

TAMPINES MERIDIAN JUNIOR COLLEGE JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME

SUGGESTED ANSWERS

CIVICS GROUP

21S

H2 CHEMISTRY

Paper 3 Free Response

Candidates answer on Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and Civics Group in the spaces at the top of the page.

Write in dark blue or black pen on the answer booklet.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A

Answer **all** questions.

Section B Answer one question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

For Examiners' Use			
Section A	Q1	/ 17	
	Q2	/ 21	
	Q3	/ 22	
Section B	Q4	/ 20	
	Q5	/20	
Total		/ 80	
Grade			

This document consists of **30** printed pages and **2** blank page.

9729 / 03 20 September 2022 2 hours

Section A

Answer **all** the questions from this section.

- **1(a)** Samples of three different oxides were added to water separately.
 - (i) State the Arrhenius theory of acids and bases.

Acids are **hydrogen-containing** substances that produce $\underline{H^+ \text{ in aqueous solution}}$ while bases are **hydroxide-containing** substances that produce $\underline{OH^- \text{ in aqueous solution}}$.

(ii) The pH value of the solution formed when sodium oxide is shaken with water is greater than the pH value of the solution formed when magnesium oxide is shaken with water. The pH of the solution formed when sulfur trioxide is shaken with water is less than both of these solutions.

Explain these observations using the Arrhenius theory. Write equations for all the reactions described. [3]

Both Na₂O and MgO produced OH⁻ when dissolved in water.

$Na_2O + H_2O \rightarrow 2NaOH$	OR	$Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$
$MgO + H_2O \rightleftharpoons Mg(OH)_2$	OR	$MgO + H_2O \rightleftharpoons Mg^{2+} + 2OH^{-}$

However, <u>NaOH</u> is <u>much more soluble</u> in water than <u>Mg(OH)</u>₂ so the <u>[OH⁻] is higher</u> and thus pH value is higher.

OR

<u>NaOH dissociates fully</u> while <u>Mg(OH)</u>₂ dissociates partially so the [OH⁻] is higher and thus pH value is higher.

 SO_3 <u>dissolves</u> in water to <u>produce H^+</u>, an acidic solution. Hence, its pH value is lower than the other two oxides. $SO_3 + H_2O \rightarrow HSO_4^- + H^+$ Or $SO_3 + H_2O \rightarrow SO_4^{2-} + 2H^+$



[1]

(b) Diazomethane, CH_2N_2 , reacts with water to give methanol and nitrogen gas.

$$CH_2N_2 \ + \ H_2O \ \rightarrow \ CH_3OH \ + \ N_2$$

When 2.50×10^{-3} mol of CH₂N₂ was added into water, the volume of nitrogen gas evolved at various time intervals after the start of the reaction were measured. At the end of the reaction, 60 cm³ of nitrogen gas was collected. The experiment results are plotted in Fig. 1.1 below.



Fig. 1.1

Use Fig. 1.1 and the information given to show that the order of reaction with respect to [CH₂N₂] is 1.

Max volume of N₂ gas collected = 60 cm³ (100%) The two half-lives are determined from graph at volume = 30 cm³ (50%) & 45 cm³ (75%) $1^{st} t_{1/2}$ is at a volume of $\frac{1}{2} \times 60 = 30$ cm³ $2^{nd} t_{1/2}$ is at a volume of $\frac{3}{4} \times 60 = 45$ cm³

From the graph, <u> $t_{1/2}$ is constant at about 14.5 min</u> hence order of reaction with respect to [CH₂N₂] is 1.

The reaction of CH_2N_2 with water takes place in the presence of an acid. Two experiments were conducted at different pH values to investigate the kinetics of this reaction. The results are shown in Table 1.1.

Experiment	$[CH_2N_2]$ / mol dm ⁻³	pН	Relative rate
1	1.00 × 10 ⁻³	1.00	1
2	4.00 × 10 ^{−3}	1.30	2

Table 1.1

(ii) Calculate the concentration of H⁺(aq) in experiment 1 and 2.

 Experiment
 pH
 [H+] / mol dm⁻³

 1
 1.00
 10^{-1.00} = 0.100

 2
 1.30
 10^{-1.30} = 0.0501

(iii) Use the data provided to determine the order of reaction with respect to [H⁺], and hence write the rate equation for the reaction.

Experiment	$[CH_2N_2] \text{ / mol dm}^{-3}$	рН	[H ⁺] / mol dm ⁻³	Relative rate
1	1.00 × 10⁻³	1.00	0.100	1
2	4.00 × 10 ^{−3}	1.30	0.0501	2

Let rate = $k [CH_2N_2] [H^+]^x$ $\frac{rate_1}{rate_2} = \frac{k [CH_2N_2]_1^1 [H^+]_1^x}{k [CH_2N_2]_2^1 [H^+]_2^x}$ $\frac{1}{2} = \frac{(1.0 \times 10^{-3})^1 (0.100)^x}{(4.0 \times 10^{-3})^1 (0.0501)^x} \Rightarrow \frac{1}{2} = \frac{1}{4} (2)^x \Rightarrow x = 1$

OR

From Experiments **1 and 2**, when $[CH_2N_2]$ is <u>increased 4 times</u> and $[H^+]$ is <u>halved</u>, overall <u>rate is doubled</u>. Since order of reaction w.r.t. $[CH_2N_2]$ is 1, when $[CH_2N_2]$ is <u>increased 4</u> times, rate should have <u>increased 4 times</u>. Since $(4)^1 \times (\frac{1}{2})^1 = 2$, this means that when $[H^+]$ is <u>halved</u>, <u>rate is halved</u>.

Hence order of reaction w.r.t. [H+] is 1.

Rate = k [CH₂N₂] [H⁺] (allow for ECF)

[1]

(c) Pure magnesium needed for making alloys can be obtained by the electrolysis of molten magnesium chloride as shown in Fig. 1.2.



Write the half-equations, including state symbols, for the reactions occurring at the graphite and iron electrodes. Label your equations clearly to indicate the reaction occurring at the graphite and iron electrode respectively.

Graphite electrode / anode:	$2Cl^{-}(l) \rightarrow Cl_{2}(g) + 2e^{-}$
Iron electrode / cathode:	$\mathrm{Mg}^{2+}(l)$ + 2e ⁻ $ ightarrow$ Mg (l)

- (ii) Draw and label the direction of electron flow in the cell on Fig. 1.2. [1]
- (iii) Calculate the mass of magnesium obtained if a current of 3.00 A is supplied for 10.0 h.

 $Q = I \times t$ = 3.00 × 10.0 × 3600 = 108 000C

Amount of Mg = $\frac{l t}{n F} = \frac{108\ 000}{2 \times 96500} = 0.5596$ mol

Mass of Mg = 0.5596 × 24.3 = **<u>13.6 g</u>**

 (iv) A gas is continuously passed over the molten magnesium in the electrolytic cell to provide an inert environment. Suggest a gas that can be used for this.

Helium, argon or any suitable noble gas. (Do not accept nitrogen gas)

[2]

(v) Molten magnesium chloride in the cell is being replaced with aqueous magnesium chloride. Using relevant data from the *Data Booklet*, state and explain the reactions taking place at both electrodes when this change is made.

At the cathode, (reduction) $Mg^{2+} + 2e \rightleftharpoons Mg$ $E^{\circ} = -2.38 \vee$ $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^ E^{\circ} = -0.83 \vee$ At the anode, (oxidation) $Cl_2 + 2e^- \rightleftharpoons 2Cl^ E^{\circ} = + 1.36 \vee$

 $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\circ = + 1.23 V$

For MgCl₂(aq),

At the cathode,

• <u>H₂O is preferentially reduced</u> to produce <u>H₂(g)</u> as <u>*E*[•] (H₂O/H₂) is more positive</u> <u>than *E*[•] (Mg/Mg²⁺). (including quoted E values)</u>

At the anode,

• <u>H₂O is preferentially oxidised</u> to produce $O_2(g)$ as <u>*E*^e (O₂ /H₂O) is less positive</u> than <u>*E*^e (Cl₂ /Cl⁻). (including quoted E values)</u>

[Total: 17]

- **2** Chromium is a steely-grey, hard and dense transition element. Its name came from the Greek word 'chrδma', which means colour, because many of its compounds are coloured.
- (a) Define *transition element*. [1]

A transition element is a *d* block element that <u>forms at least one stable ion with</u> <u>partially-filled *d* subshell.</u>

- (b) Transition elements have significant higher density and melting point compared to the main group metals.
 - (i) Briefly explain why transition elements exhibit higher density. [1]

Transition elements have relatively <u>smaller atomic radius</u> and <u>higher relative atomic</u> <u>mass</u> than main group metals. Hence they have **higher mass per unit volume**.

(ii) Explain why the melting point of chromium is significantly higher than the melting point of calcium.

Both Ca and Cr have giant metallic structures.

In Cr, <u>the 3d and 4s electrons are involved in delocalisation</u> but in Ca, <u>only the s</u> <u>electrons are involved in the delocalisation</u> in metallic bonding. A larger amount of energy is needed to overcome the stronger metallic bonding

in Cr to melt the metal.

Hence Cr has a higher melting and boiling point than Ca.

[1]

(c) Anhydrous chromium(III) chloride may be prepared by the chlorination of chromium metal.

$$Cr(s) + \frac{3}{2}Cl_2(g) \rightarrow CrCl_3(s)$$

The thermodynamic data at 298 K are given in the table below.

Substance	$\Delta S_{\rm f}^{ m e}$ / J mol ⁻¹ K ⁻¹	$\Delta H_{\rm f}^{\rm e}$ / kJ mol ⁻¹
CrCl ₃	-236.0	-556.6

(i) Explain the significance of the sign of ΔS_{f}^{\bullet} .

Sign of ΔS_{f}^{e} is negative as there is a <u>decrease in disorder due to decrease in the</u> <u>number of gaseous particles</u> from 1.5 mol of $Cl_2(g)$ to 0 mol of gas.

(ii) Using the information above, calculate ΔG° for the formation of $CrCl_{3}(s)$. [1]

$$\Delta G_{\rm r}^{\rm e} = \Delta H_{\rm r}^{\rm e} - T\Delta S_{\rm r}^{\rm e}$$

= -556.6 - (298) $\left(-\frac{236}{1000}\right)$
= - 486 kJ mol⁻¹ or - 486 000 J mol⁻¹ (3 sf or 4 sf with units)

(iii) Using your answer from (c)(ii), suggest whether the ratio of [product] / [reactants] at equilibrium for the formation of CrCl₃ at 298 K will be less than, equal to or greater than 1. Give a reason for your answer.

Since $\Delta G^{\circ} < 0$, the <u>forward reaction is favoured / thermodynamically feasible</u> and hence the <u>ratio of [product] / [reactants] becomes > 1</u>. allow ecf if $\Delta G^{\circ} > 0$ in (iii)

(iv) Comment on the effect of increasing temperature on the spontaneity of the reaction. [2]

As the **temperature of the reaction increases**, $|\Delta H| < |T\Delta S|$ OR <u>-T ΔS becomes more positive</u>

 ΔG_{r}° becomes positive. Therefore, reaction becomes <u>non-spontaneous</u> at high temperature. [1]





Fig. 2.1

Using relevant E^o values from the Data Booklet, explain why the blue solution slowly turns green in air.

$\begin{array}{c} Cr^{3+} + e^{-} \rightleftharpoons Cr^{2+} \\ \hline O_2 + 4H^+ + 2e^{-} \rightleftharpoons 2H_2O \end{array}$	<i>E</i> [₽] = −0.41 V <i>E</i> [₽] = + 1.23 V	E ^e oxid E ^e red
E^{e}_{cell} = 1.23 - (-0.41) = <u>+1.64</u> V		

Since $E_{cell}^{\circ} > 0$, reaction is spontaneous and the <u>blue $Cr^{2+} / [Cr(H_2O)_6]^{2+}$ is oxidised to</u> green $Cr^{3+} / [Cr(H_2O)_6]^{3+}$.

(ii) State the type of reaction and write a balanced equation to account for the observation when a small amount of aqueous sodium hydroxide was added to a solution **W**. [2]

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When sodium hydroxide, OH^- was added, W [Cr(H_2O)_6]^{3+} undergoes <u>precipitation</u> to form grey green ppt of Cr(OH)_3
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	[Cr(H₂O)₀] ³⁺ + 3OH⁻ ⇒	Cr(OH) ₃ + 6 H ₂ O
OR	Cr³+ (aq) + 3OH⁻ (aq) ,	Cr(OH)₃
OR	[Cr(H₂O) ₆]³+ + 3OH⁻ ,	Cr(OH) ₃ (H ₂ O) ₃ + 3 H ₂ O

(iii) Suggest the formula of the chromium containing species in X and Y. [2]

X: $[Cr(OH)_6]^{3-}$ accept $[Cr(OH)_4]^{-}$ Y: $Cr_2O_7^{2-}$

(iv) State, with reasoning, the role of hydrogen peroxide in Fig. 2.1.

 H_2O_2 is an <u>oxidising agent</u>. Cr is oxidised as <u>the oxidation number of Cr from +3 in</u> [Cr(OH)₆]³⁻ to <u>+6 in CrO₄²⁻</u>.

(e) Chromium(III) picolinate is a chemical compound with the formula Cr(C₅H₄N(CO₂))₃, commonly abbreviated as CrPic₃. It is sold as a nutritional supplement to treat type-2 diabetes and promote weight loss.

The structure of the bidentate ligand picolinate is shown below.



Draw the structure of chromium(III) picolinate.

[1]

[1]



accept structure without the charges shown

- (f) Aluminium hydroxide, $Al(OH)_3$, was used as white pigment for paints. $Al(OH)_3$ has a solubility of 2.90 × 10⁻⁹ mol dm⁻³ in pure water.
 - (i) Write the expression for the solubility product, K_{sp} , of A*l*(OH)₃ and calculate its solubility product in pure water. [3]

Let the solubility of $Al(OH)_3$ in **mol dm**⁻³ be s $Al(OH)_3$ (s) $\implies Al^{3+}$ (aq) + $3OH^-$ (aq) **s** 3s $K_{sp} = [Al^{3+}] [OH^-]^3$ $K_{sp} = (s)(3s)^3$ $K_{sp} = 27 \ s^4 = 27 \ (1.56 \times 10^{-8})^4$ $K_{sp} = 1.91 \times 10^{-33} \ \text{mol}^4 \ \text{dm}^{-12}$

 $K_{sp} = [Al^{3+}][OH^{-}]^{3}$

(ii) How would you expect the solubility of Al(OH)₃ in excess NaOH to compare with that in pure water? Briefly explain your answer with an equation with state symbols. [2]

 $Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

In excess sodium hydroxide, $\underline{Al(OH)_3 \text{ forms}}$ a soluble <u>complex</u> ion, $\underline{Al(OH)_4}^-$. The solubility of $\underline{Al(OH)_3}$ is <u>higher</u> in NaOH (aq) as compared to pure water.

[Total: 21]

3(a) Outline the mechanism of the reaction between hydrogen cyanide, HCN and propanal, CH₃CH₂CHO, to form 2-hydroxybutanenitrile, CH₃CH₂CH(OH)CN.

Include all the necessary charges, dipoles, lone pairs and curly arrows. [3]

Nucleophilic addition





- (b) Compound P is an isomer of propanal and it forms a yellow precipitate when reacted with alkaline aqueous iodine.
 - P can be converted to compound S as shown in Fig. 3.1.





(i) Suggest structures for the compounds P, Q and R.

P: (CH₃)₂CO

Q: (CH₃)₂C(OH)CN

R: (CH₃)₂C(OH)COOH

(ii) Suggest reagents and conditions for each of the steps I, II and III. [3]

step I: HCN, trace NaOH (aq) OR NaCN (aq), cold

step II: HCl (aq) / H₂SO₄ (aq) heat

step III: CH₃CH₂OH, conc. H₂SO₄, heat

(iii) Suggest a suitable carbonyl compound which can be used to form CH₃CH₂CH₂CH(OH)CO₂CH₂CH₃ using the 3-stage synthesis shown in Fig. 3.1. [1]

CH₃CH₂CH₂CHO

[3]

(c) Compound **T** is another isomer of propanal and it contains two different functional groups.

T reacts with cold alkaline KMnO₄ to form propane-1,2,3-triol.



propane-1,2,3-triol

(i) Give the displayed formula of **T**.



(ii) Draw the structure of the compound U formed when propane-1,2,3-triol reacts with hot acidified K₂Cr₂O₇.



(iii) How would you expect the acidity of compound U to compare with that of propane-1,2,3-triol? Briefly explain your answer. [2]

<u>**U**</u> (carboxylic acid) is **a stronger acid** than propane-1,2,3-triol (alcohol).

- The carboxylate anion (RCOO⁻) is resonance stabilised but not the alkoxide
- Hence, the <u>carboxylate anion is more stable than alkoxide ion</u>.
- There is a greater tendency for the carboxylic acid to ionise compared to alcohol.

[1]

(d) Triglycerides are triesters formed from a glycerol (propane-1,2,3-triol) and three fatty acid (carboxylic acid) molecules.

A natural triglyceride with three different fatty acid chains is shown below.



A particular triglyceride, **J**, in castor oil produces glycerol (1 mol) and compound **K**, $C_{18}H_{34}O_3$ (3 mol) when heated with dilute sulfuric acid.

K decolourises bromine in an organic solvent. On gentle oxidation, **K** gives **L**, $C_{18}H_{32}O_3$, which gives an orange precipitate with 2,4-dinitrophenylhydrazine.

Warming **K** with concentrated sulfuric acid gives a compound **M**, $C_{18}H_{32}O_2$. On treating **M** with hot concentrated KMnO₄, $CH_3(CH_2)_5COOH$, $HO_2C(CH_2)_7CO_2H$ and CO_2 are produced.

Suggest structures for **K**, **M** and **J**. For each reaction, state the type of reaction described and the functional group present in each compound. [8]

J undergoes acidic <u>hydrolysis</u> $\sqrt{}$ when heated with sulfuric acid to produce glycerol (1 mol) and compound **K**, C₁₈H₃₄O₃ (3 mol)

 \Rightarrow K contains <u>carboxylic acid</u> \checkmark functional group

K undergoes electrophilic addition $\sqrt{}$ with bromine

 \Rightarrow **K** contains <u>**alkene</u>** $\sqrt{}$ functional group</u>

K undergoes gentle oxidation to give L, $C_{18}H_{32}O_3$ and L undergoes <u>condensation</u> \checkmark to form orange ppt

⇒ L contains <u>carbonyl</u> √ functional group (or <u>aldehyde or ketone</u>)

and **K** contains primary or **secondary alcohol** $\sqrt{}$ functional group.

K undergoes <u>elimination</u> $\sqrt{}$ with warm conc. sulfuric acid to form M, C₁₈H₃₂O₂

⇒ **M** contains <u>**alkene</u>** $\sqrt{}$ functional group</u>

M, $C_{18}H_{32}O_2$ undergoes <u>oxidation</u> \checkmark with hot conc. KMnO₄ to CH₃(CH₂)₅COOH, HO₂C(CH₂)₇CO₂H and CO₂ are produced.

- \Rightarrow Based on number of carbon atoms, 2 mol of CO₂ are formed per mol of **M**
- ⇒ Hence <u>HOOCCOOH / ethanedioc acid</u> √ intermediate is formed and immediately oxidised to give the 2 mol CO₂.

M, $C_{18}H_{32}O_2$: HO₂C(CH₂)₇CH=CHCH=CH(CH₂)₅CH₃

OR $CH_3(CH_2)_5CH=CH(CH_2)_7CH=CHCO_2H$

K, C₁₈H₃₄O₃: HO₂C(CH₂)₇CH=CHCH₂CH(CH₂)₅CH₃ OH OR CH₃(CH₂)₅CH=CH(CH₂)₇CH₂CHCO₂H

OR other possible structures with OH at different C (in bold)



[Total: 22]

Section B

Answer **one** question from this section.

4(a) Carbon dioxide is the most significant greenhouse gas in Earth's atmosphere. The volume of 0.30 mol of carbon dioxide gas was measured at a temperature of 25 °C when various pressures were applied. The following results were obtained.

pressure, p / atm	volume, V / dm ³	pressure x volume, <i>p</i> V / atm dm ³
5.00	1.436	7.18
10.0	0.7015	7.02
15.0	0.4566	6.85

Table 4.1

(i) Calculate the volume, in dm³, of 0.30 mol of an ideal gas at a temperature of 25 °C and at a pressure of 12.0 atm.

pV = nRT → V =
$$\frac{n R T}{P}$$
 → V = $\frac{0.30 \times 8.31 \times (25 + 273)}{12.0 \times 101325}$
= 6.11 × 10⁻⁴ m³
= 0.611 dm³

(ii) Based on the data given in Table 4.1, estimate the value of pV when p = 12.0 atm. Hence, calculate the value of V when p = 12.0 atm. [1]

Accept any value of pV in the range of 6.90 < x < 7.00

When p = 12.0 atm, pV = 6.95

since pV = 6.95, $V = 6.95 \div 12.0 = 0.579 \text{ dm}^3$

(iii) Compare the values of V you have obtained in (a)(i) and (a)(ii). Account for the difference in the values by taking into consideration the properties of CO₂ molecules.

The volume occupied by an ideal gas significantly larger than the volume occupied by CO_2 a real gas, under similar conditions.

CO₂ has **significant intermolecular** <u>instantaneous dipole-induced dipole attraction</u> <u>between its molecules</u>, and its molecules are closer to each other and thus occupy a smaller volume than an ideal gas. (b) Dry ice is the solid form of carbon dioxide. Dry ice sublimes readily and is commonly used to preserve ice cream where mechanical cooling is unavailable.

Table 4.2 shows the standard enthalpy changes of sublimation for several substances. Enthalpy change of sublimation is the energy required to change one mole of a substance from the solid state to gaseous state.

	ΔH^{e}_{sub} / kJ mol ⁻¹
standard enthalpy change of sublimation of C(s)	+715
standard enthalpy change of sublimation of Si(s)	+456
standard enthalpy change of sublimation of CO ₂ (s)	+25.0

Table	e 4.2
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Explain the relative standard enthalpy change of sublimation for these three substances. [2]

<u>Little energy is required</u> to <u>overcome</u> the weak intermolecular <u>instantaneous dipole-induced dipole forces of attraction between CO_2 molecules</u>, hence a lot less energy is required to sublime dry ice. Comparatively, a lot more energy is required to overcome the strong and extensive covalent bonds between the atoms in C(s) and Si(s).

More energy is required to <u>overcome the stronger covalent bonds between carbon atoms</u> <u>due to better extent of orbital overlaps between carbon atoms</u>. Hence, carbon has a more endothermic standard enthalpy change of sublimation.



(c) Ibuprofen and aspirin are nonsteroidal anti-inflammatory drugs that are commonly used as painkiller and for fever reduction. Some data of ibuprofen and aspirin are shown below in Table 4.3.



(i) Ibuprofen exhibits stereoisomerism. Explain how this stereoisomerism arises. Draw the structures of these stereoisomers. [2]



Ibuprofen exhibits enantiomerism. **Enantiomerism** arises due to the presence of <u>chiral</u> <u>carbon</u> with <u>absence of</u> (internal) <u>plane of symmetry</u>.

(ii) Compare and explain the relative acidity of ibuprofen and aspirin. [1]

Aspirin is a stronger acid than ibuprofen. The conjugate base of aspirin,



The <u>negative charge of the carboxylate is delocalised</u> over the COO⁻ group and <u>into</u> the benzene ring.

(iii) Young children often find it difficult to swallow tablets. Thus, ibuprofen can also be supplied in the form of an emulsion. Given that ibuprofen is insoluble in water, an emulsifier such as *Tween 80* is used to create a homogenous mixture.



Using your knowledge from chemical bonding and the above information on the role of an emulsifier, explain clearly in terms of intermolecular forces, how *Tween 80* can create a homogenous mixture of ibuprofen in water. [2]

The numerous <u>-OH</u> and/or ether <u>polar groups</u> allow the emulsifier to form numerous <u>hydrogen bonds with water molecules</u> hence making it soluble in water, while the <u>non-polar/hydrocarbon groups</u> allow the emulsifier to <u>form extensive instantaneous</u> <u>dipole-induced dipole attractions with ibuprofen</u>.



(d) A student proposed using 2-methylpropylbenzene to synthesise ibuprofen. The reaction scheme is shown in Fig. 4.1 below.



Fig. 4.1

(i) Name the type of reactions that occur in steps 1 and 3. [2]

Step 1: Electrophilic substitution

Step 3: Nucleophilic substitution

(ii) Suggest the reagents and conditions for steps 1 and 2. [2]

Step 1: CH₃COC*l*, anhydrous A/Cl₃ catalyst, r.t.p

Step 2: <u>NaBH₄ in ethanol</u>, r.t.p. OR <u>LiA/H₄ in dry ether</u>, r.t.p.

(iii) Describe a simple chemical test that can be carried out to indicate that Step 3 of the reaction scheme is complete. [2]

Add anhydrous <u>PCl₅</u> to an aliquot of the reaction mixture. <u>No white fumes of HCl</u> formed is observed if Step 3 is complete. Also accept anhydrous $SOCl_2$

Add <u>acidified $K_2Cr_2O_7$ </u> to an aliquot of the reaction mixture and <u>heat</u>. Acidified <u> $K_2Cr_2O_7$ remains orange</u> if Step 3 is complete. Do not accept acidified KMnO₄ (due to side-chain oxidation) Step 4 in the reaction scheme involves the formation of a Grignard reagent. A Grignard reagent is useful to form new carbon-carbon bonds. The alkyl group in R-MgCl behaves like an anion, R^- . The Grignard reagent adds to a reagent via a nucleophilic addition reaction as shown below.



(iv) Suggest the identity for Reagent Z in Step 5.





Suggest the structures of intermediates ${\bf P},\,{\bf Q}$ and ${\bf R}$



[Total: 20]

[1]

[3]

- 5(a) The halogens (chlorine, bromine and iodine) are found in Group 17 of the Periodic Table.
 - (i) Copy and complete the electronic configuration for a bromine atom, Br. [1]
 - 1s²

1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁵

(ii) Hence, sketch and label all occupied valence orbitals of the bromine atom. [2]



- (iii) State and explain the trend in first ionisation energy down Group 17. [2]
 - Down Group 17, the first ionisation energy <u>decreases</u>.
 - Despite the <u>increase in nuclear charge</u>, there is also an <u>increase in the number of</u> <u>electronic shells</u> and hence <u>shielding effect</u>.
 - The valence electrons are less strongly attracted to the nucleus and
 - less energy is required to remove a valence electron.
- (iv) By considering the relative positions of iodine, ₅₃I, and lead, ₈₂Pb, in the Periodic Table, and their first ionisation energies given in the *Data Booklet*, suggest a value for the first ionisation energy of astatine, ₈₅At. Explain your answer. [2]
 - <u>900 kJ mol⁻¹</u> (accept any value between 750 to 950 kJ mol⁻¹)
 - First I.E. of astatine should be <u>lower than that of iodine (1010 kJ mol⁻¹) as it is below iodine</u> in Group 17, and <u>higher than that of Pb</u> (716 kJ mol⁻¹) as <u>ionisation energy generally</u> increases across a period.

(b) The Period 3 elements sodium, aluminium and silicon, react with chlorine gas to produce chlorides with varying chemical properties.

Describe what would be observed when water is added to separate samples of NaCl, $AlCl_3$ and SiCl₄. Suggest the pH of the resulting solutions and write equations where appropriate. [3]

- NaCl dissolves in water to form a colourless solution
- of <u>**pH 7**</u>.
- A/Cl₃ dissolves in water and undergoes cation hydrolysis to form a colourless solution
- of <u>pH 3</u>.
- $A_lC_{l_3}(s) + 6H_2O(l) \rightarrow [A_l(H_2O_6)]^{3+}(aq) + 3C_l^{-}(aq)$ [hydration]
- $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$ [cation hydrolysis] OR $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$
- SiC*l*₄ <u>reacts with water / hydrolyses in water</u> to form <u>white fumes</u> of HC*l* and a white precipitate of SiO₂.
- The resultant solution has a pH of 2.
- SiC $l_4(l)$ + 2H₂O (l) \rightarrow SiO₂(s) + 4HCl (aq)

(c) At 450 K, phosphorus pentachloride, $PCl_5(g)$, decomposes to form phosphorus trichloride, $PCl_3(g)$, and chlorine, $Cl_2(g)$. A *dynamic equilibrium* is established as shown.

 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Delta H = +124 \text{ kJ mol}^{-1}$

[1]

(i) Explain what is meant by the term *dynamic equilibrium*.

It is when the <u>rate of forward reaction is equal to the rate of backward reaction</u> in a **reversible reaction**.

The <u>concentrations of the reactants and products remain constant</u> even though the substances are still reacting.

(ii) Suggest, with reasoning, the effect of increasing temperature on the percentage of $PCl_5(g)$ that decomposes. [1]

With an <u>increase in temperature, the equilibrium position will shift right to absorb</u> <u>heat OR the forward endothermic reaction is favoured</u>.

Hence, the percentage of PCI₅(g) that decomposes increases.

When 2.00 mol of PC $l_5(g)$ are decomposed at 450 K and 1.00 × 10⁵ Pa, the resulting equilibrium mixture contains 0.900 mol of C $l_2(g)$.

(iii) Write the expression for the equilibrium constant, K_{p} , for the decomposition of PC $l_5(g)$.[1]

 $K_{p} = \frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})}$

(iv) Determine the partial pressures of each of the gases at equilibrium. Hence, calculate the value of K_p and state its units. [3]

	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$		
Initial amount (mol)	2.00	0	0
Change in amount (mol)	-0.900	+0.900	+0.900
Equilibrium amount (mol)	1.10	0.900	0.900

Total amount of gases at equilibrium = 1.10 + 0.900 + 0.900 = 2.90 mol

Partial pressure of $PCl_5 = \frac{1.10}{2.90} \times (1.00 \times 10^5) = 3.793 \times 10^4 Pa$ Partial pressure of $PCl_3 = = \frac{0.900}{2.90} \times (1.00 \times 10^5) = 3.103 \times 10^4 Pa$ Partial pressure of $Cl_2 = \frac{0.900}{2.90} \times (1.00 \times 10^5) = 3.103 \times 10^4 Pa$

$$K_{\rm p} = \frac{(p_{\rm PCl_3})(p_{\rm Cl_2})}{(p_{\rm PCl_5})} = \frac{(3.103 \times 10^4)(3.103 \times 10^4)}{(3.793 \times 10^4)}$$

= 2.54 x 10⁴ Pa



(d) Nitrogen mustard gas was stockpiled as a chemical warfare agent in World War II. However, it was not deployed in combat.

It was proposed that the synthesis of nitrogen mustard can be carried out via the following synthetic pathway as shown in Fig. 5.1.



Fig. 5.1

- (i) Suggest the reagents and conditions necessary for an optimal yield in Step 2 in Fig. 5.1.
 [1]
 Limited NH₃ dissolved in ethanol, heat in a sealed tube
- (ii) Is X in nitrogen mustard more likely to be Cl or I? Explain your answer. [1]

X is likely to be <u>CI.</u> The <u>C-I bond is weaker than the C-CI bond</u> and hence **breaks more easily**. Hence, iodine is more likely to react with NH_3 in step 2.



Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used in the first step as shown in Fig. 5.2.



- (iii) By considering Step 1 of the reaction pathway in Fig. 5.2, explain why this method of synthesis is not likely to be feasible. [2]
 - The <u>lone pair of electrons on the halogen atom</u> is <u>delocalised into the C=C bond</u>, hence <u>strengthening the carbon-halogen bond</u> / giving it a <u>partial double bond</u> <u>character.</u>
 - Hence, the C–X bond does not break readily, and <u>CH₂I=CH₂Cl is not susceptible</u> towards nucleophilic substitution by reagent A.

OR

- The <u>electron rich C=C bond repels the lone pair of electrons on nucleophile and</u> prevents it from approaching C atom of the C-X bond.
- Hence, <u>CH₂I=CH₂Cl is not susceptible towards nucleophilic substitution</u> by reagent A.

[Total: 20]

