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 $\underline{OH^- \text{ in aqueous solution}}$. [1]

Markers' Comments

- Some candidates confuse the Arrhenius theory with the Bronsted Lowry and Lewis Theory of acids and bases. Candidates are reminded to do their bookwork and learn the definitions well.
- (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	$MgO + H_2O \rightleftharpoons Mg^{2+} + 2OH^-$

[1] for both equations

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. [1]

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.

SO₃ <u>dissolves</u> in water to <u>produce H⁺</u>, an acidic solution. Hence, its pH value is lower than the other two oxides. SO₃ + H₂O \rightarrow HSO₄⁻ + H⁺

Or SO₃ + H₂O \rightarrow **SO**₄²⁻ + 2H⁺ [1] for equation and explanation

Markers' Comments

- Candidates need to make clear reference to the Arrhenius theory in answering this part to link to the H⁺ and OH⁻ produced in the solution.
- Candidates need to take note that the higher [OH⁻] and hence higher pH of the solution formed from dissolving Na₂O as compared to that of MgO is due to full dissociation of the NaOH and partial dissociation of MgOH)₂ respectively.

(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%) 1st t_{1/2} is at a volume of ½ × 60 = 30 cm³ 2nd t_{1/2} is at a volume of ¾ × 60 = 45 cm³ [1] for clear construction lines on graph with labelling of t_½ From the graph, <u>t_{1/2} is constant at about 14.5 min</u> [1] hence order of reaction with respect to [CH₂N₂] is 1. Markers' Comments • Candidates need to take note that this is a product–time graph. To determine a set of 2 half-lives, the first one is at half the maximum volume of 60 cm³. 0 $-\frac{t_{\frac{N}{2}}}{2} \rightarrow \frac{x}{2} \rightarrow \frac{t_{\frac{N}{2}}}{4} \rightarrow \frac{3x}{8}$ (where x is 60 cm³ in this case) • t_½ is constant Tampines Meridian Junior College 2022 JC2 Preliminary Examination H2 Chemistry

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	рН	[H⁺] / mol dm⁻³	
	1	1.00	10 ^{-1.00} = 0.100	
	2	1.30	10 ^{-1.30} = 0.0501	[1] for both
Markers' Comments • pH = 1.00 $\Rightarrow -\log_{10} [H^+] = 1.00 \Rightarrow [H^+] = 10^{-1.00} = 0.100$				

(iii) Use the data provided to determine the order of reaction with respect to [H⁺], and hence write the rate equation for the reaction. [2]

Experiment	$[CH_2N_2] \text{ / mol dm}^{-3}$	pН	[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 $(4)^1 \times (1/2)^1 = 2$, this means that when $[H^+]$ is <u>halved</u>.

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

Rate = k [CH₂N₂] [H⁺] [1] (allow for ECF)

Markers' Comments

• Candidates are reminded to read the questions carefully and not miss out on answering either of the two parts asked in the question to determine both the order of reaction w.r.t H⁺ as well as to give the rate equation.

Markers' Comments

- Since Cl₂ gas is produced at the graphite electrode, oxidation of Cl⁻ took place and hence the graphite electrode is the anode. Flow of electrons is from the graphite anode to the iron electrode (cathode).
- (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:	$2Cl^{-}(l) \rightarrow Cl_{2}(g) + 2e^{-}$	[1]	
	Iron electrode / cathode:	$Mg^{2+}(l)$ + 2e ⁻ $ ightarrow$ Mg (l)	[1]	
	 Markers' Comments Candidates need to take note that the that magnesium and magnesium chlo 	states of Mg^{2*} , Cl^- and Mg are liqu ride are in the molten state.	id since it was given in the questio	'n
(ii)	Draw and label the direction o	f electron flow in the cell on Fi	g. 1.2. [1]

(iii) Calculate the mass of magnesium obtained if a current of 3.00 A is supplied for 10.0 h.

[2]

 $Q = I \times t$ = 3.00 × 10.0 × 3600 [1] = 108 000C

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

Mass of Mg = 0.5596 × 24.3 = <u>13.6 g</u> [1]

 (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. [1] Do not accept nitrogen gas.
Markers' Comments

Nitrogen gas is not accepted as magnesium nitride might be formed.

(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 $E^{\circ} = -2.38$ V

 $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad E^{\oplus} = -0.83 V$ At the anode, (oxidation) $Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^{\oplus} = +1.36 V$ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^{\oplus} = +1.23 V$

For MgCl₂(aq),

At the cathode,

 <u>H₂O is preferentially reduced</u> to produce <u>H₂(g)</u> as <u>E^e (H₂O/H₂) is more positive</u> than <u>E^e (Mg/Mg²⁺)</u>. [1] (including quoted E^e values)

At the anode,

 <u>H₂O is preferentially oxidised</u> to produce <u>O₂(g)</u> as <u>E^o (O₂ /H₂O) is less positive</u> than <u>E^o (Cl₂ /Cl⁻)</u>. [1] (including quoted E^o values)

Markers' Comments	
• In the presence of an aqueous medium, H ₂ O is present and hence H ₂ O can also be	,
discharged at the respective electrodes. Candidates need to extract the relevant eq	uations
from the Data Booklet and quote the E^{Θ} values in deciding what reactions will take	place at
the electrodes.	[10tal: 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 partially-filled d subshell.</u> [1]
 Markers' Comments
 - Candidates are reminded to memorise definitions accurately as many gave incomplete or unnecessary descriptions. IUPAC defines transition elements as an element having a d subshell that is partially filled with electrons
- (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.** [1]

Markers' Comments Density = mass/volume and hence both factors affecting density should be addressed. Candidates are also reminded to do their book work accurately and not confuse terms which look similar e.g. density and charge density.

(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.

[1]

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. [1] 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.

Markers' Comments

• A sizeable number of candidates had the misconception that melting of the metals involved ionisation energy and brought in terms such as nuclear charge and shielding effect. These candidates are reminded to distinguish between the various processes (e.g. ionisation, melting, decomposition etc.) and accurately identify the forces of attraction that are being overcome in these processes.

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

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

[1]

Sign of ΔS_f^o 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. [1]

Markers' Comments A sizeable number of candidates misinterpreted the question and gave a generic explanation on what ΔS means and even mentioned about the spontaneity of the reaction (which is predicted by ΔG, not ΔS). Candidates should contextualise their answers and account for the negative sign of ΔS_f to the reaction.

(ii) Using the information above, calculate ΔG° for the formation of $CrCl_3$ (s). [1]

$$\Delta G_{\rm r}^{\,\rm e} \qquad = \Delta H_{\rm r}^{\,\rm e} - T \Delta S$$

$$=-556.6-(298)\left(-\frac{236}{100}\right)$$

= - 486 kJ mol⁻¹ [1] or - 486 000 J mol⁻¹ (3 sf or 4 sf with units)

Markers' Comments

- This question was generally well-attempted as most candidates could remember the formula relating ΔG to ΔH and ΔS .
- (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>. [1]

Markers' Comments

• This question was generally well-attempted. Only a handful of candidates had the misconception that the reaction is spontaneous if ∆G>0.

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



(d)

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

 $Cr^{3+} + e^{-} \rightleftharpoons Cr^{2+} \qquad E^{\oplus} = -0.41 \text{ V} \qquad E^{\Theta}_{\text{oxid}}$ $O_{2} + 4H^{+} + 2e^{-} \rightleftharpoons 2H_{2}O \qquad E^{\oplus} = +1.23 \text{ V} \qquad E^{\Theta}_{\text{red}}$ $E^{\Theta}_{\text{cell}} = 1.23 - (-0.41)$ = +1.64 V [1]

Since $E_{cell}^{\circ} > 0$, reaction is spontaneous and the <u>blue $Cr^{2+} / [Cr(H_2O)_6]^{2+}$ is oxidised to</u> green $Cr^{3+} / [Cr(H_2O)_6]^{3+}$. [1]

Markers' Comments

- It is necessary to calculate the E^e_{cell} value in order to prove that the reaction is feasible.
- Candidates who had poor understanding of the flow chart used the wrong species (e.g. Cr metal, Cr₂O₇²⁻) to account for the observation.
- (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]

When sodium hydroxide, OH^- was added, **W** [Cr(H₂O)₆]³⁺ undergoes <u>precipitation</u> [1] to form grey green ppt of Cr(OH)₃

	[Cr(H₂O) ₆] ³⁺ + 3OH [−] ⇒	Cr(OH) ₃ + 6 H ₂ O [1] (also accept single arrow)
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
OR	Cr₂(SO₄)₃ + 6NaOH 🛛 🛁	2Cr(OH) ₃ + 3 Na ₂ SO ₄

Markers' Comments

• The common error for the type of reaction was ligand exchange. This is a precipitation reaction as the greygreen <u>solid</u> was formed due to SMALL amount of NaOH added. A ligand exchange reaction involves the substitution of one or more ligands in a complex ion with one or more different ligands.

• A sizeable number of candidates also struggled to give the correct equation for the precipitation reaction.

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

X: $[Cr(OH)_6]^{3-}$ [1] accept $[Cr(OH)_4]^{-}$ Y: $Cr_2O_7^{2-}$ [1]

 Markers' Comments Candidates struggled to deduce the correct identities of X and Y, refer to flow chart for explanation. Candidates need to be cognisant of how the different ligands will affect the overall charge on the complex ion. Oxidation number of Cr in X is still +3, it did not change with the addition of NaOH. 	
v) State, with reasoning, the role of hydrogen peroxide in Fig. 2.1.	1
[1]
H ₂ O ₂ is an oxidising agent. Cr is oxidised as the oxidation number of Cr increased	
<u>from +3 in</u> [Cr(OH) ₆] ^{3−} to <u>+6 in CrO₄^{2−}. [1]</u>	
Markers' Comments	1
• Catalyst was commonly suggested as the role of hydrogen peroxide. This is incorrect as there is no indication of the hydrogen peroxide being regenerated. Candidates should realised oxidation had occurred,	

[2]

(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.

0

Markers' Comments

- Many candidates did not realise that the N atom also has a lone pair of electrons that can be donated to the central Cr³⁺ ion.
- Candidates are reminded to check the structure of the ligands they have drawn against the given structure as there were many instances of missing double bonds, having only 5 atoms in the ring, and incorrect positions of the COO- substituent.



- (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 Al(OH)₃ and calculate its solubility product in pure water. [3]

 $K_{\rm sp} = [Al^{3+}][OH^{-}]^{3}[1]$ **Markers' Comments** • Even though this was a basic question, Let the solubility of Al(OH)₃ in **mol dm⁻³** be s many candidates did not read the question carefully and used the value of $Al(OH)_3$ (s) $\Longrightarrow Al^{3+}$ (aq) + $3OH^-$ (aq) 2.90×10^{-9} as the solubility product (K_{sp}) 3**s** value and tried to calculate the solubility. Candidates need to distinguish between $K_{\rm sp} = [Al^{3+}] [OH^{-}]^3$ solubility product and solubility. $K_{sp} = (s)(3s)^3$ $K_{\rm sp} = 27 \ s^4 = 27 \ (2.90 \times 10^{-9})^4$



 $K_{\rm sp} = 1.91 \times 10^{-33} [1] \text{ mol}^4 \text{ dm}^{-12} [1]$

(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) [1]
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In excess sodium hydroxide, <u>Al(OH)₃ forms</u> a soluble <u>complex</u> ion, Al(OH)₄-.

The solubility of Al(OH)₃ is <u>higher</u> in NaOH (aq) as compared to pure water. [1]

Markers' Comments	
• This question was poorly attempted as many candidates did not realise that AI(OH)₃ is soluble in excess	
NaOH (if you cannot recall, this is in the QA notes!) due to the formation of the complex ion, Al(OH)4 ⁻ .	
Hence, many candidates used the common ion effect to explain the decreased solubility of Al(OH) ₃ in	
excess NaOH, which is incorrect.	
	!

[Total: 21]



[3]

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.

Nucleophilic addition [1]



step 1 and was not regenerating the CN- ion in step 2.

• Candidates are reminded to learn standard mechanism well.

(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.



CH₃CH₂CH₂CHO [1]

(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.



(i) Give the displayed formula of T.



[1] do not award mark if not displayed formula

Markers' Comments

• Candidates did not read the question carefully. Many candidates did not show the single bond between O and H for the hydroxy group. Candidates are reminded to show ALL bonds for displayed formula.

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



Markers' Comments

• Common incorrect answer was to form aldehyde when the primary alcohol is oxidised. Candidates should be aware that **without distillation**, the aldehyde will be oxidised to carboxylic acid.

(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 (carboxylic acid) is a stronger acid than propane-1,2,3-triol (alcohol). [1]

- The <u>carboxylate</u> (RCOO⁻) is resonance stabilised but not the alkoxide
- Hence, the <u>carboxylate is more stable than alkoxide</u>. [1]

• There is a greater tendency for the carboxylic acid to ionise compared to alcohol.

Markers' Comments

• The acidity of -OH containing organic compound (alcohol, phenol or carboxylic acid) is an important concept. Many candidates did not give a clear comparison and did not use exact key phrases in their answers. Candidates are expected to do their bookwork well. (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 carbonyl √ functional group (or aldehyde or ketone)

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

 \Rightarrow **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 (not 1 mol) of CO₂ are formed per mol of M
- ⇒ Hence <u>HOOCCOOH / ethanedioc acid</u> $\sqrt{}$ intermediate is formed and immediately oxidised to give the 2 mol CO₂.
- [5] 9 to 11 √
- [4] 7 to $8\sqrt{}$
- [3] 5 to $6\sqrt{}$
- [2] 3 to $4\sqrt{}$
- [1] 1 to 2 √
 - **M**, $C_{18}H_{32}O_2$: HO₂C(CH₂)₇CH=CHCH=CH(CH₂)₅CH₃[1]
 - OR $CH_3(CH_2)_5CH=CH(CH_2)_7CH=CHCO_2H$



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



Markers' Comments

- A number of candidates were unable to correctly identify the organic reactions (type of reaction and functional group involved) with typical reagents, indicate a lack of sufficient preparation. Candidates are expected to do their bookwork well to have a proficient overview of the organic reactions.
- Answers should be unambiguous; where a compound may be subjected to multiple reagents / reactions, candidates should ensure the reagents are also indicated to show appropriate understanding and referencing.
- Functional groups should be identified by name (not merely drawing the respective functional group fragment).
- It would not be possible to have two sets of terminal alkenes in **M** to result in 2 moles of CO₂ since carboxylic acid must be present in **K** and **M**. A very few candidates appreciated the further oxidation of ethanedioic acid due to KMnO₄ as a possible intermediate fragment.

[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, <i>p</i> / atm	volume, V / dm ³	pressure x volume, pV / 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. [1]

$$pV = nRT \Rightarrow V = \frac{n R T}{P} \Rightarrow V = \frac{0.30 \times 8.31 \times (25 + 273)}{12.0 \times 101325}$$
$$= 6.11 \times 10^{-4} \text{ m}^{3} \qquad \text{Note: 1 m}^{3} = 1000 \text{ dm}^{3}$$
$$= 0.611 \text{ dm}^{3} \text{ [1]}$$
Markers' Comments
Some candidates still struggled with converting variables correctly to their SI units before using them in the Ideal Gas Equation.
Pressure, p in Pa (1 atm = 101325 Pa); Volume , V in m³ (1 m³ = 1000 dm³)
Temperature, T in K (°C = +273 K); Volume , n in mol ; R (Ideal Gas Constant) = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}

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

Since p = 12.0 atm is between 10.0 atm and 15.0 atm, pV value should be between 6.85 and 7.02. Accept any value of *p*V in the range of **6.90** $\leq x \leq 7.00$

Markers' Comments

Ма

Generally, candidates did well for this question. Many were able to estimate the value of pV and calculate the value of V correctly.

In this case, the approach of using $p_1V_1 = p_2V_2$ is not applicable as it is clear from the data given that $pV \neq constant.$ _____

(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 is significantly larger than the volume occupied by CO_2 a real gas, under similar conditions.

CO₂ has significant intermolecular instantaneous dipole-induced dipole attraction between its molecules, and its molecules are closer to each other and thus occupy a smaller volume than an ideal gas. [1]

Markers' Comments Many candidates were able to explain why CO₂ behave non-ideally. However, some candidates wrongly identified that CO₂ is a polar molecule. CO₂ is **NON-POLAR**.and hence only has weak intermolecular instantaneous dipole-induced dipole forces of attractions.

(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.

Table	4.2
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	∆ <i>H</i> ^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

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

<u>Little energy is required</u> to <u>overcome the weak intermolecular instantaneous dipole-induced dipole forces of attraction between CO_2 molecules</u>, hence a lot less energy is required to sublime dry ice, hence a much less endothermic ΔH^{e}_{sub} . [1] Comparatively, a lot more energy is required to overcome the strong and extensive covalent bonds between the atoms in C(s) and Si(s) giant molecular structure.

More energy is required to <u>overcome the stronger covalent bonds between carbon atoms</u> <u>due to better extent of orbital overlap between carbon atoms</u>. [1] Hence, carbon has a <u>more endothermic ΔH^{e}_{sub} .</u>

Markers' Comments

Weaker responses failed to compare the ΔH_{sub}^{e} of Si and C, both of which have giant molecular structure. Many candidates could not explain the difference in the covalent bond strength of C-C and Si-Si.

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(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. <u>Enantiomerism</u> arises due to the presence of <u>chiral carbon</u> with <u>absence of</u> (internal) <u>plane of symmetry</u>. [1]



[1] for correct representation of the two enantiomers

Markers' Comments

Weaker responses failed to explain fully why ibuprofen exhibits enantiomerism. Many candidates omitted the requirement of having no internal plane of symmetry.

Some candidates also forgot how to represent enantiomerism using the "tetrahedral" representation of using dash and wedge.

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

[1]





<u>Conjugate</u>

<u>Aspirin is a stronger acid</u> than *ibuprofen*. The <u>conjugate base of aspirin, is more</u> <u>stable</u> than the conjugate base of *ibuprofen*,.

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

[1] for relative acidity and explanation of the stability of conjugate base

Markers' Comments

This question was poorly attempted. Many candidates did not discuss and explain the relative stability of the conjugate base of the two acids. Weak responses merely compared and interpreted the pKa values given.

Many candidates failed to notice that the carboxylic acid is attached directly to the benzene ring. The benzene ring facilitates the delocalization of the negative charge on the carboxylate anion.

(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 ether <u>polar groups</u> allow the emulsifier to form numerous <u>hydrogen bonds with water molecules</u> [1] 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>. [1]

Markers' Comments

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This question was poorly attempted. Many candidates did not understand the role of an emulsifier. An emulsifier needs to be able to form interactions with both the solvent (H_2O) and the solute (ibuprofen) to form a homogenous mixture. Since it was mentioned that ibuprofen is insoluble in water, it is likely that the main IMF in ibuprofen that affects its solubility should be instantaneous dipole-induced dipole forces of attractions.

[2]

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



- (i) Name the type of reactions that occur in steps 1 and 3. [2]
 - Step 1: <u>Electrophilic substitution</u> [1]
 - Step 3: <u>Nucleophilic substitution</u> [1]
- (ii) Suggest the reagents and conditions for steps 1 and 2.
 - Step 1: <u>CH₃COC*l*, anhydrous A*l*C*l*₃ catalyst, r.t.p [1]</u>
 - Step 2: <u>NaBH₄ in ethanol</u>, r.t.p. OR <u>LiA/H₄ in dry ether</u>, r.t.p. OR <u>H₂ (g), Pt / Pd</u>, r.t.p. OR <u>H₂ (g), Ni, high temp. & pressure</u> [1]
- (iii) Describe a simple chemical test that can be carried out to indicate that Step 3 of the reaction scheme is complete. [2]

Add <u>Na metal</u> to an aliquot of the reaction mixture. [1] <u>No effervescence of H_2 (g)</u> if Step 3 is complete. [1]

Add <u>anhydrous PCl₅</u> to an aliquot of the reaction mixture. [1] <u>No white fumes of HCl</u> <u>formed is observed</u> if Step 3 is complete. [1] Also accept anhydrous SOCl₂

Add <u>acidified $K_2Cr_2O_7$ </u> to an aliquot of the reaction mixture and <u>heat</u>. [1] Acidified <u> $K_2Cr_2O_7$ remains orange</u> if Step 3 is complete. [1] Do not accept acidified KMnO₄ (due to side-chain oxidation)

Markers' Comments

To show that the reaction in step 3 is complete, it is more important to show that there is no alcohol remaining rather than the presence of the chloroalkane. Thus, chemical tests for alcohols are relevant in this question and the negative observations will be conclusive that the reaction is complete.

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lodoform test is not suitable in this context as the OH^- in the alkaline $I_2(aq)$ with the heat, will result in the chloroalkane undergoing some degree of nucleophilic substitution to form back the alcohol.

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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-MgC*l* 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.

Reagent Z: CO₂ [1]





2-methylpropylbenzene undergoes a four-step reaction as shown below. (e)



Suggest the structures of intermediates P, Q and R



step 1: KMnO₄ (aq), H₂SO₄ (aq), heat; (oxidation)

step 2: conc. HNO₃, conc H₂SO₄, heat (electrophilic substitution)

step 3: Br₂, FeBr₃ catalyst, heat (electrophilic substitution)

step 4: Sn in excess conc HCl, heat, followed by careful addition of NaOH (aq) (reduction)



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2022 H2 Chem Prelim P3 (Ans)

- 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]



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



[2] – all 4 labelled orbitals (x, y, z axes required to show 3D shape of orbitals) [1] – 2 of 4 labelled orbitals

Markers' Comments
Candidates are expected to score in this basic question.
Valence orbitals refer to orbitals in outermost quantum shell, i.e. both 4s and 4p orbitals.

(iii) State and explain the trend in first ionisation energy down Group 17.

[2]

[2]

- Down Group 17, the first ionisation energy decreases.
- 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.

[2] – all 4 points; [1] – any 2 points

Markers' Comments

• This is a standard concept. In the syllabus objective 5b(ii), it is specified that the decreasing trend in first I.E down a Group should be explained in terms of increasing number of electronic shells, shielding effect <u>and</u> nuclear charge. Some students missed out key phrases. Candidates are reminded to do their bookwork well.

- (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> (any value between 750 to 975 kJ mol⁻¹ is accepted) [1]
 - Astatine has <u>lower first I.E. than iodine</u> (1010 kJ mol⁻¹) as it is <u>below iodine</u> in Group 17, and <u>higher first I.E. than Pb</u> (716 kJ mol⁻¹) as <u>ionisation energy generally</u> increases across a period. [1]
 Markers' Comments
 - Many candidates were able to suggest a reasonable value for first I.E. of astatine. Explanations were however often unclear or incomplete.
- (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>.
- AICl₃ dissolves in water and undergoes cation hydrolysis to form a colourless solution
- of <u>pH 3</u>.

OR

- $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^{-}(aq)$ [hydration]
- $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$ [cation hydrolysis]
 - $[Al(H_2O)_6]^{3+}(aq) + H_2O(I) \implies [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq)$
- SiCl₄ <u>reacts with water / hydrolyses in water</u> to form <u>white fumes</u> of HCl and a white precipitate of SiO₂.
- The resultant solution has a pH of 2.
- SiC l_4 (I) + 2H₂O(I) \rightarrow SiO₂(s) + 4HCl(aq)

[3] - 8 to 9 points [3] - 8 to 9 points [2] - 4 to 7 points [1] - 2 to 3 points [0] - 0 to 1 points oxides. Candidates are reminded to do their bookwork well.



(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.

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

(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 <u>reversible reaction</u> OR the <u>concentrations of the reactants and products remain</u> <u>constant even though the substances are still reacting</u>. [1]

Markers' Comments

- This is a common definition question. Candidates are reminded to do their bookwork well.
- (ii) Suggest, with reasoning, the effect of increasing temperature on the percentage of PCl_5 (g) that decomposes. [1]

By Le Chatelier's principle, with an <u>increase in temperature</u>, <u>the equilibrium position</u> <u>will shift right to absorb heat</u> OR <u>the forward endothermic reaction is favoured</u>. Hence, the <u>percentage of PCI₅(g) that decomposes increases</u>. [1]

Markers' Comments

• Most candidates correctly applied the Le Chatelier's principle.

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 $Cl_2(g)$.

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

$$K_{\rm p} = \frac{(p_{\rm PCl_3})(p_{\rm Cl_2})}{(p_{\rm PCl_6})}$$
[1]

(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

[1] Correct eqm amount (mol)

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

Partial pressure of PC
$$l_5 = \frac{1.10}{2.90} \times (1.00 \times 10^5) = 3.793 \times 10^4 \text{ Pa}$$

Partial pressure of PC $l_3 = \frac{0.900}{2.90} \times (1.00 \times 10^5) = 3.103 \times 10^4 \text{ Pa}$
Partial pressure of C $l_2 = \frac{0.900}{2.90} \times (1.00 \times 10^5) = 3.103 \times 10^4 \text{ Pa}$

[1] for all partial pressures

$$\mathcal{K}_{p} = \frac{(p_{\mathsf{PC}l_{3}})(p_{\mathsf{C}l_{2}})}{(p_{\mathsf{PC}l_{5}})} = \frac{(3.103 \times 10^{4})(3.103 \times 10^{4})}{(3.793 \times 10^{4})} = \frac{2.54 \times 10^{4} \,\mathsf{Pa}}{2.54 \times 10^{4} \,\mathsf{Pa}}$$
[1] with units

Markers' Comments
The context described is a constant pressure system, where total pressure is maintained at 1.00 × 10⁵ Pa. Hence, ICE table should be in moles of substance, and partial pressure, p_A = (mole fraction of A) x P_{total}.
Unless otherwise specified, units of K_p should follow units given in question, i.e. 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
 [1]

(ii) Is X in nitrogen mustard more likely to be Cl or I? Explain your answer. [1]

X is likely to be <u>Cl.</u> The <u>C-I bond is weaker than the C-Cl bond</u> and hence **breaks more easily**. Hence, iodine is more likely to react with NH_3 in step 2. [1]

• Candidates need to interpret the question carefully. **X** is the halogen atom that <u>remained</u> on nitrogen mustard (i.e. unreacted) after the nucleophilic substitution reaction 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> [1]
 - Hence, the C–X bond does not break readily, and <u>CH₂I=CH₂Cl is not susceptible</u> towards nucleophilic substitution by reagent A. [1]

OR

Markers' Comments

- 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. [1]
- Hence, <u>CH₂I=CH₂Cl is not susceptible towards nucleophilic substitution</u> by reagent A. [1]

[Total: 20]
Markers' Comments
This question involves an extension of the concept of the unreactivity of halogenoarenes towards nucleophiles.