ANDERSON SERANGOON JUNIOR COLLEGE



2023 JC2 PRELIMINARY EXAMINATION

NAME:	()	CLASS: 23 /

CHEMISTRY

Paper 2 Structured Questions

9729/02 14 September 2023 2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register 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. 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		
	1	/19
2	2	/9
aper	3	/11
–	4	/17
	5	/19
-	Total	/ 75

This document consists of 20 printed pages and 4 blank pages.

Answer all the questions.

1 The common chlorides of Period 3 elements are shown in Table 1.1.

Period 3 chloride	NaC <i>l</i>	AlCl ₃	SiCl ₄	PCl ₅
Bonding		С		
Structure		S		
pH of aqueous solution		3		

(a) A 3.30 g sample of a Period 3 chloride is heated to 500 K in a sealed flask of 250 cm³. At this temperature, the chloride is a gas and the pressure in the flask is 323 kPa.

Assuming the gas behaves ideally, calculate the M_r of the Period 3 chloride. Hence, use the chlorides given in Table 1.1 to deduce its formula.

[2]

- (b) (i) Complete Table 1.1 by
 - identifying the bonding shown by each chloride under standard conditions. Use C = covalent, I = ionic, M = metallic
 - identifying the structure shown by each chloride under standard conditions. Use G = giant, S = simple
 - stating the pH of the aqueous solution of each chloride at 298 K.

[3]

(ii) At certain temperature, aluminium chloride exists as Al_2Cl_6 molecules. Draw the structure of Al_2Cl_6 . State how the shape with respect to each Al atom changes from $AlCl_3$ to Al_2Cl_6 .

[2]

(iii) SCl₂ is also a chloride of Period 3 element.

It is a cherry-red liquid that reacts vigorously with water to form a strongly acidic solution.

Use this information to deduce the bonding and structure shown by SCl₂.

Structure:	
Bonding:	
Explanation:	
	 [2]

 SCl_2 is formed when sulfur, S_8 , reacts with an excess of chlorine in a series of steps.

step 1	$S_8(s) + 4Cl_2(g) \rightarrow 4S_2Cl_2(I)$	$\Delta H_{\rm r} = -58.2 \text{ kJ mol}^{-1}$
step 2	$S_2Cl_2(I) + Cl_2(g) \implies 2SCl_2(I)$	$\Delta H_{\rm r} = -40.6 \text{ kJ mol}^{-1}$

(iv) Calculate the enthalpy change of formation, ΔH_{f} , of SCl₂(I).

$$\frac{1}{8}S_8(s) + Cl_2(g) \to SCl_2(l) \qquad \Delta H_f$$

[2]

(v) State the effect of a decrease in pressure on the position of equilibrium in step 2. Explain your answer.

•••••	 	 	 	
	 	 	 	[1]

(c) Sulfur also reacts with chlorine to form S_2Cl_2 .

Fig. 1.1 shows one of the constitutional isomers of S_2Cl_2 .

Fig. 1.1

(i)	Define the term constitutional isomer.
	[1]
(ii)	 Using the isomer of S₂Cl₂ shown in Fig 1.1, state the oxidation number of S. suggest a value for the Cl–S–S bond angle. Explain your answer.
	[3]
(iii)	 Draw the 'dot-and-cross' diagram of another isomer of S₂Cl₂, given that one of the S atoms has an oxidation number of zero.

• the other S atom is the central atom.

[1]

- (d) SO_3 can react with SCl_2 to form liquid $SOCl_2$ and another gas which turns aqueous acidified potassium manganate(VII) from purple to colourless.
 - (i) Write a balanced chemical equation for the reaction between SO_3 and SCl_2 .

.....[1]

(ii) Draw the organic product formed when compound A is reacted with SOCl₂.



[1]

[Total: 19]

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2 (a) Phthalic anhydride is an important industrial chemical for the synthesis of phthalic esters, which are used as plasticisers to soften plastics.



Phthalic anhydride

Phthalic acid (C₈H₆O₄)

The reactivity of phthalic anhydride is similar to that of acyl chloride. Hydrolysis of phthalic anhydride produces phthalic acid, which is an aromatic dicarboxylic acid that can ionise in two stages, each with its associated pK_a value as shown in Table 2.1.

Table	2.1
-------	-----

$C_8H_6O_4 \implies C_8H_5O_4^- + H^+$	р <i>К_{а1}</i> = 2.89
$C_8H_5O_4^- \Longrightarrow C_8H_4O_4^{2-} + H^+$	р <i>К_{а2}</i> = 5.51

(i) Suggest reagents and conditions for hydrolysis of phthalic anhydride to form phthalic acid.

.....[1]

(ii) Suggest two reasons why the pK_{a2} of phthalic acid is higher than its pK_{a1} .

- (b) A student pipetted 10 cm³ of 0.50 mol dm⁻³ of phthalic acid into a conical flask and 20.00 cm³ of 0.50 mol dm⁻³ of potassium hydroxide, KOH, was required for complete neutralisation.
 - (i) Calculate the pH of 0.50 mol dm⁻³ solution of phthalic acid, ignoring the effect of pK_{a2} .

[1]

(ii) Calculate the pH of a solution which contains both phthalic acid and potassium hydrogen phthalate, C₈H₅O₄K in equal concentration.

[1]

(iii) Determine the volume of potassium hydroxide that has been added when the solution in the conical flask contains only potassium hydrogen phthalate.

[1]

- (iv) Using information from Table 2.1,
 - calculate the K_b of potassium hydrogen phthalate, C₈H₅O₄K.
 - calculate the K_{a2} of phthalic acid.

Hence, suggest if an aqueous solution of potassium hydrogen phthalate is acidic or alkaline.

[Total: 9]

3 (a) Lucas Test is used to distinguish between primary, secondary and tertiary alcohols.

Table 3.1 shows the observations on adding reagents of Lucas Test (concentrated hydrochloric acid and zinc chloride as catalyst) to separate samples of three alcohols to form chloroalkanes.

alcohol	observation on adding conc. HCl and $ZnCl_2$
(CH₃)₃COH	immediate cloudiness appears in the solution
CH ₃ CH ₂ CH(OH)CH ₃	cloudiness apparent within 5 minutes
CH ₃ CH ₂ CH ₂ CH ₂ OH	no cloudiness apparent unless warmed

(i) The cloudiness is due to the formation of two immiscible layers. Suggest why cloudiness appears in the solution after the reaction is complete.

......[1]

(ii) The three stages of the Lucas Test using $(CH_3)_3COH$ are described in Table 3.2.

Complete Table 3.2 by suggesting the mechanism involved in stage 2 **only**. Show the structure of the intermediate and movement of electron pairs by using curly arrows in your answer.

stage	description of stage	equation		
1	acid–base reaction between alcohol and conc. HC <i>l</i> to form protonated alcohol	$\bigvee^{OH} + HCl \longrightarrow \bigvee^{\oplus} H_2 + Cl^{\ominus}$		
2	heterolytic fission of C–O bond in protonated alcohol to form a carbocation intermediate			
3	reaction of intermediate carbocation with C <i>I</i> ⁻ to form the chloroalkane	$: Cl \ominus \longrightarrow Cl$		

Table 3.2

(iii) With reference to the information provided in Table 3.2, suggest why primary alcohol such as CH₃CH₂CH₂CH₂OH does not give cloudiness in Lucas Test.

.....[1] Other than the use of Lucas Test, suggest how (CH₃)₃COH and CH₃CH₂CH₂CH₂CH₂OH (iv) can be differentiated by using another chemical test. Include reagents and conditions and state the observations that will be made.[2]

- (b) One of the alcohols listed in Table 3.1 undergoes elimination to form three isomeric alkenes **B**, **C** and **D** of molecular formula, C_4H_8 .
 - (i) Identify the alcohol and draw the skeletal formula of alkenes **B**, **C** and **D**.

Alcohol:



(ii) 20 cm³ of alkene with formula C_4H_8 undergoes complete combustion in an oxygenrich environment. There is a reduction in volume of $x \text{ cm}^3$. When the residual gaseous mixture is treated with sodium hydroxide solution, there is a further reduction in volume of $y \text{ cm}^3$.

Determine the values of *x* and *y*.

(All measurement of volumes is done at room temperature and pressure.)

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4 Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

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The solubility products of the chloride, bromide and iodide of silver are given in Table 4.1.

Salt	value of solubility product at 298 K
AgC <i>l</i>	2.0 x 10 ⁻¹⁰
AgBr	5.0 x 10 ⁻¹³
AgI	to be calculated

Table 4.1

(a) (i) Write an expression for the solubility product, K_{sp} of silver iodide.

.....[1]

(ii) Given the solubility of silver iodide, AgI is 8.9 x 10^{-9} mol dm⁻³, calculate a value for K_{sp} of silver iodide. Leave your answer to **two** significant figures.

When a precipitate is formed, ΔG_{ppt}^{e} is given by the following expression.

$$\Delta G_{ppt}^{\Theta} = 2.303 \text{ RT} \log_{10} K_{sp}$$

(iii) Use the data above to calculate $\Delta \textit{G}_{ppt}^{e},$ for silver chloride.

[1]

(iv) For silver fluoride, AgF, $K_{sp} = 1.006 \text{ mol}^2 \text{ dm}^{-6}$ at 298 K. Use the ΔG_{ppt}^{e} expression given to determine whether silver fluoride is soluble in water at 298 K.

Explain your answer.

(b) (i) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added.

With the aid of suitable equations only, explain the chemistry that is occurring during these reactions. Include state symbols in your equations.

(ii) When aqueous sodium bromide was added to the resultant mixture from (b)(i), a cream precipitate is obtained. Explain the observation made using information from Table 4.1.

 (c) Silver bromide dissolves in an aqueous solution of $S_2O_3^{2-}$ ions to form the complex ion $[Ag(S_2O_3)_2]^{3-}$. The $S_2O_3^{2-}$ ions act as monodentate ligands here.

equilibrium 1 $\operatorname{AgBr}(s) + 2S_2O_3^{2-}(aq) \Longrightarrow [\operatorname{Ag}(S_2O_3)_2]^{3-}(aq) + \operatorname{Br}^{-}(aq)$

(i) Define the term *ligand*.

......[1]

(ii) Write an expression for the equilibrium constant, K_c , for equilibrium 1.

.....[1]

Stability constant of a complex, K_{stab} , is the equilibrium constant for its formation as shown below. It is a measure of the relative stability of complex compared to its aqua complex.

$$[Ag(H_2O)_2]^+(aq) + 2L^{m-}(aq) \implies [AgL_2]^{(1-2m)}(aq) + 2H_2O(I) \qquad K_{stab}$$
(where m = 0, 1 or 2)

Table 4.2 lists the numerical values for the stability constant of three silver(I) complexes with 3 different ligand, L^{m-} .

m	L ^{m-}	silver(I) complex	numerical value of K_{stab}
0	NH_3	[Ag(NH ₃) ₂] ⁺	1.6 × 10 ⁷
1	CN⁻	[Ag(CN) ₂] ⁻	$5.3 imes 10^{18}$
2	S ₂ O ₃ ²⁻	[Ag(S ₂ O ₃) ₂] ³⁻	2.9×10^{13}

Table 4.2

(iii) Use your answer from (c)(ii) and relevant data from Table 4.1 and 4.2 to calculate the K_c for equilibrium 1.
 (Note that [Ag(H₂O)₂]⁺(aq) is equivalent to [Ag⁺])

(iv) An aqueous solution containing Ag^+ is added to a solution containing equal concentrations of $CN^-(aq)$, $NH_3(aq)$ and $S_2O_3^{2-}(aq)$. The mixture is left to reach equilibrium.

Deduce, in decreasing order, the relative concentrations of $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$ and $[Ag(S_2O_3)_2]^{3-}$ present in the resulting mixture. Explain your answer.

(i) State the electronic configuration of a Ag⁺ ion.
(ii) Hence, suggest why the silver(I) complexes in Table 4.2 are colourless.

(e) In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

Using the axes in Fig. 4.1, draw fully-labelled diagrams of the following.

- One of the d orbitals at the lower energy level in an octahedral complex.
- One of the d orbitals at the higher energy level in an octahedral complex.



lower energy level



higher energy level

[2]

[Total: 17]

(d)

Fig. 4.1

5 (a) NH_3 is produced from N_2 and H_2 in the presence of a catalyst. When N_2 and H_2 is heated in a sealed reactor, the following equilibrium is established.

 $N_2(g) + 3H_2(g) \implies 2NH_3(g)$

(i) Write an expression of the K_{p} for this equilibrium.

.....[1]

(ii) In an experiment, N_2 and H_2 are placed in a sealed reactor in the molar ratio 1:3.

Fig. 5.1 shows the variation in the amounts of N_2 and NH_3 in the system with time. The reactor is maintained at a temperature of 750 K and the total pressure is 200 atm.



Use the information provided above and data from Fig. 5.1 to calculate the value of K_p for the equilibrium at 750 K, stating its units.

(b) The Strecker amino acid synthesis, is a method for the synthesis of amino acids by the reaction of an aldehyde with ammonia is shown below. Isoleucine can be prepared via Strecker synthesis as shown below.

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$$\begin{array}{cccc} CH_{3} & 0 & CH_{3} \\ CH_{3}-CH_{2}-CH-C-H & \overrightarrow{step 1} \end{array} & CH_{3}-CH_{2}-CH-CH-NH_{2} & \overrightarrow{step 2} \end{array} & CH_{3}-CH_{2}-CH-CH=NH \\ & step 3 & HCN \\ CH_{3}-CH_{2}-CH-C-COOH & \overleftarrow{step 4} & U \\ CH_{3}-CH_{2}-CH-C-COOH & \overrightarrow{step 4} & U \\ H & step 4 & C_{6}H_{12}N_{2} \\ & soleucine \end{array}$$

(i) Suggest the type of reaction occurring in steps 1 and 2.

Step 1:[2]

- (ii) The mechanism of the reaction in step 1 proceeds via the following stages:
 - Nucleophilic attack of ammonia on the carbonyl carbon forming an intermediate (with a negative charge on O atom and a positive charge on N atom).
 - 2. The intermediate abstract a proton from the neighboring nitrogen and form the product.

Draw the mechanism for step 1. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

[2]

(iii) Suggest why step 1 produces a mixture which is optically inactive.

.....[2]

(iv) Draw the structure of compound U, $C_6H_{12}N_2$.

(v)



An amino acid, Tyrosine can be prepared from aldehyde V via Strecker synthesis. Draw the structure of aldehyde V.

(vi) When one mole of CH₃COC*l* is added to one mole of tyrosine, two different isomeric products, X and Y, are formed.
Y forms violet complex with neutral FeC*l*₃ while X does not.
Draw the structures of X and Y.

[2]

[1]

[1]

(c) Cysteine and serine are naturally occurring amino acids found in proteins with the following structures.



Thiols having the structure R-SH, undergoes similar reactions as alcohols but are generally more acidic than alcohols.

(i) The thiol group in cysteine has a pK_a value of 8.18. The remaining pK_a values of cysteine are 1.96 and 10.28.

Draw the structure of the predominant species of cysteine at pH 9.0.

[1]

(ii) Suggest a pH at which the predominant species of cysteine is a zwitterion. Draw the structure of the zwitterion.

рН :



[2]

(iii) The pK_a value of the alcohol group in serine is 13.00.

Suggest a reason why the pK_a value for the thiol group in cysteine is lower than that for the alcohol group in serine.

.....[1]

(iv) Cysteine and serine can form a dipeptide. Draw the structure of this dipeptide.

[1]

[Total: 19]

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