Anderson Serangoon Junior College 2020 JC2 Preliminary Examinations H2 Chemistry (9729) Suggested Mark Scheme for Paper 2

- 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.

K: 1s² 2s² 2p⁶ 3s² 3p⁶ 4s¹ Cu: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹

(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]

[1]

[2]

No of protons in ${}^{64}_{29}$ Cu = 29 No of electrons in ${}^{64}_{29}$ Cu = 29 No of neutrons in ${}^{64}_{29}$ Cu = 35

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Mass of one atom {}^{64}_{29}Cu = (29x1.67x10<sup>-27</sup>) + (29x9.11x10<sup>-31</sup>) + (35x1.67x10<sup>-27</sup>)
= 1.07 x 10<sup>-25</sup> kg
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(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.

 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

explanation: It is the <u>highest energy orbital</u> / <u>the electron in this orbital is less attracted</u> <u>to the nucleus</u>.

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













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

The amount of heat <u>evolved or absorbed</u> when <u>one mole</u> of a substance is formed from its <u>constituent elements</u>, all in their standard states at <u>298 K and 1 bar</u>.

(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 . [3]



$$= -2035 \text{ kJ mol}^{-1}$$

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

Calculate ΔS^{Θ} for the reaction, and explain its sign.

 $\Delta G^{\Theta} = \Delta H^{\Theta} - T\Delta S^{\Theta}$ -284 = -251 - (298) ΔS^{Θ} ΔS^{Θ} = +0.111 kJ mol-1 K-1 = +111 J mol-1 K-1

 ΔS^{Θ} is <u>positive</u>, indicating an <u>increase in ways of arranging the particles and distributing</u> <u>energy</u> as the reaction results in a <u>change</u> from regular arrangement in the <u>solid</u> state to ions in the <u>aqueous</u> state.

[Total: 13]

[2]

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. [1]

A heterogeneous catalyst provides active <u>sites</u> where the butane molecules could be <u>adsorbed</u> via temporary bonds. This <u>weakens the covalent bonds in butane</u> and <u>lowers the</u> <u>activation energy</u> which increases the rate of reaction. OR

The <u>adsorption increases the concentration of the reactant molecules</u> at the catalyst surface and allows <u>more reactant molecules</u> to come into close contact with proper orientation for reaction to take place.

(b) Butane gas was added to an enclosed vessel, at 373 K and at constant pressure. 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

 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.

pV = nRT $p = \left(\frac{n}{V}\right)RT \quad (IMPT: V \text{ is in } m^{3}!)$ $p_{\text{butane}} = \frac{(0.30)(8.31)(373)}{1 \times 10^{-3}} 0.30 \times (10^{-1})^{-3} \times 8.31 \times 373$ $= \frac{930000 \text{ Pa} (3 \text{ sig fig})}{1 \times 10^{-3}}$ $p_{2-\text{methylpropane}} = \frac{(0.70)(8.31)(373)}{1 \times 10^{-3}}$ = 2170000 Pa (3 sig fig)

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

 $K_{p} = \frac{p_{2\text{-methylpropane}}}{p_{\text{butane}}}$ $= \frac{2170000}{930000}$ = 2.33

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

partial pressure of butane remains unchanged / constant.

- (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]

(Free radical substitution) Initiation: $Br_2 \xrightarrow{uv} 2Br$

Propagation:

$$\begin{array}{cccc} \mathsf{Br} \bullet & \mathsf{CH}_3 & & \mathsf{CH}_3 \\ \mathsf{Br} \bullet & \mathsf{CH}_3 \overset{\mathsf{I}}{\underset{\mathsf{H}}{\mathsf{C}}} - \mathsf{CH}_3 & \longrightarrow & \mathsf{CH}_3 \overset{\mathsf{I}}{\underset{\mathsf{C}}{\mathsf{C}}} - \mathsf{CH}_3 & + \mathsf{HBr} \end{array}$$

$$\begin{array}{c} \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{C} \\ \mathsf{-} \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{C} \\ \mathsf{-} \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{C} \\ \mathsf{-} \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{CH}_3 \\ \mathsf{-} \\ \mathsf{-} \\ \mathsf{-} \\ \mathsf{CH}_3 \\ \mathsf{-} \\ \mathsf{-} \\ \mathsf{-} \\ \mathsf{-} \\ \mathsf{-} \\ \mathsf{CH}_3 \\ \mathsf{-} \\$$

Termination:

$$2Br \bullet \longrightarrow Br_{2}$$

$$CH_{3}$$

$$CH_{3}C - CH_{3} + Br \bullet \longrightarrow CH_{3}C - CH_{3}$$

$$Br$$

$$CH_{3}C - CH_{3} + Br \bullet \longrightarrow CH_{3}C - CH_{3}$$

$$Br$$

$$CH_{3}C - CH_{3} \longrightarrow H_{3}C - CH_{3} - CH_{3}$$

$$CH_{3}C - CH_{3} - CH_{3}$$

$$CH_{3}C - CH_{3} - CH_{3}$$

- (ii) Suggest why it is not possible to make iodoalkanes by this method.
- [1]
- lodoalkanes cannot be made by free–radical substitution as the <u>first propagation</u> <u>step is endothermic</u> ($\Delta H = 410 - 299 = +111 \text{ kJ mol}^{-1}$)
- OR Less energy is evolved from the formation of the weak H–I bond (299 kJ mol⁻¹) compared to that of H–Br (366 kJ mol⁻¹).
- OR Enthalpy change for the reaction is endothermic (+22 kJ mol⁻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.

 $CH_3CH_2Cl + NaI \implies CH_3CH_2I + NaCl$ 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]

Sodium chloride being insoluble can be easily removed, causing the [NaC*l*] to be low. This will cause the equilibrium position to shift to the right to form more NaC*l*, allowing the reaction to go almost to completion.

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 [CH₃CH₂C <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. [3]

$$\frac{rate_2}{rate_1} = \frac{k(3.0 \times 10^{-3})^x (4.0 \times 10^{-3})^y}{k(1.0 \times 10^{-3})^x (2.0 \times 10^{-3})^y} = \frac{1.8 \times 10^{-10}}{3.0 \times 10^{-11}}$$
$$\left(\frac{3}{1}\right)^x \left(\frac{2}{1}\right)^y = \frac{18}{3}$$
$$\binom{3^x}{2^y} = 6$$
$$x = \underline{1}, y = \underline{1}$$

Therefore order of reaction with respect to CH_3CH_2Cl is <u>1</u> and order of reaction with respect to NaI is <u>1</u>.

Rate = k [CH₃CH₂Cl] [NaI]

Alternative method

Comparing expt 1 and 2, when $[CH_3CH_2Cl]$ doubled and [NaI] tripled, the rate of reaction increased by a factor of 6.

If x = 0 and y = 1, rate of reaction will increase by a factor of 2 If x =1 and y = 0, rate of reaction will increase by a factor of 3 If x =1 and y = 1, rate of reaction will increase by a factor of $(3)^{1}(2)^{1} = 6$ If x =1 and y = 2, rate of reaction will increase by a factor of $(3)^{1}(2)^{2} = 12$ If x =2 and y = 1, rate of reaction will increase by a factor of $(3)^{2}(2)^{1} = 18$

[Total: 14]

- 3 (a) Iron reacts with
 - chlorine, Cl_2 to form iron(III) chloride FeC l_3 .
 - 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. [2]

Element	<i>E</i> ⊖ / V
$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36
$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$	+0.54

Down the Group, $E^{\bullet}_{x_2/X^-}$ becomes <u>less positive</u>. Hence, decreasing tendency for X₂ to be reduced to X⁻. The <u>oxidising power</u> of halogens <u>decreases</u> from <u>Cl₂ to I₂</u>.

Due to the strong oxidising power of $\underline{Cl_2}$, it is able to oxidise iron (oxidation number 0) to iron(III) chloride (oxidation number of Fe= +3). I₂ is a weaker oxidising agent, and can oxidise iron (oxidation number 0) to iron(II) iodide (oxidation number of Fe = +2).

(b) Sea water from the Dead Sea is known to contain Br⁻(aq).

AgNO₃(aq) of known concentration can be gradually added to the sea water to determine concentration of $Br^{-}(aq)$ in it. A small quantity of aqueous potassium chromate(VI), K₂CrO₄, 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 bromide ions are precipitated.

Table 3.1		
	colour	K _{sp}
AgBr	cream	5.35 x 10 ⁻¹³ mol ² dm ⁻⁶
Ag ₂ CrO ₄	red	3.01 x 10 ⁻¹² mol ³ dm ⁻¹²

(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.

AgBr for precipitation to occur, $[Ag^+][Br^-] > K_{sp} (AgBr)$ min. $[Ag^+] = \frac{5.35 \times 10^{-13}}{0.06}$ = 8.92 x 10⁻¹² mol dm⁻³

Ag₂CrO₄, for precipitation to occur, $[Ag^+]^2 [CrO_4^{2-}] > K_{sp} (Ag_2CrO_4)$ min. $[Ag^+] = \sqrt{\frac{3.01 \times 10^{-12}}{0.01}}$ = **1.73 x 10^{-5 mol dm^{-3}}** [2]

(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]

[Ag⁺] required for Ag₂CrO₄ to ppted out = 1.73 x 10⁻⁵ mol dm⁻³ [Br⁻] remaining when Ag₂CrO₄ starts to ppt out = $\frac{5.35 \times 10^{-13}}{1.73 \times 10^{-5}}$ = 3.09 x 10⁻⁸ mol dm⁻³

% of Br⁻ ppted out as AgBr = $\frac{0.06 - (3.09 \times 10^{-8})}{0.06} \times 100\% \approx 100\%$

For a solution containing 0.06 mol dm⁻³ of Br⁻, K_2CrO_4 is able to determine the end point of the titration very accurately as shown below, thus it is a suitable indicator.

(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. [3]

No. of mol of Cl^- in 25 cm³ = 0.0500 X 0.0224 = 1.12 x 10⁻³ mol No. of mol of Cl^- in 100 cm³ = 1.12 x 10⁻³ X 4 = 4.48 x 10⁻³ mol

Mass of $Cl^- = 4.48 \times 10^{-3} \times 35.5 = 0.159 \text{ g}$ Mass of S = 0.303 - 0.159 = 0.144 g

No. of mol of S = $0.144 / 32.1 = 4.49 \times 10^{-3}$ mol Mole ratio of S : Cl = 1 : 1 Empirical formula = SC/

(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]

 Mg^{2+} has <u>high charge density</u> (due to small ionic radius and high charge) thus has <u>high</u> <u>polarising power</u>. Hence, $MgCl_2$ undergoes <u>hydration and partial hydrolysis</u>, producing a slightly acidic solution. pH of resulting solution = <u>6.5</u>

 PCl_5 undergoes <u>complete hydrolysis</u> due to the <u>presence of energetically accessible vacant</u> <u>3d orbitals on phosphorus which can accommodate lone pair from water molecules</u>. pH of resulting solution = <u>1 or 2</u>

 $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

[Total: 12]

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, I_3^- , has a linear structure. Draw a 'dot–and–cross' diagram to show the bonding in a triiodide ion [1]



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

Since I_2 is much more soluble in cyclohexane than it is in water, [I₂(aq)] decreases as it <u>dissolves in cyclohexane</u> (and is removed from the aqueous layer). Hence, by Le Chatelier's Principle, the <u>position of equilibrium 1 shifts left</u>. [I₃⁻(aq)] <u>decreases</u> and [I⁻(aq)] increases.

- (iii) Explain in terms of types of the intermolecular forces involved, why cyclohexane and water are immiscible. [2]
 - Energy released due to the formation of weak instantaneous dipole-induced dipole interactions (or permanent dipole-induced dipole) between cyclohexane and water is unable to compensate for the energy absorbed to break the stronger <u>hydrogen</u> bonding between the water molecules (and instantaneous dipole-induced dipole interactions between cyclohexane molecules).
 - Hence, cyclohexane is insoluble in water
- (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

9729/02/H2

(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. [2]

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

Reduction : $2e + I_3 \rightarrow 3I^-$ Oxidation: $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

$$E^{\Theta}_{cell} = E^{\Theta}_{red} - E^{\Theta}_{oxd}$$

= +0.536 - (0.09)
= +0.446 V

 $\Delta G = - nFE^{\Theta}_{cell}$ = -2(96500)(0.446) = -86078 J mol⁻¹ = -86.1 kJ mol⁻¹

(ii) Construct the overall equation for the reaction between ascorbic acid and triiodide. [1]

 $\begin{array}{l} C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e \\ I_3^- + 2e \rightarrow 3I^- \end{array}$

Overall: $C_6H_8O_6 + I_3^- \rightarrow C_6H_6O_6 + 2H^+ + 3I^-$

(iii) Using the information provided, determine the mass of ascorbic acid in the food product. [3]

$$\begin{split} IO_3^- + 8\Gamma^- + 6H^+ &\rightarrow 3I_3^- + 3H_2O \\ C_6H_8O_6^- + I_3^- &\rightarrow C_6H_6O_6 + 2H^+ + 3I^- \\ I_3^- + 2S_2O_3^{2-} &\rightarrow 3\Gamma^- + S_4O_6^{2-} \\ Amount of S_2O_3^{2-} &= (25.60/1000) \times 0.04 = 0.001024 \text{ mol} \\ Amount of unreacted I_3^- &= 0.000512 \text{ mol} \\ Amount of KIO_3 &= (20/1000) \times 0.01 = 0.0002 \text{ mol} \\ Amount of I_3^- \text{ initially} &= 0.00002 \times 3 = 0.0006 \text{ mol} \\ Amount of I_3^- \text{ reacted} &= 0.0006 - 0.000512 = 0.000088 \text{ mol} \\ Amount of C_6H_8O_6 \text{ in sample} &= 0.000088 \text{ mol} \\ Mass of C_6H_8O_6 \text{ in sample} &= 0.000088 \times (72+8+96) \\ &= 0.0154 \text{ g} \end{split}$$

[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 scheme 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 [1]

liquid vegetable oil	linoleic acid
undesired lard like product	stearic acid
soft and spreadable product	oleic acid

(ii) Suggest the reagents and conditions for step 1 in Fig. 5.1. [1]

(limited) hydrogen gas, nickel catalyst, heat Or hydrogen gas, nickel catalyst, (r.t.p.)



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]

Oleic acid cis-trans isomerism

(b) Fig. 5.2 shows a reaction scheme involving compound E.





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

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



[2]

(iii)

- (ii) Hence, suggest reagents and conditions for steps I, II and III in Fig. 5.2.
 - step I LiA*l*H₄ in dry ether, rt
 - step II II: NaBH₄ (in methanol) or H₂, Pt, rt or H₂, Ni, heat step III (excess) conc. H₂SO₄, heat
- (iii) Suggest a two-step synthetic route to form compound J from E.



First step: HCN with trace amount of NaOH or NaCN, cold Second step: H_2 gas, Ni catalyst, heat or H_2 , Pt, rt

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





[Total: 14]

[3]

[3]

[2]

ASRJC JC2 PRELIM 2020

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.

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

Diphenylamine, $(C_6H_5)_2NH$, dissolves in liquid naphthalene which lowers the melting point of naphtalene. 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.

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

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

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.

Table	6.1
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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

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

An increasing amount of diphenylamine <u>increases the disruption to the lattice of</u> <u>naphthalene</u>. There is an <u>increasing weakening of the instantaneous dipole– induced</u> <u>dipole attraction between naphthalene molecules</u>. Hence, <u>decreasing the amount of</u> <u>energy required</u> to overcome the intermolecular forces of attraction between naphthalene molecules.

(accept explanation in terms of increased in entropy leading to depression in melting point T = $\frac{\Delta H}{\Delta S}$)

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





(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. [2]

Gradient = $\frac{-0.02 - (-0.22)}{(2.85 \times 10^{-3}) - (3.05 \times 10^{-3})}$ = -1000 K⁻¹ Gradient = $-\frac{\Delta H_{\text{fusion}}}{2.30 \times \text{R}}$ $\Delta H_{\text{fusion}} = \text{Gradient} \times -2.30 \times \text{R}$ = -1000 × -2.30 × 8.31 = +19113 J mol⁻¹ = +19.1 kJ mol⁻¹ (3 sig fig)

9729/02/H2

(b) Fig. 6.2 shows ΔH_1 , ΔH_{fusion} and ΔH_{mixing} relationship in an energy cycle.



Fig. 6.2

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. [2]

 ΔH_1 will be <u>more positive</u> than ΔH_{fusion} .

Since $\Delta H_1 = \Delta H_{\text{fusion}} + \Delta H_{\text{mixing}}$ and ΔH_{mixing} is positive.

- (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]

Y become smaller since n_D becomes larger.

(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]

 ΔH_{fusion} will be <u>more positive</u>.

This is because <u>logY</u> is more negative.

(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.



napthalene

(i) Use the information above to explain why naphthalene is an aromatic molecule. [1]

Naphthalene has (10 sp² hybridised C in a bicyclic, planar ring and) <u>10 delocalised π electrons</u> where <u>n = 2</u>.

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]

Since pyrrole is aromatic, <u>lone pair</u> on the N atom resides in the <u>unhybridised p orbital</u> and forms delocalised π electron cloud. Hence, N in pyrrole is <u>sp² hybridised</u>.

OR

cyclic planar \Rightarrow trigonal planar about N, therefore sp²

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

base	K₀ / mol dm ⁻³
pyridine	1.70 × 10 ^{−9}
diphenylamine	6.03 × 10 ⁻¹³

Table 6.2

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

[2]

The lone pair of electrons on N atom in diphenylamine is delocalised into the π electron cloud of the benzene ring while the lone pair of electron on N in pyridine is not. This decreases the availability of the lone pair of electrons on N atom to accept a proton in diphenylamine. Hence, diphenylamine is a weaker base with a lower K_b value.

[Total: 12]