

RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CHEMISTRY
Paper 1 Multiple Choice

9729/01
19 September 2024
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, glue or correction fluid.

Write your name, class and index number in the spaces provided on the Answer Sheet.

There are **thirty** 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.

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

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

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

How many molecules are present in 1 cm³ of methane gas under room temperature and pressure?

A $\frac{6.02 \times 10^{23}}{24000}$

B $\frac{6.02 \times 10^{23}}{22400}$

C $\frac{22400}{6.02 \times 10^{23}}$

D $\frac{24000}{6.02 \times 10^{23}}$

- 2 When 20 cm³ of a gaseous hydrocarbon was completely burnt in 130 cm³ of oxygen in an enclosed vessel, the volume of gas remaining after the reaction was 100 cm³. This volume was decreased to 40 cm³ under the same conditions when the resulting mixture was passed through aqueous sodium hydroxide. All gas volumes are measured at room temperature and pressure.

What is the formula of the hydrocarbon?



- 3 What do the ions ¹⁸O²⁻ and ¹⁹F⁻ have in common?

A They have more electrons than neutrons.

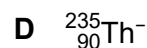
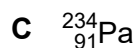
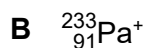
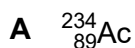
B They have 10 neutrons in their nuclei.

C They have an outer electronic configuration of 3s² 3p⁶.

D They contain the same number of nucleons in their nuclei.

- 4 In beta-minus decay, a neutron in the nucleus of an atom is converted into a proton and a beta particle (electron). This increases the atomic number by 1 while the mass number remains unchanged.

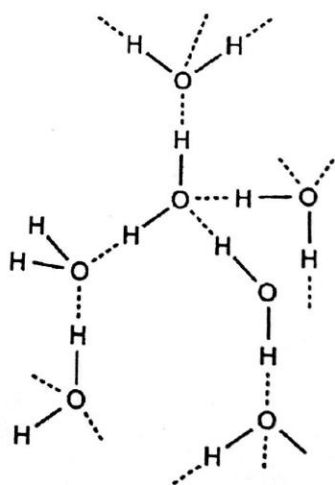
Thorium-234, ²³⁴₉₀Th, undergoes beta-minus decay. What is the resulting species after the decay process?



- 5 Water has a higher boiling point than hydrogen fluoride.

What is the major reason for this?

- A** The O–H bond in water is stronger than the F–H bond in hydrogen fluoride.
B A water molecule contains more electrons than a hydrogen fluoride molecule.
C On average, there are more hydrogen bonds between water molecules than there are between hydrogen fluoride molecules.
D A hydrogen fluoride molecule is more polar than a water molecule.
- 6 The diagram shows the structure of part of a crystal of ice.



Which statement is correct?

- A** The open structure of ice causes ice to be denser than water.
B The hydrogen bonds are stronger than the O–H covalent bonds.
C Two electrons from each oxygen are involved in forming hydrogen bonds.
D Each oxygen atom is tetrahedrally bonded to four hydrogen atoms through covalent or hydrogen bonds.

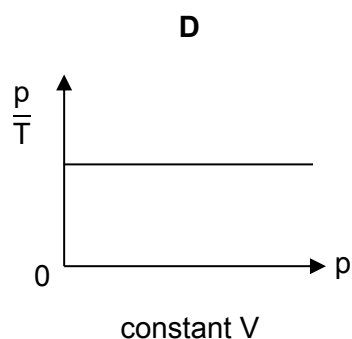
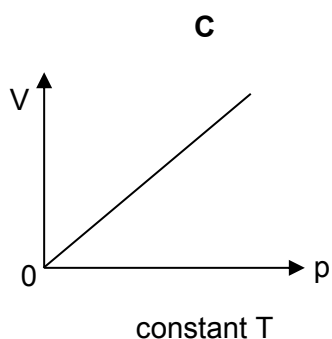
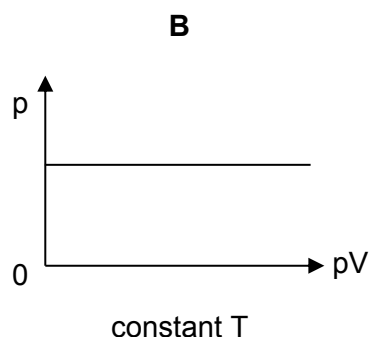
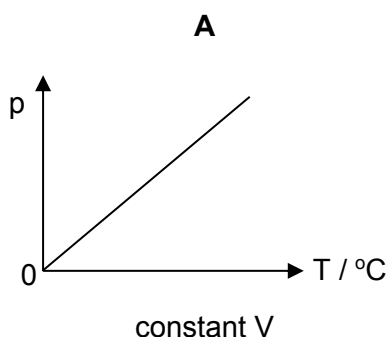
- 7 Compound E, $C_3H_2Cl_2$, is non-cyclic.

Which statements are correct for E and all its non-cyclic isomers?

- 1 There are 6 σ and 2 π bonds present.
- 2 The optically active isomers each contain a chiral carbon.
- 3 There is a total of five non-cyclic isomers, including stereoisomers.

A 1 and 2 **B** 1 and 3 **C** 2 and 3 **D** 1 only

- 8 Which graph is correct for a fixed mass of an ideal gas?



- 9 Which row correctly describes the general trends from sodium to chlorine across Period 3 of the Periodic Table?

	atomic radius	electronegativity	1 st ionisation energy
A	increases	decreases	decreases
B	decreases	increases	decreases
C	decreases	increases	increases
D	increases	increases	increases

- 10 Elements L and M are in Period 3 of the Periodic Table.

The oxide of L dissolves sparingly in water. The pH of the solution of the chloride of L is higher than that of the chloride of M.

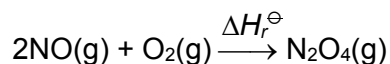
Which row correctly shows the identities of L and M?

	L	M
A	Mg	Al
B	Mg	Na
C	Na	Si
D	Na	S

- 11 Which property of X_2 increases down the group for $X = Cl, Br$ or I ?

- A** volatility
- B** bond length
- C** bond energy
- D** oxidising power

- 12 The standard enthalpy change of the following reaction, ΔH_r^\ominus , can be calculated using the data in the table.

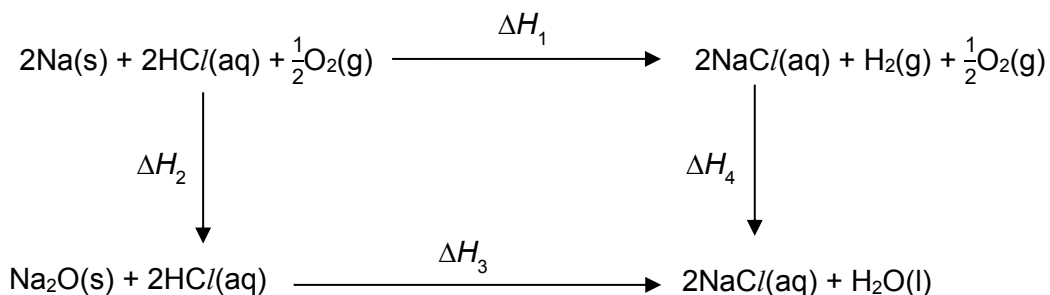


equation	$\Delta H^\ominus / \text{kJ mol}^{-1}$
$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO(g)$	+91
$\frac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g)$	+34
$2NO_2(g) \longrightarrow N_2O_4(g)$	-58

What is the value of ΔH_r^\ominus ?

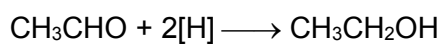
- A** -172 kJ mol^{-1} **B** -115 kJ mol^{-1} **C** -56 kJ mol^{-1} **D** -1 kJ mol^{-1}

- 13 Hydrochloric acid can react with sodium and sodium oxide to give different products.

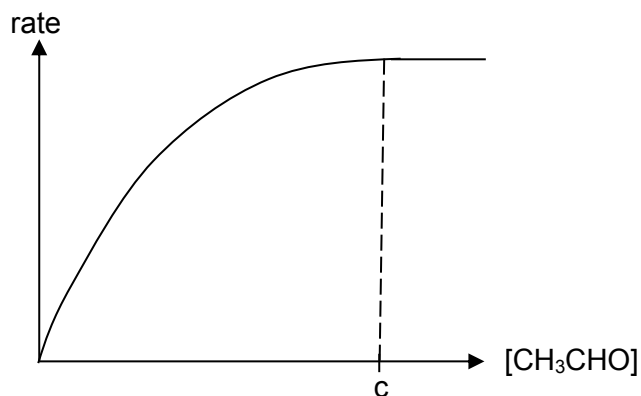


Which statement is correct?

- A $\Delta H_1 + \Delta H_2$ is always positive.
 B $\Delta H_3 + \Delta H_4$ is always positive.
 C $\Delta H_3 - \Delta H_4 - \Delta H_1$ is always negative.
 D $\Delta H_2 + \Delta H_3 - \Delta H_1$ is always negative.
- 14 The following reaction is catalysed by an enzyme.



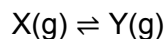
The graph shows how the rate of the reaction varies with $[\text{CH}_3\text{CHO}]$.



Which statement is correct when $[\text{CH}_3\text{CHO}] = c$?

- A There are no more enzyme active sites available.
 B The order of reaction with respect to $[\text{CH}_3\text{CHO}]$ is 1.
 C As more $\text{CH}_3\text{CH}_2\text{OH}$ is produced, the reaction slows down.
 D All the CH_3CHO has been used up and the reaction stops.

- 15 X(g) is placed in a sealed vessel and allowed to reach equilibrium at constant temperature.



Under the same conditions, which statements are correct?

- 1 Given that X and Y behave as ideal gases, $K_c = K_p$.
- 2 $\frac{P_Y}{P_X}$ at equilibrium is the same if Y(g) is used initially instead of X(g).
- 3 Adding more X(g) causes the partial pressures of both gases to be higher at the new equilibrium.

A 1, 2 and 3 **B** 1 and 2 only **C** 1 and 3 only **D** 2 and 3 only

- 16 20.0 cm³ of 0.100 mol dm⁻³ of dilute nitric acid was titrated against 0.100 mol dm⁻³ of aqueous ammonia.

Which volume of aqueous ammonia is required to produce a buffer with maximum buffering capacity?

A 10.0 cm³ **B** 20.0 cm³ **C** 30.0 cm³ **D** 40.0 cm³

- 17 A 1.00 mol dm⁻³ solution of CH₃COO⁻ was prepared at 50 °C.

K_a for ethanoic acid = 1.63×10^{-5} mol dm⁻³ and $pK_w = 13.3$ at 50 °C.

What is the pH of this solution at 50 °C?

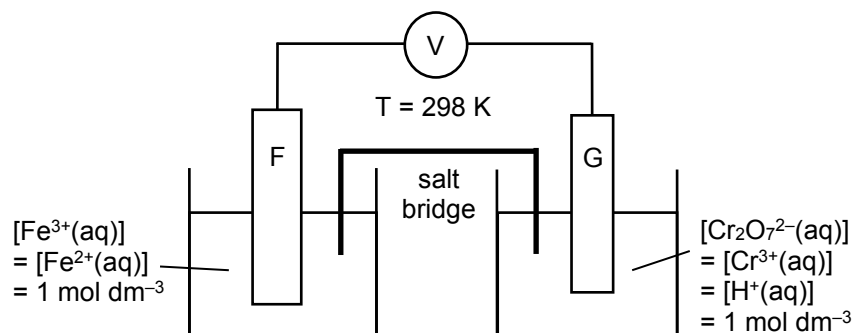
A 4.26 **B** 9.04 **C** 9.39 **D** 9.74

- 18 Which substance will cause the formation of a precipitate when added to a saturated solution of magnesium carbonate?

- A** NaCl(s)
- B** H₂O(l)
- C** K₂CO₃(s)
- D** HCl(aq)

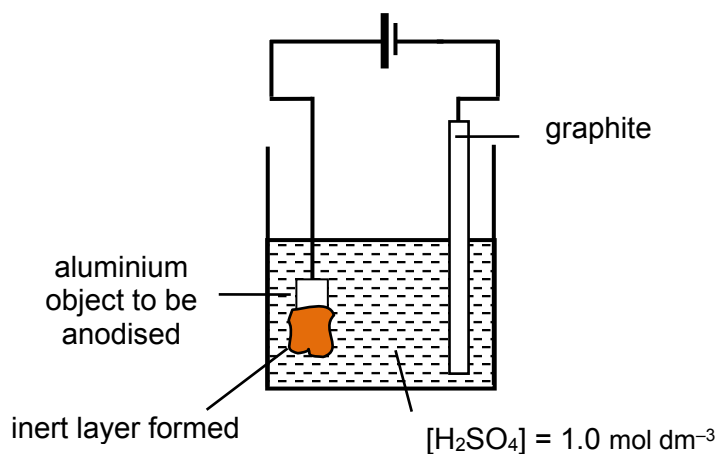
- 19 Use of the Data Booklet is relevant to this question.

Which row gives the standard cell potential on the voltmeter and the correct direction of electron flow in the connecting wire?



	$E^\ominus_{\text{cell}} / \text{V}$	direction of flow
A	+0.56	F to G
B	+0.56	G to F
C	-0.56	F to G
D	-0.56	G to F

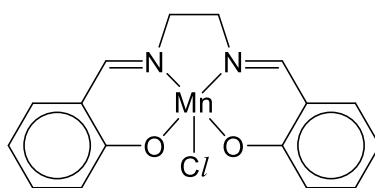
- 20 The process of coating aluminium objects with an inert layer via electrolysis is called anodising. The set-up used for anodising aluminium is shown.



Which statement is correct?

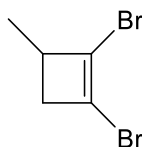
- A** The mass of the cathode increases.
- B** Water is preferentially reduced to form oxygen gas at the anode.
- C** Water is preferentially reduced to form hydrogen gas at the cathode.
- D** The gas formed at the anode reacts to form an inert layer on the object to be anodised.

- 21 Which statement is correct about the properties of both potassium and copper?
- A Both elements have similar density.
 B Both elements can form compounds that are white in colour.
 C Both elements form stable compounds with the metal having an oxidation state of +2.
 D Both elements use electrons from two subshells for metallic bonding.
- 22 The Mn-salen complex protects cells from oxidative damage and improves the mitochondrial function of neurons.



Which statements regarding the Mn-salen metal complex are correct?

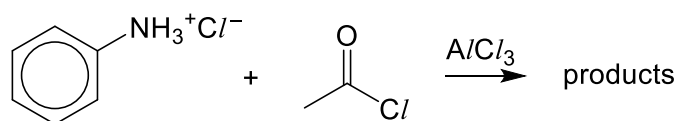
- 1 The shape about Mn is octahedral.
 - 2 Mn has an oxidation number of +3 in the complex.
 - 3 The complex contains a monodentate ligand and a tetradentate ligand.
- A 2 only B 3 only C 1 and 2 D 2 and 3
- 23 Which statements correctly identify the features of the following compound?



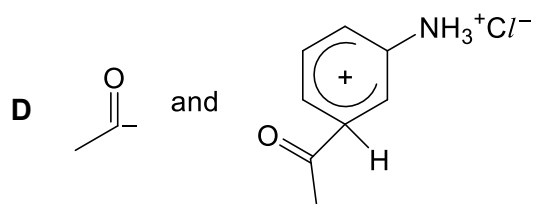
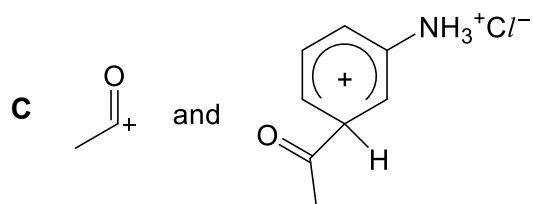
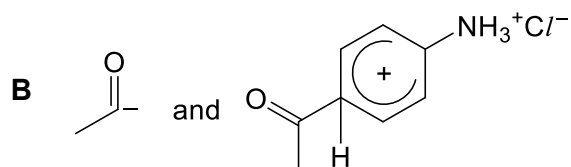
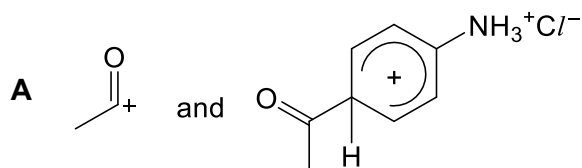
- 1 It is planar.
 - 2 It exists as enantiomers.
 - 3 It exists as cis-trans isomers.
- A 1 only B 2 only C 1 and 3 D 2 and 3

24 Use of the Data Booklet is relevant to this question.

The reaction between phenylammonium chloride and ethanoyl chloride proceeds via several stages with two intermediates.




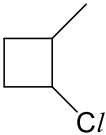

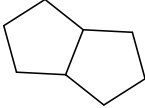
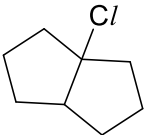
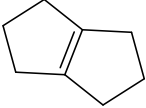
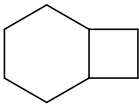
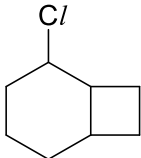
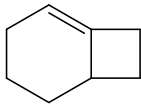
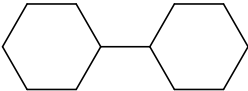
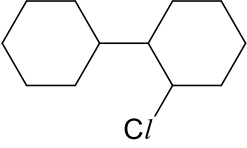
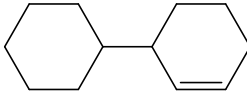
What could be the intermediates formed to produce the major product for this reaction?



- 25** P reacts with chlorine in the presence of ultraviolet light to produce only four monochlorinated compounds, excluding stereoisomers.

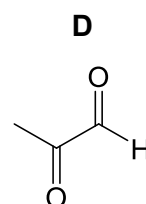
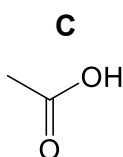
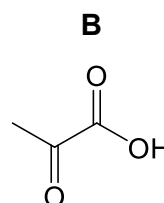
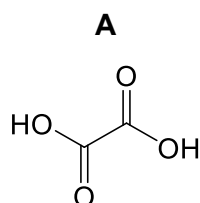
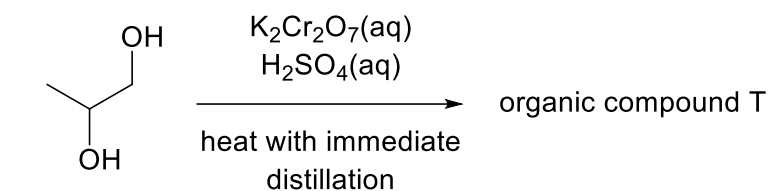
Q, one of the monochlorinated compounds, reacts with hot ethanolic KOH to produce R as a major product.

What are the possible structures of P, Q and R?

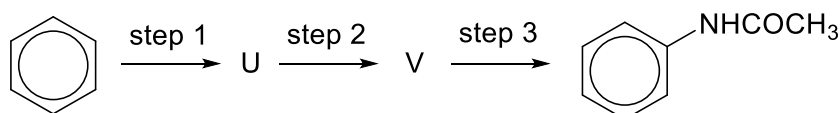
	structure of P	structure of Q	structure of R
1			
2			
3			
4			

- A** 1 and 2 only **B** 2 and 3 only **C** 1 and 3 only **D** 1, 3 and 4

26 What could be the identity of compound T?

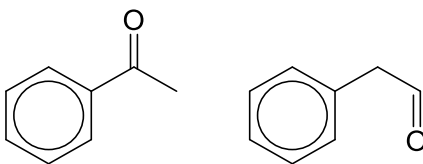


27 Which row shows the correct reagents and conditions for this synthesis?



	step 1	step 2	step 3
A	Br ₂ , FeBr ₃	excess NH ₃ , heat in sealed tube	CH ₃ COC/
B	conc. HNO ₃ , H ₂ SO ₄ , heat	LiAlH ₄	CH ₃ COC/
C	conc. HNO ₃ , H ₂ SO ₄ , heat	Sn, HCl	CH ₃ COOH, conc. H ₂ SO ₄ , heat
D	conc. HNO ₃ , H ₂ SO ₄ , heat	Sn, HCl	CH ₃ COC/

- 28 Which reagents and conditions would allow these two compounds to be distinguished from each other?



- 1 2,4-DNPH
- 2 Tollens' reagent, heat
- 3 Fehling's reagent, heat
- 4 KMnO_4 , H_2SO_4 , heat

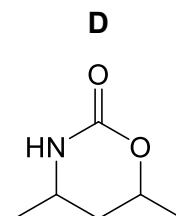
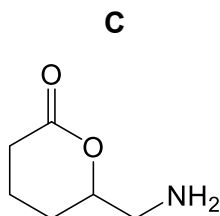
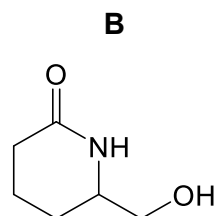
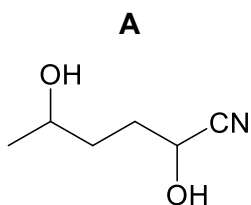
A 1 and 2 **B** 2 and 3 **C** 2 and 4 **D** 3 and 4

- 29 J is an organic compound with the formula $\text{C}_6\text{H}_{11}\text{O}_2\text{N}$.

It reacts with excess HCl(aq) to form a mixture containing the compound with the formula $\text{C}_6\text{H}_{12}\text{O}_2\text{NCI}$.

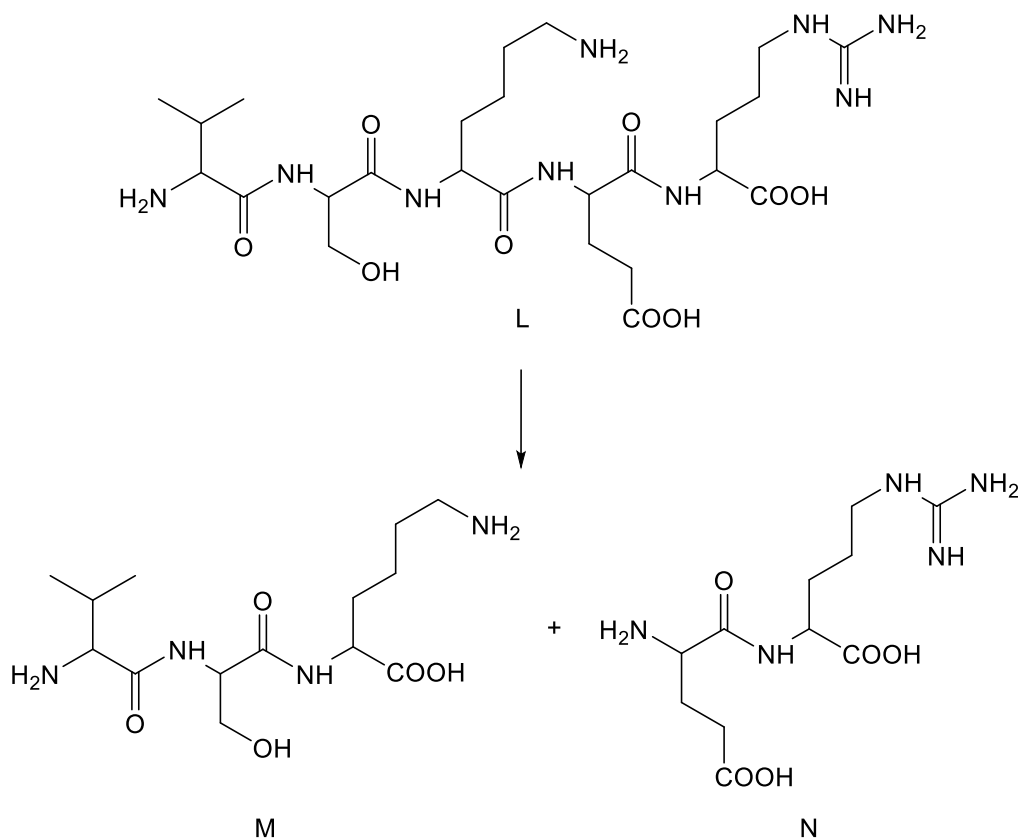
Upon heating this mixture, a product with the formula $\text{C}_6\text{H}_{14}\text{O}_3\text{NCI}$ is formed.

What could be the identity of J?

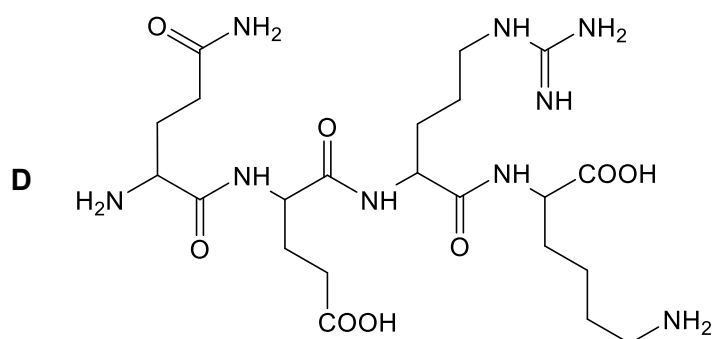
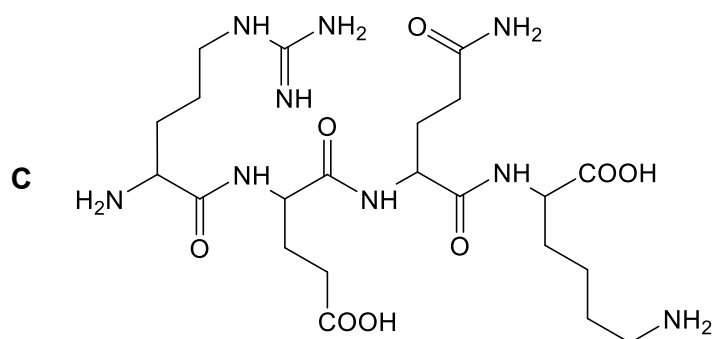
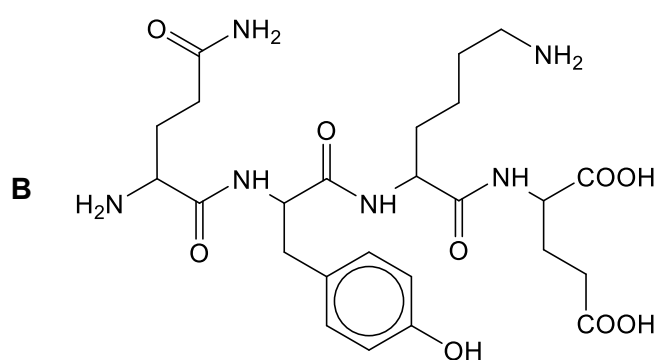
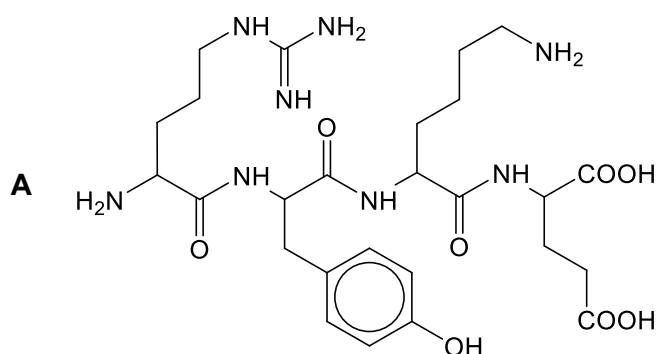


- 30** Trypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains a positively charged group.

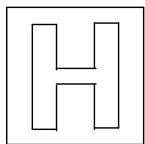
For example, the pentapeptide L produces only two compounds M and N. This is because the $-(CH_2)_4-NH_2$ group on the side chain is basic and can be protonated to a $-(CH_2)_4-NH_3^+$ group.



Which tetrapeptide would give 3 different products when hydrolysed by trypsin?



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RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/02

Paper 2 Structured Questions

10 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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 in the spaces at the top of this page.

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 in the spaces provided on the Question Paper.

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

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.

For Examiner's Use	
1	/ 15
2	/ 19
3	/ 22
4	/ 19
Total	/ 75

This document consists of **24** printed pages.

Answer **all** questions in the space provided.

1 Boron and its compounds have diverse applications across industries.

(a) (i) Write an equation to represent the fourth ionisation energy of boron.

..... [1]

(ii) Explain why the fourth ionisation energy of boron is much higher than that of carbon.

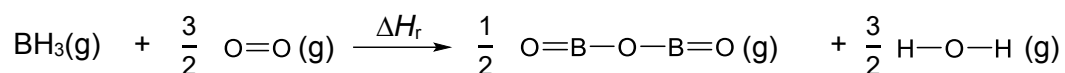
.....

 [2]

(b) Borane, BH_3 , is a useful compound of boron.

Borane undergoes complete combustion in excess oxygen to form boron trioxide, B_2O_3 , as shown in equation 1.

equation 1



(i) Draw a dot-and-cross diagram of the BH_3 molecule.

[1]

(ii) State the shape and bond angle in BH_3 .

..... [2]

- (iii) Table 1.1 shows some bond energy data.

Table 1.1

bond	bond energy / kJ mol^{-1}
B–B	293
B–H	330
B–O	536
B=O	837

Use the data in Table 1.1, together with data from the *Data Booklet*, to calculate the enthalpy change, ΔH_r , for the reaction in equation 1.

[2]

- (iv) Boron trioxide, B_2O_3 , is a relatively inert glass-like solid at 298 K.

The standard enthalpy change of combustion of borane, $\text{BH}_3(\text{g})$, is more exothermic than ΔH_r . Explain why.

.....

 [1]

- (c) At certain temperatures, BH_3 dimerises into diborane, B_2H_6 . Similarly, AlCl_3 also dimerises to form Al_2Cl_6 .

(i) Explain why AlCl_3 can undergo dimerisation.

.....

 [1]

(ii) By considering the shape around the Al atom, state the change in hybridisation of the Al atom when AlCl_3 dimerises to Al_2Cl_6 .

..... [1]

Fig. 1.1 shows the structure of B_2H_6 .

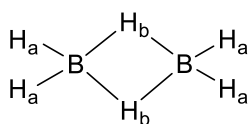


Fig. 1.1

(iii) The central hydrogen atoms, H_b , bond to both boron atoms. Two electrons are shared across the three atoms in $\text{B-H}_b\text{-B}$.

Explain why the B-H_b bond is longer than B-H_a bond.

.....

 [1]

(d) Borazine, $B_3N_3H_6$, is similar in structure to benzene and consists of a six-membered ring with alternating boron and nitrogen atoms.

- (i) The borazine structure can be represented by two different resonance structures, **X** and **Y**, as shown in Fig. 1.2. The arrow \longleftrightarrow indicates that the actual structure of borazine is somewhere in between these two structures.

Complete Fig. 1.2 by adding curly arrows to structure **X**.

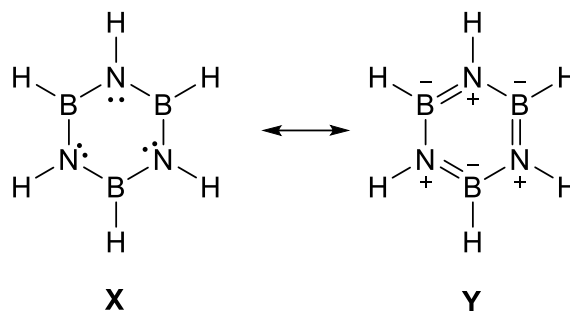


Fig. 1.2

[1]

- (ii) Explain why borazine is less resonance stabilised than benzene.

.....
 [1]

- (iii) Borazine undergoes addition reactions due to the less resonance stabilised structure.

X accounts for the major products formed from addition reactions of borazine.

When one mole of **X** reacts completely with three moles of HCl , compound **Z** is formed as the only product. Draw the structure of **Z**.

[1]

[Total: 15]

- 2 Water chemistry plays a critical role in the well-being of fishes in an aquarium. Fish waste releases ammonia into water which is toxic to fish. During nitrification, ammonia is broken down by beneficial bacteria into less toxic nitrate ions as shown in Fig. 2.1.

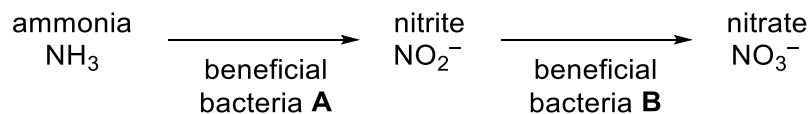
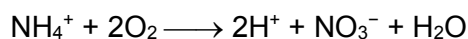


Fig. 2.1

- (a) (i) Under acidic conditions, the equation for nitrification is shown.



Use relevant standard redox potentials from the *Data Booklet* to show that this reaction is spontaneous under standard conditions.

[1]

- (ii) Despite nitrification being spontaneous under the conditions in an aquarium, the presence of beneficial bacteria is necessary for any appreciable breakdown of NH_4^+ to be observed.

Suggest the role of beneficial bacteria in the nitrification process.

..... [1]

- (b) Setting up a new aquarium involves establishing colonies of beneficial bacteria in the tank before fish are added. Ammonia is added daily and the concentrations of different water parameters are monitored. Fig. 2.2 shows a graph of some water parameters over 35 days.

The presence of the respective products in Fig. 2.1 indicates that the beneficial bacteria has been established.

Fish can only be safely added after the concentration of NO_2^- increases then decreases to 0 ppm as NO_2^- is also toxic to fish.

The total ammonia nitrogen, TAN, measured is the sum of the concentrations of NH_3 and NH_4^+ .

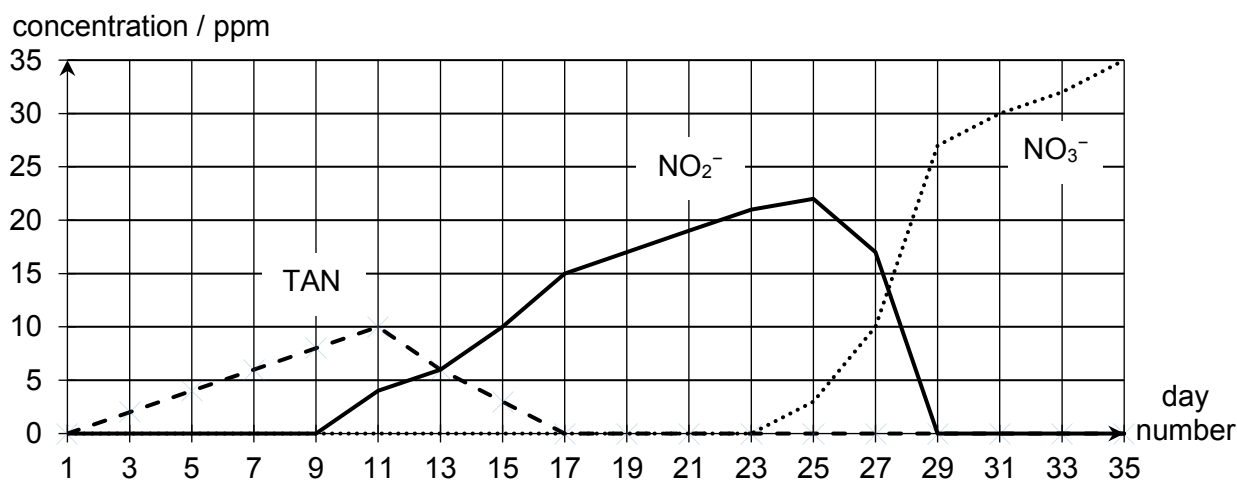


Fig. 2.2

- (i) State the day number that first indicates that beneficial bacteria **A** is established.

..... [1]

- (ii) State the day number that is first safe for the addition of fish.

..... [1]

- (iii) On day 35, 25% of the tank water is replaced with water that is free of NO_3^- .

Calculate the new concentration of NO_3^- , in ppm.

[1]

- (iv) At pH 7.4, ammonia released by fish waste exists as a mixture of NH_3 and NH_4^+ . The mole fraction of ammonia in the mixture, z , can be calculated as follow.

$$z = \frac{[\text{NH}_3]}{\text{TAN}}$$

Calculate z for a sample of tank water at pH 7.4 on day 11.

The $\text{p}K_a$ for $\text{NH}_4^+(\text{aq})$ is 9.25.

[2]

- (c) In another aquarium, the tank water's buffering capacity is due to the presence of carbonate, CO_3^{2-} , and bicarbonate, HCO_3^- .

- (i) Write two equations to show how the tank water behaves as a buffer when small amounts of $\text{OH}^-(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ are separately added to it.

.....

..... [2]

- (ii) The nitrification process produces H^+ which can cause the pH of tank water to decrease.

Carbonate hardness is a measure of the total concentration of CO_3^{2-} and HCO_3^- .

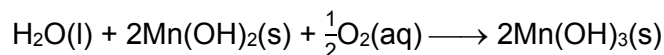
Suggest why tank water with a higher carbonate hardness is better at maintaining its pH.

.....

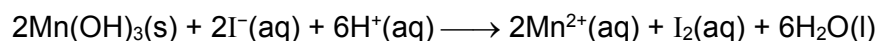
..... [1]

- (d) The recommended range for the concentration of dissolved oxygen in aquarium water samples is 1.50×10^{-4} to $5.00 \times 10^{-4} \text{ mol dm}^{-3}$.

The concentration of dissolved oxygen in aquarium water can be determined by first adding $\text{Mn(OH)}_2(\text{s})$ to the water.



Excess $\text{I}^-(\text{aq})$ is then added and the following reaction occurs to produce I_2 .



The I_2 produced can then be titrated with a standard solution of sodium thiosulfate using starch as an indicator.



- (i) A 100 cm^3 of sample of aquarium water containing dissolved oxygen required 13.40 cm^3 of $0.0100 \text{ mol dm}^{-3}$ sodium thiosulfate solution to reach the end point.

Calculate the concentration of dissolved oxygen in this sample, in mol dm^{-3} , and hence determine if it falls within the recommended range.

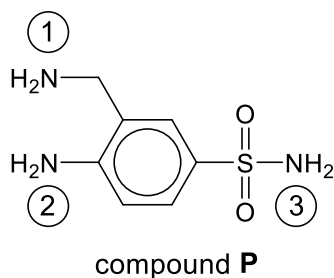
[3]

- (ii) Azide, N_3^- , is added to the titration in (d)(i) to prevent NO_2^- in aquarium water from reacting with I^- . N_3^- reacts with NO_2^- to give nitrogen gas as the only nitrogen-containing product.

With the aid of half-equations, write a balanced equation for the reaction between N_3^- and NO_2^- under acidic conditions.

.....
.....
.....
..... [2]

- (e) Compound **P** can be used to test for NO_2^- and has a sulfonamide functional group, $-\text{SO}_2\text{NH}_2$, that has similar basicity to an amide.



Describe and explain the relative basicities of the three nitrogen-containing groups in compound **P**.

[4

[Total: 19]

3 This question explores the reactions of short-chain hydrocarbons and halogenoalkanes.

- (a) 3-Methylbut-1-ene reacts with chlorine gas in the dark to give compound **D**, as shown in Fig. 3.1.

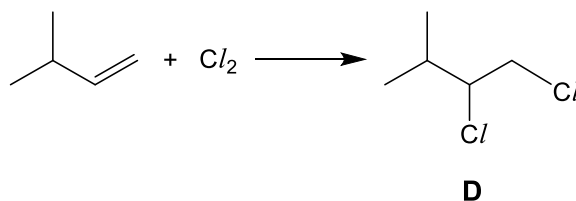


Fig. 3.1

- (i) Draw the three-dimensional structures of the two enantiomers of **D**.

[1]

- (ii) By considering the shape of the intermediate formed during the reaction in Fig. 3.1, explain whether the product mixture rotates plane-polarised light.

.....

.....

.....

.....

..... [2]

Fig. 3.2 shows the electrophilic addition of bromine to alkenes via a different type of intermediate from that in Fig. 3.1.

The stereochemistry of the product depends on the stereochemistry of the starting alkene.

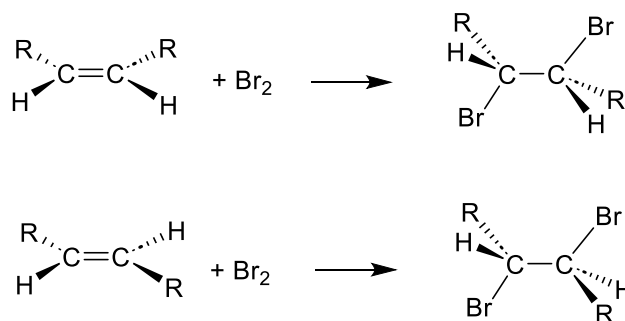


Fig. 3.2

- (iii) A meso compound contains more than one chiral carbon with an internal plane of symmetry.

When an alkene **E**, C_4H_8 , reacts with liquid bromine in the dark, a meso compound is produced.

With reference to Fig. 3.2, deduce the three-dimensional structures of **E** and the product.

E	product

[2]

- (b) Rearrangement may occur when a carbocation is formed in a reaction. This typically involves the migration of a hydride or an alkyl group from a carbon adjacent to the positively charged carbon.

Fig. 3.3 shows the reaction between 3-methylbut-1-ene and hydrogen bromide.

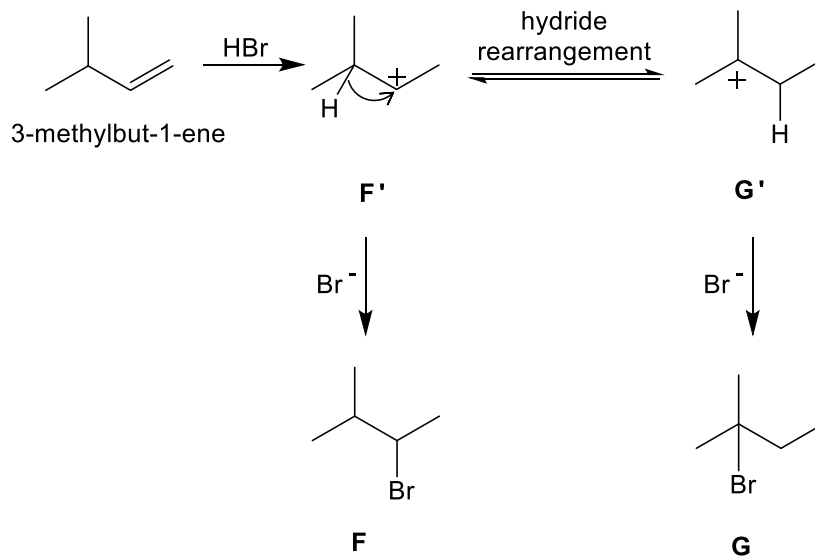


Fig. 3.3

- (i) Using the concept of electronic effect, explain why **G** is produced in a larger proportion.

.....

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.....

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..... [2]

The reaction in Fig. 3.4 proceeds via the S_N1 mechanism. Alkyl rearrangement results in the formation of **K** and **L**.

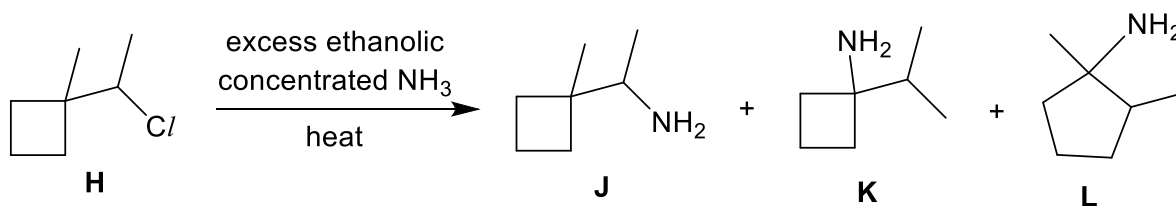


Fig. 3.4

(ii) On Fig. 3.5, draw a curly arrow for step B to show the alkyl rearrangement. [1]

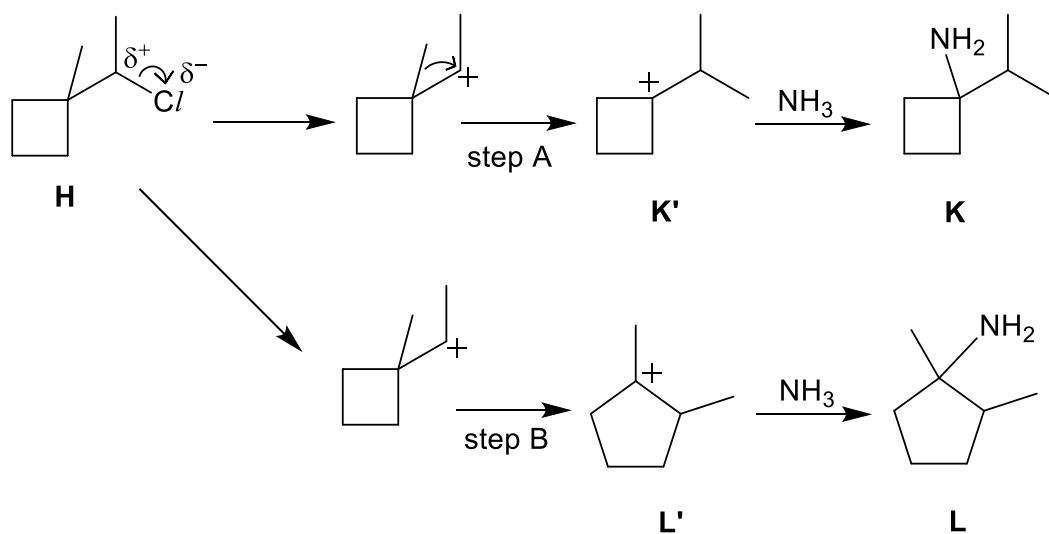


Fig. 3.5

(iii) Deduce whether **K** or **L** is the major product. Explain your answer.

.....

 [1]

- (c) Alkenes react with borane, BH_3 , in the presence of hydrogen peroxide to give an alcohol, as shown in Fig. 3.6.

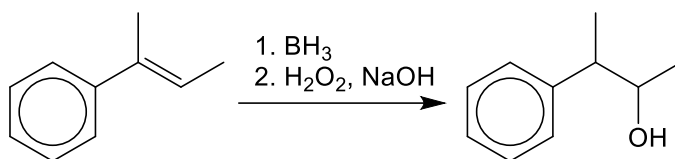


Fig. 3.6

- (i) Use this information to complete the reaction scheme involving 3-methylbut-1-ene in Fig. 3.7. Draw the structures of **M** and **P** and state the reagent for step 2.

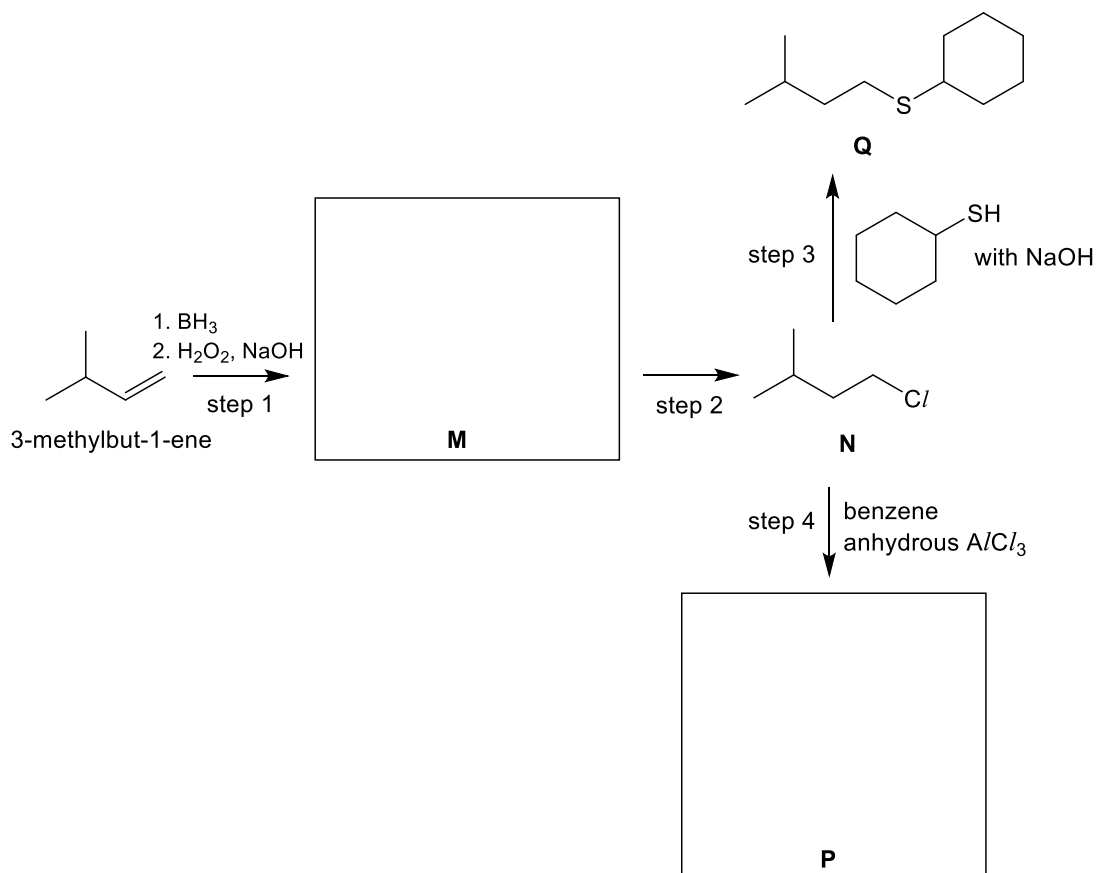


Fig. 3.7

reagent for step 2: [3]

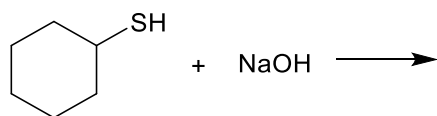
- (ii) Give the systematic name for compound **N**.

..... [1]

- (iii) State the type of reaction occurring in step 4.

..... [1]

- (iv) The reagents used in step 3 are involved in an acid-base reaction. Complete the equation below.



[1]

- (v) Based on your answer in (c)(iv), describe the mechanism to show the formation of **Q** from **N**.

Show all the partial charges, relevant lone pairs and show the movement of electron pairs by using curly arrows.

You may represent **N** as $\text{R}-\text{CH}_2\text{Cl}$.

[3]

3-Methylbut-1-ene can react to form compounds **S** and **T**.



- (vi) Suggest a simple chemical test to distinguish between **S** and **T**.

.....

.....

.....

..... [2]

- (d) 3-Methylbut-1-ene is a precursor to the production of chlorofluorocarbons, CFCs, which were once used as refrigerant fluids and propeller aerosols.

- (i) Indiscriminate use of CFCs has resulted in ozone depletion.

Briefly explain how CFCs contribute to ozone depletion.

.....

 [1]

CFCs have been gradually replaced by hydrofluorocarbons, HFCs.

Table 3.1 provides some information regarding CFC-11 and HFC-23.

Table 3.1

name	structure	GWP
HFC-23	CHF_3	14800
CFC-11	CFCI_3	4750

Global warming potential, GWP, indicates the amount of heat trapped by 1 tonne of a gas relative to the amount of heat trapped by 1 tonne of CO_2 over a specified period.

- (ii) Explain how the replacement of CFCs by HFCs is detrimental to the environment.

.....
 [1]

[Total: 22]

- 4 (a) (i) Define the terms *order of reaction* and *rate constant*.

.....

.....

.....

.....

.....

..... [2]

Question 4 continues on page 20.

When ethanal, CH_3CHO , reacts with hydroxyl radicals, $\bullet\text{OH}$, the reaction shown in equation 1 takes place.



The reaction was studied at 298 K and the initial $[\text{CH}_3\text{CHO}]$ was much higher than $[\bullet\text{OH}]_0$, the initial concentration of $\bullet\text{OH}$.

In this experiment, the ratio of concentration of $\bullet\text{OH}$ at a particular time, relative to its initial concentration, is represented by $\frac{[\bullet\text{OH}]}{[\bullet\text{OH}]_0}$.

Fig. 4.1 shows the graph of $\frac{[\bullet\text{OH}]}{[\bullet\text{OH}]_0}$ against time for this experiment.

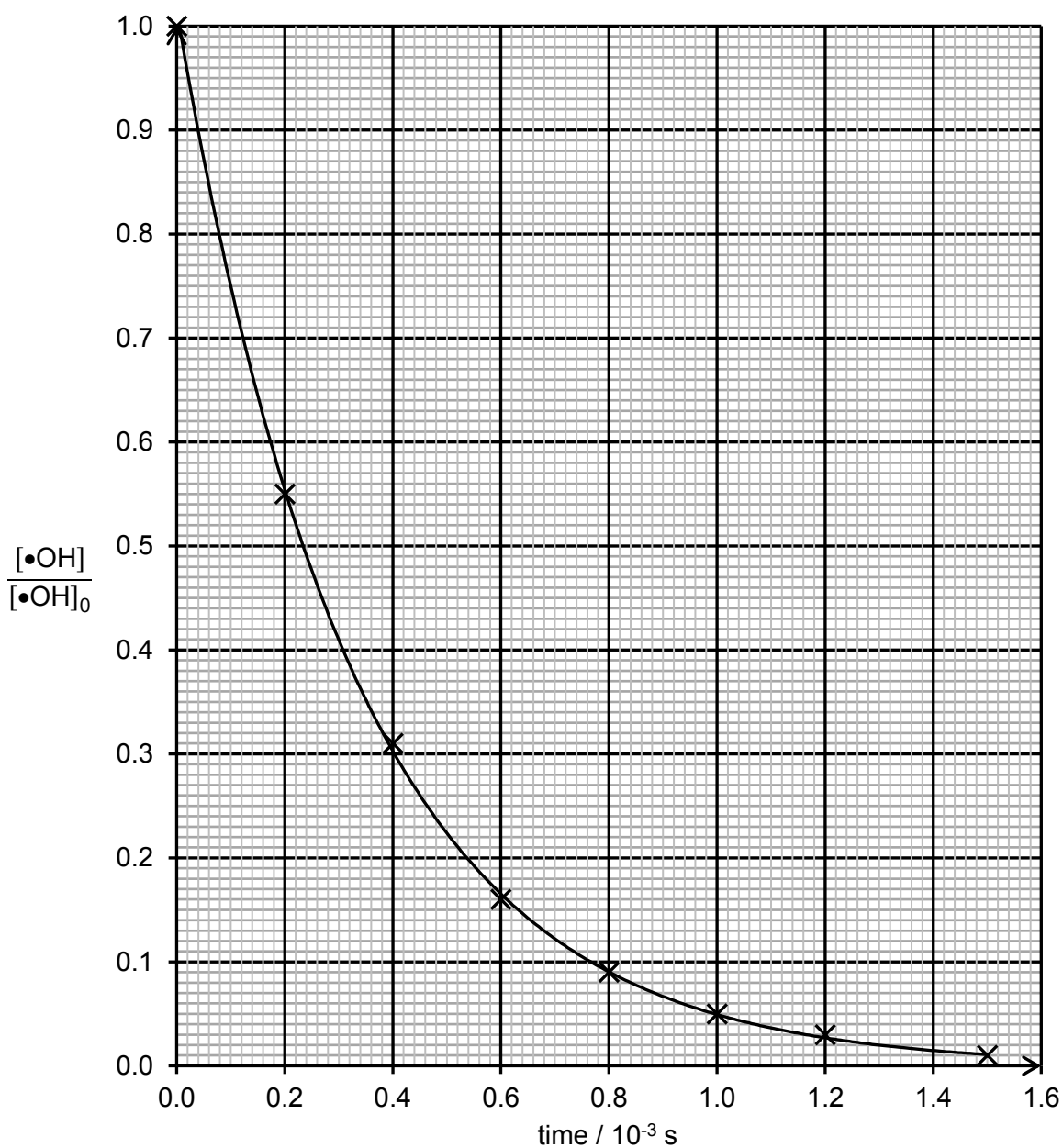


Fig. 4.1

- (ii) Use Fig. 4.1 to determine the order of reaction with respect to $\bullet\text{OH}$.

Assume that $\frac{[\bullet\text{OH}]}{[\bullet\text{OH}]_0}$ is equivalent to the concentration of $\bullet\text{OH}$.

[2]

The reaction is known to follow pseudo-order kinetics, where the pseudo-order rate constant, $k' = k[\text{CH}_3\text{CHO}]^n$.

More experiments were conducted to explore the relationship between k' and the concentration of CH_3CHO . The results of these experiments are shown in Fig. 4.2.

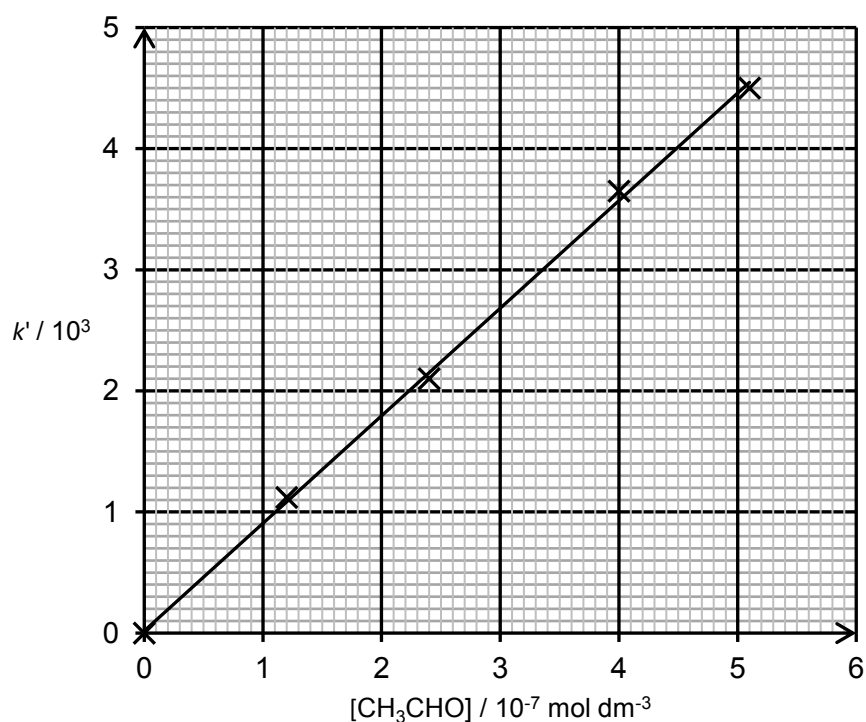


Fig 4.2

- (iii) Use Fig. 4.2 to deduce the order of reaction with respect to CH_3CHO , and hence determine the value of the rate constant, k , for the reaction.

[2]

- (iv) Hence, write the rate equation for the reaction in equation 1.

..... [1]

- (v) It is proposed that the reaction shown in equation 1 takes place in a single, elementary step. Using your answer in (a)(iv), suggest if you agree with this proposal, giving your reasons.

.....
.....
..... [1]

- (vi) Suggest how the presence of a catalyst would affect the magnitudes of the rate constant, k , and activation energy, E_a , of the reaction in equation 1.

.....
..... [1]

(b) The hydroxyl radical, $\bullet\text{OH}$, is often referred to as the “detergent” of the atmosphere, as it eliminates pollutants and greenhouse gases like CH_4 by reacting with them via free radical substitution.

- The first step of this reaction involves the removal of a hydrogen atom from CH_4 by $\bullet\text{OH}$, forming water and a methyl radical.
- The second step involves the reaction of the methyl radical with O_2 , forming a radical with an $\text{O}-\text{O}$ single bond as the only product.

The radical formed then undergoes further reactions to form more stable molecules such as CH_3OH and HCHO .

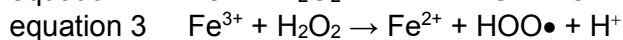
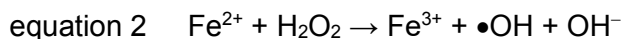
(i) Use the information given above to draw the first and second steps of the mechanism for the reaction between $\bullet\text{OH}$ and CH_4 . Use curly arrows to show movement of electrons.

[4]

(ii) Draw the labelled energy profile diagram for the first two steps of the reaction between $\bullet\text{OH}$ and CH_4 , given that the overall enthalpy change for the first and second steps is exothermic. Label the overall enthalpy change, ΔH , on your diagram.

[2]

- (c) $\bullet\text{OH}$ may be generated by Fenton's reagent, which is an aqueous mixture of hydrogen peroxide, H_2O_2 , and iron(II) sulfate, FeSO_4 . The reactions shown in equations 2 and 3 take place in the mixture.



- (i) Write the equation for the overall reaction.

..... [1]

- (ii) Using equations 2 and 3, deduce the role of Fe^{2+} in the overall reaction. Explain your reasoning.

.....

.....

..... [2]

- (iii) Fenton's reagent is used to generate $\bullet\text{OH}$ in the study of organic reactions.

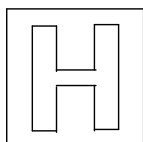
However, after a small amount of $\bullet\text{OH}$ is generated, "quenching" or stopping of the reaction progress is sometimes required.

Suggest a method of "quenching" the reaction, without changing the temperature.

.....

..... [1]

[Total: 19]



RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

17 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

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

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.

For Examiner's Use					
Section A		Section B		Total	
1	/ 20	(Circle the question you have answered)		/ 80	
2	/ 20	4	/ 20		
3	/ 20	5	/ 20		

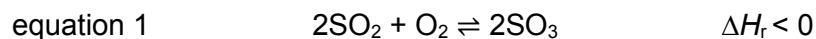
This document consists of **29** printed pages and **3** blank pages.

Section A

Answer **all** the questions in this section.

1 Contrails are the visible clouds that form in a line behind an aircraft during its flight.

(a) One of the reactions involved in the formation of contrails is shown in equation 1.



(i) Write the expression for the equilibrium constant, K_c , for equation 1, stating its units. [1]

(ii) At 450 °C, a sealed 1.00 dm³ flask is found to contain an equilibrium mixture of gases as shown in Table 1.1.

Table 1.1

	SO ₂	O ₂	SO ₃
amount / mol	0.500	0.100	4.60

Use these data to calculate K_c for the reaction in equation 1. [2]

(iii) Using information from **(a)(ii)**, calculate the total pressure, in MPa, of the gaseous mixture at equilibrium. Assume that the gases behave ideally. [1 MPa = 10⁶ Pa] [1]

(iv) Hence, calculate the equilibrium partial pressure, in MPa, of SO₃. [1]

(v) Calculate the amount of oxygen that must be added to the mixture to increase the amount of SO₃, at equilibrium, to 4.70 mol at the same temperature. [2]

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- (b)** Another sealed flask contains the same gaseous mixture in equation 1.

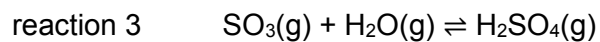
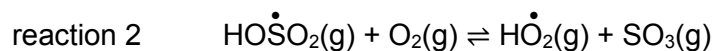
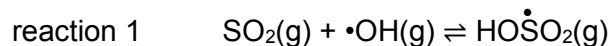
- (i) Explain how an increase in temperature affects the equilibrium amount of SO_2 . [2]
- (ii) The system is initially at equilibrium at $t = 0$ s. At time $= t_1$, the temperature of the system increases sharply. Equilibrium is re-established at time $= t_2$.

Sketch a labelled graph of both the forward and backward rates of the reaction against time. You may use f and b to label the forward and backward rates respectively. [2]

[illegible]

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- (c) Contrail formation depends on the proportion of H_2SO_4 produced in the exhaust gases of an airplane. The reactions to produce H_2SO_4 are shown below.



The higher the proportion of H_2SO_4 , the more contrails are formed.

Fig. 1.1 shows how ΔG_r^\ominus for reaction 1 varies with temperature, T , of the exhaust gases.

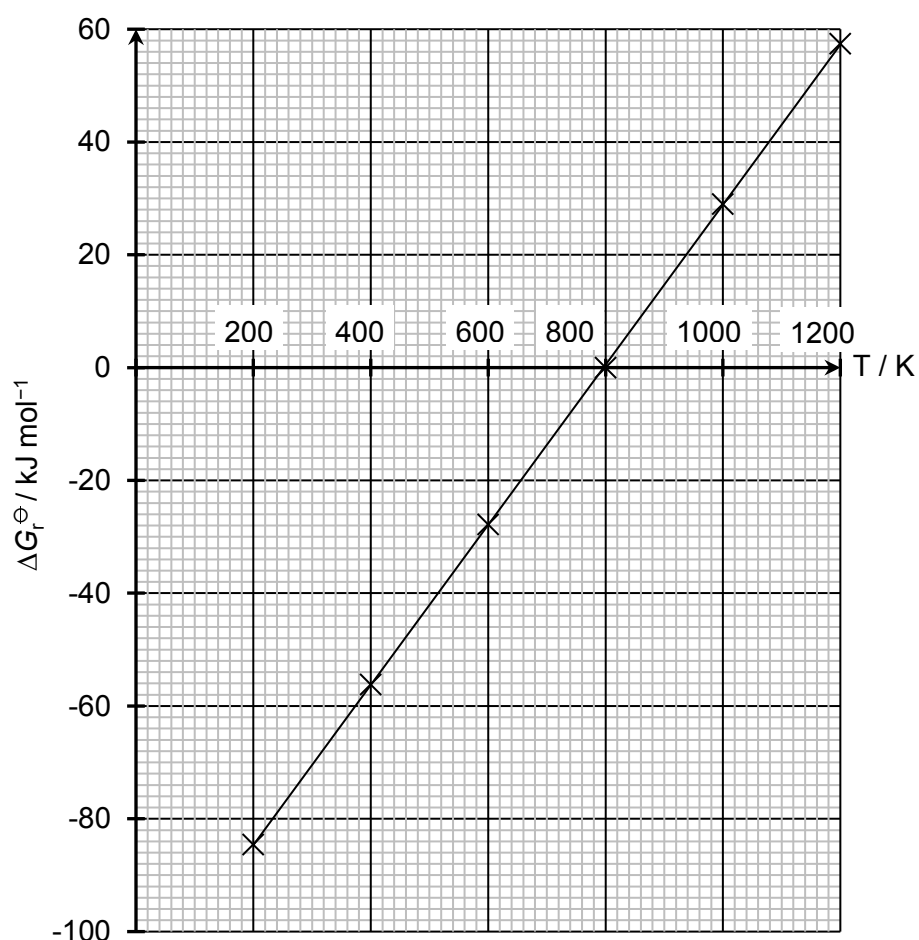


Fig. 1.1

- (i) State the minimum temperature at which reaction 1 is no longer spontaneous. [1]
- (ii) Explain, in terms of position of equilibrium, the effect of increasing temperature on the proportion of H_2SO_4 produced in the exhaust gases. [2]

- [illegible]

- (e) Liquefaction is the process by which gases are converted to liquids. Some gases can be liquefied at a given temperature by applying a sufficiently high pressure.

However, when the temperature is higher than the critical temperature, T_c , gases cannot be liquefied regardless of the pressure applied.

The table below shows the value of T_c for some gases.

Table 1.2

gas	formula	$T_c / ^\circ\text{C}$
carbon dioxide	CO ₂	31.0
steam	H ₂ O	374

- (i) Explain why above T_c , gases cannot be liquefied regardless of the pressure applied. [1]

- (ii) Explain why the critical temperature of steam is higher than that of carbon dioxide. [2]

[illegible]

[Total: 20]

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- 2 (a) (i) Define the term *standard enthalpy change of formation of a substance*. [1]
- (ii) Use the data from Table 2.1, together with data from the *Data Booklet*, to construct a Born-Haber cycle to calculate the standard enthalpy change of formation of solid sodium hydrogencarbonate, NaHCO_3 .

Table 2.1

	value / kJ mol^{-1}
lattice energy of sodium hydrogencarbonate, $\text{NaHCO}_3(\text{s})$	-656.0
standard enthalpy change of atomisation of $\text{Na}(\text{s})$	+107.5
standard enthalpy change of formation of gaseous hydrogencarbonate ion, $\text{HCO}_3^-(\text{g})$	-896.3

[4]

- (iii) The standard enthalpy change of solution of sodium hydrogencarbonate, NaHCO_3 , is $+18.7 \text{ kJ mol}^{-1}$.

Calculate the temperature change when 11.2 g of sodium hydrogencarbonate ($M_r = 84.0$) is fully dissolved in 100 cm^3 of water. [2]

- (iv) Given that the dissolution of sodium hydrogencarbonate is spontaneous at 298 K, state the sign of ΔS^\ominus for this reaction. Explain your reasoning without reference to any calculation. [1]
- (v) Suggest whether hydrogencarbonate ion or hydroxide ion would have the more exothermic standard enthalpy change of hydration. Explain your answer. [1]

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- (b) (i) Write an expression for the solubility product, K_{sp} , of copper(II) carbonate, stating its units. [1]

Equal volumes of 0.1 mol dm^{-3} lead(II) nitrate and 0.2 mol dm^{-3} copper(II) nitrate are mixed in a beaker.

Table 2.2 shows the numerical values of the solubility products, K_{sp} , of lead(II) carbonate and copper(II) carbonate at 298 K.

Table 2.2

substance	numerical value of K_{sp}
lead(II) carbonate	7.40×10^{-14}
copper(II) carbonate	1.40×10^{-10}

Solid sodium carbonate is gradually added into the beaker until the first precipitate is seen.

- (ii) With relevant calculations, show that lead(II) carbonate is the first precipitate to form. [2]

- (iii) Describe and explain what you would see when $\text{NH}_3(\text{aq})$ is added slowly to a solution containing $\text{Cu}^{2+}(\text{aq})$ ions, until $\text{NH}_3(\text{aq})$ is in excess.

Write equations for any reactions that occur. [4]

- (c) The continual increase in carbon dioxide emission has caused changes to marine ecosystems in the ocean.

Carbonic acid is formed when carbon dioxide is dissolved in water. The carbonic acid formed can further dissociate to give hydrogencarbonate ions and carbonate ions.

The mole fractions of H_2CO_3 , HCO_3^- and CO_3^{2-} are dependent on the pH of the solution, as shown in Fig. 2.1.

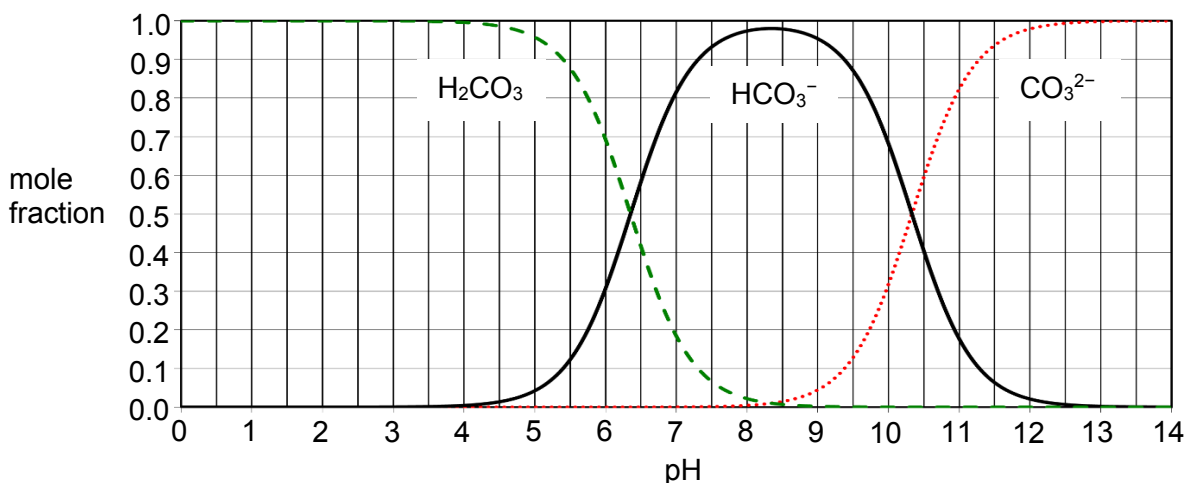


Fig. 2.1

- (i) A sample of water was analysed and the mole fraction of carbonate ion, CO_3^{2-} , was determined to be 0.05.

Use Fig. 2.1 to estimate the concentration of hydrogen ions present in the sample. [1]

- (ii) On Fig. 2.1, indicate with an 'x', the pK_a of HCO_3^- . Draw a construction line to show how you obtained your answer. [1]

- (iii) The composition of the shells of crustaceans is mainly made up of calcium carbonate.

Using the information in (c), suggest why it is increasingly difficult for crustaceans to build their shells as the emission of carbon dioxide increases. [2]

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[Total: 20]

- 3 (a)** Explain why 2-chloropropanoic acid is more acidic than 2-iodopropanoic acid. [2]

[illegible]

- (b)** Compound **R** can be synthesised from cyclohexanol in three steps as shown in Fig. 3.1.

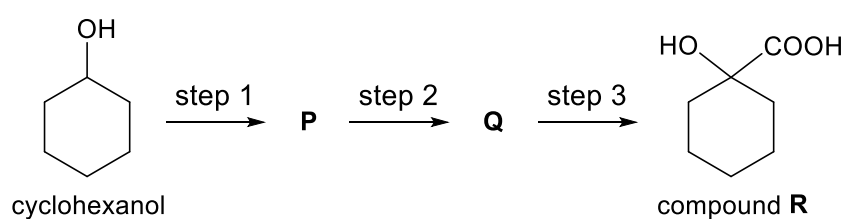


Fig. 3.1

- (i) Suggest structures for the organic compounds **P** and **Q**. [2]

- (ii) Suggest reagents and conditions for each of the steps 1, 2 and 3. [3]

This image shows a single sheet of white paper with ten evenly spaced horizontal dotted lines, typical of primary school handwriting practice paper. The lines are thin and black, extending across the full width of the page. There are no margins, text, or other markings on the paper.

- (c) Compound **S**, $C_8H_{12}O_4$, is a neutral, sweet-smelling oil. It does not give any orange precipitate with 2,4-DNPH.

Samples of compound **S** are reacted separately with

- cold alkaline $KMnO_4$ forming an organic compound **T**, $C_8H_{14}O_6$
- hot acidic $KMnO_4$ forming **U**, $C_2H_4O_2$, as the only organic product
- hot aqueous KOH forming organic compound **V**, C_2H_6O , and salt **W**, $C_4O_4H_2K_2$.

Compound **V** gives a yellow precipitate with alkaline aqueous iodine.

Suggest possible structures for **S**, **T**, **U**, **V** and **W**.

[5]

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- (d) The cycloaddition of azides, $R-N_3$, to alkynes, compounds with a $C\equiv C$ group, requires prolonged heating to form triazole. The mechanism of this cycloaddition reaction is shown in Fig. 3.2.

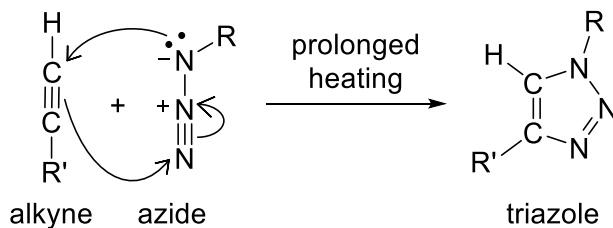


Fig. 3.2

Suggest why the alkyne requires prolonged heating to react with an azide which is a nucleophilic reagent. [1]

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- (e) Unlike straight-chain alkynes, cyclooctynes undergo cycloaddition with azides under mild conditions. This is useful in applications involving the tagging of living cells with fluorescent molecules as shown in Fig. 3.3.

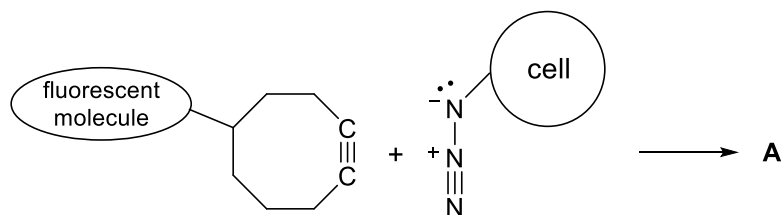


Fig. 3.3

- (i) Suggest the structure of product **A**. [1]
- (ii) Suggest a reason why cycloaddition can take place under mild conditions when cyclooctyne is used. [1]

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- (f) Cu(I) complexes were discovered to catalyse the cycloaddition reaction in Fig. 3.2, leading to the 2022 Nobel Prize for Chemistry.

Some steps of the copper-catalysed cycloaddition are shown in Fig. 3.4, where [Cu] represents a Cu-complex.

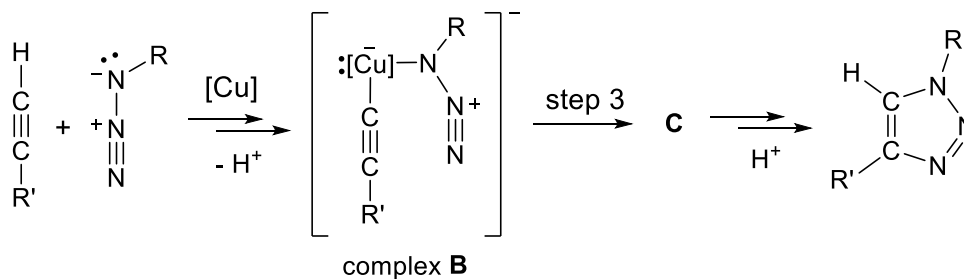


Fig. 3.4

- (i) The alkyne and azide are coordinated to Cu in complex **B**.

Explain why in complex **B**,

- ① the azide becomes a stronger electrophile;
- ② the alkyne is more susceptible to electrophilic attack.

[2]

- (ii) In step 3, the formation of compound **C** from complex **B** takes place in a single step.
- An electron pair moves from Cu to form a Cu–C π bond.
 - An electron pair moves from the alkyne $\text{C}\equiv\text{C}$ to the azide to form a new C–N bond.
 - A strained 6-membered ring is formed.

On Fig. 3.4, draw three curly arrows on complex **B** to show the mechanism of step 3. [2]

- (iii) Suggest the structure of compound **C**. [1]

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[Turn Over

Section B

Answer **one** question from this section.

- 4 (a) Explain why an aqueous solution of Cu^{2+} ions is coloured while an aqueous solution of Zn^{2+} ions is colourless. [4]

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- (b) Bromine is a stronger oxidising agent than iodine.

Suggest a simple chemical reaction that can be carried out to support this statement.
Write relevant equations for the reactions that occur. [3]

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(c) Fig. 4.1 shows a voltaic cell made up of $\text{Cu}^{2+} / \text{Cu}$ and $\text{VO}_2^+ / \text{VO}^{2+}$ half-cells.

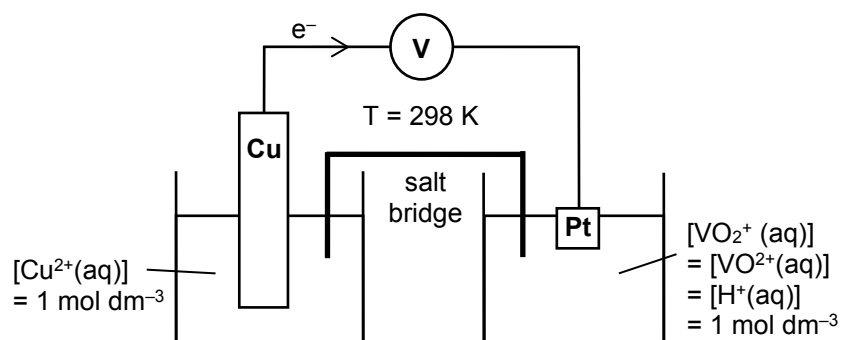


Fig. 4.1

- (i) Define the term standard cell potential, $E^{\ominus}_{\text{cell}}$. [1]
- (ii) Write the overall equation and calculate ΔG^{\ominus} for this voltaic cell. [2]
- (iii) Use of the *Data Booklet* is relevant to this question.

Suggest the effect on E_{cell} if the following changes are imposed:

- ① Solid sodium carbonate is added to the $\text{Cu}^{2+} / \text{Cu}$ half-cell.
- ② Water is added to the $\text{VO}_2^+ / \text{VO}^{2+}$ half-cell. [4]

[illegible]

Redox flow batteries are rechargeable devices which are used for energy storage and the electrolytes are pumped through an electrochemical cell to transform chemical energy into electrical energy.

The zinc-bromine flow battery (ZBFB) is a widely used redox flow battery where the electrolyte containing aqueous zinc bromide is continuously pumped through.

Fig. 4.2 shows the schematic diagram of a ZBFB.

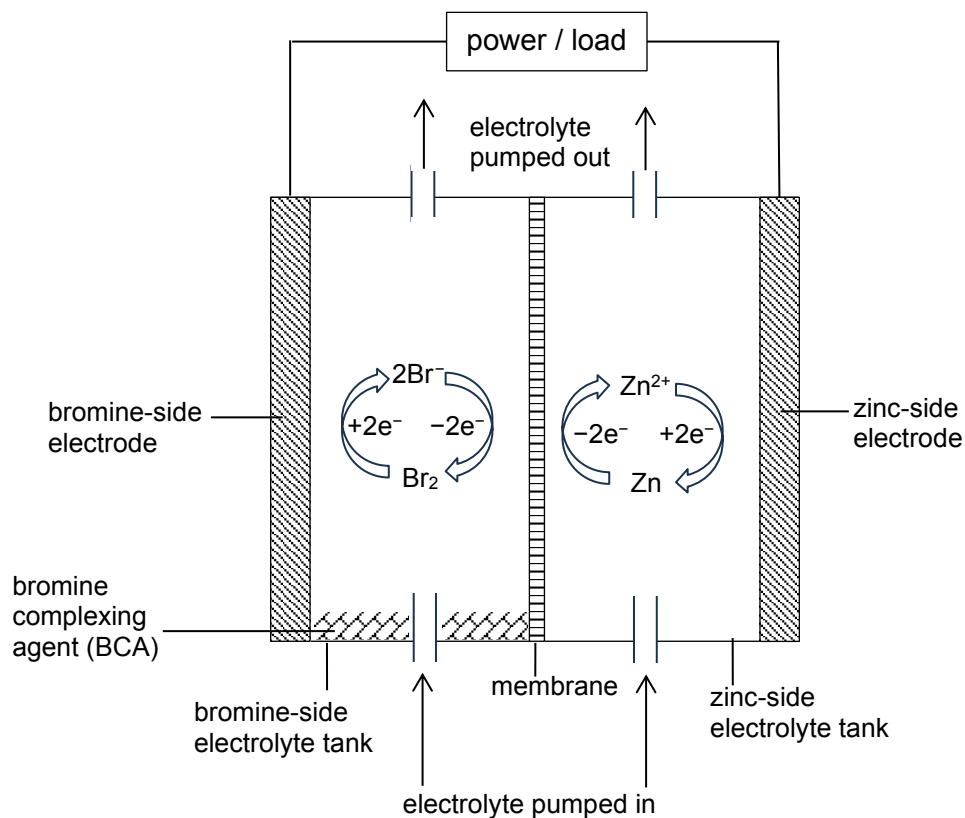


Fig. 4.2

- (d) The membrane serves to keep the two electrolytes separate. Explain why the membrane needs to allow selected ions to flow through. [1]

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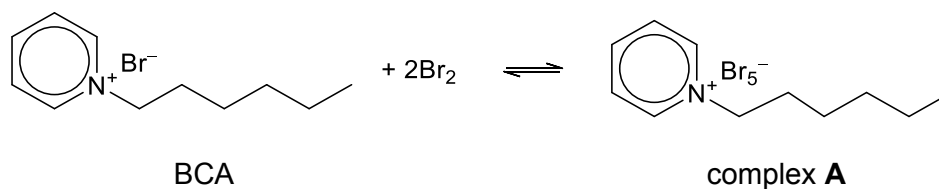
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- (e)** During the charging process, bromine is produced at the positive electrode.

A bromine complexing agent (BCA) is added to the bromine-side electrolyte tank.

BCA reacts with bromine as shown in the following equation.



- (i) Suggest why it is necessary to add BCA to the bromine-side electrolyte tank. [1]

- (ii) Explain why complex **A** is immiscible with the aqueous electrolyte. [2]

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- (f) During the charging process, zinc is deposited on the negative electrode.

Calculate the time, in hours, needed to deposit 1.00 kg of zinc on the electrode given that the charging current is 32.0 A and the charging process has an efficiency of 80.0%. [2]

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[Total: 20]

5 This question is about nickel and its complexes.

(a) Briefly explain why the electrical conductivity of Ni is higher than that of s-block elements. [1]

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(b) Nickel is widely used as a heterogenous catalyst in the reduction of alkenes.

(i) State the feature of Ni that allows it to act as a heterogenous catalyst. [1]

(ii) Explain clearly how Ni increases the rate of the reaction. [3]

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[illegible]

- (d) Nickel forms many complexes with a co-ordination number of 4 and 6 which exist in either tetrahedral, square planar or octahedral geometry. Fig. 5.2 shows the relative energy levels of d-orbitals in octahedral and square planar geometry.

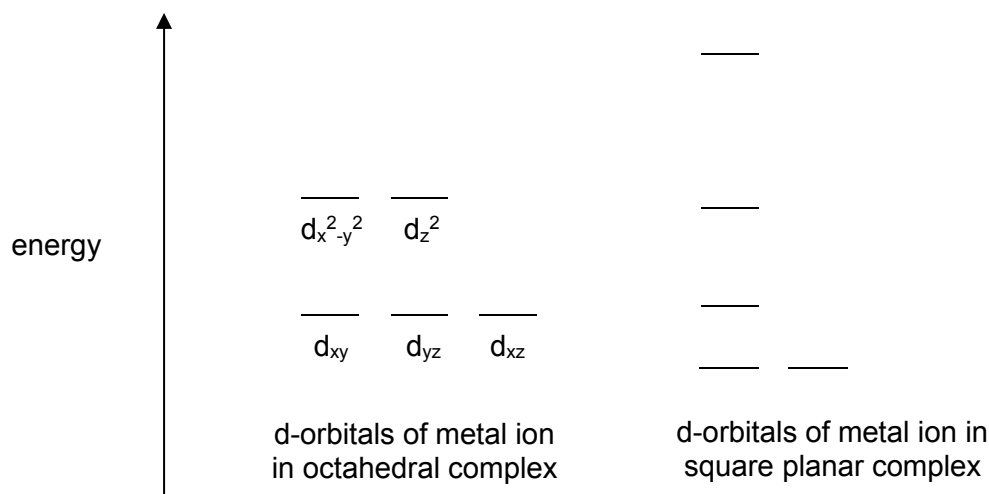


Fig. 5.2

- (i) Write the electronic configuration of Ni^{2+} ion. [1]
- (ii) With reference to Fig. 5.2, explain the relative energy levels of the d-orbitals in an octahedral complex. [2]
- (iii) By considering your answer in (d)(ii), state which 3d-orbital has the highest energy level in a square planar complex. [1]

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

[illegible]

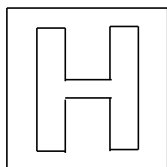
[illegible]

CANDIDATE
NAME

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CLASS

24S0



RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CHEMISTRY

9729/04

Paper 4 Practical

21 August 2024

2 hours 30 minutes

Do NOT turn over the Question Booklet until you are told to do so.

READ THESE INSTRUCTIONS FIRST.

Write your name and class on the space provided when instructed to do so.
Give details of the practical shift and laboratory where appropriate, in the space provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The number of marks is given in brackets [] at the end of each question or part question.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 23 and 24.

Shift	
Laboratory	
Bench Number	

For Examiner's Use	
Question	Marks
1	/ 15
2	/ 13
3	/ 14
4	/ 13
Total	/ 55

This document consists of **21** printed pages and **3** blank pages.

Answer **all** the questions in the spaces provided.

1 Determination of the molar enthalpy change of solution, ΔH_{sol} , of FA 1

FA 1 is solid anhydrous magnesium sulfate, MgSO_4 .

When added to water, **FA 1** dissolves and the temperature of the solution rises. Some of the heat energy released from the dissolution of **FA 1** is absorbed by the calorimeter. To determine the molar enthalpy change of solution, ΔH_{sol} , of **FA 1**, you will first need to determine the heat capacity of the calorimeter.

The heat capacity of the calorimeter, C_{cal} , is the amount of heat energy required to change its temperature by 1°C . The calorimeter used in this experiment comprises two polystyrene cups supported by a 250 cm^3 glass beaker.

(a) (i) Determination of the heat capacity of the calorimeter, C_{cal}

When hot water is added to the calorimeter containing room temperature water, heat energy from the hot water is used to raise the temperature of the calorimeter and the room temperature water. To determine the heat capacity of the calorimeter, C_{cal} , you will measure the maximum temperature rise when hot water is added to room temperature water in the calorimeter.

You are to carry out the experiment and record all values of temperature, T , to an appropriate level of precision in Table 1.1.

Procedure

1. Place a polystyrene cup inside a second polystyrene cup and place both cups in a 250 cm^3 glass beaker.
2. Use a 50 cm^3 measuring cylinder to transfer 50 cm^3 of room temperature water into the polystyrene cup.
3. Carefully stir the water in the polystyrene cup with a thermometer. Read and record the temperature of the room temperature water, T_1 . Leave the thermometer in the polystyrene cup.
4. Use a 100 cm^3 glass beaker to collect approximately 60 cm^3 of hot water from the hot water dispenser.

Note: Use a paper towel to hold the hot apparatus. Handle all hot apparatus with care.

5. Use the 50 cm^3 measuring cylinder to measure 50 cm^3 of hot water from the 100 cm^3 glass beaker. Place another thermometer into the measuring cylinder. Read and record the temperature of the hot water, T_2 . Remove the thermometer from the hot water.
6. **Immediately** add the hot water from the measuring cylinder to the room temperature water in the polystyrene cup. Carefully stir the combined water using the thermometer and record the maximum temperature reached, T_3 .
7. Empty the polystyrene cup and dry it using the paper towel.

Table 1.1

temperature of room temperature water, $T_1 / ^\circ\text{C}$	
temperature of hot water, $T_2 / ^\circ\text{C}$	
maximum temperature of combined water, $T_3 / ^\circ\text{C}$	

- (ii) Calculate the heat energy lost by the hot water and the heat energy gained by the room temperature water using the values you obtained in (a)(i).

Assume that the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, and that the density of water is 1.00 g cm^{-3} .

heat energy lost by the hot water =

heat energy gained by the room temperature water =
[2]

- (iii) The heat energy absorbed by the calorimeter during the experiment can be determined from the following equation.

Heat energy absorbed by the calorimeter
= heat energy lost by hot water – heat energy gained by room temp water

Calculate the heat energy absorbed by the calorimeter and hence determine the heat capacity of the calorimeter, C_{cal} .

Use the values you obtained from (a)(i) and (a)(ii).

heat energy absorbed by the calorimeter =

heat capacity of calorimeter, C_{cal} =
[2]

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(b) (i) Determination of the molar enthalpy change of solution, ΔH_{sol} , of FA 1

In this experiment, you will measure the temperature of the water in a polystyrene cup at regular time intervals, before and after **FA 1** is added. You will analyse your results graphically to obtain an accurate value for the temperature change caused by the dissolution of **FA 1**.

You will use this value to calculate the total heat change, q , of the solution and the calorimeter, and hence determine the molar enthalpy change of solution, ΔH_{sol} , of **FA 1**.

In the space provided on page 6, prepare tables in which to record for your experiment:

- all weighings to an appropriate level of precision
- all values of temperature, T , to an appropriate level of precision
- all values of time, t , recorded to 0.5 min.

It is important that you measure each temperature at the specified time.

Procedure

1. Weigh the capped container containing solid **FA 1**. Record the mass in your table on page 6.
2. Place a polystyrene cup inside a second polystyrene cup and place both cups in a 250 cm³ glass beaker.
3. Use a measuring cylinder to transfer 100 cm³ of room temperature water into the polystyrene cup.
4. Carefully stir the water in the polystyrene cup with the thermometer. Read and record the temperature, T . Start the stopwatch ($t = 0.0$ min). The stopwatch must be left to run for the rest of the experiment.
5. Continue to stir the water in the polystyrene cup. Read and record T every 0.5 minute for two minutes.
6. At **exactly** 2.5 minutes, transfer all the solid **FA 1** to the polystyrene cup. Stir the solution but do not read T .
7. Continue to stir the solution. Read and record T at $t = 3.0$ min and every 0.5 min until $t = 8.0$ min.
8. Reweigh the empty capped container. Record this mass in your table on page 6.

Results

[3]

- (ii) Plot a graph of temperature, T , on the y-axis against time, t , on the x-axis, on the grid in Fig. 1.1.

Draw a best-fit straight line taking into account all of the points before $t = 2.5$ min.

Draw another best-fit straight line taking into account all of the points after the temperature of the solution has started to fall steadily.

Extrapolate (extend) both lines to $t = 2.5$ min.

[3]

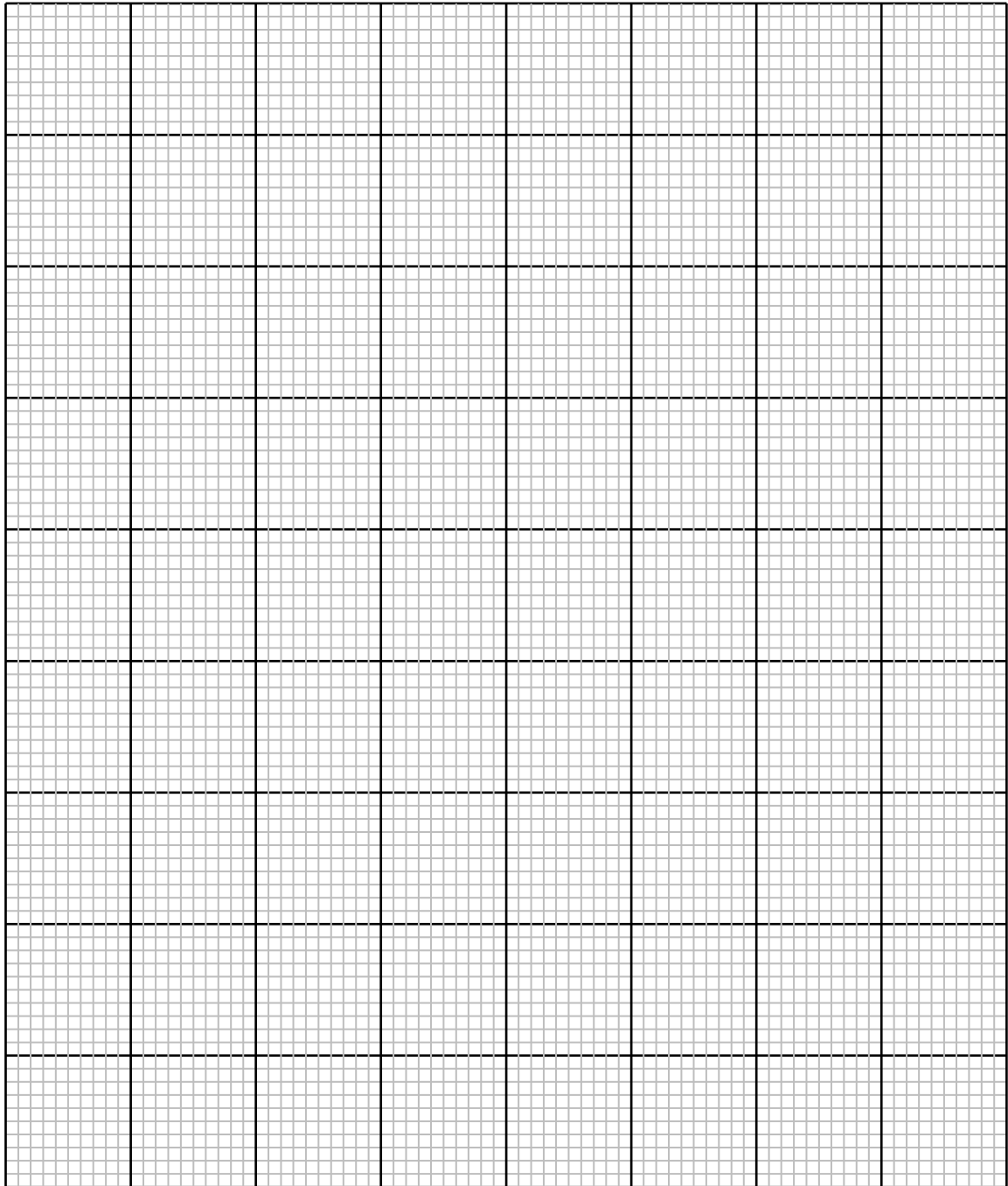


Fig. 1.1

- (iii) From your graph, read the minimum temperature, T_{\min} , and the maximum temperature, T_{\max} , at $t = 2.5$ min. Record these values in the spaces below.

Calculate the temperature change, ΔT , at $t = 2.5$ min.

$$T_{\min} = \dots\dots\dots$$

$$T_{\max} = \dots\dots\dots$$

$$\Delta T = \dots\dots\dots$$

[1]

- (iv) Calculate the total heat change, q , of the solution and the calorimeter as your sample of **FA 1** dissolved.

Use the values you obtained from (a)(iii) and (b)(iii).

Assume that the specific heat capacity of the solution is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, and that the density of the solution is 1.00 g cm^{-3} .

If you were unable to answer (a)(iii), you may assume the numerical value of the heat capacity of calorimeter, C_{cal} is 100 (this is not the correct value).

$$\text{total heat change, } q = \dots\dots\dots [1]$$

- (v) Determine the molar enthalpy change of solution, ΔH_{sol} , of **FA 1**.

Use the values you obtained from (b)(i) and (b)(iv).

Include the sign of ΔH_{sol} in your answer.

[A_r : Mg, 24.3 S, 32.1 O, 16.0]

$$\Delta H_{\text{sol}} = \dots\dots\dots [2]$$

(c) Heat loss to the surroundings is not accounted for in (a)(i).

Explain how this error affects the ΔH_{sol} of **FA 1** obtained in (b)(v).

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..... [1]

[Total: 15]

2 Qualitative Analysis

(a) Organic Chemistry Analysis

FA 2 is an aqueous solution of an organic compound, **W**, which contains two different functional groups.

You will perform tests to identify the functional groups in **W** and hence deduce its possible structure.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

Test and identify any gases evolved.

If there is no observable change, write **no observable change**.

Preparation of hot water bath

Fill a 250 cm³ glass beaker with about 150 cm³ of water from the water dispenser. Use this beaker of hot water for tests **1** and **2** in Table 2.1.

(i) Carry out the following tests. Carefully record your observations in Table 2.1.

Table 2.1

tests		observations
1	Add 1 cm depth of FA 2 into a clean test-tube. To this test-tube add 10 drops of sodium hydroxide followed by iodine solution, dropwise, until a permanent orange colour is present. Warm the test-tube in the beaker of hot water for 2 minutes.	
2	Add 1 cm depth of FA 2 into a clean test-tube. Add 8 drops of Fehling's solution. Warm the test-tube in the beaker of hot water for 3 minutes.	
3	Test solution FA 2 with Universal Indicator paper.	

[3]

- (ii) The molecular formula of **W** is $\text{C}_3\text{H}_6\text{O}_2$. Using your observations in Table 2.1, draw the displayed formula for **W**.

[1]

(b) Inorganic Chemistry Analysis

FA 3 is an aqueous solution which contains two cations listed in the *Qualitative Analysis Notes*. **FA 3** also contains nitrate ions and another anion listed in the *Qualitative Analysis Notes*.

You will perform tests to identify the two cations and the unknown anion in **FA 3**.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

Test and identify any gases evolved.

If there is no observable change, write **no observable change**.

- (i) Carry out the following tests. Carefully record your observations in Table 2.2.

Table 2.2

tests		observations
1	<p>Using a 10 cm³ measuring cylinder, add 2 cm³ of FA 3 into a clean boiling tube.</p> <p>Using another 10 cm³ measuring cylinder, measure out 7 cm³ of aqueous sodium hydroxide. Slowly with shaking, add this completely to FA 3.</p> <p>Stir the contents of the boiling tube with a glass rod.</p> <p>Filter the mixture into a clean test-tube. The filtrate will be used for test 4.</p> <p>While waiting, proceed to tests 2 and 3.</p>	
2	<p>Add 1 cm depth of FA 3 into a clean test-tube.</p> <p>Add 2 cm depth of aqueous sodium carbonate.</p>	

tests		observations
3	<p>Add 1 cm depth of FA 3 into a clean test-tube.</p> <p>Add 1 cm depth of aqueous silver nitrate.</p> <p>Filter the mixture and discard the filtrate. Wash the residue by pouring deionised water through it. Discard the washings.</p> <p>Place the filter funnel containing the residue into a test-tube containing 1 cm depth of dilute nitric acid.</p> <p>Carefully add aqueous ammonia to the filter funnel until it covers the residue.</p> <p>The filtrate will collect in the test-tube containing the dilute nitric acid.</p>	
4	<p>Add 1 cm depth of the filtrate from test 1 into a clean test-tube.</p> <p>Add dilute sulfuric acid drop-wise, until in excess.</p>	

[6]

- (ii) Identify the two cations and the unknown anion in **FA 3** and state the evidence for each cation and the anion by completing Table 3.2.

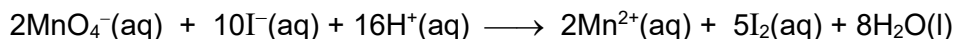
Table 3.2

cation	evidence
anion	evidence

[3]

[Total: 13]

- 3 The reaction between potassium manganate(VII) and excess acidified potassium iodide is shown.



The iodine liberated reacts with sodium thiosulfate solution.



In this experiment, you are required to determine the concentration of potassium manganate(VII) in solution **P**. You are **not** provided with solution **P**.

FA 4 is $0.100 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

FA 5 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4 .

FA 6 is $0.500 \text{ mol dm}^{-3}$ potassium iodide, KI .

FA 7 is a diluted solution of **P**.

Starch indicator.

- (a) (i) You are to titrate **FA 7** with **FA 4** using starch as indicator.

Titration of FA 7 with FA 4

1. Fill the burette with **FA 4**.
2. Pipette 25.0 cm^3 of **FA 7** into a 250 cm^3 conical flask.
3. Using separate measuring cylinders, transfer to the conical flask
 - 25.0 cm^3 of **FA 5**,
 - 20.0 cm^3 of **FA 6**.
4. Titrate the liberated iodine with **FA 4** until the solution is pale yellow. Then add 6 drops of starch solution and carry on the titration until the deep blue colour is just discharged. **Swirl** the reaction mixture **continuously** during the titration.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat the titration until at least two consistent results are obtained.

Titration results

[3]

- (ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{\text{FA 4}}$, to be used in your calculations. Show clearly how you obtained this value.

$V_{\text{FA 4}} = \dots\dots\dots$ [3]

(b) Calculations

- (i) Calculate the amount of iodine produced in the reaction between 25.0 cm³ of **FA 7** and 20.0 cm³ of **FA 6**.

amount of iodine = $\dots\dots\dots$ [2]

- (ii) Calculate the amount of KMnO_4 which reacted to produce the amount of I_2 determined in (i).

amount of $\text{KMnO}_4 = \dots\dots\dots$ [1]

- (iii) **FA 7** is a diluted solution of **P**, in which 34.50 cm^3 of **P** was made up to 250 cm^3 with deionised water in a graduated flask.

Calculate the molar concentration of KMnO_4 in solution **P**.

molar concentration of $\text{KMnO}_4 = \dots\dots\dots$ [2]

- (iv) Calculate the mass of KMnO_4 needed to prepare 1.00 dm^3 of **P**.

[A_r : K, 39.1 Mn, 54.9 O, 16.0]

mass of $\text{KMnO}_4 = \dots\dots\dots$ [1]

- (c) (i) Solution **P** was actually prepared by dissolving 21.0 g of KMnO_4 in 1.00 dm^3 of solution.

Calculate the difference between the actual value and your answer to **(b)(iv)** as a percentage of the actual value.

percentage = $\dots\dots\dots$ [1]

- (ii) A student suggested that the experiment would be more accurate if a burette was used to measure the volume of **FA 6**.

State and explain whether you agree with the student.

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.....[1]

[Total: 14]

4 Planning

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ reacts with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ to give the purple complex ion, $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$, as shown in equation 4. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is abbreviated as *en*.



It is possible to determine the concentration of a solution of $[\text{Ni}(\text{en})_3]^{2+}$ using spectrometry.

A series of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ solutions of known concentrations are prepared and treated with a large excess of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ to form $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$ of different concentrations. For each concentration of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$, a spectrometer is used to measure the absorbance of light by $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$. Absorbance is directly proportional to the concentration of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$.

A graph of absorbance against concentration of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$ is then plotted. This graph is known as a calibration line. By comparing the absorbance of a solution of unknown concentration with the calibration line, the concentration of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$ in the unknown solution can be determined.

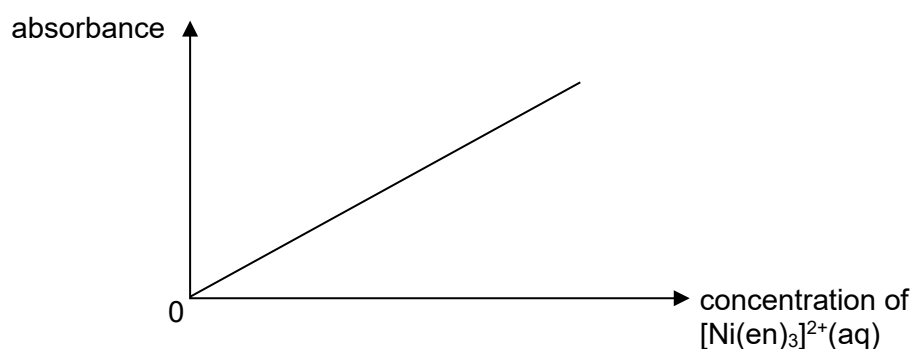


Fig 4.1

- (a) Explain why $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ must be used in large excess in the preparation of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$ to obtain the calibration line.

.....

[1]

- (b)** Using the information given above, write a plan to prepare 100 cm³ each of the following solutions.

solution	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} / \text{mol dm}^{-3}$
1	1.00×10^{-3}
2	8.00×10^{-4}
3	6.00×10^{-4}
4	4.00×10^{-4}
5	2.00×10^{-4}

You may assume that you are provided with:

- **FA 8**, $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$;
- the apparatus normally found in a school or college laboratory.

..... [2]

To determine a value for K_c , 25.0 cm³ each of $2.00 \times 10^{-3} \text{ mol dm}^{-3} [\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and $6.00 \times 10^{-3} \text{ mol dm}^{-3} \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ are mixed to produce a solution of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$. The absorbance of this solution is then measured. Using the calibration line in Fig 4.1, the concentration of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$ can be determined. This can be used to calculate the concentrations of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ in the equilibrium mixture and hence K_c .

The relationship between K_c and temperature in kelvin, T , is represented by the following equation.

$$\ln K_c = -\frac{\Delta H}{R} \left(\frac{1}{T} \right) + \frac{\Delta S}{R}$$

R is the molar gas constant with a value of $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

ΔH is the enthalpy change of reaction.

ΔS is the entropy change of reaction.

A plot of $\ln K_c$ against $1/T$ can then be used to graphically determine ΔH and ΔS .

- (c) Plan an investigation to determine the effect of temperature, T , on the equilibrium constant, K_c , of the reaction between $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$.

You may assume that you are provided with:

- **FA 8**, $2.00 \times 10^{-3} \text{ mol dm}^{-3} [\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$;
- **FA 9**, $6.00 \times 10^{-3} \text{ mol dm}^{-3} \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$;
- a spectrometer;
- the apparatus normally found in a school or college laboratory.

In your plan you should include:

- an outline of how you would prepare a solution of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$,
- an outline of how you would determine the concentration of $[\text{Ni}(\text{en})_3]^{2+}(\text{aq})$ in the solution at different temperatures,
- brief but specific details of how the concentrations, in mol dm^{-3} , of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ in the equilibrium mixture can be determined, and how you would use these concentrations to determine K_c for one of your chosen temperatures.

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- (d) (i) Given that the reaction between $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq})$ is exothermic, sketch a graph you would expect to obtain on the axes in Fig 4.2.

Explain your answer.



Fig 4.2.

Explanation

.....

[2]

- (ii) Describe how you would use your graph in 4(d)(i) to determine values for ΔH and ΔS .

.....

[2]

[Total: 13]

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Qualitative Analysis notes*[ppt. = precipitate]***(a) Reactions of aqueous cations**

cation	reaction with	
	NaOH(aq)	NH ₃ (aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	ammonia produced on heating	–
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.
chromium(III), Cr ³⁺ (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	blue-ppt. soluble in excess giving dark blue solution
iron(II), Fe ²⁺ (aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe ³⁺ (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

<i>anion</i>	<i>reaction</i>
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$)
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$)
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$)
nitrate, $\text{NO}_3^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; NO liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown NO_2 in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	SO_2 liberated on warming with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

(c) Tests for gases

<i>gas</i>	<i>test and test result</i>
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

<i>halogen</i>	<i>colour of element</i>	<i>colour in aqueous solution</i>	<i>colour in hexane</i>
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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