

RIVER VALLEY HIGH SCHOOL JC 2 PRELIMINARY EXAMINATION

H2 CHEM	IST	̈́RΥ					972	9/02
CENTRE NUMBER	S				INDEX NUMBER			
CLASS	2	2	J					
CANDIDATE NAME								

Paper 2 Structured Questions

13 September 2023

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, class and name on all the work that 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.

DO NOT WRITE IN ANY BARCODES.

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

The use of an approved scientific calculator is expected, where appropriate. A Data Booklet is provided.

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

For Examiner's Use								
Question Number	1	2	3	4	5	6		
Marks	12	12	13	7	13	18		
significant figures			units				Total	75

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

1

(a) Over one million tonnes of chromium are produced in the world each year and about 30% of it is used in electroplating. In an electroplating experiment, as shown by the set up below, an aqueous solution containing chromium(III) sulfate was electrolysed using a piece of pure chromium and the metal object to be electroplated as the electrodes.



(i) Identify the anode in this reaction.

(ii) A square piece of chromium sheet has a dimension of 0.100 m \times 0.100 m and a depth of 1000 atoms.

Assume that each chromium atom occupies a length of 3.00×10^{-12} m, calculate how long it will take for 90.0 % of the chromium sheet to be used when a constant current of 4.00 A is provided.

(iii) The experiment was repeated using dilute sulfuric acid and a piece of pure aluminium in place of chromium sheet.

Explain why the aluminium electrode gained mass. Write relevant equations to support your answer.

..... [2] The successive ionisation energies, in kJ mol⁻¹, of an element **X** are given (b) below. 1012, 1907, 2914, 4964, 6274, 21267, 25431, 29872 (i) With the aid of an equation involving **X**, explain the term *first ionisation* energy. [1] (ii) Explain the general increase in successive ionisation energies of any atom. [2] (iii) Deduce which group of the Periodic Table X belongs to. [2] (iv) Hence, write the electronic configuration of **X**, given that **X** is in Period 3. [1]

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[Total: 13]

[Turn over

2 (a) Methylamine is a weak base with a pK_b value of 3.38 at 298 K. It reacts with water and boron trifluoride in acid-base reactions.

$$CH_3NH_2 + H_2O = CH_3NH_3^+ + OH^-$$
$$CH_3NH_2 + BF_3 \rightarrow CH_3NH_2BF_3$$

(i) State the type of base that methylamine is acting as in each reaction. Explain your answer.

With	H ₂ O:
With BF ₃ :	
- · · · · · · · · · · · · · · · · · · ·	

(ii) Calculate the pH of 0.10 mol dm⁻³ of methylamine in water at 298 K.

- (b) A buffer solution can be made from methylamine and its salt, methylammonium chloride. A suitable reagent of concentration 0.10 mol dm⁻³ is added to 50 cm³ of 0.10 mol dm⁻³ methylamine to obtain the buffer solution.
 - (i) Name a suitable reagent that **reacts** with methylamine to form the buffer solution.

.....[1]

(ii) Show that the ratio of the salt to base concentration needed to maintain the buffer at pH 11.1 is 0.33.

[1]

(iii) Hence, calculate the volume, in cm^3 , of the suitable reagent to be added to form a buffer with a pH of 11.1.

Leave your answer to 1 decimal place.

- (c) FA 1 and FA 2 are either $MgCO_3$ or $BaCO_3$. The following tests were carried out to establish their identities.
 - Test 1: When **FA 1** was heated to 500 °C, a gas was produced.
 - Test 2: FA 2 produced the same gas only when heated to 1000 °C.
 - Test 3: The residues produced in tests 1 and 2 were then added to water separately. The residue obtained from test 1 formed a solution of pH 8 while the residue obtained from test 2 formed a solution of pH 14.

With reference to the observations in Test 1 and Test 2, deduce the identities of **FA 1** and **FA 2**. Describe the reactions of residues with water in Test 3.

Write balanced equations for any reactions that occurred.

	[4]
-	

[Total: 12]

[Turn over

- 8
- **3** (a) 1,3–dibromopropane is the starting compound for a 4–step reaction pathway which produces compound **H**. The pathway is shown below.



Compound **F** has a molecular formula of $C_3H_4O_2$. Compound **F** gives a black precipitate when heated with $[Ag(NH_3)_2]^+(aq)$.

(i) State the IUPAC name of compound **H**.

(ii) State the reagents and conditions for reactions 1, 2 and 3.

Reaction	Reagents and conditions
1	
2	
3	

[3]

[3]

(iii) Give the structures of **E**, **F** and **G**.

Compound	Structure
E	
F	
G	

Use a suitable diagram, showing relevant orbitals, to show that the H atoms in compound ${\bf J}$ are not in the same plane.

[1]

(v) Compound J can isomerise into compound K which has three carbon atoms in different chemical environments.

Give the structure of compound K.

[1]

(b) In contrast to compound H, lysine, an amino acid, is a naturally-occuring molecule.



lysine

(i) Amino acids can exist as zwitterions.

Zwitterions are found to be:

- solids under room temperature and pressure.
- soluble in water.

Explain these observations.

[2]

(ii) The pK_a values in lysine are 2.35, 9.16 and 10.7.

Give the structure of the dominant species when lysine is placed in buffer solutions of pH 6.0 and 9.5 respectively.

pH 6.0	pH 9.5

[2]

[Total: 13]

11

4 Thiourea is a reagent used to prepare thiol and urea. Benzhydryl thiol can be synthesised by reacting benzhydryl bromides with thiourea, NH₂CSNH₂, as shown Fig. 4.1. The rate of reaction is independent of [thiourea].



12

(iv) Suggest the mechanism for the reaction occurring in stage 1. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

(b) Explain how the rate of reaction differs from the reaction of benzhydryl chloride with thiourea.

[1] [Total: 7]

- 5
- Esters generally can undergo hydrolysis with water, but the rate of reaction is too slow to be of use for kinetic analysis. Therefore, the hydrolysis is usually done via catalysis with dilute acid or alkali, accompanied with heating.
 - (a) A kinetic study of an acid-catalysed hydrolysis of 0.0100 mol dm⁻³ methyl acetate, is being conducted.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

The hydrolysis reaction is carried out using 0.100 mol dm^{-3} hydrochloric acid at room temperature and pressure. Aliquots are drawn periodically from the reaction mixture and titrated against 0.100 mol dm^{-3} sodium hydroxide, with phenolphthalein as the indicator.

The results are shown in Table 5.1.

Time / min	V _t / cm ³	V_{∞} – V_t / cm ³	$\lg \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$
0	26.50	14.00	0.00
10	28.10	12.40	0.0527
20	29.20	11.30	0.0930
30	31.00	9.50	0.168
40	31.30	9.20	0.182
50	31.50	9.00	0.192
60	32.20	8.30	0.227
∞	40.50	0.00	

Table 5.1

where

 V_0 = titre value at time = 0 min

 V_t = titre value at time t

 V_{∞} = titre value at the end of the reaction

The hydrolysis of methyl acetate shows pseudo first order kinetics.

The rate constant for pseudo first order reactions, k, can be determined by:

$$k' = \frac{2.303}{t} \lg \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

Thus, for this experiment, k = k [HC*l*], where k is the actual rate constant of the hydrolysis of methyl acetate.

(i)	Explain why the hydrolysis of methyl acetate is pseudo zero order with respect to HC <i>l</i> .	
		[1]
(ii)	Explain why the values of V_t increase over time.	
		[1]
(iii)	State the significance of the V_{∞} – V_t term.	
		[1]
(iv)	By plotting a suitable graph using the given data, the actual rate	

(iv) By plotting a suitable graph using the given data, the actual rate constant, k, can be determined. Suggest how the graph can be plotted to determine the value of k. You may sketch a graph to illustrate.

[2]

(b) The hydrolysis of an ester in alkaline medium is known as saponification. A strong base, such as NaOH or KOH, is used to catalyse this process.



The mechanism of the hydrolysis is thought to involve the following steps:

- Step 1: OH⁻ undergoes reaction with ester to form only one intermediate, which is an alkoxide.
- Step 2: The unstable alkoxide intermediate undergoes a reaction to produce R'O⁻ ion and RCOOH.
- Step 3: Protonation of the R'O⁻ ion yields an alcohol and a carboxylate ion.

Complete Fig. 5.1 below to suggest the mechanism for the base-catalysed hydrolysis of methyl acetate, CH₃COOCH₃.

Show the structural formulae of the intermediates, relevant lone pairs of electrons, dipoles and charges involved, and indicate the movement of electrons by using curly arrows.





[3]



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(c) A simplified energy profile diagram is proposed for the saponification process, as shown in Fig. 5.2.



(iii) Indicate the position of the alkoxide intermediate in Fig. 5.2. [1]

The next two questions pertain to points **X**, **Y** and **Z** indicated on Fig. 5.2.

(iv) Explain why the enthalpy change of reaction from X to Y is zero.

(v) Considering the chemical species labelled in Fig. 5.2, suggest a reason why Z is at a lower energy level than X and Y. [1] 6 (a) Define *transition element*.

.....[1]

(b) Cobalt(II) ions in aqueous state exists as hydrated complex ions, $[Co(H_2O)_6]^{2+}(aq)$. The water ligands can be substituted by other ligands through ligand exchange reaction. An example of such exchange reaction is $[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \Rightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(I)$.

Assuming that the concentration of water is approximately constant in the aqueous state, write an expression for equilibrium constant, K_s , for the above ligand exchange reaction.

[1]

(c) Ligand exchange reaction for aqueous cobalt(II) ions occurs in a stepwise manner. The first step of the process is shown below:

$$[Co(H_2O)_6]^{2+}(aq) + NH_3(aq) = [Co(H_2O)_5(NH_3)]^{2+}(aq) + H_2O(I)$$

The process continues until all H₂O ligands are substituted by NH₃ ligands. 50.0 cm³ of 0.200 mol dm⁻³ NH₃(aq) was added to 50.0 cm³ of 0.200 mol dm⁻³ aqueous cobalt(II) ions. The lg K_c for the formation of $[Co(H_2O)_5(NH_3)]^{2+}$ is 1.30.

Calculate the concentration of $[Co(H_2O)_6]^{2+}(aq)$ and $[Co(H_2O)_5(NH_3)]^{2+}(aq)$ in the equilibrium mixture.

(For a quadratic equation $ax^2 + bx + c = 0$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$)

[2]

(d) The values of $\lg K_s$ for some cobalt complexes are shown in Table 6.1.

complex	colour	lg <i>K</i> s
[Co(SCN) ₄] ^{2–} (aq)	bright blue	3.00
$[Co(NH_3)_6]^{2+}(aq)$	light brown	5.11
[Co(NH ₃) ₆] ³⁺ (aq)	dark reddish brown	16.3
[Co(edta)] ^{2–} (aq)	pink	35.2

When NH_3 was added to a solution of $[Co(SCN)_4]^{2-}$, a ligand exchange reaction occurs:

 $[Co(SCN)_4]^{2-}(aq) + 6NH_3(aq) = [Co(NH_3)_6]^{2+}(aq) + 4SCN^{-}(aq)$

(i) Show that the K_c for the above ligand exchange reaction is 129.

(ii) Heating a bright blue solution of $[Co(SCN)_4]^{2-}$ turns it light brown.

State and explain whether the above ligand exchange reaction is endothermic or exothermic.

[2]

[2]

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(iv) Explain why [Co(NH₃)₆]²⁺ and [Co(NH₃)₆]³⁺ have *different colours*.

(e) In Crystal Field Theory, one of the measurements that determines the arrangement of the 3d electrons in the octahedral crystal field is the ligand-field stabilisation energies (LFSE). LFSE is given by:

$$\mathsf{LFSE} = (0.4\mathsf{x} - 0.6\mathsf{y}) \times \Delta E$$

- where x = total number of electrons in the lower energy d-orbitalsy = total number of electrons in the higher energy d-orbitals $\Delta E = \text{energy gap between the two energy levels}$
- (i) Fig. 6.1 shows the relative energy levels of d orbitals in an octahedral crystal field. Consider the orientation of d orbitals in an octahedral complex, explain their relative energy levels using Crystal Field Theory.





 [2]

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Complexes exist in two spin states.

In a *high spin* state, the electrons of the central metal occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a *low spin* state, the lower energy d-orbitals are filled first, with pairing, if necessary, before the higher energy d-orbitals are used.

(ii) Calculate the LFSE for the metal ions in an octahedral crystal field with the following configurations:



(f) Fig. 6.2 shows the variation in standard enthalpy change of hydration of M²⁺ ions (high spin state) from vanadium to zinc. The straight line shows the expected trend when the LFSE has been subtracted from the plotted experimental data involving these ions in an octahedral crystal field.



Fig. 6.2

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[2]

(i)	Explain the trend in the standard enthalpy change of hydration.					
		[1]				
(ii)	Suggest why there is no deviation from the linear trend for the metal cations with atomic numbers 25 and 30.					
		[1]				
	[Total: 18					

Additional answer space

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

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