ANDERSON SERANGOON JUNIOR COLLEGE

2020 PRELIMINARY EXAMINATION

NAME:	()	CLASS: 20 /

CHEMISTRY

Paper 2 Structured Questions

9729/02

15 September 2020

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.

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		
aper 2	1	/ 13
	2	/ 14
	3	/ 12
	4	/ 10
à	5	/ 14
	6	/ 12
	Total	/ 75

This document consists of 23 printed pages and 1 blank page.

Answer all the questions in the spaces provided.

- 1 One early nineteenth century Periodic Table had copper placed in the same group as potassium because they both formed +1 ions.
 - (a) State the full electronic configurations of potassium and copper atoms.

.....[1]

(b) (i) The mass of an atom is the sum of the masses of all subatomic particles it contains.

Calculate the mass, in kg, of **one** atom of $^{64}_{29}$ Cu. Quote relevant values from the *Data Booklet* and give your answer to three significant figures.

[2]

(ii) During the process of ionisation, a Cu atom loses an electron.

 $Cu(g) \rightarrow Cu^{+}(g) + e^{-}$

State the electronic configuration of Cu⁺. Explain your answer.

1s ²	
explanation	
	[2]

(iii) On the Cartesian axes given in Fig. 1.1, sketch the shape of the following three 3d orbitals found in copper atom.













[2]

(c) (i) Define the term standard enthalpy change of formation.

.....[1]

(ii)

Table 1.1

enthalpy change	value / kJ mol ⁻¹
standard enthalpy change for P(s) + $2O_2(g) + 3e^- \rightarrow PO_4^{3-}(aq)$	-1284
standard enthalpy change for $K(s) \to K^{\scriptscriptstyle +}(aq) + e^{\scriptscriptstyle -}$	-251
standard enthalpy change for $K_3PO_4(s) \rightarrow 3K^+(aq) + PO_4^{3-}(aq)$	-2

Using a labelled energy cycle, and the enthalpy values given in Table 1.1, determine the standard enthalpy change of formation of solid potassium phosphate, K_3PO_4 .

(iii) The value of ΔG^{Θ} at 298 K for K(s) \rightarrow K⁺(aq) + e⁻ is –284 kJ mol⁻¹.

Using data from Table 1.1, calculate ΔS^{Θ} for the reaction, and explain its sign.

.....[2]

[Total: 13]

[3]

Question 2 starts on the next page.

5

2 2-methylpropane, (CH₃)₂CHCH₃, is an important precursor for petrochemical industry. Butane, CH₃(CH₂)₂CH₃, can be converted to 2-methylpropane in the presence of a suitable heterogeneous catalyst.

 $CH_3(CH_2)_2CH_3(g) \iff (CH_3)_2CHCH_3(g)$ equilibrium 1

(a) Explain briefly how a heterogeneous catalyst increases the rate of equilibrium 1.

(b) Butane gas was added to an enclosed vessel at 373 K. The concentration of butane and 2-methylpropane was measured at regular time intervals and a graph was plotted as shown in Fig. 2.1.



Fig. 2.1

(i) Using information from Fig. 2.1, calculate the partial pressures of butane and 2-methylpropane in the mixture at equilibrium. You may assume that both gases behave ideally.

(ii) Write the K_p expression of *equilibrium 1* and calculate its value.

[2]

(c)	State how the partial pressure of butane will change when argon is added to the enclosed vessel at constant volume.
	[1]

- (d) Bromine reacts with alkanes in the presence of light.
 - (i) Outline the mechanism of the reaction between 2–methylpropane and bromine to form 2–bromo–2–methylpropane.

[3]

(ii) Suggest why it is not possible to make iodoalkanes by this method.

.....[1]

(e) lodoalkanes can be made by warming a chloroalkane with a solution of sodium iodide in propanone, in which sodium chloride is almost insoluble.

$$CH_3CH_2Cl + NaI \iff CH_3CH_2I + NaCl$$
 equilibrium 2

(i) By considering the equation for *equilibrium 2*, suggest why the reaction goes almost to completion, despite the C–I bond being weaker than the C–C*l* bond.

.....[1]

A student performed two experiments to investigate the effect of changes in concentration on the rate of this reaction.

The initial concentration and rate data obtained for each experiment is given in Table 2.1.

experiment	initial [CH ₃ CH ₂ C <i>l</i>] / mol dm ⁻³	initial [NaI] / mol dm ⁻³	initial rate / mol dm ⁻³ s ⁻¹
1	1.0 x 10 ^{−3}	2.0 x 10 ^{−3}	3.0 x 10 ⁻¹¹
2	3.0 x 10 ^{−3}	4.0 x 10 ^{−3}	1.8 x 10 ⁻¹⁰

Table 2.1

(ii) Determine the order of reaction with respect to each reactant and hence deduce the rate equation for this reaction. Use data from Table 2.1 to explain your answers.

- chlorine, Cl₂ to form iron(III) chloride FeCl₃.
- iodine, I₂ to form iron(II) iodide, FeI₂.

Using the information provided, suggest how the reactivity of chlorine and iodine as oxidising agent varies down the group. Relate this variation to relevant E^{Θ} values and the changes in oxidation numbers.

 (b) Sea water from the Dead Sea is known to contain bromide ions, Br.

AgNO₃(aq) of known concentration can be gradually added to a sample of sea water to determine the concentration of Br⁻ in it. A small quantity of aqueous potassium chromate(VI), K_2CrO_4 , of concentration 0.01 mol dm⁻³ is added as an indicator.

The end–point of this titration is determined when the indicator forms a coloured precipitate with silver ions after all the Br^{-} ions are precipitated. Table 3.1 lists some information of the two precipitates.

	colour	K _{sp}
AgBr	cream	5.35 x 10 ⁻¹³ mol ² dm ⁻⁶
Ag_2CrO_4	red	3.01 x 10 ⁻¹² mol ³ dm ⁻¹²

Table	3.1
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(i) AgNO₃(aq) is added to separate solutions containing 0.06 mol dm⁻³ Br⁻(aq) and 0.01 mol dm⁻³ CrO₄²⁻(aq) respectively.

Calculate the concentration of Ag⁺ required to cause precipitation of

- AgBr
- Ag₂CrO₄

in each of the solutions.

ſ	2	1
-		-

(ii) Using the data in Table 3.1 and your answer in (b)(i), explain why K₂CrO₄ can be used as an indicator in this titration.

	 	 	 	 	[2]

(c) When a stream of chlorine is passed over heated sulfur, it reacts to form an orange chloride of sulfur, **D**, which has an unpleasant smell.

0.303 g of **D** is completely hydrolysed with water. All the chlorine atoms present in **D** are converted to chloride ions. The solution is diluted to 100 cm^3 .

A 25.00 cm³ sample of this solution requires 22.40 cm³ of 0.0500 mol dm⁻³ aqueous silver nitrate for complete precipitation of the chloride ion.

Calculate the empirical formula of **D**. Show all your working.

(d)	Explain the differences in the reaction of water with magnesium chloride and with phosphorus
	pentachloride. Suggest the pH of the resulting solutions, and write equations.

.....[3] [Total: 12] Question 4 starts on the next page.

4 (a) lodine and iodide ions undergo the following equilibrium in aqueous solution.

 $I_2(aq) + \Gamma(aq) \implies I_3^-(aq)$ equilibrium 1

Cyclohexane and water are immiscible. Molecular iodine, I_2 , is more soluble in cyclohexane than it is in water. An equal volume of cyclohexane is added to an aqueous solution in which $[I_3^-(aq)]$ and $[I^-(aq)]$ are both 1.00 mol dm⁻³.

(i) Triiodide ions, I₃⁻, has a linear structure.
 Draw a 'dot–and–cross' diagram to show the bonding in a triiodide ion.

(ii) Explain in terms of types of the intermolecular forces involved, why cyclohexane and water are immiscible.

(iii) Describe and explain the effect of adding cyclohexane on *equilibrium 1*. [2]

[1]

(b) In food chemistry, substances known as antioxidants are reducing agents. Ascorbic acid, C₆H₈O₆, commonly known as vitamin C is thought to retard potentially damaging oxidation of living cells.

The mass of ascorbic acid in a food product can be determined by means of an iodometric titration. The analysis involved reacting ascorbic acid with excess triiodide, I_3^- which is prepared by combining potassium iodide, KI and potassium iodate, KIO₃, in acidic solution according to the following stoichiometry.

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O$$
 equation 1

In the preparation of triiodide, excess KI is reacted with 20 cm³, 0.01 mol dm⁻³ of KIO₃.

The triiodide produced will oxidise ascorbic acid to dehydroascorbic acid, $C_6H_6O_6$, and itself reduced to iodide ions.

Subsequently, the unreacted triiodide is determined by reacting with 25.60 cm³ of 0.04 mol dm⁻³ thiosulfate ions, $S_2O_3^{2-}$.

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$
 equation 2

(i) The electrode reaction for the standard I_3^-/I^- half cell is

$$I_3^{-}(aq) + 2e^{-} \implies 3I^{-}(aq) \qquad E^{\Theta} = +0.536V$$

With reference to the *Data Booklet*, determine the E_{cell}^{Θ} and ΔG^{Θ} of equation 2.

$$E_{cell}^{\Theta}$$
 =V

$$\Delta G^{\Theta} = \dots kJ \text{ mol}^{-1} [2]$$

(ii) Construct the overall equation for the reaction between ascorbic acid and triiodide.

.....[1]

(iii) Using the information provided, determine the mass of ascorbic acid in the food product.

[3] [Total: 10] **5** (a) Margarine is a non-dairy food product created as a substitute for butter. While originally made from animal fat in 1800s, margarine is now produced from liquid vegetable oils. During the process, the unsaturated fatty acids present in the oils undergo partial hydrogenation.

Complete hydrogenation would produce fully saturated fatty acids and lead to a lard-like product that is too hard to spread on toast. Conditions can be adjusted to ensure some double bonds are hydrogenated while others are left in place resulting in a soft and spreadable product.

Fig. 5.1 shows the reaction that occurs during the production of margarine.



Fig. 5.1

(i) Using the information provided and Fig. 5.1, state which organic acid is likely present in liquid vegetable oil undesired lard like product soft and spreadable product [1] Suggest the reagents and conditions for step 1 in Fig. 5.1. (ii)[1] (iii) С elaidic acid It is known that elaidic acid is a by-product during the process. State which acid in Fig. 5.1 is isomeric with elaidic acid and name the type of isomerism involved.

.....[2]

17

(b) Fig. 5.2 shows some reaction schemes involving compound **E** (where R represents a side chain).





(i) Compound H has a molecular formula $C_9H_8O_2$.

Suggest the structures of compound **G** and **H**.

G	н
	[2]

(ii) Hence, suggest reagents and conditions for steps I, II and III in Fig. 5.2.

step I	
step II	
step III	[3]
	[*]

(iii) Suggest a two-step synthetic route to form compound J from E.

[3]

(iv) Write an equation for the reaction of **E** with alkaline aqueous iodine.

.....[2] [Total: 14] **6** Naphthalene, C₁₀H₈, is an aromatic organic compound that is a solid at room temperature and pressure.

The enthalpy change of fusion, ΔH_{fusion} , of naphthalene is the enthalpy change that occurs when naphthalene melts. It cannot be directly measured.

 $C_{10}H_8(s) \implies C_{10}H_8(l)$

The melting point of naphthalene depends on its purity. When diphenylamine, $(C_6H_5)_2NH$, is dissolved in liquid naphthalene, it lowers the melting point of naphthalene. By varying the amount of diphenylamine and measuring the melting points of the different mixtures, the enthalpy change of fusion of naphthalene can be calculated.

(a) The equation that links the melting point of a naphthalene–diphenylamine mixture with its enthalpy change of fusion, ΔH_{fusion} , is shown.

$$\log Y = A - \frac{\Delta H_{\text{fusion}}}{2.30 \times \text{RT}_{\text{m}}}$$

 $\begin{array}{l} Y = \text{mole fraction of naphthalene} \\ R = \text{molar gas constant} \\ T_m = \text{melting point of naphthalene in K} \\ A \text{ is a constant} \end{array}$

Mole fraction of naphthalene, Y is calculated as shown.

$$Y = \frac{n_N}{n_N + n_D}$$

 n_N = amount in moles of naphthalene n_D = amount in moles of diphenylamine

The melting point and freezing point of a substance are the same. The melting point, T_m , of a substance can be found by recording the temperature at which the substance freezes, measured when crystals first start to appear on cooling.

Table 6.1 shows the results of a series of experiments using 0.100 mol of naphthalene and different amount of diphenylamine.

amount of diphenylamine, n _D / mol	temperature at which crystals appear, T _m / K
0.00	353
0.0088	349
0.0178	345
0.0266	341
0.0355	338
0.0444	334
0.0533	331
0.0621	329
0.0769	325

Table 6.1

(i) Suggest why the melting point decreases as the amount of diphenylamine in the mixture increases.



Using the results in Table 6.1, log Y and $\frac{1}{T_m}$ are calculated. A graph is then plotted to show

the relationship between log Y and $\frac{1}{T_m}$. Fig. 6.1 shows a graph of log Y against $\frac{1}{T_m}$.





(ii) Calculate the gradient of the graph in Fig. 6.1 and hence, determine the value of the enthalpy change of fusion of naphthalene, ΔH_{fusion} , in kJ mol⁻¹.





State how the value of ΔH_1 compares to the value of ΔH_{fusion} if the mixing of naphthalene and diphenylamine is endothermic. Explain your answer.

- (c) A student incorrectly used a value for the M_r of diphenylamine that is too low. This produced incorrect values for the mole fraction, Y used to obtain the graph in Fig. 6.1.
 - (i) Deduce the effect this error will have on the calculated values of Y.

.....[1]

(ii) The student uses the incorrectly calculated value of Y from (c)(i) in the determination of $\Delta H_{\text{fusion.}}$

Predict how the student's calculated value of ΔH_{fusion} will be different from the actual value. Explain your answer.

.....[2]

(d) Both naphthalene and diphenylamine contain aromatic system that obey Hückel's rule.

This rule states that an aromatic molecule is a cyclic, planar molecule that contains (4n+2) delocalised π electrons, where n is 0 or a positive integer (1, 2, 3 etc.). Benzene is an example of an aromatic molecule as it contains 6 delocalised π electrons where n = 1.

The Kekulé structure of naphthalene is shown below.



naphthalene

(i) Use the information above to explain why naphthalene is an aromatic molecule.

.....[1]

Pyrrole is another aromatic compound that obeys Hückel's rule.



(ii) Deduce the type of hybridisation present in the N atom in pyrrole. Explain your answer.

......[1]

(e) The basicities of pyridine and diphenylamine, $(C_6H_5)_2NH$, are different. Table 6.2 lists the K_b values for both bases.

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base	$K_{ m b}$ / mol dm ⁻³	
pyridine	1.70 × 10 ^{−9}	
diphenylamine	6.03 × 10 ⁻¹³	

Explain the relative magnitudes of the K_b values in Table 6.2.

.....[2]

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