

RAFFLES INSTITUTION
2022 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/02

Paper 2 Structured Questions

14 September 2022

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	/ 19
2	/ 20
3	/ 19
4	/ 17
Total	/ 75

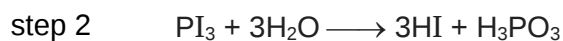
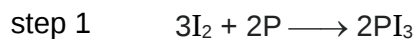
This document consists of **24** printed pages and **4** blank pages.

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

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1 This question is about the compounds of iodine and their reactions.

(a) Hydrogen iodide is a primary source of iodine in chemical reactions. It can be synthesised from iodine via the following two steps.



Given that 65 cm^3 of HI gas is collected at standard temperature and pressure, calculate the mass of iodine reacted.

[2]

(b) (i) Explain the trend and variation in the boiling points of the hydrogen halides shown in the table below.

hydrogen halide	HF	HCl	HBr	HI
boiling point / °C	+20	-85	-67	-35

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..... [2]

- (ii) Describe and explain the trend in the thermal stability of HCl , HBr and HI .

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..... [2]

- (c) Iodate(V) ion, IO_3^- , is commonly used as an oxidising agent in chemical reactions.

- (i) Draw a 'dot-and-cross' diagram of IO_3^- .

[1]

- (ii) With reference to the Valence Shell Electron Pair Repulsion theory, state and explain the shape and bond angle about the iodine atom in IO_3^- .

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..... [2]

Both iodate(V) and iodide ions can be obtained via the disproportionation of iodine under alkaline conditions.

- (iii) Using oxidation numbers, or otherwise, construct a balanced chemical equation for the disproportionation of iodine under alkaline conditions.

..... [1]

- (d) IO_3^- can be converted to periodic acid, HIO_4 .

HIO_4 can be used to split alcohols with two adjacent hydroxy groups, such as glycol **A**.

Fig. 1.1 shows the splitting of glycol **A** by HIO_4 to form ethanal and butanone, via an intermediate **B**.

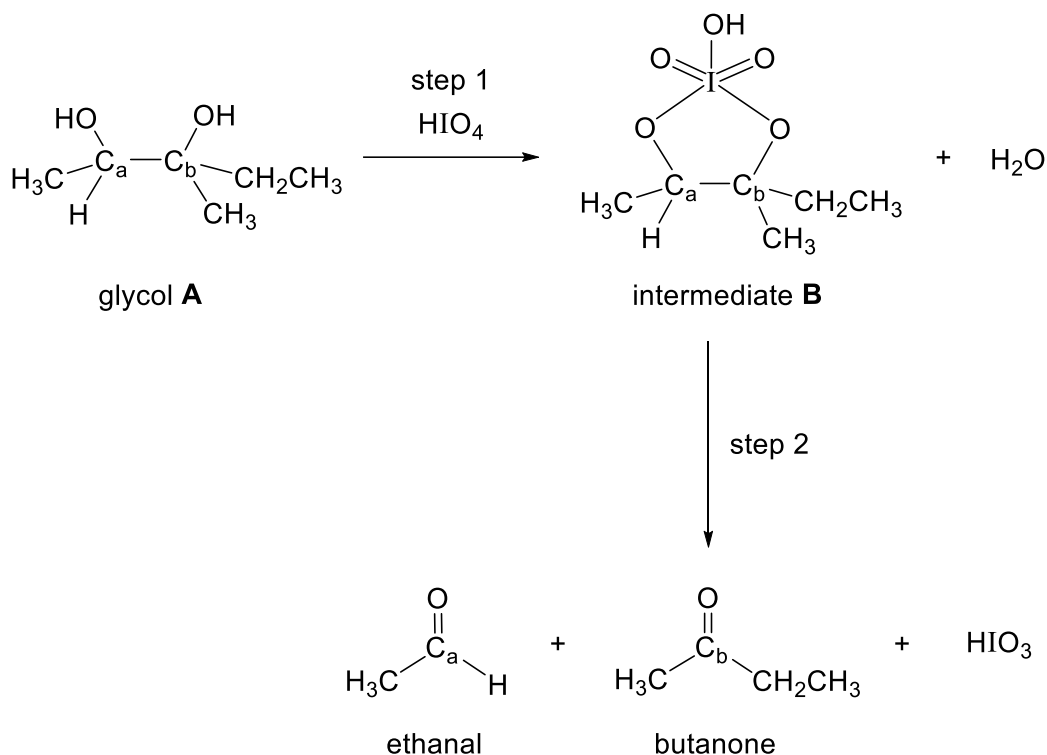


Fig. 1.1

- (i) On intermediate **B** in Fig. 1.1, draw three curly arrows to indicate the movement of electron pairs for step 2. [1]
- (ii) By considering the hybridisation of the atoms, compare the $\text{C}_a\text{--H}$ bond strength in glycol **A** and in ethanal. Explain your answer.

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..... [2]

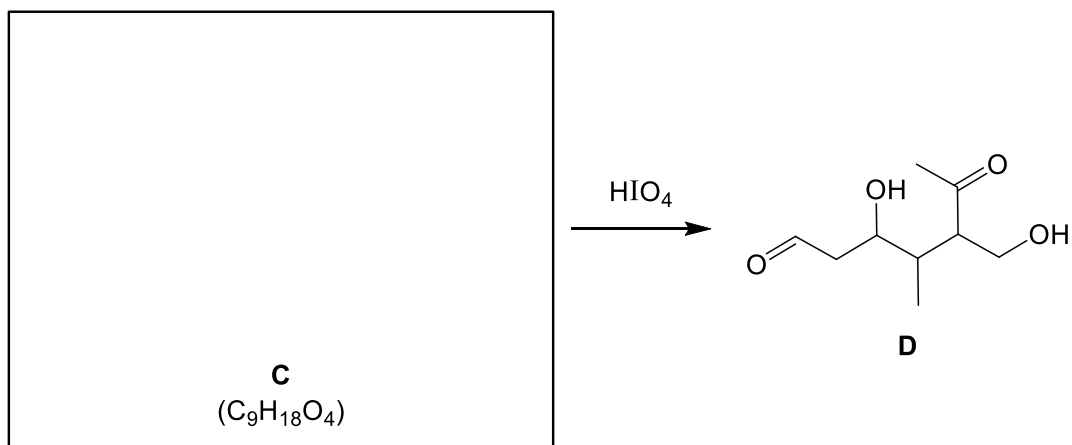
- (iii) Draw a labelled diagram to show all the valence orbitals of C_a and O in ethanal and how they overlap to form the C_a=O bond.

Assume that the O atom in ethanal is sp² hybridised.

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[2]

- (iv) Compound **C** reacts with HIO₄ to form compound **D** as shown below.



Draw the skeletal formula of compound **C** in the box provided.

[1]

- (v) Butanone reacts with HCN in the presence of trace amount of KOH.

Describe the mechanism for this reaction, showing all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

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[3]

[Total: 19]

- 2 Nitrogen dioxide, NO_2 , is a highly reactive gas due to the presence of an unpaired electron on the nitrogen atom.

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- (a) (i) State three basic assumptions of the kinetic theory as applied to an ideal gas.

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..... [2]

- (ii) Fig. 2.1 shows how $\frac{pV}{T}$ varies with pressure for 1 mol of ideal gas and 1 mol of NO_2 at T_1 K.

On Fig. 2.1, sketch a graph to show how $\frac{pV}{T}$ varies with pressure for 1 mol of NO_2 at a higher temperature of T_2 K. Label your graph as **(a)(ii)** and explain your answer.

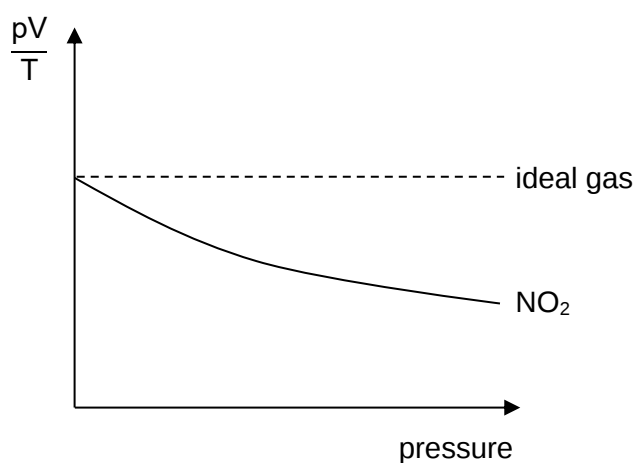


Fig. 2.1

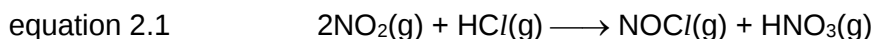
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..... [2]

- (b) Nitrogen dioxide undergoes the following gas phase reaction with hydrogen chloride, as shown in equation 2.1.



To study the kinetics for this reaction, three separate experiments were carried out in a vessel of fixed volume at a constant temperature of 500 K. The initial concentrations of NO_2 and HCl are shown in Table 2.1.

Table 2.1

experiment	initial $[\text{NO}_2]$ / mol dm^{-3}	initial $[\text{HCl}]$ / mol dm^{-3}
1	1.00	0.05
2	0.50	0.05
3	0.50	0.01

To monitor the progress of the reaction for each experiment, the total pressure in the vessel was measured at regular time intervals and the corresponding concentrations of NOCl were calculated.

Fig. 2.2 shows how the concentration of NOCl varies with time for experiments 1 and 2.

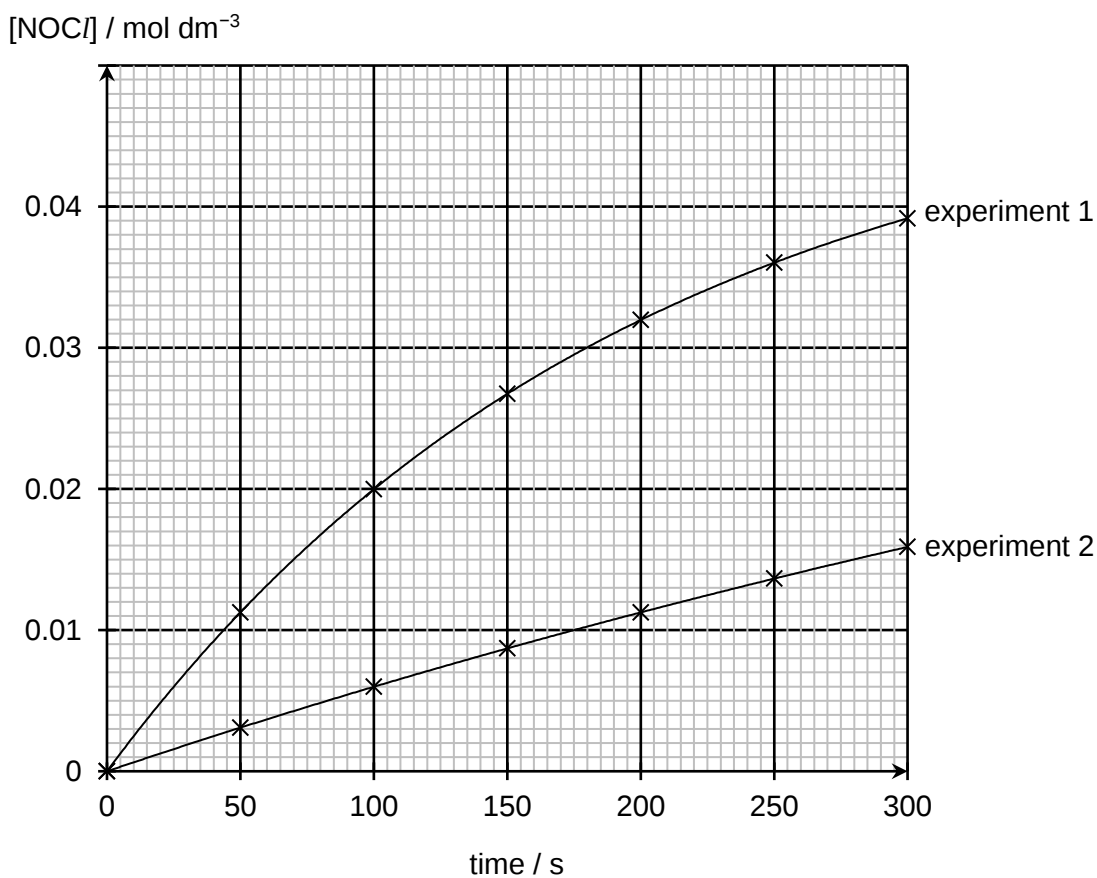


Fig. 2.2

- (i) With reference to Fig. 2.2, calculate the mole fraction of NOCl present in the vessel for experiment 1 at $t = 200$ s.

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use*

[2]

- (ii) Calculate the total pressure, in Pa, in the vessel for experiment 1 at $t = 200$ s.
You may assume that all the gases behave ideally.

[2]

- (iii) Using Fig. 2.2, determine the initial rate of reaction for experiments 1 and 2.
Hence, deduce the order of reaction with respect to NO_2 .

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use

[2]

- (iv) State the final concentration of NOCl in the vessel for experiment 1 if the reaction were to proceed to completion.

..... [1]

- (v) Hence, determine the order of reaction with respect to HCl .

Show your working, including construction lines on Fig. 2.2.

[1]

- (vi) The half-life of the reaction in experiment 2 was found to be 540 s.

With reference to Table 2.1, suggest how the half-life of the reaction in experiment 3 will compare to that of experiment 2. Explain your answer.

.....

 [2]

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- (c) N_2O_4 can undergo dissociation to form NO_2 , which then reacts with ethene to form 1,2-dinitroethane. The reaction mechanism consists of three steps as shown in Fig. 2.3.

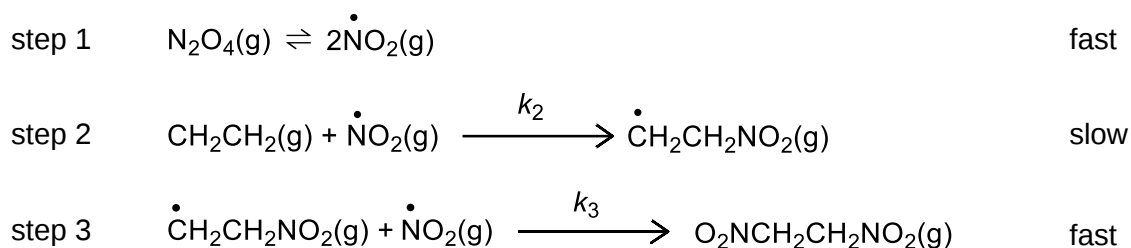


Fig. 2.3

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

..... [1]

- (ii) Name the type of reaction occurring in (c)(i).

..... [1]

- (iii) The dissociation of N_2O_4 in step 1 of the mechanism rapidly reaches equilibrium due to the use of solid platinum which acts as a heterogeneous catalyst.

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use

Outline the mode of action of the platinum catalyst in the dissociation of N_2O_4 .

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..... [2]

- (iv) The equilibrium constant for step 1 of the mechanism is K_c .

Write an expression for $[\text{NO}_2]$ in terms of K_c .

[1]

- (v) Using your answer in (c)(iv) and the mechanism in Fig. 2.3, write the overall rate equation for the reaction.

[1]

[Total: 20]

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- 3 COVID-19 is an illness caused by the virus SARS-CoV-2, which was first identified amid an outbreak of respiratory illness cases in 2019.

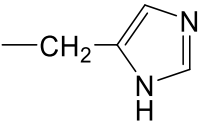
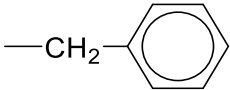
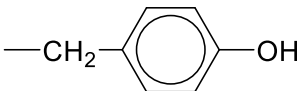
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In November 2021, a new Omicron variant was found to be the most transmissible variant compared to the previous variants, such as the Delta variant.

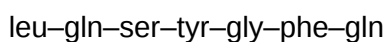
- (a) The differences in the transmissibility of the variants are due to their varying amino acid sequences in a specific region **X** of their peptide chains.

Some of the amino acids present in the variants are listed in Table 3.1.

Table 3.1

name	abbreviation	formula of side chain (R in R-CH(NH ₂)CO ₂ H)
arginine	arg	
glutamine	gln	-CH ₂ CH ₂ CONH ₂
glutamic acid	glu	-CH ₂ CH ₂ COOH
glycine	gly	-H
leucine	leu	-CH ₂ CH(CH ₃) ₂
phenylalanine	phe	
serine	ser	-CH ₂ OH
tyrosine	tyr	

A heptapeptide found in region **X** of the Delta variant has the sequence shown below.



The heptapeptide was partially hydrolysed by heating with a concentrated solution of sodium hydroxide. The partial hydrolysis produced a mixture of dipeptides.

- (i) Upon acidification of the dipeptides, leu-glu and phe-glu were obtained instead of leu-gln and phe-gln.

By referring to Table 3.1, suggest why this is so.

.....
 [1]

- (ii) Ser-tyr was also one of the dipeptides formed.

Draw the structure of this dipeptide at pH 13.

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[1]

Another heptapeptide found in region X of the Omicron variant was also subjected to hydrolysis under the same conditions.

The initial partial hydrolysis of this heptapeptide produced the tetrapeptides shown below.

tyr-ser-phe-arg, arg-ser-tyr-ser, leu-arg-ser-tyr

- (iii) Deduce the sequence of amino acids in this heptapeptide.

..... [1]

Increasing evidence suggests that gut health may be compromised in COVID-19 patients. One indicator of bad gut health is high levels of trimethylamine.

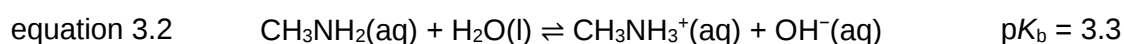
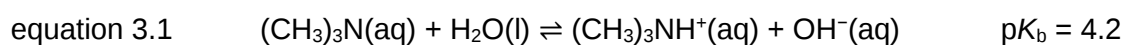
Both trimethylamine, $(\text{CH}_3)_3\text{N}$, and methylamine, CH_3NH_2 , behave as bases in the gaseous and aqueous phases.

(b) (i) Explain why, in the gaseous phase, $(\text{CH}_3)_3\text{N}$ is a stronger base than CH_3NH_2 .

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 [1]

In aqueous solution, the following equilibria are established.



(ii) State the predominant interaction, other than hydrogen bonding, between $(\text{CH}_3)_3\text{NH}^+$ and water.

..... [1]

(iii) Compared to $(\text{CH}_3)_3\text{NH}^+$, CH_3NH_3^+ has a stronger interaction with water.

With reference to your answer in **(b)(ii)**, explain why this is so.

.....

 [1]

(iv) Hence, suggest why the $\text{p}K_{\text{b}}$ of CH_3NH_2 is lower than that of $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

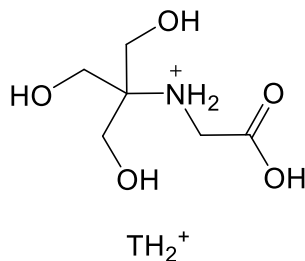
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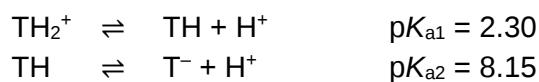
Antigen-based rapid diagnostic test kits have been used to detect the SARS-CoV-2 virus.

- (c) The test kit includes a vial containing a buffer solution prepared from tricine, TH.

The structure of protonated tricine, TH_2^+ , is shown below.



The acid dissociation involving TH_2^+ and TH and their corresponding pK_a values at 25 °C are shown below.



- (i) TH exists as a solid at room temperature.

Draw the structure of TH and explain why it has a high melting point.

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..... [2]

The buffer solution is prepared by dissolving 0.1 mol of solid tricine, TH, in 1.0 dm³ of aqueous sodium hydroxide. The pH of this buffer is 8.78.

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- (ii) Calculate the concentration of aqueous sodium hydroxide used in the preparation of this buffer solution.

[2]

- (iii) Explain how a more dilute buffer solution of the same volume will compare in terms of buffering capacity.

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..... [1]

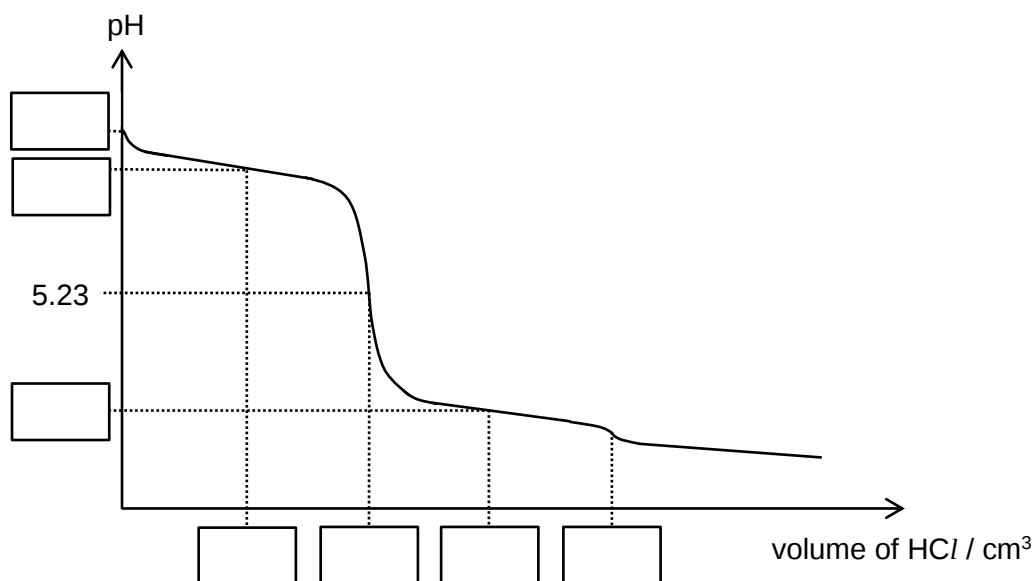
- (d) 10 cm³ of 0.1 mol dm⁻³ of the deprotonated tricine, T⁻, was titrated against 0.1 mol dm⁻³ of HCl from a burette.

- (i) Calculate the pH of 0.1 mol dm⁻³ of T⁻ solution at 25 °C.

[2]

- (ii) Using your answer in (d)(i) and information in (c), fill in the boxes below with the correct pH values and HCl volumes.

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use



[2]

- (iii) Methyl red is used as the indicator for determining the first end-point for this titration. It changes colour from red at pH 4.4 to yellow at pH 6.2.

Explain why methyl red is suitable for determining the first end-point.

Hence, state the colour change at the first end-point of the titration.

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 [2]

- (iv) Suggest why the second end-point cannot be determined by titration.

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 [1]

[Total: 19]

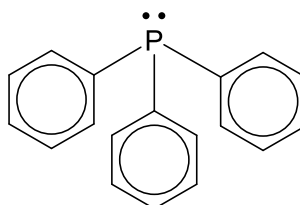
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- 4 Nickel, copper and their compounds have many uses such as coinage metals, electrical components and catalysts.

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- (a) Nickel forms complexes readily, one of which has the formula $\text{NiCl}_2(\text{PPh}_3)_2$.

The structure of triphenylphosphine, PPh_3 , is shown below.



PPh_3

There are two main isomers of $\text{NiCl}_2(\text{PPh}_3)_2$ which co-exist in equilibrium as shown in equation 4.1.

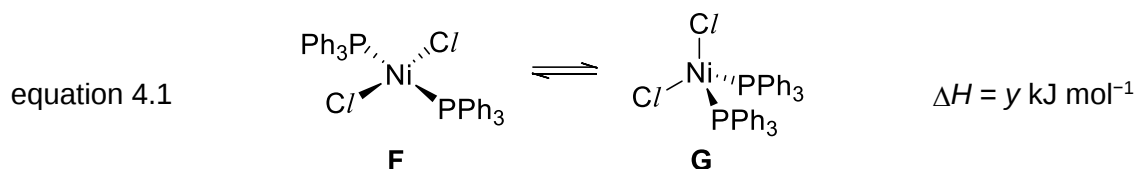


Table 4.1 gives some information about isomers **F** and **G**.

Table 4.1

isomer	F	G
geometry	square planar	tetrahedral
colour	red	blue

- (i) The proportion of **G** to **F** increases with temperature.

Deduce whether y in equation 4.1 has a positive or negative value.

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..... [1]

Nickel has an oxidation state of +2 in $\text{NiCl}_2(\text{PPh}_3)_2$.

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(ii) State the electronic configuration of a Ni^{2+} ion.

..... [1]

The five 3d orbitals in Ni^{2+} are split differently in complexes with square planar and tetrahedral geometries as shown in Fig. 4.1.

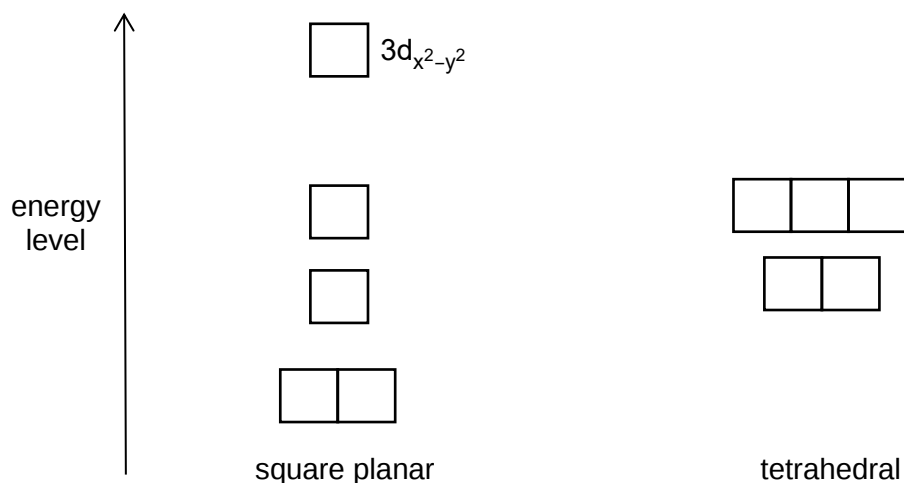
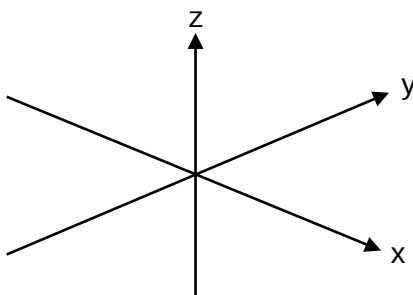


Fig. 4.1

(iii) The $3d_{x^2-y^2}$ orbital in a complex with square planar geometry has the highest energy level among the five 3d orbitals, as shown in Fig. 4.1.

Draw the $3d_{x^2-y^2}$ orbital in the axes provided.

Explain why the $3d_{x^2-y^2}$ orbital in **F** has the highest energy level.



..... [2]

- (iv) A paramagnetic substance contains one or more unpaired electrons and is attracted to an external magnetic field.

G is paramagnetic but **F** is not.

On Fig. 4.1, draw the distribution of the 3d electrons of Ni^{2+} ion in both the square planar and tetrahedral geometries. [2]

- (v) Explain why **F** and **G** have different colours.

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..... [2]

- (vi) Compound **H** is the *cis*-isomer of **F**.

Draw the structure of **H**.

Hence, suggest why **G** converts to **F** rather than to **H** in the backward reaction of equation 4.1.

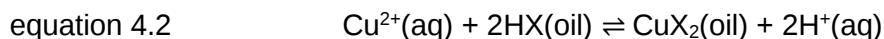
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- (b) Mine water from copper mines contains appreciable quantities of Cu^{2+} ions from which valuable copper can be recovered.

To separate Cu^{2+} ions from other impurities in a sample of mine water, an organic acid dissolved in oil, $\text{HX}(\text{oil})$, is mixed with the mine water.

HX reacts with Cu^{2+} to form a complex, CuX_2 , which is soluble in oil but not in water.

An equilibrium is established as shown in equation 4.2.



- (i) State a feature of ligand X^- which enables CuX_2 to be soluble in oil but not in water.

.....
 [1]

To determine the concentration of CuX_2 in oil, a calibration curve is first obtained by finding the absorbance of known concentrations of CuX_2 in oil, as shown in Fig. 4.2.

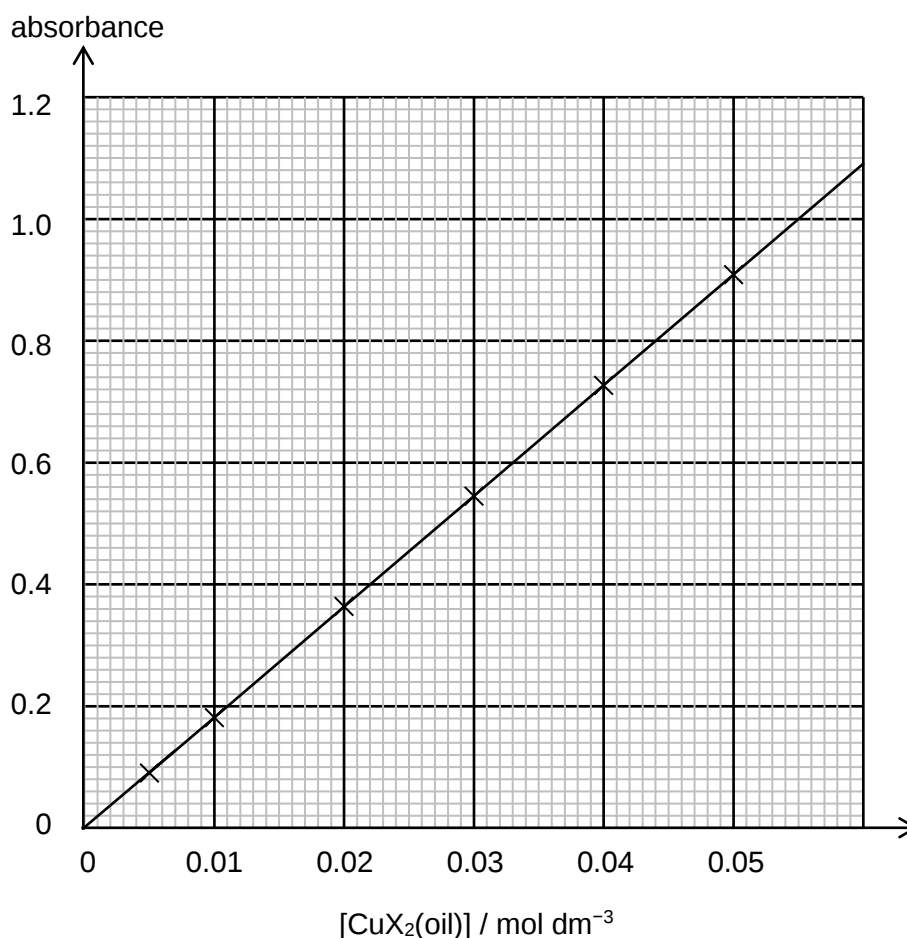


Fig. 4.2

A 1 dm³ solution of HX in oil is mixed with 2 dm³ mine water containing Cu²⁺ ions and allowed to reach equilibrium at pH 3 at 25 °C.

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- (ii) CuX₂(oil) formed at equilibrium is found to have an absorbance of 0.82.

Using Fig. 4.2, find the concentration of CuX₂(oil) at equilibrium.

[1]

The K_c expression for the reaction in equation 4.2 is shown below.

$$K_c = \frac{[\text{CuX}_2(\text{oil})] [\text{H}^+(\text{aq})]^2}{[\text{Cu}^{2+}(\text{aq})] [\text{HX}(\text{oil})]^2}$$

- (iii) At 25 °C, the value of K_c is 2.1×10^{-2} .

Given that [HX(oil)] in the equilibrium mixture is 0.20 mol dm⁻³ and using your answer in (b)(ii), calculate the concentration of copper(II) ions remaining in the mine water.

Hence, calculate the percentage of copper extracted from the mine water.

[2]

- (iv) With reference to equation 4.2, suggest how Cu^{2+} can be released from the CuX_2 molecules in the oil solution back into aqueous solution.

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..... [1]

- (c) Some copper ornaments are tarnished due to the formation of solid copper(II) sulfide, CuS .

The CuS tarnish can be removed by using metal polishes containing aqueous ammonia.

With the aid of equations, explain how the aqueous ammonia in the metal polish can remove the CuS tarnish.

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..... [2]

[Total: 17]

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