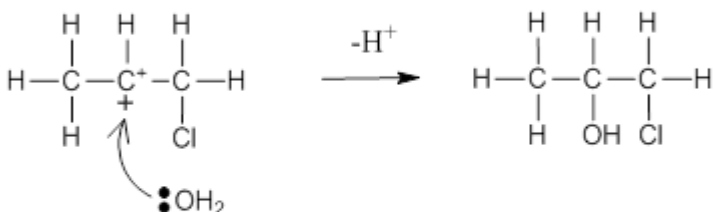
Answer: D

The reaction proceeds via electrophilic addition, during which a carbocation intermediate is

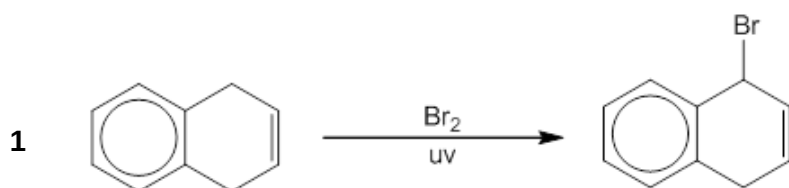
formed.

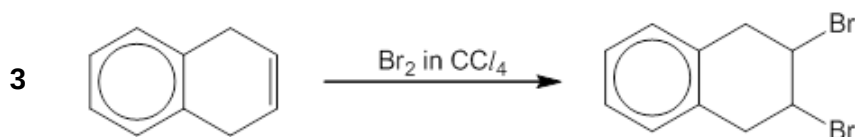


The carbocation reacts with the different nucleophiles present, giving rise to only these possible products.



37 Which of the following reactions will not give a good yield of the desired product?

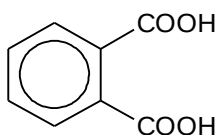




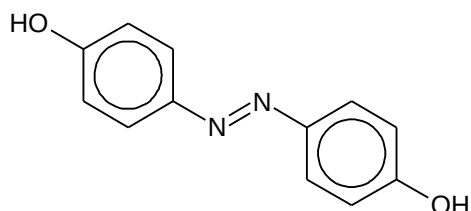
Answer: B

Both reactions 1 and 2 will not give a good yield of the desired product.

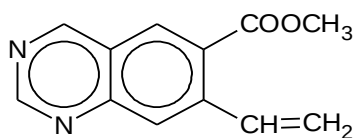
Reaction 1 is free radical substitution which can lead to multiple substitution due to the numerous C–H bonds present.

In reaction 2,  will be formed by the oxidation of the two side chains of the benzene structure.

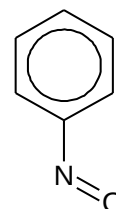
38 The three compounds **E**, **F** and **G** have the following structures?



E



F



G

Which statements about **E**, **F** and **G** are correct?

- 1 **E** and **G** have the same empirical formula.
- 2 **E** and **F** are isomers
- 3 The M_r of **F** is exactly twice that of **G**

Answer: A

Option 1 is correct.

The molecular formula of **E** is $C_{12}H_{10}N_2O_2$

The molecular formula of **G** is C_6H_5NO

Therefore, the empirical formula of **E** and **G** are the same, C_6H_5NO

Option 2 is correct.

The molecular formula of **E** is $C_{12}H_{10}N_2O_2$

The molecular formula of **F** is $C_{12}H_{10}N_2O_2$

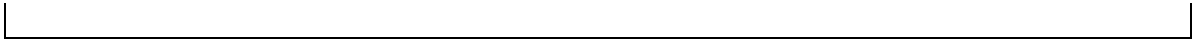
Therefore, **E** and **F** have the same molecular formula but different structural formula. They are isomers.

Option 3 is correct.

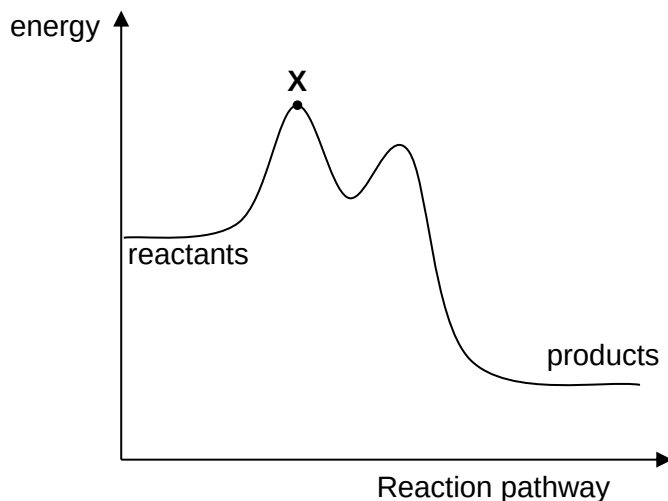
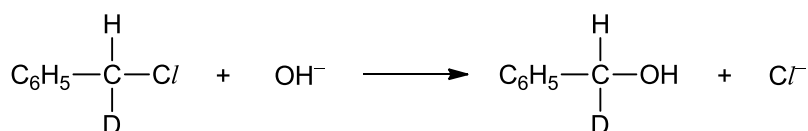
The molecular formula of **F** is $C_{12}H_{10}N_2O_2$

The molecular formula of **G** is C_6H_5NO

Since **F** has twice the number of atoms of each element in **G**, the M_r of **F** is exactly twice that of **G**.

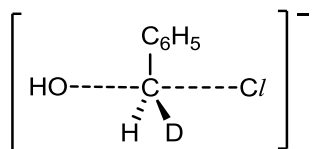


- 39 The energy profile for the following reaction is shown below. [D = ^2H]



Which conclusions can be drawn?

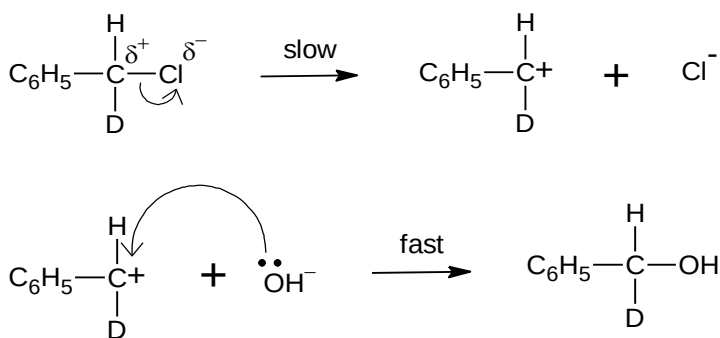
- 1 The product has no effect on the rotation of plane polarised light.
- 2 The rate of reaction can be increased by increasing concentration of OH^- .
- 3 The structure of the transition state at point X is



Answer: D

Option 1 is correct.

The graphs shows 2-steps in the mechanism. Hence, it is $\text{S}_{\text{N}}1$ mechanism.



The carbocation intermediate formed is planar, allowing OH^- to approach from either side of the plane, forming equimolar amount of both enantiomers. Therefore, the product does not display any optical activity due to the rotation of polarised light cancelling off each other

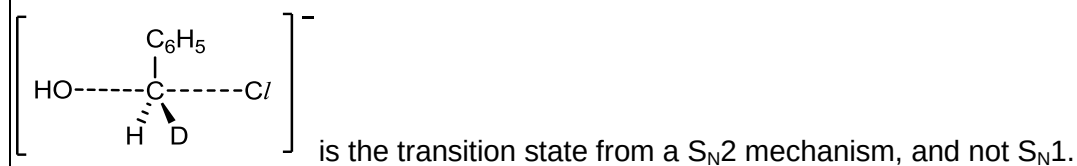
due to being equal but opposite in direction of rotation.

Option 2 is not correct.

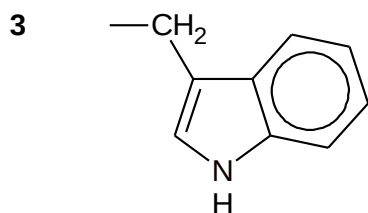
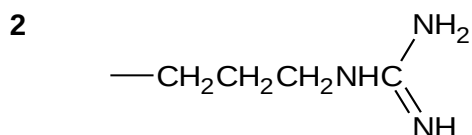
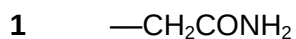
From the slow step of the mechanism, $\text{rate} = k[\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{D}]$

Therefore, the rate of reaction is independent of $[\text{OH}^-]$.

Option 3 is not correct.



- 40 Which groups within an amino acid are able to form a cross-chain link to stabilise the tertiary structure of a protein?



Answer: A

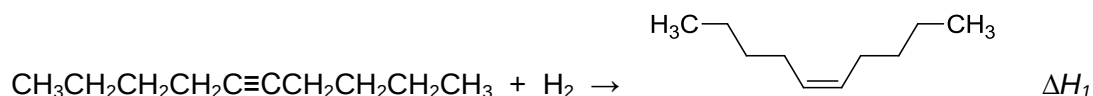
All of the above shown are R groups of α -amino acids which are used to stabilise the tertiary structure of a protein.

Answer **all** the questions.

1 Planning (P)

The selective partial hydrogenation of alkynes, which contain $\text{C}\equiv\text{C}$ triple bonds, to cis-alkenes represents an importance class of chemical transformations that have found extensive uses such as in bioactive molecules, in lubricants as well as in the syntheses of organic intermediates.

The partial hydrogenation of 5-decyne forms cis-dec-5-ene and the reaction is as shown :



The enthalpy change for hydrogenation of 5-decyne, ΔH_1 cannot be measured directly in the laboratory. You are required to plan an experiment to find the enthalpy change for hydrogenation of 5-decyne, ΔH_1 via Hess's Law.

The enthalpy change for the combustion of hydrogen is -286 kJ mol^{-1} . 5-decyne and cis-dec-5-ene are both liquids at standard conditions.

- (a) Based on the given information and the equation above, state **two** enthalpy changes that are necessary to calculate ΔH_1 .

Enthalpy change for combustion of 5-decyne and enthalpy change for combustion of cis-dec-5-ene.

- (b) Using the information given above and your answer in (a), you are required to write a plan to determine a value for the enthalpy change for hydrogenation of 5-decyne, ΔH_1 .

You may assume that you are provided with

- liquid 5-decyne
- liquid cis-dec-5-ene
- copper calorimeter
- two spirit lamps with a 5 cm-wick each
- deionised water
- a lighter
- thermometer
- apparatus normally found in a school or college laboratory

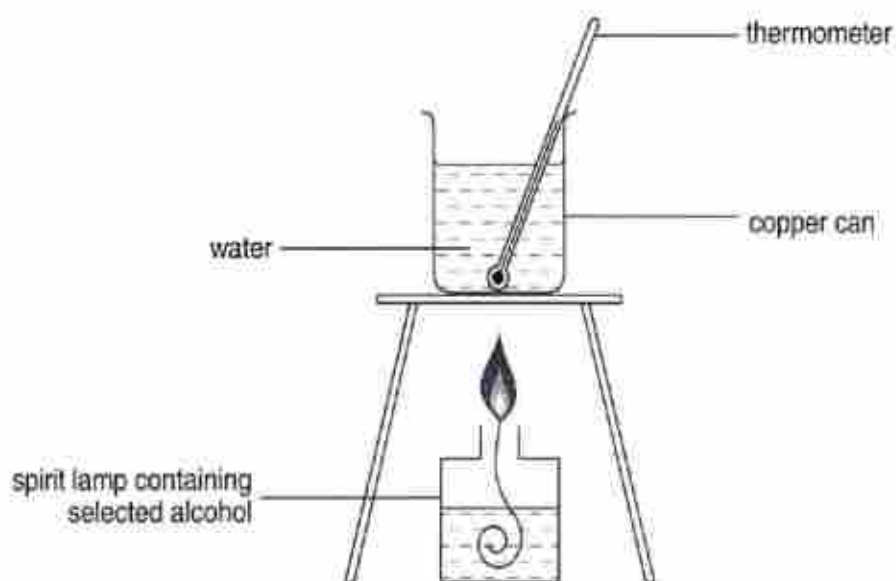
Your plan should contain the following:

- a diagram of the experimental set-up
- appropriate quantities of chemicals and solutions

- all essential experimental details

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**Diagram
of
the
experimental
set-up**



5-decyne

Procedure:

1. Using a 100 cm³ measuring cylinder, measure 100 cm³ of water into the copper calorimeter provided. Place the thermometer and record the initial temperature of water in the calorimeter.
2. Add 5-decyne to the spirit lamp until it is about half filled. Weigh using a weighing balance and record the total mass.
3. Place the spirit lamp under the calorimeter and light the wick of the lamp.
4. Stir the water with the thermometer until there is a rise of about 5°C. Extinguish the flame and record the final temperature of the water.
5. Reweigh the spirit lamp and content and record the final mass.
6. Repeat the whole procedure with cis-dec-5-ene.

- (c) List the measurements that have to be tabulated and recorded to calculate the value of enthalpy change for hydrogenation of 5-decyne, ΔH_1 . In your answer, you need to show how these measurements are used to obtain the value of ΔH_1 .

You may assume the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and density of water is 1 g cm^{-3} .

Tables used to tabulate and record experimental data:

Mass of spirit lamp and 5-decyne before combustion / g	A
Mass of spirit lamp and 5-decyne after combustion / g	B

Mass of spirit lamp and cis-dec-5-ene before combustion / g	C
Mass of spirit lamp and cis-dec-5-ene after combustion / g	D

Temperature of water in calorimeter (for experiment involving 5-decyne) before combustion / °C	E
Temperature of water in calorimeter (for experiment involving 5-decyne) after combustion / °C	F

Temperature of water in calorimeter (for experiment involving cis-dec-5-ene) before combustion / °C	G
Temperature of water in calorimeter (for experiment involving cis-dec-5-ene) after combustion / °C	H

Treatment of results:

Mass of 5-decyne combusted = (A–B) g

Amount of 5-decyne combusted, $n = (A-B)/\text{molar mass of 5-decyne} = X \text{ mol}$

Rise in temperature, $\Delta T = (F-E) \text{ K}$

Volume of water used = 100 cm^3

Density of water = 1 g cm^{-3}

Mass of water = 100 g

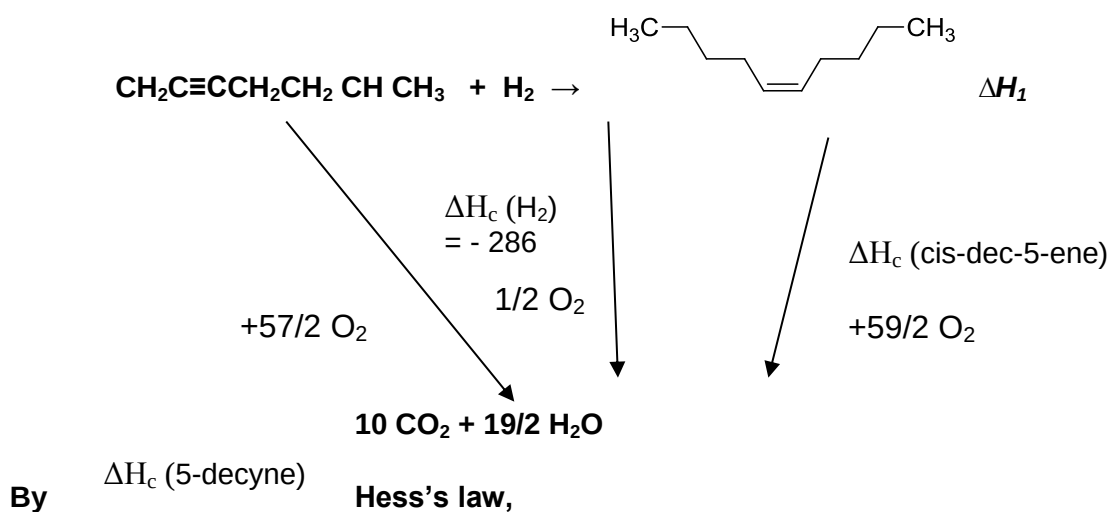
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Assume no heat loss to surroundings and negligible heat capacity of copper calorimeter

Heat evolved from combustion, q = heat absorbed by water = $mc\Delta T$
 $= (100)(4.18)(\Delta T) \text{ J}$

Enthalpy change for combustion of 5-decyne = $-(q/n) \text{ kJ mol}^{-1}$

Repeat same steps for cis-dec-5-ene



$$\Delta H_1 = \Delta H_c(5\text{-decyne}) + \Delta H_c(\text{H}_2) - \Delta H_c(\text{cis-dec-5-ene})$$

$$\Delta H_1 = \Delta H_c(5\text{-decyne}) - 286 - \Delta H_c(\text{cis-dec-5-ene})$$

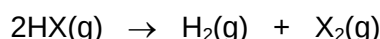
[Total: 12]

- 2 Eighty-five percent of all pharmaceutical agents and vitamins involve chlorine chemistry; many drugs require chlorine, fluorine, or bromine to be effective.

Data about the halides are given below.

Halide (X)	pK _a (HX)	Percentage of HX decomposed at 2000°C	Boiling point of HX / °C	Dipole moment of C–X / D	K _a (HOX) at 298K
F	+3	6×10^{-5}	19.5	1.82	
Cl	–7	4×10^{-1}	–84.2	1.08	2.9×10^{-8}
Br	–9	4	–67.1	0.82	2.4×10^{-9}
I	–10	30	–35.1	0.44	

- (a) Hydrogen halides decompose at high temperature according to the equation:



Use relevant data from the *Data Booklet*, explain the trend indicated by percentage decomposition of HX.

Bond energies of HX in kJ mol^{–1} in decreasing order:

HF – 562 ; HCl – 431; HBr – 366; HI – 299

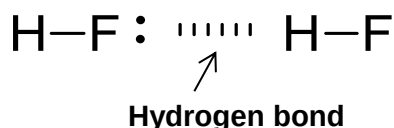
shows decreasing bond strength from HF to HI.

Covalent bond strength decreases from HF to HI is due to increasing atomic radius of F to I, leading to less effective overlap of orbitals from F to I with H.

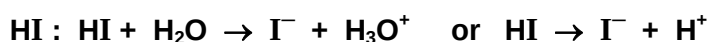
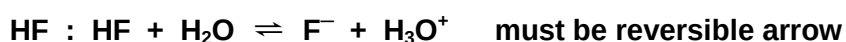
Hence thermal stability decreases in the order HF, HCl, HBr, HI and percentage decomposition increases from HF to HI as indicated in the table.

- (b) The boiling point of HF is higher than the rest of the hydrogen halides despite it being the smallest molecule. By means of a diagram, indicate the interaction between two molecules of HF that leads to this significant difference.

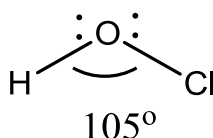




- (c) When dissolved in water, the hydrogen halides show different pK_a values. Write balanced equations to represent the extent of ionisation of HF and HI in water.



- (d) (i) Draw a diagram to illustrate the shape of oxoacid, HOCl , indicating clearly the bond angle.



shape : bent

bond angle: 105°

- (ii) Using the information from the table, state which of the two acids, HOCl or HOBr is stronger?

HOCl is a stronger acid as its K_a value is larger than that of HOBr .

- (iii) Hypoiodous acid has the formula HOI . Predict and explain whether HOI is a stronger or weaker acid than the acid you identified in (d)(ii).

HOI is a weaker acid. The conjugate base OCI^- is more stable than OI^- . This is due to Cl being more electronegative hence more electron withdrawing and disperses the negative charge on oxygen to a larger extent, stabilising OCI^- . Hence HOCl ionises more than HOI .

OR

HOI is a weaker acid. The conjugate base OI^- is less stable than OCI^- . This is due to I being less electronegative hence less electron withdrawing disperses the negative charge on oxygen to a smaller extent. Hence HOI ionises less than HOCl .

- (iv) Some solid NaOCl solution is dissolved in a solution of HOCl at 298 K. The pH

of this mixture is determined to be 6.48. Calculate the ratio of OCl^- to HOCl in this mixture.

Using $\text{pH} = \text{pK}_a + \lg \left(\frac{[\text{OCl}^-]}{[\text{HOCl}]}\right)$

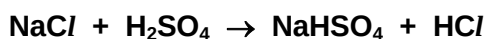
$$6.48 = -\lg (2.9 \times 10^{-8}) + \lg \left(\frac{[\text{OCl}^-]}{[\text{HOCl}]}\right)$$

$$\frac{[\text{OCl}^-]}{[\text{HOCl}]} = 0.0876$$

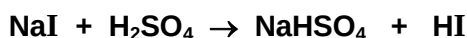
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(e) The halides can react with concentrated sulfuric acid.

- (i) When concentrated sulfuric acid was warmed with sodium chloride, white fumes of hydrogen chloride was evolved. Write a balanced equation for the reaction.



- (ii) The method described in **e(i)** cannot be used to prepare hydrogen iodide. Describe what you would observe when sodium iodide is heated with concentrated sulfuric acid. Explain the chemistry behind it, and give any relevant equations.



Black solid and violet fumes of I_2 seen and pungent (or rotten egg smell) H_2S evolved.

HI is a stronger reducing agent than HCl.

HI is oxidized to iodine, hence pure HI cannot be obtained.

[Total: 20]

- 3 (a) AlCl_3 is a compound of interest to scientists due to its industrial applications. For example, AlCl_3 can react with molten aluminium to form AlCl(g) . This is a useful procedure as the AlCl formed can be used to recover useful metalloids from their compounds.

Typically, the reaction has to be carried out in the presence of argon instead of air.

- (i) The reaction has to be carried out in an atmosphere of argon. Suggest a reason for the need of argon.

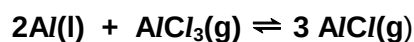
To prevent oxygen in air from reacting with molten aluminium.

Consider the reaction between $\text{AlCl}_3(\text{g})$ and molten aluminium that was carried out at 1573 K :



In the reaction vessel, 0.200 mol of $\text{AlCl}_3(\text{g})$ was reacted with 0.400 mol of molten Al. When the reaction system achieved equilibrium with a total pressure of 1.50 atm, it was determined that 0.200 mol of molten Al remained in the vessel.

- (ii) Write an expression for the equilibrium constant, K_p for reaction 1 and hence calculate its value at 1573 K.



n_i/mol	0.400	0.200	0
n_c/mol	-0.200	-0.100	+ 3/2 x 0.200
n_e/mol	0.200	0.100	0.300

Total number of moles of gases at equilibrium = 0.100 + 0.300 = 0.400 mol

$$K_p = (P_{\text{AlCl}})^3 / (P_{\text{AlCl}_3}) = (0.3/0.4 \times 1.5)^3 / (0.1/0.4 \times 1.5) = 3.80 \text{ atm}^2$$

The same reaction vessel was heated to 1700 K rapidly in a way such that no reaction took place during the short interval of heating. The reaction system was allowed to re-establish equilibrium. It was found that the partial pressure of $\text{AlCl}_3(\text{g})$ was 0.390 atm when the equilibrium was re-established.

- (iii) Using the information from a(ii), determine the partial pressures of $\text{AlCl}_3(\text{g})$ and $\text{AlCl}(\text{g})$ at the instant when the reaction was heated to 1700 K, before the equilibrium was re-established. You can assume that the gases behave ideally and the volume of vessel is unchanged.

PV = nRT, since V, R and n are constant, $P \propto 1/T$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Thus,

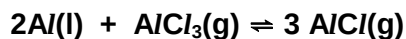
$$\frac{P_{AlCl}}{1700} = \frac{\frac{0.300}{0.400} \times 1.5}{1573}$$

$$P_{AlCl} = 1.22 \text{ atm}$$

$$\frac{P_{AlCl_3}}{1700} = \frac{\frac{0.100}{0.400} \times 1.5}{1573}$$

$$P_{AlCl_3} = 0.405 \text{ atm}$$

- (iv) Using the calculated values from a(iii), calculate K_p of the reaction at 1700 K. Hence, explain whether reaction 1 is endothermic or exothermic.



$$P_i/\text{atm} \quad - \quad 0.405 \quad 1.22$$

$$P_c/\text{atm} \quad - \quad -0.015 \quad +0.045$$

$$P_e/\text{atm} \quad - \quad 0.390 \quad 1.265$$

$$K_p = (1.265)^3 / 0.390 = 5.19 \text{ atm}^2$$

K_p value is larger at 1700K compared to 1573K showing forward reaction is favoured. By Le Chatelier's Principle, reaction 1 equilibrium position has shifted to the right to remove excess heat.

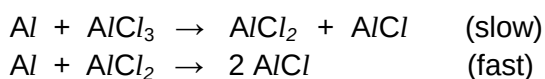
Hence reaction 1 is endothermic.

- (v) The rate equation for reaction between Al and $AlCl_3$ is shown below.

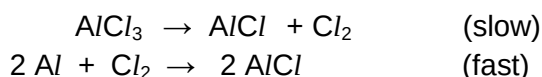
$$\text{rate} = k[AlCl_3][Al]$$

Suggest which of the two mechanisms shown is a possible mechanism for the reaction.

Mechanism 1:

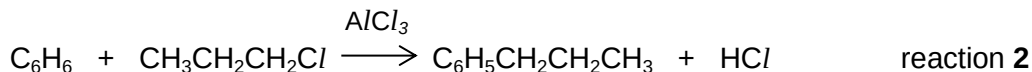


Mechanism 2:



Mechanism 1 is the possible mechanism. It tallies with the rate equation where one mole of Al reacts with 1 mole of AlCl₃ in the slow step.

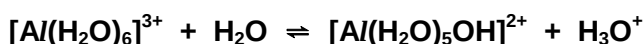
- (b) Anhydrous AlCl₃ is often used as a catalyst in the Friedel-Crafts alkylation of benzene.



- (i) Explain why AlCl₃ can act as a catalyst in Friedel-Crafts alkylation.

Al has empty 3p orbital (or empty p orbital) to accept a lone pair of electrons when generating electrophile.

- (ii) With the aid of an equation, explain the need to have anhydrous condition when AlCl₃ is used for reaction 2.



AlCl₃ will dissolve (or undergoes hydration) in water to form [Al(H₂O)₆]³⁺ which then undergoes hydrolysis in water.

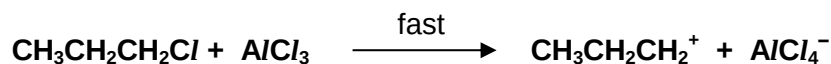
- (iii) Use information from the *Data Booklet*, calculate the enthalpy change of reaction for reaction 2.

$$\begin{aligned} \Delta H &= [\text{BE}(\text{C}-\text{H}) + \text{BE}(\text{C}-\text{Cl})] - [\text{BE}(\text{H}-\text{Cl}) + \text{BE}(\text{C}-\text{C})] \\ &= (410 + 340) - (431 + 350) = -31 \text{ kJ mol}^{-1} \end{aligned}$$

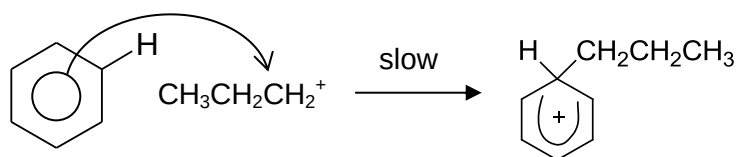
- (iv) Describe the mechanism for the formation of C₆H₅CH₂CH₂CH₃ in reaction 2, showing clearly the movement of electrons and partial charges.

Electrophilic substitution

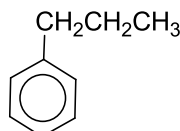
Step 1: Generation of strong electrophile

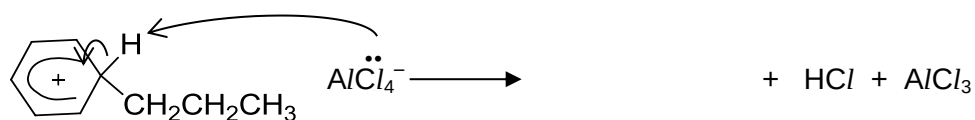


Step 2: Electrophilic attack on ring to form a carbocation intermediate

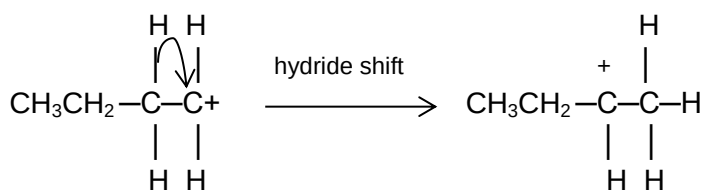


Step 3: Restoring the benzene ring and regeneration of catalyst





One key limitation of the alkylation reaction is that a mixture of products tends to form despite using only one type of halogenoalkane. For primary halogenoalkane, this is due to the occurrence of a process known as hydride shift which results in rearrangement of primary carbocation intermediates as shown :

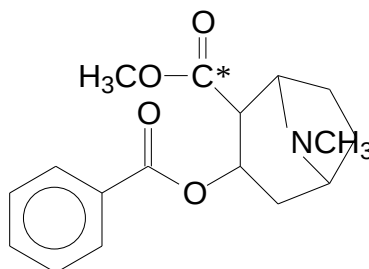


- (v) Explain why hydride shift occurs for primary halogenoalkane.

Hydride shift leads to a more stable secondary carbocation as there are more electron donating alkyl groups directly bonded to positively charged carbon. Hence the positive charge in the carbocation is dispersed.

[Total: 22]

- 4 (a) Cocaine, $\text{C}_{17}\text{H}_{21}\text{NO}_4$, was first used as a local anaesthetic. It is also a powerful stimulant. Its structure is as shown:



cocaine

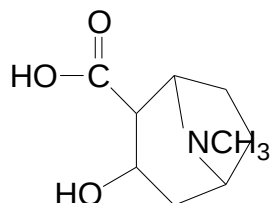
- (i) State the functional groups, other than phenyl ring, present in cocaine.

Ester and tertiary amine

- (ii) State the hybridisation of the carbon atom labelled with the asterisk (*).

sp^2

- (b) Student X was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound A.



compound A

Student X suggested the following steps:

Step 1	Methylbenzene is oxidised with hot, acidified KMnO_4 to give benzoic acid.
Step 2	Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step 1 with phosphorus pentachloride.
Step 3	Benzoyl chloride is reacted with compound A at room temperature.
Step 4	The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid at room conditions.

Explain why steps 2 and 4 of the synthetic route will not work.

In step 2, phosphorus pentachloride will be hydrolysed in the presence of aqueous solution. (or phosphorus pentachloride will react with water)

Heat is required for step 4.

- (c) Cocaine is sold in its protonated hydrochloride salt, known as cocaine hydrochloride. Suggest a possible reason for this.

It has a higher melting point and is more stable.

(d) Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is converted back to cocaine before smoking.

(i) Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine.

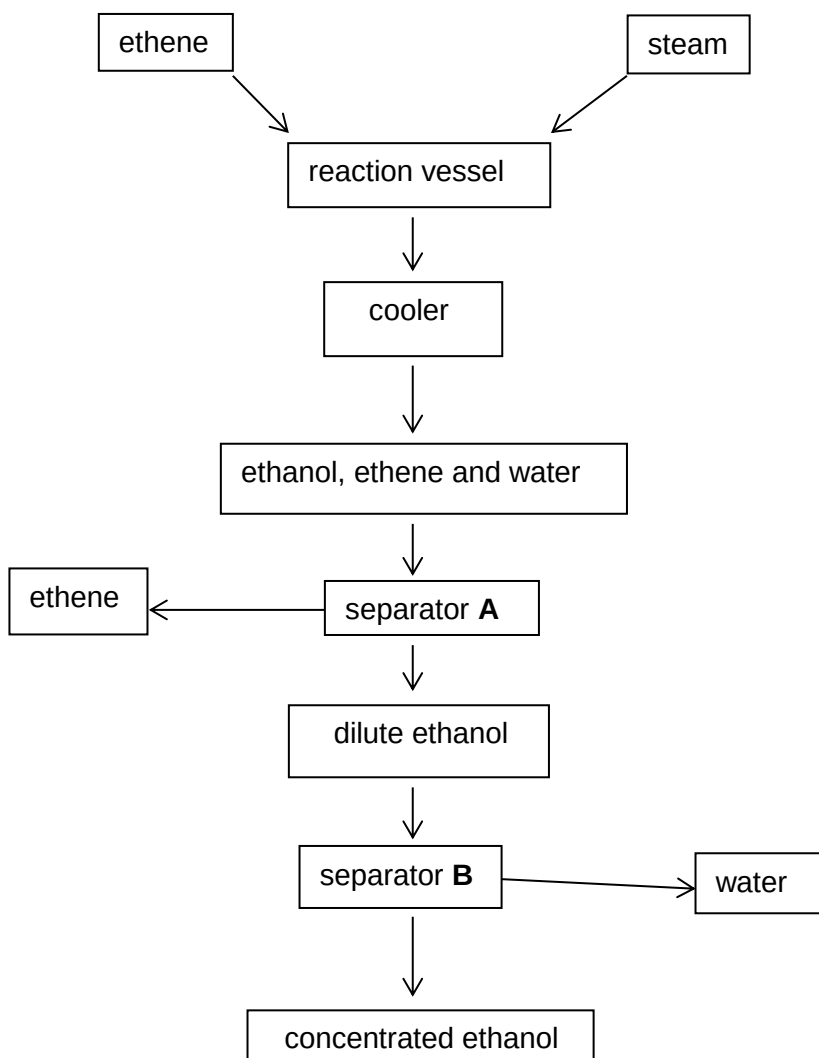
NaOH(aq)

(ii) Suggest a suitable solvent to extract cocaine and separate it from its salt.

Ether (or any other organic solvent less polar than water)

[Total: 7]

5 An industrial method for the production of ethanol, C_2H_5OH , is outlined in the following flow diagram.



(a) (i) Unreacted ethene is removed in separator A. Suggest how the separated ethene could be used to increase the efficiency of the overall process of the manufacture of ethanol.

The separated ethene can be returned back to the reaction vessel to produce more ethanol.

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- (ii) Name the process that takes place in separator B.

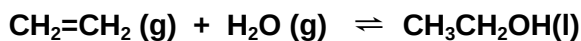
Fractional distillation (or distillation)

- (b) In the reaction vessel, ethanol is produced in an exothermic reaction.

- (i) State the reagents and conditions for the industrial preparation of ethanol from ethene.

**H₂O and concentrated H₃PO₄
300 °C, 60 atm**

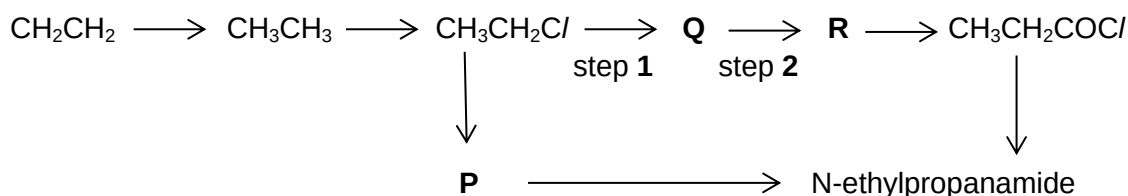
- (ii) If 1.64 kg of ethanol is produced from 10.0 kg of ethene, calculate the percentage yield of ethanol.



$$\begin{aligned} \text{Theoretical yield of} &= \frac{10 \times 1000}{12 \times 2 + 4} \times (12 \times 2 + 6 + 16) = 1.6429 \times 10^4 \text{ g} \\ &= 16.429 \text{ kg} \\ &= 16.4 \text{ kg} \end{aligned}$$

$$\text{Percentage yield} = \frac{1.64}{16.4} \times 100 = 10.0 \%$$

- (c) Ethene is used to synthesise N-ethylpropanamide as shown in the following reaction scheme:



- (i) Give the structural formulae of compounds P, Q and R.

P : CH₃CH₂NH₂

Q : CH₃CH₂CN

R : CH₃CH₂COOH

For
Examiner's
Use

- (ii)** State the reagents and conditions for steps **1** and **2**.

step 1 : ethanolic KCN, heat

step 2 : dilute sulfuric acid, heat

[Total: 11]

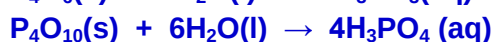
End of Paper

Answer any **four** questions

- 1 Phosphorus was first discovered by the German alchemist, Hennig Brandt's experiment with human waste, urine. Phosphorus occurs in different allotropic forms with the two common ones being white phosphorus and red phosphorus.

(a) Depending if oxygen is in excess, phosphorus reacts with oxygen to form two different oxides, phosphorus(III) oxide and phosphorus(V) oxide.

- (i) Write the equations for the reactions of phosphorus(III) oxide and phosphorus(V) oxide with water separately, including state symbols. [2]

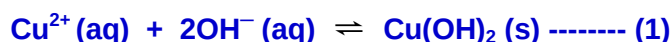
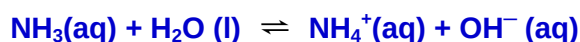


- (ii) Describe the observation when the resulting solutions from (i) are added to solid aluminium oxide. [1]

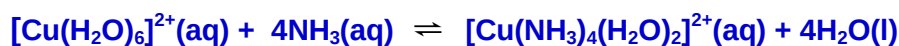
Aluminium oxide dissolves in the acidic solution to form a colourless solution.

- (b) Nitrogen, which is in the same group as phosphorus, forms an important molecule ammonia, NH_3 . NH_3 is used to make fertilisers as well as explosives.

- (i) When aqueous ammonia is gradually added to an aqueous solution containing $\text{Cu}^{2+}(\text{aq})$, several observations are seen. Describe and explain these observations and write equations where appropriate. [3]



$\text{NH}_3(\text{aq})$ undergoes hydrolysis in water to form OH^- . When a small amount of NH_3 is added, a blue precipitate of $\text{Cu}(\text{OH})_2$ is formed.



Addition of excess ammonia causes the formation of the more stable deep blue $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ion through a ligand-exchange reaction.

The reaction lowers the concentration of $\text{Cu}^{2+}(\text{aq})$ causing $\text{Cu}(\text{OH})_2$ to dissolve.

Equilibrium position (1) shifts to the left and the ionic product $< K_{\text{sp}}$.

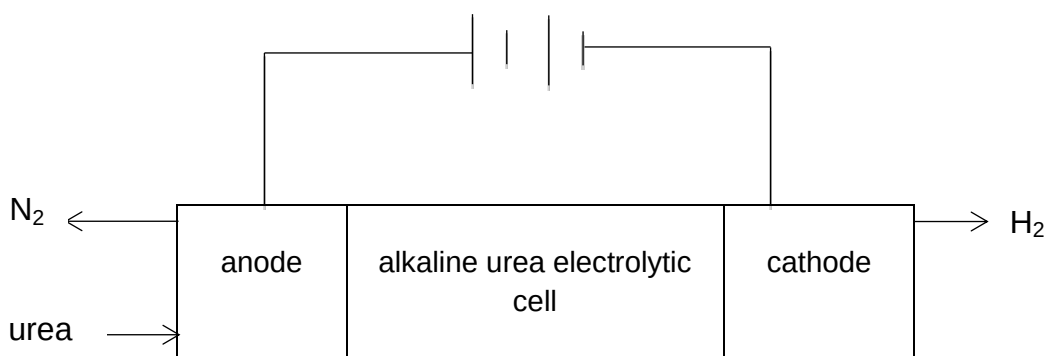
- (ii) When black copper(II) oxide is stirred with liquid ammonia, it dissolves to give a coloured solution. During this reaction the oxide ion is acting as a Bronsted-Lowry base. Suggest an equation for this reaction, and suggest the colour of the solution.

[1]

On addition of $\text{NH}_3(\text{l})$, a dark blue solution is observed as a complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is formed.

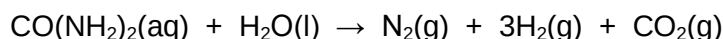


- (c) A group of researchers have recently developed an efficient way of producing hydrogen from urine, a nitrogen containing compound as shown in the diagram below.



Urea, $\text{CO}(\text{NH}_2)_2$, in aqueous KOH , which acts as the electrolyte, is oxidized at the anode to form nitrogen and carbon dioxide. At the cathode, water is reduced to hydrogen gas.

The overall equation for the urea electrolyte cell is :



- (i) Write the half equation, with state symbols, occurring at each electrode in this urea electrolytic cell.

[2]



- (ii) By considering why CO_2 is not liberated at the anode, deduce the by-product produced at the anode.

[1]

K_2CO_3 (or KHCO_3) is produced as acidic CO_2 reacts with alkaline KOH .

- (d) Nitrogen is also commonly found in organic compounds. **D**, $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$, is a neutral compound with a benzene ring. Upon reaction with hot sodium hydroxide, **E** and **F** are formed. On acidification, **E** forms $\text{C}_2\text{H}_4\text{O}_2$ which gives effervescence with sodium carbonate.

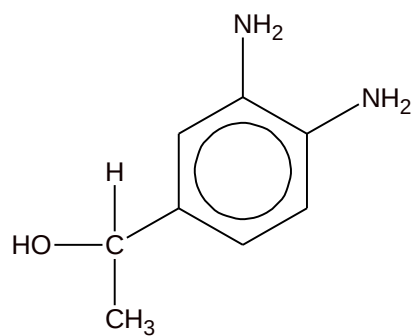
One mole of **F**, $C_8H_{12}N_2O$, reacts with one mole of aqueous sulfuric acid at room temperature. One mole of **F** is also able to decolourise three moles of aqueous bromine and gives a white ppt, **G**.

When acidified orange potassium dichromate(VI) is added to **F**, compound **H**, $C_8H_{10}N_2O$ is formed and the solution turns green. A yellow ppt is also formed when **F** and **H** is reacted with alkaline aqueous iodine separately.

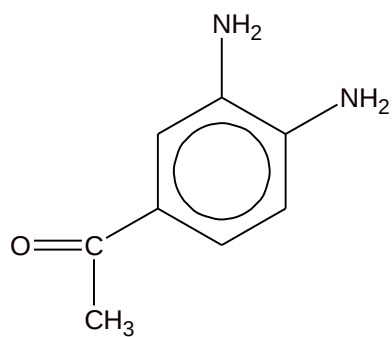
Suggest the structures for compounds **D**, **E**, **F**, **G** and **H** and explain the observations described above. You do not need to consider the positions of the substituents on the benzene ring. [10]

Statement	Type of reaction	Deduction
D reacts with hot sodium hydroxide to form E and F	✓ hydrolysis	✓ D could be ester or amide
On acidification, E forms $C_2H_4O_2$ which gives effervescence with sodium carbonate.	✓ neutralisation	✓ E is acid salt forming <u>CH_3COOH</u>
One mole of F , $C_8H_{12}N_2O$, reacts with one mole of sulfuric acid at room temperature	✓ neutralisation	✓ F is <u>basic</u> as it reacts with aq H_2SO_4 . F could be <u>phenylamine</u> . ✓ Since $F : H_2SO_4 = 1 : 1$, F has <u>2 $-NH_2$</u> .
One mole of F is able to decolourise three moles of aqueous bromine and give a white ppt, G .	✓ electrophilic substitution	✓ F contains <u>ring activating/electron donating NH_2 groups</u> attached to benzene ring ✓ This shows that <u>2,4,6 positions in the benzene are substituted</u> .
Acidified orange potassium dichromate(VI) is added to F , compound H , $C_8H_{10}N_2O$ is formed and the solution turns green.	✓ oxidation	✓ F contains a <u>secondary alcohol group</u> which is oxidised to a <u>ketone</u> in H .
A yellow ppt is also formed when F and H is reacted with alkaline aqueous iodine separately.	✓ oxidation	H has ✓ CH_3CO and F has ✓ $CH_3CH(OH)$. ✓ Yellow ppt is CHI_3 .

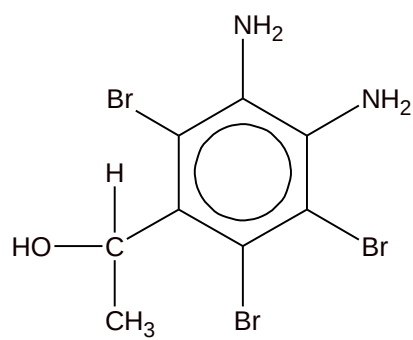
E CH_3COONa



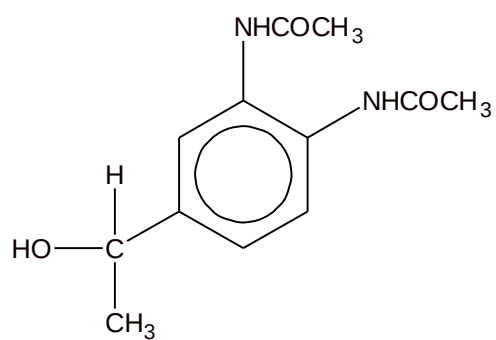
F



H



G



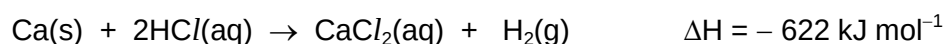
D

- 2 (a) With the aid of an equation, define the term *standard enthalpy change of formation* of calcium carbonate, CaCO_3 . [2]

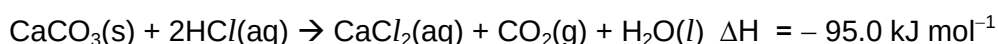
Standard enthalpy of formation of CaCO_3 is the energy released or required when 1 mole of CaCO_3 is formed from its constituent elements under standard conditions of 298 K and 1 atm.



- (b) The enthalpy change of the reaction, ΔH for the reaction shown below is determined to be -622 kJ mol^{-1} .



In a similar experiment, solid calcium carbonate reacted with an excess of hydrochloric acid and the enthalpy change of reaction was found to be -95.0 kJ per mole of calcium carbonate.

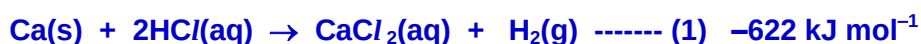


The values of enthalpy change of formation of water and enthalpy change of combustion of carbon are provided.

$$\Delta H_f^\circ(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ(\text{C}) = -394 \text{ kJ mol}^{-1}$$

Using the information given, calculate the standard enthalpy change of formation of calcium carbonate. [3]



(1) + reverse (2):



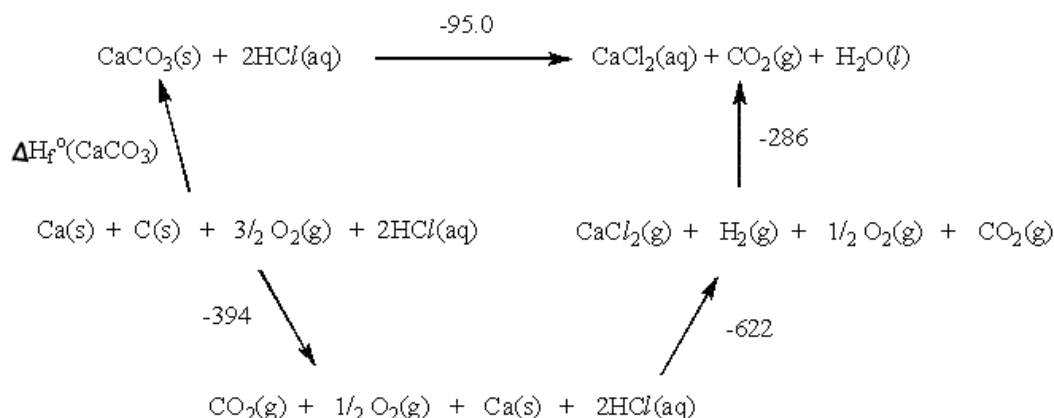
$$\Delta H_r = -622 + 95.0 = -527 \text{ kJ mol}^{-1}$$

$$-527 = [\Delta H_f^\circ(\text{CaCO}_3) + 0] - [0 + \Delta H_f^\circ(\text{CO}_2) + (\Delta H_f^\circ(\text{H}_2\text{O}))]$$

$$-527 = \Delta H_f^\circ(\text{CaCO}_3) - [(-394) + (-286)]$$

$$\Delta H_f^\circ(\text{CaCO}_3) = -1207 \text{ kJ mol}^{-1}$$

OR



Cycle

$$\begin{aligned}
 \Delta H_f^\circ(\text{CaCO}_3) &= -394 - 622 - 286 + 95.0 \\
 &= -1207 \text{ kJ mol}^{-1}
 \end{aligned}$$

- (c) Magnesium carbonate decomposes on heating according to the equation shown below. The values of the standard enthalpy change and standard entropy change of the decomposition are provided.



$$\Delta H^\circ = +117 \text{ kJ mol}^{-1} ; \Delta S^\circ = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

- (i) Why does the entropy increase when magnesium carbonate decomposes? [1]

The entropy increases due to increase in the number of gaseous particles, resulting in more disorderliness in the system and more ways of distributing the energy/arranging the particles.

- (ii) Calculate the standard Gibbs free energy change, ΔG° , for the decomposition of magnesium carbonate. Hence, comment on the spontaneity of the decomposition of magnesium carbonate at room temperature. [2]

$$\begin{aligned}
 \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
 &= +117 - \left(298 \times \frac{+175}{1000}\right) \\
 &= +117 - 52.15 \\
 &= +64.9 \text{ kJ mol}^{-1}
 \end{aligned}$$

Since ΔG° is positive, the decomposition is not spontaneous at room temperature.

- (iii) Compare the ease of thermal decomposition of magnesium carbonate with barium carbonate. [3]

MgCO₃ decomposes at a lower temperature (or more easily) than BaCO₃. This is because Mg²⁺ ion, being smaller and has higher charge density and polarising power than Ba²⁺.

Mg²⁺ is able to polarise the large electron cloud of the carbonate ion to a larger extent and weakening C-O bond more, resulting in lower thermal stability in MgCO₃.

- (d) Describe the reaction of Mg and Ca with water, giving appropriate equations with state symbols. [2]

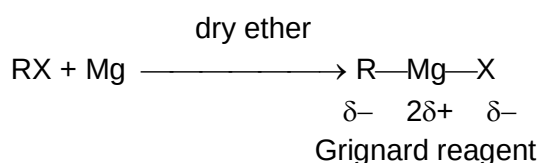
Mg reacts with slowly with hot water, effervescence observed and a white ppt is formed.



Ca reacts rapidly with cold water, effervescence observed and a colourless solution is formed.

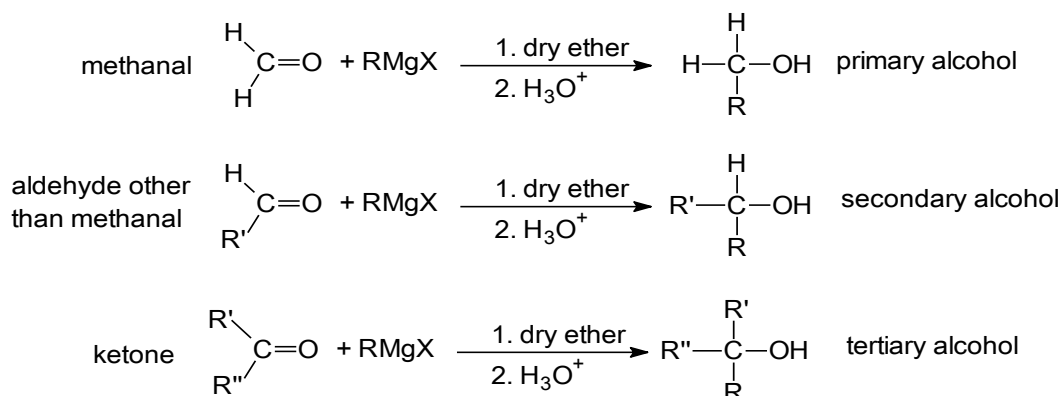


- (e) Mg reacts with halogenoalkanes, RX in dry ether, forming Grignard reagents which are important intermediates used to produce many organic compounds.

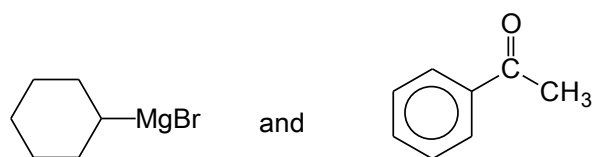


RMgX is called an organometallic compound, where R is an alkyl group and X is chlorine, bromine or iodine. R in RMgX behaves like an anion R⁻, and is strongly basic and nucleophilic.

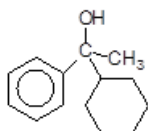
On reaction with carbonyl compounds, RMgX forms various classes of alcohols:



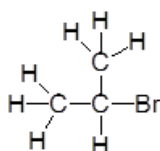
- (i) Draw the structure of the organic products formed when the following compounds are reacted:



[1]



- (ii) Give the displayed formula of the bromoalkane which can be used to form a Grignard reagent that would react with butanal to give 2-methylhexan-3-ol. [1]



- (iii) When RMgBr is reacted with ethanoyl bromide, 2 moles of RMgBr are required per mole of ethanoyl bromide and the product formed is $\text{CH}_3\text{CR}_2\text{OH}$. Explain why one mole of ethanoyl bromide reacts with two moles of RMgBr while one mole of aldehyde or ketone reacts with one mole of RMgBr . [2]

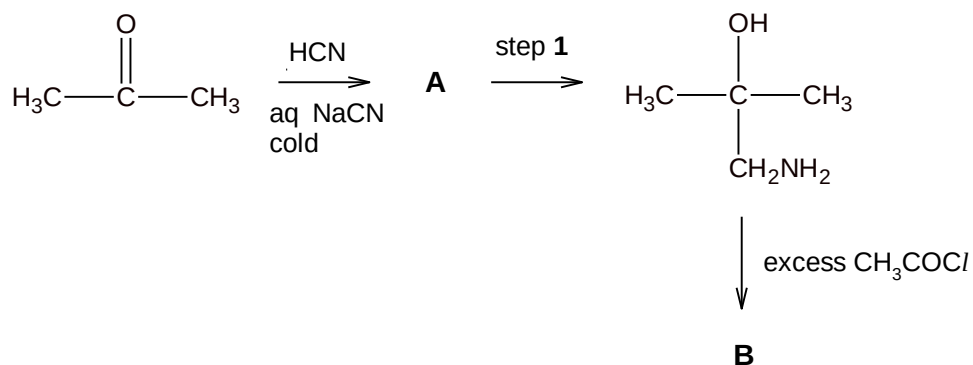
One mole of RMgBr reacts with one mole of CH_3COBr via nucleophilic substitution mechanism to form one mole of the ketone CH_3COR .

The one mole of CH_3COR formed then reacts with another mole of RMgBr to form $\text{CH}_3\text{CR}_2\text{OH}$.



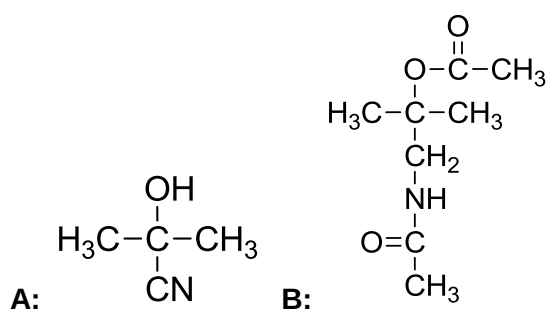
Explanation by writing the 2 equations are acceptable.

- (f) Ketones and aldehydes react with HCN via nucleophilic addition mechanism similar to the reaction with Grignard reagents. The reaction scheme below is one such example.



- (i) Draw the structures of compounds **A** and **B**.

[2]



- (ii) State the reagent and condition for step 1.

[1]

H_2 , Pt or
 H_2 , Ni, heat or
 LiAlH_4 in dry ether

[Total :20]

- 3 Transport proteins serve the function of moving other materials within an organism. They are vital to the growth and life of all living things. Haemoglobin is an iron-containing oxygen-transport protein found in the red blood cells of all vertebrates.

- (a) State the type of bonding or interactions involved in the *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins like haemoglobin. [2]

Primary Structure – covalent bonds (or amide or peptide linkage)

Secondary Structure – hydrogen bonding

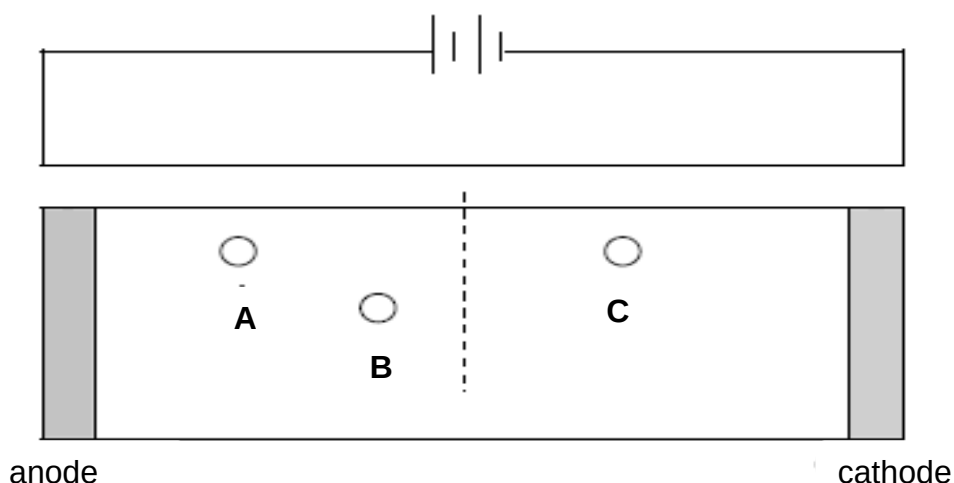
Tertiary Structure – Van der Waal's forces, ionic bond, hydrogen bonding and disulfide linkage

Quaternary Structure – Van der Waal's forces, ionic bond, hydrogen bonding and disulfide linkage

- (b) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

Amino Acids	Formula of side chain (R' in R'CH(NH ₂)CO ₂ H)	Isoelectric Point
Lysine	-(CH ₂) ₄ NH ₂	9.74
Glutamic acid	-CH ₂ CH ₂ COOH	3.15
Aspartic acid	-CH ₂ COOH	2.77

An electrophoresis experiment is ran on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.



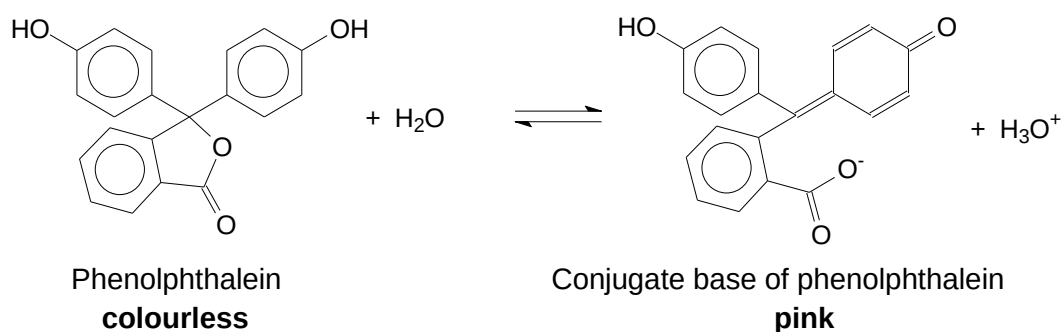
Suggest the identities of amino acids **A**, **B** and **C**.

[1]

A: Aspartic acid ; B: Glutamic acid ; C : Lysine

- (c) Haemoglobin is able to exhibit peroxidase-like activity to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base. This reaction is often used to test for the presence of blood at a crime scene.

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



The K_a of phenolphthalein is $3.00 \times 10^{-10} \text{ mol dm}^{-3}$.

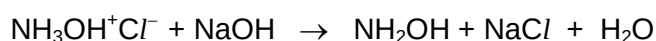
Distinct colour change for phenolphthalein occurs when half of the indicator is phenolphthalein and the other half is its conjugate base.

- (i) Calculate the pH at which phenolphthalein shows distinct colour change. [1]

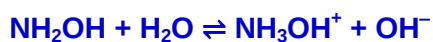
$$\text{pH} = -\lg(3 \times 10^{-10}) = 9.52$$

- (ii) The change of colour for phenolphthalein occurs over a limited range of pH and falls within ± 1.00 of the $\text{p}K_a$ value.

In an experiment, a solution of a weak acid hydroxylammonium chloride, $\text{NH}_3\text{OH}^+\text{Cl}^-$, was titrated against a solution of sodium hydroxide as shown by the equation below:



With the aid of an equation and your answer in (i), explain if phenolphthalein is a suitable indicator for this titration. [2]

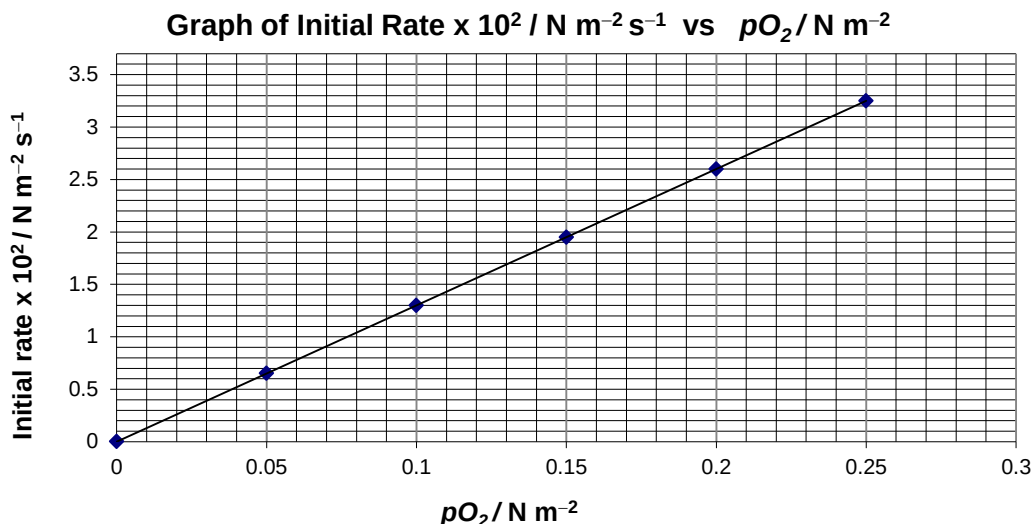


NH_2OH undergoes hydrolysis to produce OH^- hence its $\text{pH} > 7$

Phenolphthalein is suitable as the pH transition range of the indicator (8.52 – 10.52) lies within the rapid pH change over the equivalence point ($\text{pH} > 7$).

- (d) The reaction kinetics of oxygen binding to haemoglobin in human red blood cell suspension is studied. This is done by measuring the rates of uptake of oxygen by haemoglobin at different partial pressures of oxygen.

The graph of initial rate against partial pressure of oxygen was plotted below.



- (i) Using the graph above, state the order of reaction with respect to oxygen. [1]

Order of reaction with respect to O_2 is 1.

- (ii) The concentration of haemoglobin was halved and a new series of experiments was conducted at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the above graph.

Deduce the order of reaction with respect to haemoglobin? Explain your answer. [2]

Order of reaction with respect to haemoglobin is 1.

When concentration of haemoglobin was halved, change in the gradient of the graph is halved and rate of reaction was also halved.

- (iii) Using your answers to (i) and (ii), construct the rate equation for the reaction between haemoglobin and oxygen. [1]

Rate = k [haemoglobin] $[\text{O}_2]$

- (iv) Oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at $1.6 \times 10^{-6} \text{ mol dm}^{-3}$ by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to $8.0 \times 10^{-6} \text{ mol dm}^{-3}$.

Calculate the rate constant, including the unit, given that the rate of oxyhaemoglobin formation is $2.68 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 37°C . [1]

$$\text{Rate} = k [\text{haemoglobin}] [\text{O}_2]$$

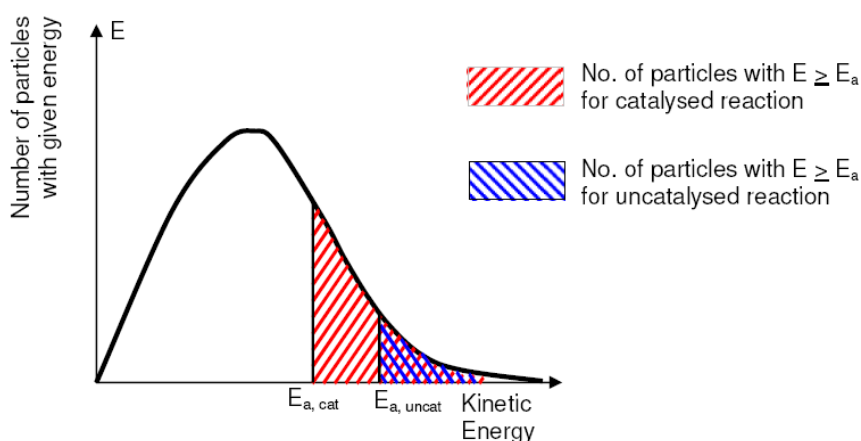
$$2.68 \times 10^{-5} = k (8.0 \times 10^{-6}) (1.6 \times 10^{-6})$$

$$k = 2.09 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

- (e) Another type of protein that transports oxygen throughout the bodies of invertebrates is *haemocyanin*, which contains two copper atoms that reversibly bind a single oxygen molecule.
- (i) *Haemocyanin* exhibits catalytic activity to catalyse the hydroxylation of monophenols to diphenols.

Using an appropriate sketch of the Maxwell-Boltzmann distribution curve, explain how the presence of *haemocyanin* increases the rate of hydroxylation of monophenols. [3]

Maxwell-Boltzmann Distribution Curve



[1]

E_a is lowered due to an alternative reaction pathway. The proportion of reactants with energy greater than or equals the activation energy increases.

Frequency of effective collisions increases, rate constant value increases and hence rate of reaction increases.

- (ii) Partial *denaturation* actually improves *haemocyanin*'s catalytic ability by providing greater access to the active site.

- 1 What is meant by the term *denaturation*?
- 2 Suggest how a weak acid might interact with *haemocyanin* to bring about denaturation.

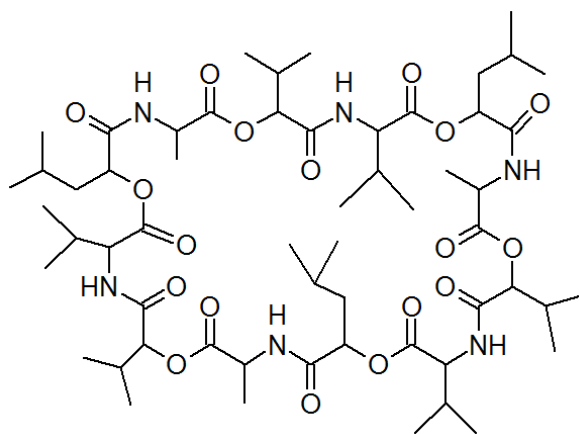
[3]

1 Denaturation refers to the breaking of weak bonds holding the secondary, tertiary and quaternary structure but not the covalent bonds within the primary

structure.

2 Protonates the anionic group, -COO^- found in side chain for example glutamic acid, [1] and disrupts ionic bond between the charged R groups of -COO^- and -NH_3^+ .

- (f) *Cereulide* is another example of a transport protein. As a natural dodecadepsipeptide ionophore, *cereulide* acts as potassium transporters, where potassium, K^+ , plays a vital role in bacterial physiology.



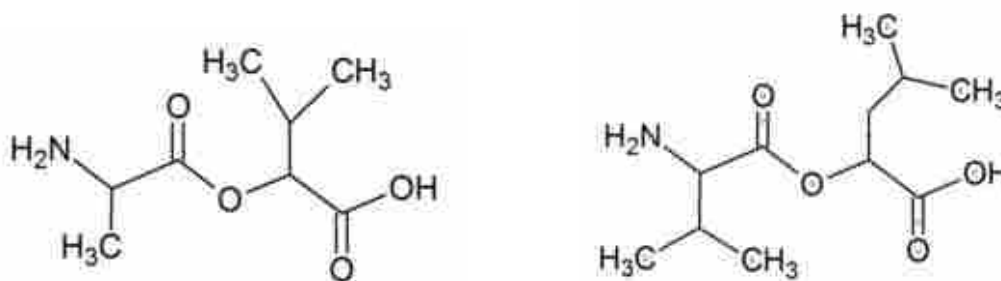
Cereulide

- (i) Apart from the peptide group, name another functional group that is present in the molecule? [1]

Ester

When treated with a peptidase enzyme, the peptide bonds in the ring are hydrolysed. Only two different products are formed.

- (ii) Out of the products formed, two of the amino acid residues are present **more than once** in the protein. Draw the structural formula of these two amino acid residues. [2]



[Total :20]

- 4 (a) Manganese is a transition element that can exist in several oxidation states.

Manganese species	Mn^{2+}	MnO_4^{2-}	MnO_4^-
Colour (in aqueous medium)	pale pink	green	purple

- (i) Write the full electronic configurations of Mn in Mn^{2+} and MnO_4^- , and explain why Mn can exhibit variable oxidation states. [2]

The electronic configuration of Mn in Mn^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

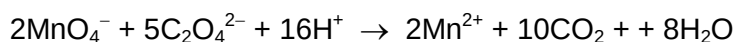
The electronic configuration of Mn in MnO_4^- is $1s^2 2s^2 2p^6 3s^2 3p^6$.

The energy difference between the 3d and 4s subshells is relatively small. Hence, a variable number of electrons can be removed. (or a variable number of electrons can be used for bond formation)

- (ii) Explain why transition elements form compounds that are coloured. [3]

In the presence of ligands, the degenerate 3d orbitals are split into two different energy levels. Since the 3d subshell is partially filled, the electrons in the lower energy 3d orbitals can absorb a photon of energy from the visible light range to promote to the higher energy 3d orbitals. The observed colour is complementary to the wavelength absorbed.

- (b) A student wanted to investigate the rate of reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ ions in an acidic medium. The reaction is shown in the equation below.



The rate of reaction was followed by mixing the following two solutions, and measuring the concentration of remaining MnO_4^- ions at fixed time intervals.

Solution A: 100 cm³ of 0.20 mol dm⁻³ ethanedioic acid, 5 cm³ of 2 mol dm⁻³ sulfuric acid, 15 cm³ of 0.20 mol dm⁻³ copper(II) sulfate and 80 cm³ of water

Solution B: 50 cm³ of 0.020 mol dm⁻³ potassium manganate(VII)

The following results were obtained.

Time/s	$[\text{MnO}_4^-] / \text{mol dm}^{-3}$
0	0.0040
10	0.0026
20	0.0016
30	0.00096
50	0.00040
75	0.00016

- (i) By means of a graphical method, determine the rate equation under the conditions whereby the reaction was conducted. [3]

Plot a graph of $[\text{MnO}_4^-]$ against time.

Determine 2 half-life from the graph and show that they have the same value or approximately the same ($t_{1/2} \approx 15\text{s}$). Refer to graph at the last page.

Rate = $k[\text{MnO}_4^-]$

- (ii) The rate of consumption of $\text{MnO}_4^-(\text{aq})$ at a particular time is $1.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. Using the equation for the reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$, calculate the rate of consumption of ethanedioate ions at that particular time? [1]

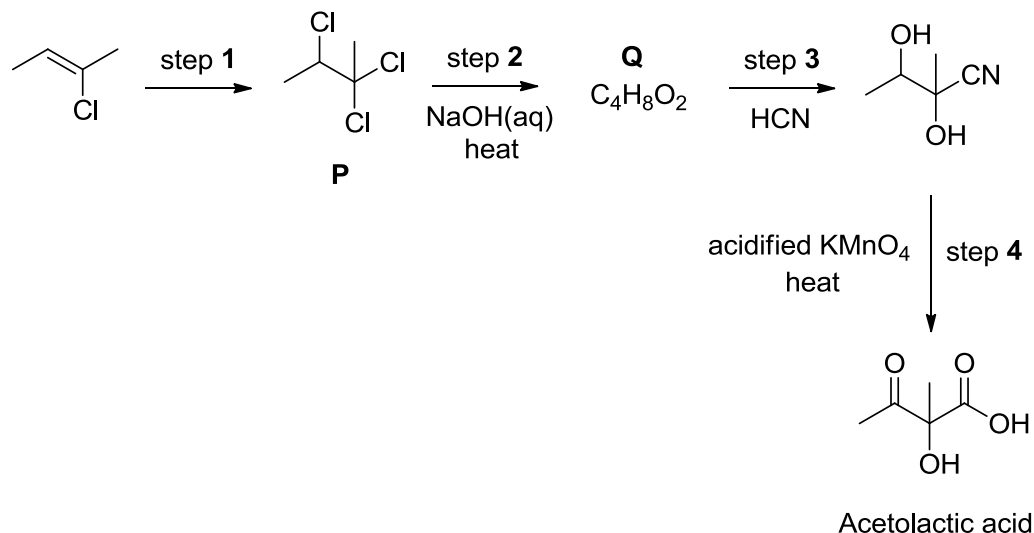
**Rate of consumption of $\text{C}_2\text{O}_4^{2-} = 5/2 \times \text{Rate of consumption of } \text{MnO}_4^-$
 $= 3.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$**

- (iii) What is the role of copper(II) sulfate in the reaction? [1]

Homogenous catalyst

(c) Potassium manganate(VII) is commonly used as an oxidising agent in organic chemistry.

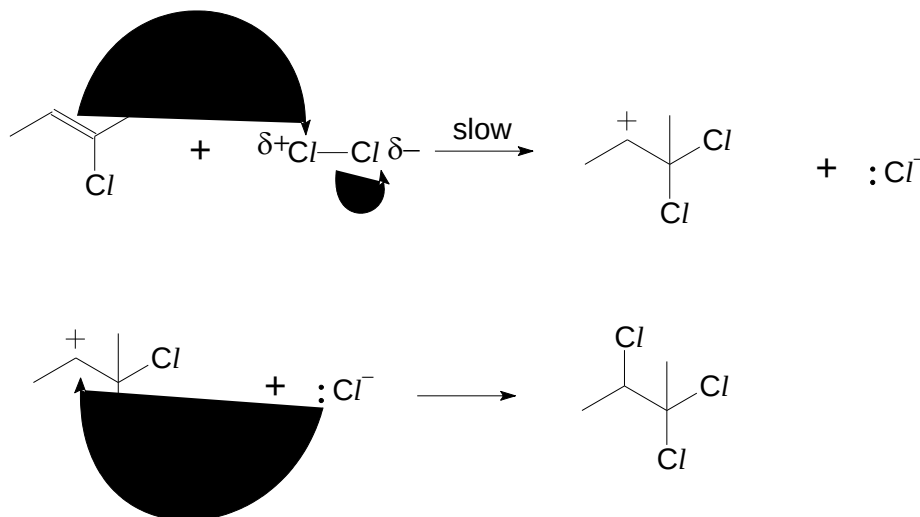
Acetolactic acid, $C_5H_8O_4$, is a precursor in the biosynthesis of the branched chain amino acids, valine and leucine. Acetolactic acid can be synthesised from 2-chlorobut-2-ene by the following reactions.



- (i) State the reagent and conditions used in step 1 and outline the mechanism for this reaction. In your answer, you should include curly arrows showing the movement of electrons and any relevant charges and dipoles. [4]

$Cl_2(g)$, or Cl_2 in CCl_4 , room temperature

Electrophilic addition

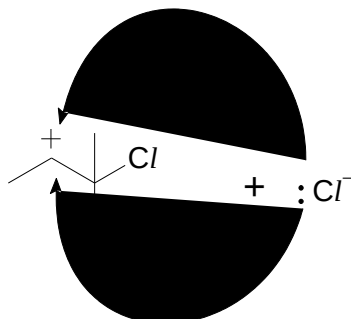


Note:

- The type of mechanism reaction must be stated.
- The mechanism arrows must be shown in the equation to illustrate the movement of electrons.
- Lone pair on the chloride ion must be clearly shown.
- Slow step and the partial charges on chlorine must be indicated in the mechanism

- (ii) Compound **P** obtained from step 1 does not rotate the plane of polarised light despite it containing a chiral carbon. Use the mechanism which you have proposed in (i), to explain this observation. [3]

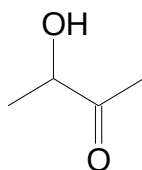
The geometry about the positively charged carbon atom of the carbocation is trigonal planar (or planar).



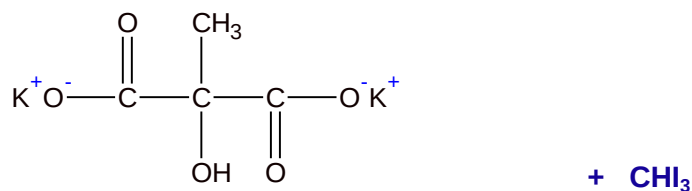
Hence, the nucleophile has equal chances of attacking the positively charged carbon atom from both above and below the plane, to produce equal amount of the 2 enantiomers, resulting an racemic mixture.

The optical activity of the two enantiomers cancel out each other completely. Thus, it is not optically active.

- (iii) Suggest the structure of compound **Q**. [1]



- (iv) Draw the organic products formed when acetolactic acid is warmed with iodine in the presence of aqueous potassium hydroxide. [2]



[Total :20]

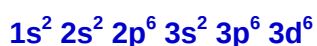
- 5 (a) New applications such as hybrid electric vehicles and power backup require rechargeable batteries that combine high energy density with high charge and discharge rate capability. One such current battery electrode material in used is LiCoO_2 .

The following cell diagram notation is a simplified illustration of the electrochemical cell.



In this cell, Li is oxidised to Li^+ while CoO_2 is reduced to LiCoO_2 . State the oxidation state of Co in LiCoO_2 and hence write the electronic configuration of Co in LiCoO_2 . [2]

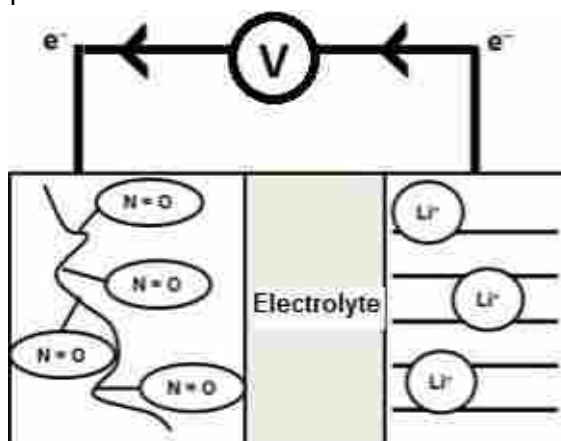
Oxidation state of Co is +3



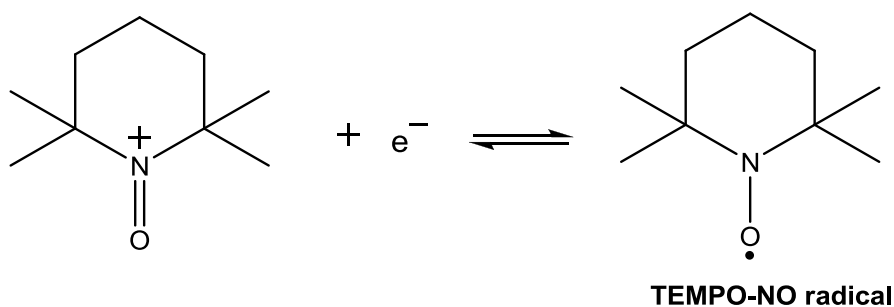
- (b) In recent years, organic radical polymers have been developed as alternatives to inorganic materials because of their light weight, flexibility and their environmentally-friendly features. With the increase in demand for thinner mobile phones and tablet computers, there is a surge to invent film-like organic-derived electrode-active battery materials to power such devices.

One such material is **TEMPO-NO radical** which is capable of repeated stable oxidation-reduction between **N=O** radicals and **N=O** cations. Its voltage when paired with a Li/Li^+ half-cell is able to reach +3.60 V which is comparable to a common lithium-ion battery.

The following is a simplified illustration of the electrochemical cell set-up.



- (i) The following half-equation represents the reaction which occurs at the organic derived electrode.



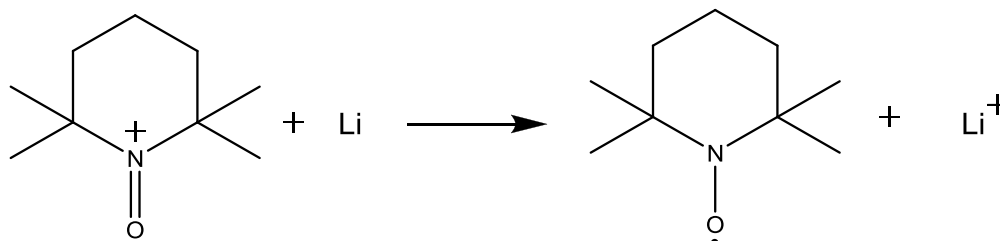
With the use of the *Data Booklet* and the information above, write the overall balanced equation for the electrochemical reaction and calculate the standard electrode potential for **TEMPO-NO** radical half cell. [3]

From Data Booklet



$$E^\circ = -3.04 \text{ V}$$

Overall equation:

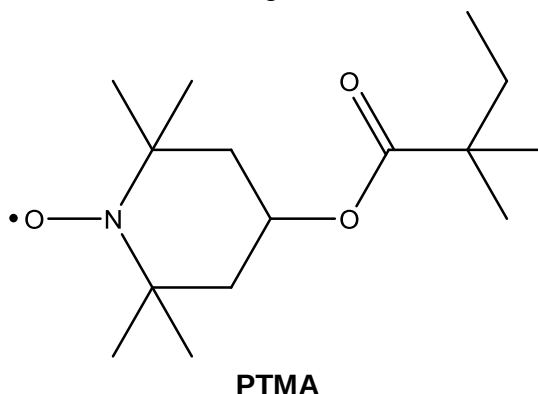


$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$$

$$+3.60 = E^\circ_{\text{reduction}} - (-3.04)$$

$$E^\circ_{\text{reduction}} = +0.56 \text{ V}$$

- (ii) In order for the radical polymer to be used as an electrode, it must not be soluble in the electrolyte. To improve the usability of **TEMPO-NO** radical, the material can be converted to **PTMA** which has the following structure:



Explain how the structure of **PTMA** will help to reduce its solubility in polar solvents like water. [3]

With the increase in carbon side chains, the electron cloud size increases and becomes more polarisable, resulting in an increase in instantaneous dipole-induced dipole (id-id) interactions in PTMA compared to TEMPO-NO radical.

Hence, the formation of hydrogen bonding between water and PTMA will not be exothermic enough to overcome the stronger id-id interaction between PTMA as well as hydrogen bonding between water molecules to dissolve it. Hence, solubility is reduced.

Alternative answer:

With the increase in carbon side chains, the induced dipole-permanent dipole interaction (or instantaneous dipole-induced dipole interaction) between the carbon side chain and water becomes the predominant interaction.

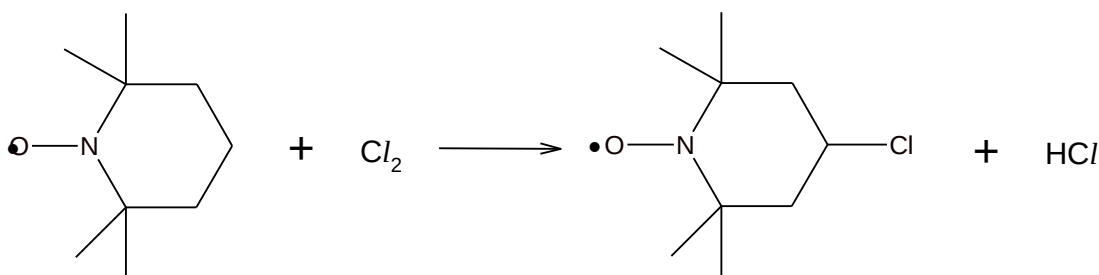
Insufficient energy is released to overcome the hydrogen bonding between water molecules as well as the stronger id-id interaction between PTMA.

- (iii) Water cannot be used as the solvent for $\text{Li}^+ \mid \text{Li}$ half cell. Write an equation to illustrate the reaction when an aqueous medium is used at the $\text{Li}^+ \mid \text{Li}$ half cell which hinders the working of the battery. [1]

Li will react with water to form LiOH



- (iv) The synthesis of **PTMA** required the mono-substitution of the **TEMPO-NO** radical with chlorine as shown in the reaction below.



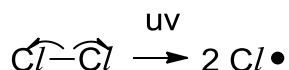
TEMPO-NO radical

Outline the mechanism for this reaction.

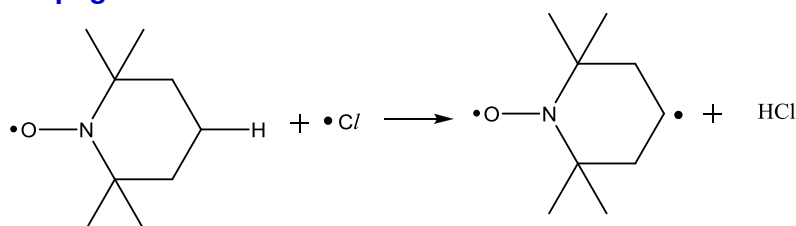
[4]

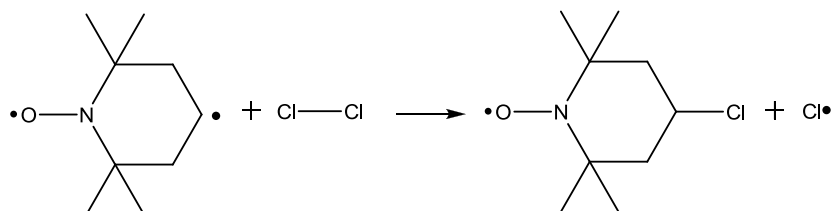
Free radical substitution

Initiation

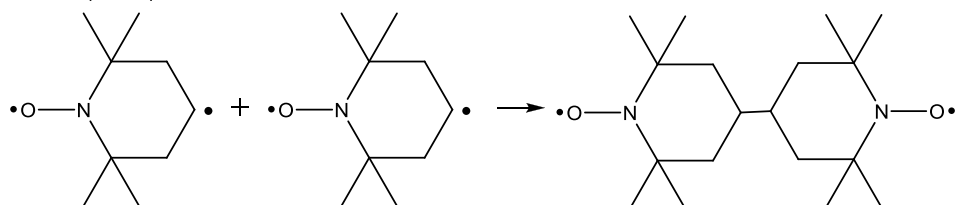
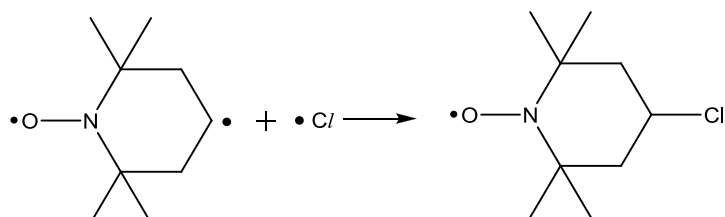
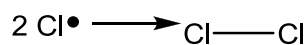


Propagation



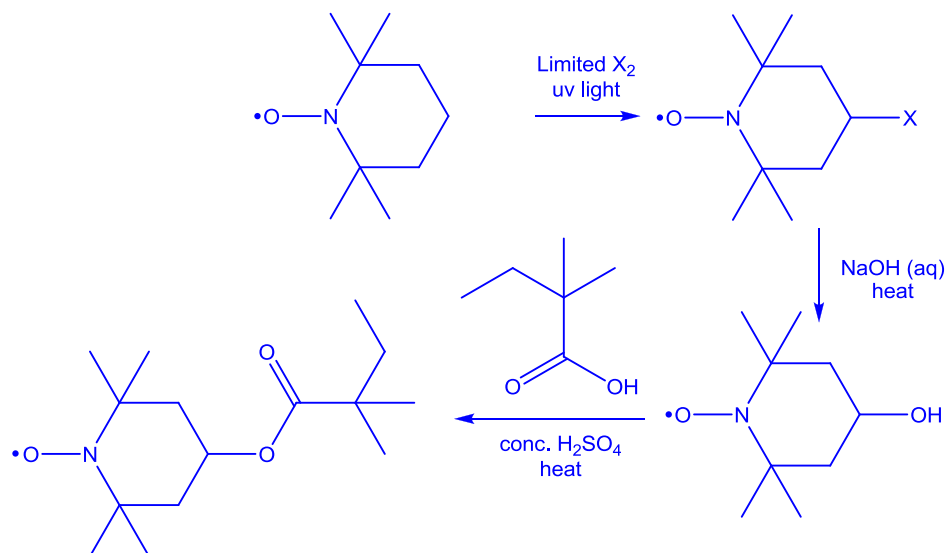


Termination (Any 2)



[1]

(v) Suggest the synthesis route for the formation of **PTMA** from **TEMPO-NO** radical. [4]



(c) When the organic radical battery is recharged, lithium ion is being converted back to lithium metal. Given that the charging process is 87% efficient, how many hours does it take to restore 1.25 g of lithium metal using a current of 3 A? [3]

$$\text{Mass of Li to be restored} = 100/87 \times 1.25 = 1.4368 \text{ g}$$

$$\text{No. of mole of Li} = 1.4367 / 6.9 = 0.20823 \text{ mol}$$

$$Q = 0.20823 \times 96500 = 20094 \text{ C}$$

$$\text{Time} = 20094 / 3 = 6698 \text{ s} = 1.86 \text{ h}$$

Or

$$\text{Mass of Li to be restored} = 100/87 \times 1.25 = 1.4367 \text{ g}$$

$$\frac{96500}{3t} = \frac{6.9}{1.4367}$$
$$t = 6697.6 \text{ s}$$
$$= 1.86 \text{ h}$$

[Total :20]



End of Paper