



ANDERSON JUNIOR COLLEGE

JC1 Promotional Examinations 2013

CHEMISTRY

Higher 2

Paper 1 Multiple Choice

9647/01

2 October 2013

45 minutes

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC/FIN number.

Shade the NRIC / FIN number.

Exam Title: JC1 Promo

Exam Details: H2 Chem / Paper 1

Date: 02/10/2013

This document consists of **12** printed pages.

Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 The famous chemist Sir Humphry Davy worked out that the formula of a yellow explosive gas was ClO_2 by decomposing it completely to form chlorine and oxygen only.

If Davy started with 200 cm^3 of ClO_2 , what volumes of chlorine and oxygen were produced at the same temperature and pressure?

	volume of chlorine / cm^3	volume of oxygen / cm^3
A	67	133
B	100	200
C	200	200
D	200	400

- 2 When dilute acid is added to an aqueous solution containing nitrite ions, NO_2^- , gases are evolved.



Which of the following statements can be deduced from the process?

- A** The $\text{H}^+(\text{aq})$ ion is oxidised by $\text{NO}_2^-(\text{aq})$ ion.
B The $\text{H}^+(\text{aq})$ ion acts as a catalyst in the process.
C The $\text{NO}_2^-(\text{aq})$ ion undergoes disproportionation.
D The $\text{NO}_2^-(\text{aq})$ ion undergoes neutralisation with $\text{H}^+(\text{aq})$ ion.
- 3 A 2.0 dm^3 sample of argon at a pressure of 300 kPa and a 1.0 dm^3 sample of helium at a pressure of 500 kPa are introduced into a 5.0 dm^3 vessel at 20°C . What is the final pressure in the vessel when the temperature is increased to 30°C ?

A 228 kPa **B** 330 kPa **C** 379 kPa **D** 550 kPa

- 4 Which of the following species **do not** have three unpaired electrons?

A Co
B Cr^{3+}
C Sc
D V^{2+}

- 5 The successive ionisation energies (I.E.) of an element **E** are given below.

	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th
I.E. / kJ mol ⁻¹	1213	3288	5200	7369	9889	13326	70330	83078

What is the likely formula of the compound that is formed when **E** reacts with Mg?

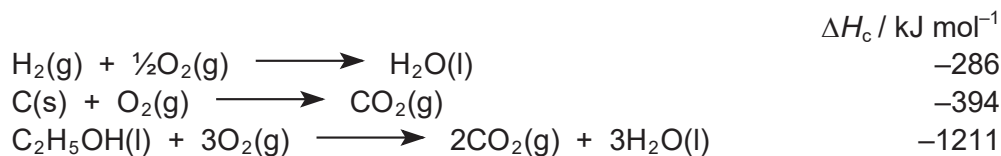
- A** Mg**E** **B** Mg**E**₂ **C** Mg₂**E** **D** Mg₃**E**₂
- 6 In which pair below does the second species have a **larger** bond angle than the first?
- A** SO₃²⁻, SO₄²⁻ **B** NO₃⁻, ClO₂⁻
- C** PH₃, AsH₃ **D** BrF₂⁻, HCN
- 7 Which of the following sets contains one ionic, one macromolecular and one simple molecular substance?
- A** aluminium chloride, diamond and silicon
- B** aluminium fluoride, aluminium chloride and graphite
- C** silicon dioxide, silicon and hydrogen chloride
- D** silicon dioxide, carbon dioxide and graphite
- 8 Consider the following four compounds:



What is the correct order of their lattice energies placing the one with the **lowest** numerical value first?

- A** LiF < LiI < MgF₂ < SrF₂
- B** LiI < LiF < MgF₂ < SrF₂
- C** LiI < LiF < SrF₂ < MgF₂
- D** SrF₂ < MgF₂ < LiI < LiF

- 9 Some enthalpy changes of combustion are given below.



What is the enthalpy change of formation of ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$?

- A -187 kJ mol^{-1}
 B -292 kJ mol^{-1}
 C -435 kJ mol^{-1}
 D -1293 kJ mol^{-1}
- 10 The reduction of nitrogen monoxide by hydrogen is shown below.



A series of experiments was carried out to determine the rate equation for the above reaction.

The results are shown in the table.

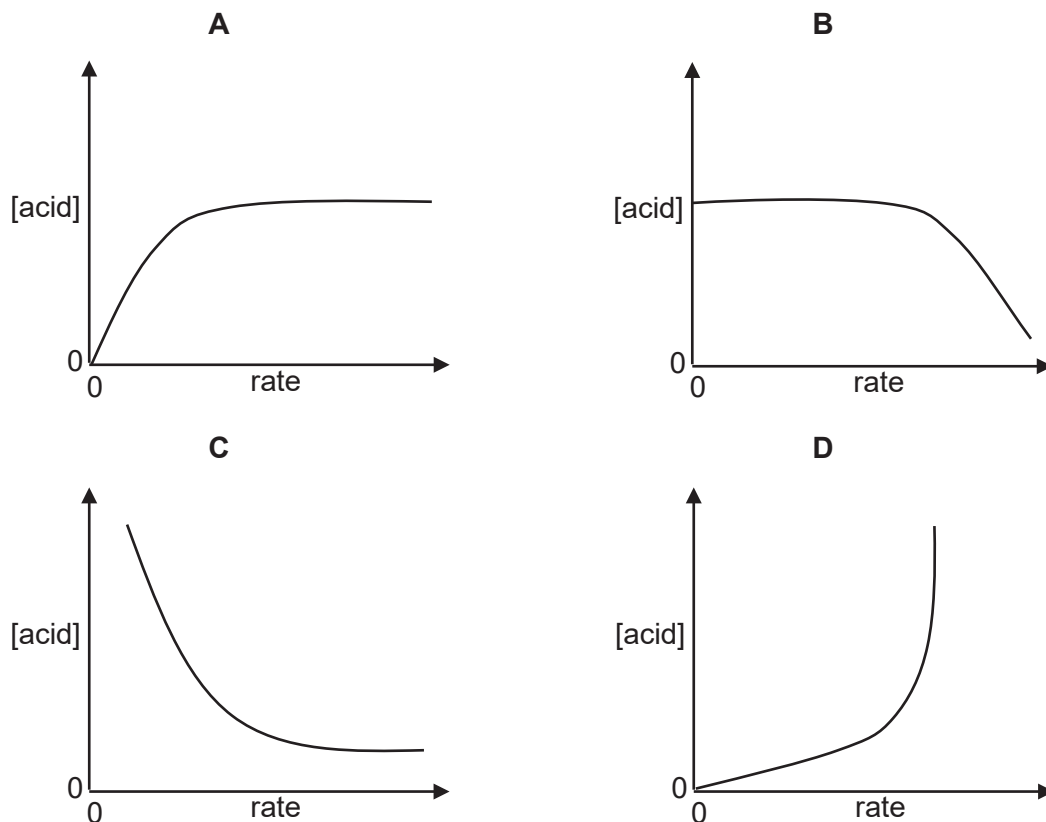
experiment	initial $[\text{H}_2] / \text{mol dm}^{-3}$	initial $[\text{NO}] / \text{mol dm}^{-3}$	rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.001	0.006	6.0×10^{-3}
2	0.002	0.006	12.0×10^{-3}
3	0.006	0.001	1.0×10^{-3}
4	0.006	0.002	4.0×10^{-3}

Which of the following shows the correct rate equation and units for the rate constant, k , for the above reaction?

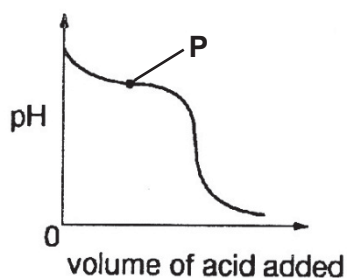
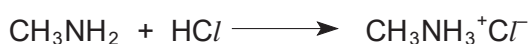
- A rate = $k [\text{NO}] [\text{H}_2]^2$, units of $k = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$
 B rate = $k [\text{NO}] [\text{H}_2]^2$, units of $k = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
 C rate = $k [\text{NO}]^2 [\text{H}_2]$, units of $k = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
 D rate = $k [\text{NO}]^2 [\text{H}_2]$, units of $k = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

- 11 In the reaction between aqueous sodium thiosulfate and dilute acid, the reaction is found to be first order with respect to acid at low acid concentration, but zero order with respect to acid at high acid concentration.

Which graph represents the experimental results?



- 12 Methylamine, CH_3NH_2 , is a weak base ($\text{p}K_b=3.38$ at 25°C). When a sample of methylamine is titrated with hydrochloric acid, the following titration graph is obtained.

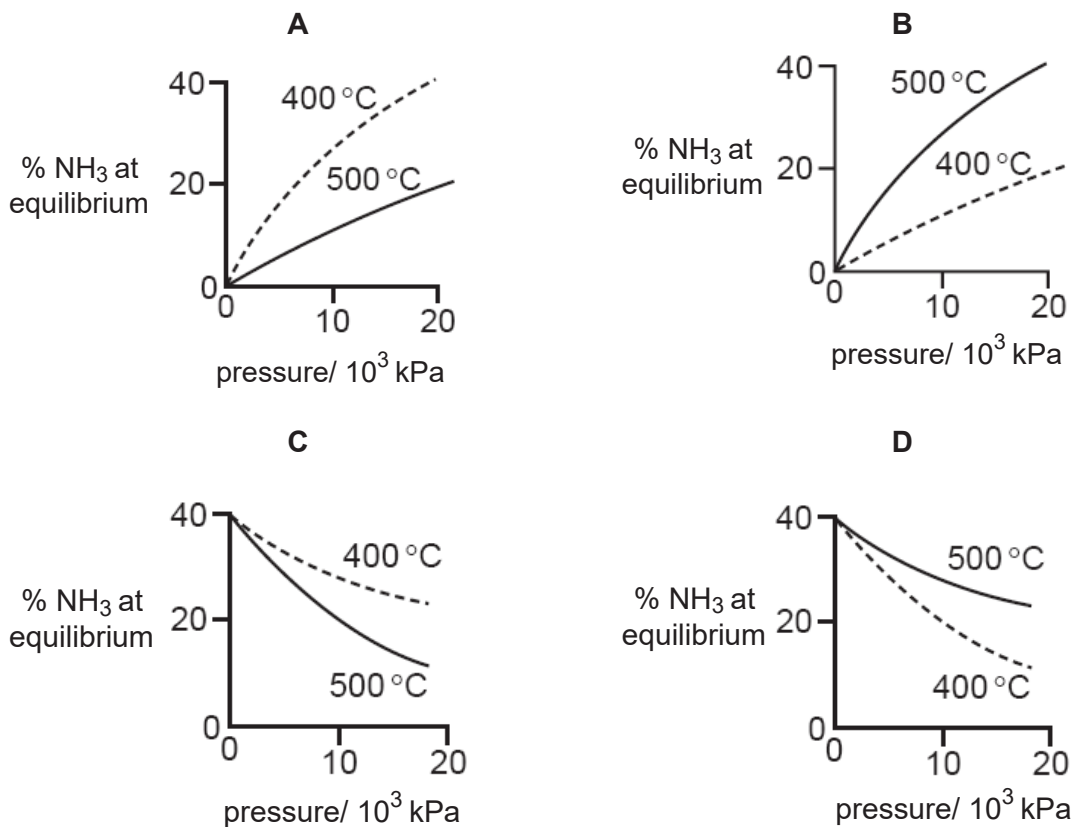


What is the explanation for the change of slope at point P?

- A A solution containing CH_3NH_2 and $\text{CH}_3\text{NH}_3^+\text{Cl}^-$ has been produced.
- B More hydroxide ions are produced as the reaction proceeds.
- C The base has been completely neutralised by the acid.
- D The reaction produces heat.

- 13 The percentage of ammonia obtainable, if equilibrium was established during the Haber process, is plotted against the operating pressure for two temperatures, 400 °C and 500 °C.

Which diagram correctly represents the two graphs?



- 14 The table below shows some data on two indicators.

indicator	approximate pH range of colour change	colour change	
		acid	alkali
bromocresol–green	3.8 – 5.5	yellow	blue
phenol–red	6.8 – 8.5	yellow	red

Which conclusion can be drawn about a solution in which bromocresol–green is blue and phenol–red is yellow?

- A It is weakly acidic.
- B It is neutral.
- C It is weakly alkaline.
- D It is strongly alkaline.

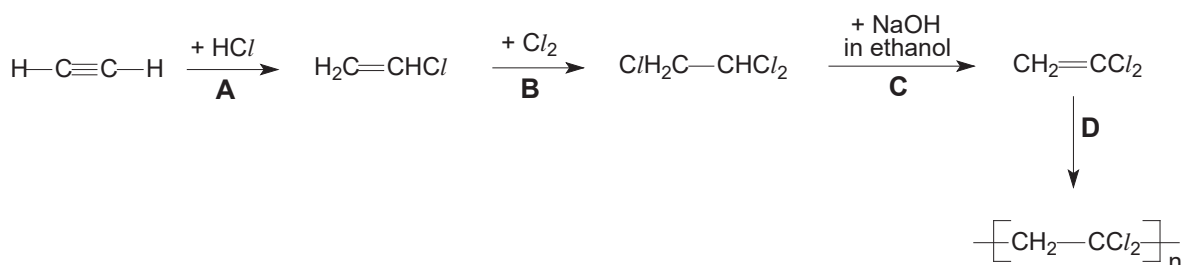
- 15 When the concentration of Ca^{2+} ions in water is greater than $10^{-5} \text{ mol dm}^{-3}$, an insoluble scum would be formed with soap.

To prevent scum formation, what is the minimum mass of sodium carbonate that should be added to 1 dm^3 of water? (K_{sp} of $\text{CaCO}_3 = 5.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$)

- A $6.4 \times 10^{-3} \text{ g}$ B $3.7 \times 10^{-2} \text{ g}$
C $4.2 \times 10^{-2} \text{ g}$ D $5.3 \times 10^{-2} \text{ g}$

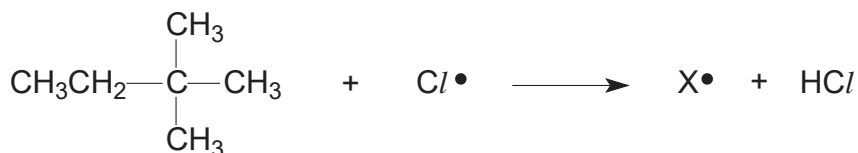
- 16 The reaction sequence shows the preparation of 1,1-dichloroethene from ethyne and its subsequent polymerisation.

In which step does the hybridisation of carbon atoms change from sp^3 to sp^2 ?



- 17 When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free-radical substitution.

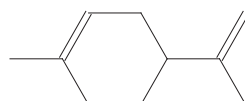
In a propagation step, the free radical X^\bullet is formed by the loss of one hydrogen atom.



How many different forms of X^\bullet are theoretically possible?

- A 1 B 2 C 3 D 4

- 18 Limonene occurs in oil of lemons and is used to flavour some citrus drinks. The structure of limonene is shown below.

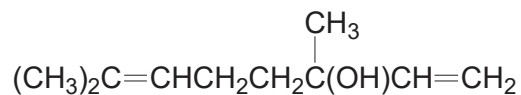


limonene

How many optical isomers will be formed when limonene is reacted with cold acidified potassium manganate(VII)?

- A 2 B 4 C 16 D 32

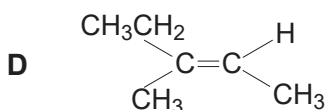
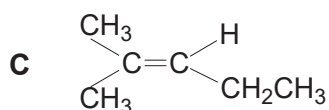
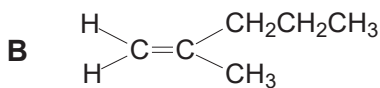
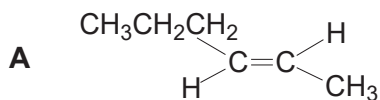
- 19 Linalool is a constituent of lavender oil and has the following structure:



Which of the following statements about linalool is correct?

- A** Its molecular formula is $\text{C}_{10}\text{H}_{20}\text{O}$.
B It can exist as three pairs of stereoisomers.
C Its molecule is planar.
D It decolourises aqueous bromine in the dark.
- 20 An alkene **Q**, on heating with an excess of concentrated acidified KMnO_4 , produces $\text{CH}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CH}_2\text{COCH}_3$ only.

Which of the following alkenes is likely to be **Q**?



Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

21 Which of the following statements are correct for the complete combustion of an alkene in excess oxygen?

- 1** The volume of oxygen required is directly proportional to the number of carbon atoms in the alkene molecule.
- 2** The volume of gas produced at 25 °C is the same for an alkane with the same number of carbon atoms under similar conditions.
- 3** At 100°C, the volume of steam produced is always twice that of carbon dioxide produced.

22 The concepts of bond energy, bond length and bond polarity are useful when comparing the behaviour of similar molecules, e.g. thermal stability.

For example, it could be said that

“Compared with the HCl molecule, the bond**R**..... of the HBr molecule is**S**.....”

Which pairs of words correctly complete the above sentence?

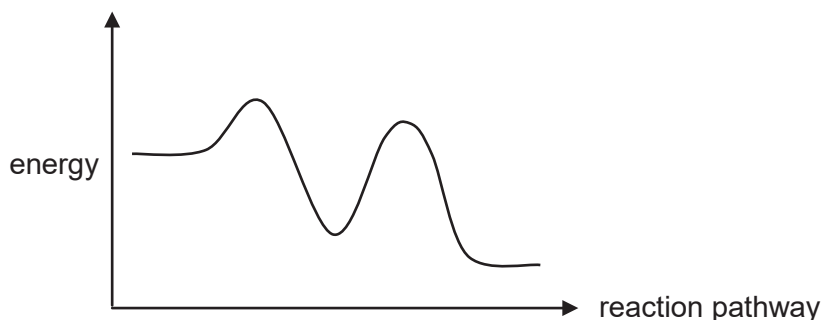
- | | R | S |
|----------|----------|----------|
| 1 | polarity | smaller |
| 2 | length | greater |
| 3 | energy | greater |

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

23 The reaction pathway diagram for a reaction that proceeds via **two** steps is shown below.



Which of the following statements are correct?

- 1** The enthalpy changes of both steps are exothermic.
- 2** The first step is fast while the second step is slow.
- 3** The activation energies of both steps are about the same.

24 The rate equation for the reaction between **X** and **Y** at a temperature of 30 °C is

$$\text{rate} = k[\text{X}]^2[\text{Y}]$$

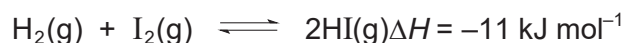
The rate constant, k , doubles with every 10 °C rise in temperature. Which of the following sets of conditions will allow the reaction to proceed with half of its original rate?

	concentration of X	concentration of Y	temperature
1	half	doubles	30 °C
2	no change	doubles	10 °C
3	doubles	half	20 °C

25 Which statements about the properties of a catalyst are correct?

- 1** A catalyst has no effect on the enthalpy change, ΔH , of the reaction.
- 2** A catalyst increases the average kinetic energy of the reacting particles.
- 3** A catalyst does not alter the mechanism of the reaction.

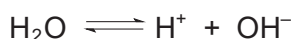
- 26** Hydrogen and iodine react in the gas phase and are allowed to reach equilibrium according to the following equation.



Which statement about this reaction at equilibrium is correct?

- 1 The yield of HI is increased by decreasing the pressure.
- 2 The value of K_c increases as temperature decreases.
- 3 The mixture will become lighter in colour if HI is removed.

- 27** Water dissociates as shown.



Given the following data at 25 °C:

	equilibrium concentration / mol dm ⁻³
H ⁺	10 ⁻⁷
H ₂ O	$\frac{1000}{18}$

Which of the following statements regarding pH, pK_a and pK_w are true?

- 1 Numerical values of $\text{pH} < pK_w < pK_a$.
- 2 Numerical values of pH, pK_a and pK_w decrease when temperature increases.
- 3 $pK_a = 2(\text{pH}) + \lg\left(\frac{1000}{18}\right)$

- 28** An enzyme, found in the stomach, operates at maximum efficiency when in an aqueous solution buffered at pH 5.

Which of the following pairs of solutions when mixed, would give the necessary buffer solution?

- 1 Equal volumes of 0.1 mol dm⁻³ CH₃CO₂H and 0.2 mol dm⁻³ CH₃CO₂⁻K⁺
- 2 Equal volumes of 0.1 mol dm⁻³ NH₃ and 0.1 mol dm⁻³ NH₄Cl
- 3 Equal volumes of 0.2 mol dm⁻³ NaOH and 0.05 mol dm⁻³ CH₃CO₂H

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 29** An acidified solution containing $0.10 \text{ mol dm}^{-3} \text{ZnSO}_4$ and $0.10 \text{ mol dm}^{-3} \text{CuSO}_4$ is saturated with H_2S at 15°C . The concentration of $\text{S}^{2-}(\text{aq})$ in the solution is then $10^{-35} \text{ mol dm}^{-3}$.

The solubility product, K_{sp} , of ZnS is $10^{-24} \text{ mol}^2 \text{ dm}^{-6}$ and that of CuS is $10^{-40} \text{ mol}^2 \text{ dm}^{-6}$ at 15°C .

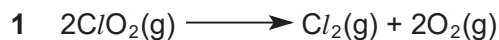
Which of the following statements correctly describes what happens in the solution?

- 1** Only CuS is precipitated.
 - 2** Only ZnS is precipitated.
 - 3** CuS is precipitated followed by ZnS .
- 30** Which of the following compounds will be produced when ethene is passed into bromine water that is mixed with aqueous sodium chloride?
- 1** $\text{BrCH}_2\text{CH}_2\text{Br}$
 - 2** $\text{ClCH}_2\text{CH}_2\text{Br}$
 - 3** $\text{ClCH}_2\text{CH}_2\text{Cl}$

H2 Chemistry 9647AJC JC1 Promotional Examinations 2013
Paper 1 – 30 marks

<i>Question Number</i>	<i>Key</i>	<i>Question Number</i>	<i>Key</i>
1	B	16	C
2	C	17	C
3	A	18	C
4	C	19	D
5	A	20	D
6	A	21	B
7	B	22	B
8	C	23	B
9	C	24	B
10	D	25	D
11	D	26	C
12	A	27	A
13	A	28	D
14	A	29	D
15	D	30	B

A	7
B	7
C	8
D	8

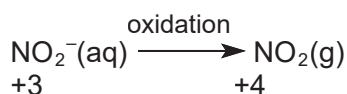
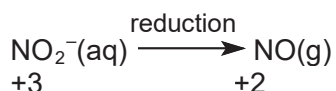


B

$$\begin{array}{ccc} n(\text{ClO}_2) & : & n(\text{Cl}_2) & : & n(\text{O}_2) \\ 2 & : & 1 & : & 2 \\ 200 \text{ cm}^3 & & 100 \text{ cm}^3 & & 200 \text{ cm}^3 \end{array}$$



C



$\therefore \text{NO}_2^-(\text{aq})$ ion undergoes disproportionation, i.e. it undergoes reduction and oxidation simultaneously.

3 $pV = nRT$

A

$$\frac{pV}{T} = \text{constant, i.e. } \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

For Ar:

$$\frac{300 \times 2.0}{(20 + 273)} = \frac{p_2 \times 5}{(30 + 273)}$$

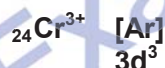
$$p_2 = 124.1 \text{ kPa}$$

For He:

$$\frac{500 \times 1.0}{(20 + 273)} = \frac{p_2 \times 5}{(30 + 273)}$$

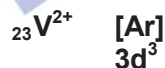
$$p_2 = 103.4 \text{ kPa}$$

$$\therefore \text{Final pressure in vessel} = 124.1 + 103.4 \approx 228 \text{ kPa}$$



$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow
\uparrow	\uparrow	\uparrow		

C



\uparrow				
\uparrow	\uparrow	\uparrow		



A

7th electron is removed from the next inner quantum shell.

\Rightarrow 6 valence electrons

\Rightarrow E is in Group VI and forms E^{2-} ion

\therefore Likely formula of the compound formed when E reacts with Mg is MgE .

- 6 SO_3^{2-} ($\sim 107^\circ$); SO_4^{2-} ($\sim 109.5^\circ$)
 NO_3^- ($\sim 120^\circ$); ClO_2^- ($\sim 105^\circ$)
 PH_3 ($\sim 107^\circ$); AsH_3 ($< 107^\circ$)

A

[Note: P is more electronegative than As \Rightarrow bonding electrons in P–H bond are drawn more towards P \Rightarrow more crowding of electron density around P atom \Rightarrow more inter–electronic repulsion between the electron pairs around the P atom \Rightarrow larger bond angle than in AsH_3]

BrF_2^- (180°); HCN (180°)

- 7 A : simple molecular, macromolecular, macromolecular
 B : ionic, simple molecular, macromolecular
 C : macromolecular, macromolecular, simple molecular
 D : macromolecular, simple molecular, macromolecular

B

8 L.E. $\propto \frac{q^+q^-}{r_+ + r_-}$

C

- Mg^{2+} and Sr^{2+} have a larger ionic charge than Li^+
- Mg^{2+} has a smaller ionic radius than Sr^{2+}
- F^- has a smaller ionic radius than I^-



C

$$\begin{aligned} \Delta H_f[\text{C}_2\text{H}_5\text{OH(l)}] &= \Sigma \Delta H_c(\text{reactants}) - \Sigma \Delta H_c(\text{products}) \\ &= [2(-394) + 3(-286) + 0] - [(-1211)] \\ &= -435 \text{ kJ mol}^{-1} \end{aligned}$$

- 10 Comparing Expt. 3 and 4, order of reaction w.r.t. NO is 2.
 Comparing Expt. 1 and 2, order of reaction w.r.t. H_2 is 1.

D

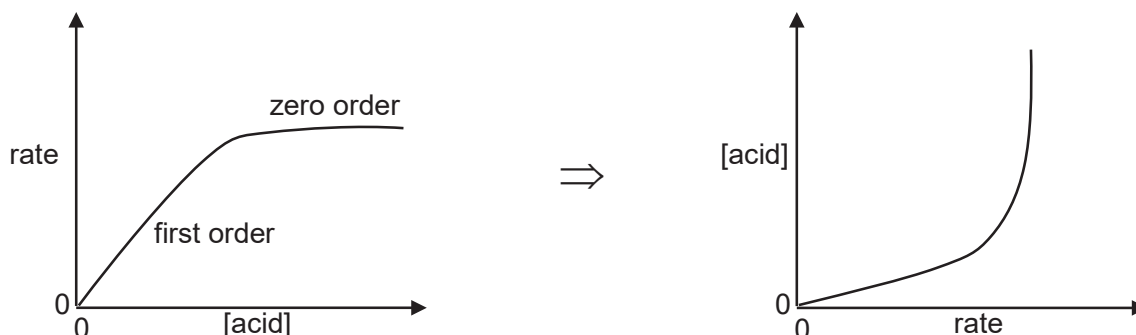
$$\therefore \text{rate} = k [\text{NO}]^2 [\text{H}_2]$$

$$\text{Units of } k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})} = \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

- 11 Note that the y-axis is [acid] and x-axis is rate.

D

From the given information, if rate is plotted against [acid] the graph will be as follows:



- 12 Maximum buffer capacity occurs at point **P** where equal concentrations of CH_3NH_2 (weak base) and its salt ($\text{CH}_3\text{NH}_3^+\text{Cl}^-$) have been produced when CH_3NH_2 is titrated against HCl . A buffer at its maximum capacity is most effective in maintaining its pH. **A**

- 13 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \Delta H < 0$ (exothermic) **A**

By Chatelier's Principle,

- **when pressure increases**, the position of equilibrium (POE) shifts right to decrease pressure by producing fewer gas molecules \Rightarrow % NH_3 at equilibrium increases
- **when temperature increases**, POE shifts left (as backward endothermic reaction is favoured) to reduce temperature by absorbing the extra heat \Rightarrow % NH_3 at equilibrium decreases

- 14
- | | | | |
|-------------------|--------|---|------|
| | yellow | | blue |
| bromocresol-green | 3.8 | – | 5.5 |
| | yellow | | red |
| phenol-red | 6.8 | – | 8.5 |

pH range of solution : 5.5 – 6.8 \Rightarrow **weakly acidic**

- 15 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ **D**

Ionic product = $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$

To prevent scum formation, $[\text{Ca}^{2+}]_{\text{in water}} \leq 10^{-5} \text{ mol dm}^{-3}$

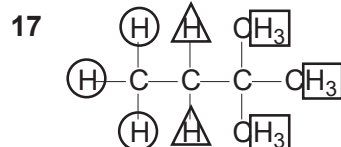
$$\begin{aligned} (10^{-5}) \times [\text{CO}_3^{2-}]_{\text{in water}} &= 5.0 \times 10^{-9} \\ [\text{CO}_3^{2-}]_{\text{in water}} &= 5.0 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

$n(\text{CO}_3^{2-})$ in 1 dm^3 water = $5.0 \times 10^{-4} \text{ mol}$

$n(\text{Na}_2\text{CO}_3)$ that should be added = $5.0 \times 10^{-4} \text{ mol}$

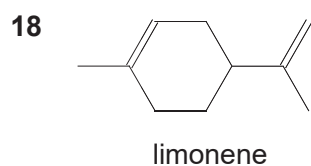
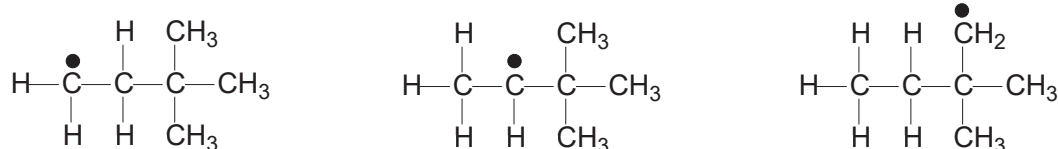
mass of Na_2CO_3 that should be added = $5.0 \times 10^{-4} \times 106.0 = 5.3 \times 10^{-2} \text{ g}$

- 16
- $$\begin{array}{ccccccc} \text{H}-\text{C}\equiv\text{C}-\text{H} & \xrightarrow[\text{A}]{+\text{HCl}} & \text{H}_2\text{C}=\text{CHCl} & \xrightarrow[\text{B}]{+\text{Cl}_2} & \text{ClCH}_2\text{CHCl}_2 & \xrightarrow[\text{C}]{+\text{NaOH in ethanol}} & \text{CH}_2=\text{CCl}_2 \\ \text{sp} \quad \text{sp} & & \text{sp}^2 \quad \text{sp}^2 & & \text{sp}^3 \quad \text{sp}^3 & & \text{sp}^2 \quad \text{sp}^2 \\ & & & & & & \downarrow \text{D} \\ & & & & & & \left[\underset{\text{sp}^3}{\text{CH}_2}-\underset{\text{sp}^3}{\text{CCl}_2} \right]_n \end{array}$$
- C**



C

The 3 different forms of X•are:



cold KMnO_4/H^+



C

No. of chiral centres in product = 4

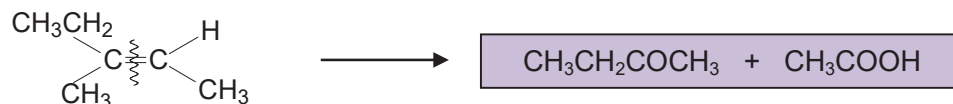
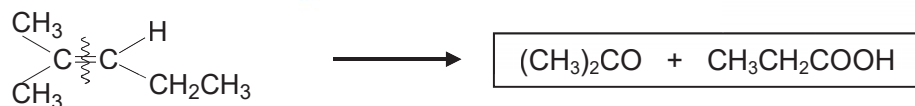
\therefore No. of optical isomers = $2^4 = 16$

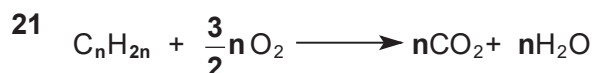
- 19
- Its molecular formula is $\text{C}_{10}\text{H}_{18}\text{O}$
 - It can exist as one pair of stereoisomers (optical isomers)
 - Its molecule is non-planar; it's tetrahedral w.r.t. each sp^3 carbon atom
 - The alkene functional group in linalool undergoes electrophilic addition with aq. Br_2 in the dark

D



D





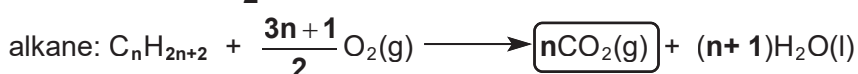
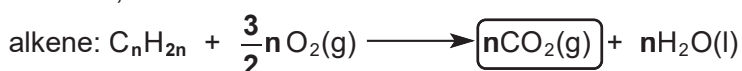
B

$$n(C_nH_{2n}) : n(C) : n(O_2)$$

$$1 : n : \frac{3}{2}n$$

∴ Volume of $O_2(g)$ required is directly proportional to the no. of carbon atoms, n , in the alkene molecule (Option 1 is correct).

At 25 °C,



∴ Volume of gas produced (CO_2 only) at 25 °C is the same for an alkane with same no. of carbon atoms (Option 2 is correct).

At 100 °C,

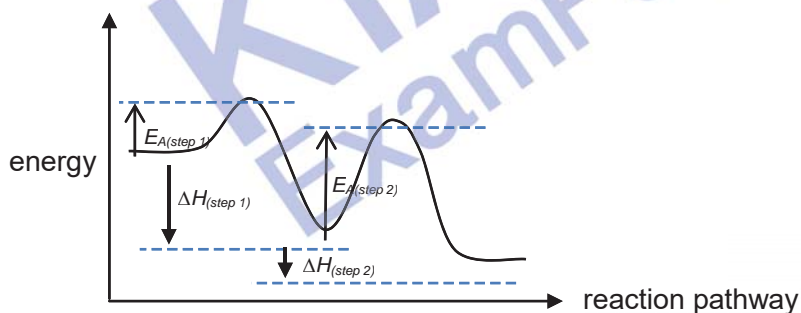


∴ Volume of steam produced is the same as that of CO_2 produced (Option 3 is incorrect).

- 22
- Br is less electronegative than Cl \Rightarrow bond polarity of H–Br is smaller (Option 1 is correct)
 - Br has a larger atomic radius than Cl \Rightarrow bond length of H–Br is greater (Option 2 is correct)
 - H–Br is a weaker bond than H–Cl \Rightarrow bond energy of H–Br is smaller (Option 3 is incorrect)

B

23 B



- ΔH of both steps are exothermic, i.e. < 0 (Option 1 is correct)
- E_A of first step is lower than that of second step \Rightarrow first step is fast; second step is slow (Option 2 is correct; Option 3 is incorrect)

- 24 At 30 °C, B
 $\text{rate} = k [\text{X}]^2 [\text{Y}]$

if original $[\text{X}] = a \text{ mol dm}^{-3}$ & original $[\text{Y}] = b \text{ mol dm}^{-3}$

original rate = ka^2b

when $[\text{X}]$ is halved & $[\text{Y}]$ doubled,

new rate = $k (a/2)^2 (2b) = (ka^2b) / 2 \Rightarrow$ rate is halved (Option 1 is correct)

At 10 °C,

rate = $(k/4)[\text{X}]^2 [\text{Y}]$ since k doubles with every 10 °C rise in temperature

when $[\text{X}]$ is unchanged & $[\text{Y}]$ doubled,

new rate = $(k/4) (a)^2 (2b) = (ka^2b) / 2 \Rightarrow$ rate is halved (Option 2 is correct)

At 20 °C,

rate = $(k/2)[\text{X}]^2 [\text{Y}]$

when $[\text{X}]$ is doubled & $[\text{Y}]$ halved,

new rate = $(k/2) (2a)^2 (b/2) = ka^2b \Rightarrow$ rate is unchanged (Option 3 is incorrect)

- 25 D
- Catalyst only lowers the activation energy of the reaction (Option 1 is correct)
 - Increase in temperature increases the average KE of the reacting particles, not catalyst (Option 2 is incorrect)
 - Catalyst alters the mechanism of the reaction by providing an alternative reaction pathway of a lower activation energy (Option 3 is incorrect)

- 26 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $\Delta H = -11 \text{ kJ mol}^{-1}$ C
 violet steamy white

- No change in the no. of moles of gaseous reactants and products, hence yield of HI is unaffected by pressure changes (Option 1 is incorrect)
- As temperature decreases, POE shifts right (exothermic reaction is favoured) to release heat. More product (HI) will be formed. Hence K_c increases since $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$. (Option 2 is correct)
- When HI is removed, POE shifts right to produce more HI $\Rightarrow [\text{I}_2]$ decreases hence the mixture will become lighter in colour (Option 3 is correct)

- 27 $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Delta H > 0$ A

$$\text{pH} = -\lg [\text{H}^+] = -\lg (10^{-7}) = 7$$

$$\text{p}K_w = -\lg K_w = -\lg ([\text{H}^+][\text{OH}^-]) = -\lg (10^{-7} \times 10^{-7}) = 14$$

$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{(10^{-7})^2}{(1000/18)} = 1.8 \times 10^{-16} \Rightarrow \text{p}K_a = -\lg (1.8 \times 10^{-16}) = 15.7$$

$\therefore \text{pH} < \text{p}K_w < \text{p}K_a$ (Option 1 is correct)

When temperature increases, POE shifts right (forward endothermic reaction is favoured) to absorb the extra heat $\Rightarrow [\text{H}^+] \uparrow, [\text{OH}^-] \uparrow, [\text{H}_2\text{O}] \downarrow$

$\therefore \text{pH} \downarrow$

$\text{p}K_a \downarrow (K_a \uparrow)$

$\text{p}K_w \downarrow (K_w \uparrow)$ (Option 2 is correct)

$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{[\text{H}^+]^2}{[\text{H}_2\text{O}]}$$

$$-\lg K_a = -\lg \left(\frac{[\text{H}^+]^2}{[\text{H}_2\text{O}]} \right) \quad (\text{Option 3 is correct})$$

$$= -2 \lg[\text{H}^+] + \lg[\text{H}_2\text{O}]$$

$$\text{p}K_a = 2(\text{pH}) + \lg\left(\frac{1000}{18}\right)$$

- 28 • A mixture of $\text{CH}_3\text{CO}_2\text{H}$ and CH_3CO_2^- forms an acidic buffer ($\text{pH} < 7$) (Option 1 is correct) D
 • A mixture of NH_3 and NH_4^+ forms an alkaline buffer ($\text{pH} > 7$) (Option 2 is incorrect)
 • When equal volumes of 0.2 mol dm^{-3} NaOH and 0.05 mol dm^{-3} $\text{CH}_3\text{CO}_2\text{H}$ are mixed, the resulting solution contains the excess NaOH and CH_3CO_2^- which do not make up a buffer (Option 3 is incorrect)

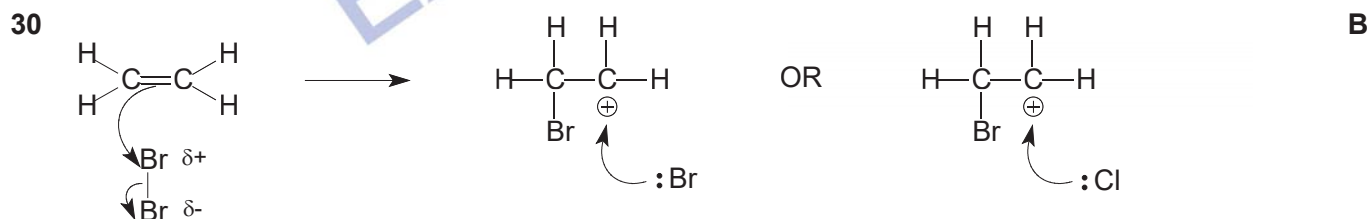
- 29 $[\text{Zn}^{2+}] = [\text{ZnSO}_4] = 0.10 \text{ mol dm}^{-3}$ D
 $[\text{Cu}^{2+}] = [\text{CuSO}_4] = 0.10 \text{ mol dm}^{-3}$

$$[\text{S}^{2-}]_{\text{in solution}} = 10^{-35} \text{ mol dm}^{-3}$$

ionic product: $[\text{Zn}^{2+}][\text{S}^{2-}] = (0.10)(10^{-35}) = 1 \times 10^{-36} < K_{\text{sp}}$ of $\text{ZnS} \Rightarrow \text{ZnS is not precipitated}$

ionic product: $[\text{Cu}^{2+}][\text{S}^{2-}] = (0.10)(10^{-35}) = 1 \times 10^{-36} > K_{\text{sp}}$ of $\text{CuS} \Rightarrow \text{CuS is precipitated}$

\therefore Only CuS is precipitated (only Option 1 is correct)



$\text{Br}(\delta+)$ acts as the electrophile for the electrophilic addition of ethene. Hence the possible products formed include: $\text{BrCH}_2\text{CH}_2\text{Br}$ and $\text{ClCH}_2\text{CH}_2\text{Br}$ (Options 1 & 2)

Note: $\text{ClCH}_2\text{CH}_2\text{Cl}$ is not formed due to the absence of $\text{Cl}(\delta+)$ to act as the electrophile.

NAME: _____ PDG: _____ Register No: _____



ANDERSON JUNIOR COLLEGE

JC1 Promotional Examinations 2013

CHEMISTRY

9647/02

Higher 2

2 October 2013

Paper 2 Structured & Free Response Questions

2 hours 25 minutes

Candidates answer Section A on the Question Paper.

Additional Materials: Data Booklet
 Writing Paper

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

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

Section A

Answer **ALL** questions in the spaces provided.

Section B

Answer **ALL** questions on separate writing paper.

Begin each question on a fresh sheet of paper.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use				
Paper 2	1		Paper 1	/ 30
	2			
	3		Paper 2	/ 90
	4			
	5		Final Marks	/ 120
	6			/ 100
	7		Grade	

This document consists of **16** printed pages.

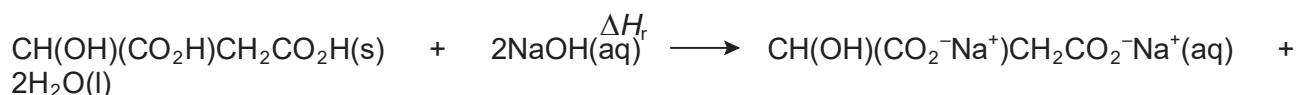
Section A

Answer **all** the questions in this section in the spaces provided.

1 Planning (P) – You should spend **no more** than 20 minutes on this question.

Discovered in 1785, malic acid, with the formula $\text{CH}(\text{OH})(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$, is a naturally occurring compound found in many fruits. It is used in many types of food, especially candy intended to be very sour or bitter.

A student was given a bottle of malic acid crystals and $1.00 \text{ mol dm}^{-3} \text{ NaOH(aq)}$. He was asked to determine the enthalpy change of reaction, ΔH_r , between malic acid and NaOH as shown below.



The student was provided with the following:

- a thermometer with 0.2°C division
- a 200 cm^3 Styrofoam cup with a lid
- a digital stopwatch
- common apparatus found in a school or college laboratory

Dataloggers are **not** provided.

- (a) Given that ΔH_r has an approximate value of -96 kJ mol^{-1} , suggest a suitable mass of malic acid that the student could use to obtain a temperature change of 8.0°C .

Justify your answer with relevant calculations.

You may assume that 4.18 J is required to raise the temperature of 1.0 cm^3 of any solution by 1 K .

$[M_r \text{ of malic acid} = 134.0]$

- (b) Write a plan that the student could use to determine the enthalpy change of reaction, ΔH_r , between malic acid and NaOH(aq).

In your plan you should:

- allow for the plotting of a suitable graph to correct for heat transfer with the surroundings
- include appropriate apparatus, masses and volumes of reagents, using your answer in part (a)
- draw a well-labelled diagram to show the experimental set-up

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[4]

- (c) Sketch a graph that you would expect to obtain in the experiment. Indicate clearly on the graph the temperature change of the reaction.

[2]

[Total: 8]

- 2 (a) The van der Waals' equation as shown below is often used to account for the discrepancies between experimental and theoretical behaviour of real gases.

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

p is the actual pressure, V the volume, T the temperature, n the amount of substance (in moles), and R the gas constant. The van der Waals' constants a and b are characteristic of the substance and are independent of temperature.

- (i) Given that the van der Waals' constants a and b for sulfur dioxide, SO_2 , is $0.687 \text{ Pa m}^6 \text{ mol}^{-2}$ and $5.68 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ respectively, calculate the actual pressure, p , exerted by 1 mole of SO_2 in a 0.5 dm^3 container at 25°C .

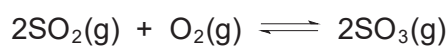
- (ii) Calculate the pressure exerted by SO_2 as described in (a)(i) if it obeys the ideal gas law.

- (iii) Suggest a reason for the discrepancy in the pressures obtained in (a)(i) and (a)(ii).

.....
.....

[3]

- (b) The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen.



The reaction is carried out at 500°C in a 10.0 dm^3 vessel. At the start of the reaction, 4 moles of SO_2 and 2 moles of O_2 are introduced into the vessel. When equilibrium is established, it is found that 2% of SO_2 remains unconverted.

- (i) Calculate the equilibrium concentrations of the three gases.

- (ii) Hence determine the value of the equilibrium constant, K_c , for this reaction at 500°C .

- (iii) When the same reaction is carried out at 700 °C, it is found that 10% of SO₂ remains unconverted. Deduce whether the reaction is endothermic or exothermic. Explain your answer.

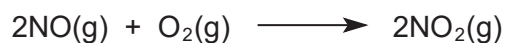
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[6]
[Total: 9]

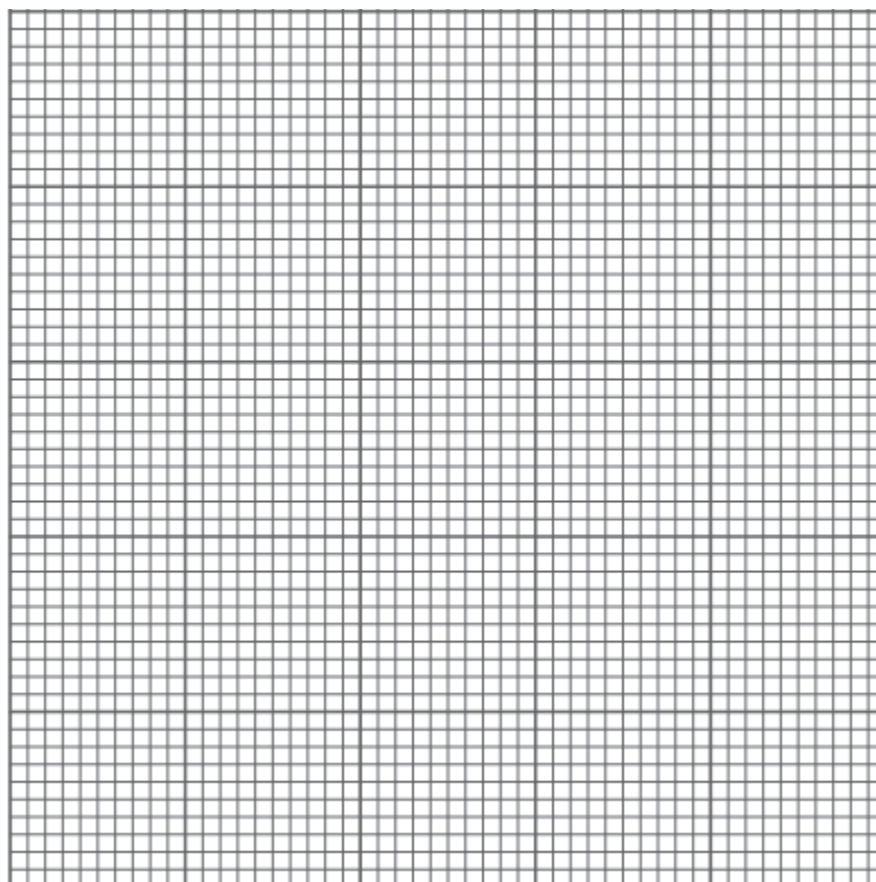
- 3 (a) Nitrogen monoxide is readily converted into nitrogen dioxide.



An investigation was carried out to determine the order of reaction with respect to oxygen. The following results were obtained.

Experiment	1	2	3	4	5
Initial rate / atm s^{-1}	1.08	2.16	3.06	3.60	4.14
Initial total pressure / atm	3.10	3.70	4.20	4.50	4.80
Initial partial pressure of NO / atm	2.50	2.50	2.50	2.50	2.50
Initial partial pressure of O_2 / atm					

- (i) Complete the above table.
- (ii) Hence use the data in the table to plot a suitable graph on the grid below to determine the order of reaction with respect to oxygen.



- (iii) What is the order of reaction with respect to oxygen? Explain your answer with reference to the shape of the graph obtained in (a)(ii).

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- (iv) What can be deduced from the gradient of the graph obtained in (a)(ii)? Calculate its value, and hence the half-life of this reaction.

[8]

- (b) With the aid of an appropriate diagram, explain how an increase in temperature increases the rate of this reaction.

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[3]

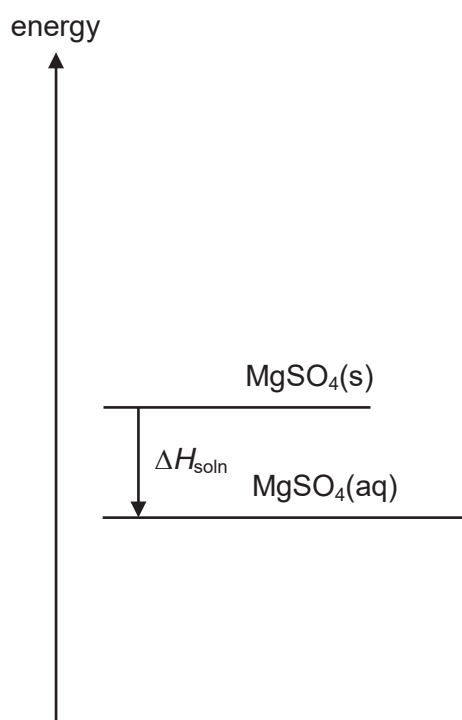
- 4 (a) The enthalpy change of solution, ΔH_{soln} , of anhydrous magnesium sulfate can be calculated from an energy level diagram involving enthalpy changes of hydration, ΔH_{hyd} , and lattice energy.

$$\text{lattice energy of MgSO}_4 = -2959 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}} \text{ of Mg}^{2+} = -1890 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}} \text{ of SO}_4^{2-} = -1160 \text{ kJ mol}^{-1}$$

- (i) Complete the energy level diagram below, labelling all the enthalpy changes involved and the chemical species at each stage.



- (ii) Use the given data and the diagram in (a)(i) to calculate the enthalpy change of solution, ΔH_{soln} , of anhydrous magnesium sulfate.

- (b) Data concerning magnesium and other Group II elements of the Periodic Table, at 298 K, are given in the table below.

	Mg	Ca	Sr	Ba
ΔH_{hyd} of M^{2+} / kJ mol^{-1}	-1890	-1650	-1480	-1365
ΔS_{hyd} of M^{2+} / $\text{J mol}^{-1} \text{K}^{-1}$	-293	-238	-222	-188
solubility of sulfate / mol per 100 g water	1.8×10^{-1}	4.7×10^{-3}	7.1×10^{-5}	9.4×10^{-7}

When the sulfate has dissolved, the anions and cations are each surrounded by a number of water molecules. The formation of these hydrated ions is an exothermic process.

- (i) Draw simple diagrams to show how a water molecule can be attached to a magnesium cation, and to a sulfate anion. Label each diagram clearly to show the type of interaction involved.

Mg^{2+} cation	SO_4^{2-} anion
-------------------------	--------------------------

- (ii) Suggest why ΔH_{hyd} of M^{2+} becomes less negative from Mg^{2+} to Ba^{2+} .

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- (iii) Use the data above to calculate ΔG_{hyd} of Ca^{2+} at 298 K.

- (iv) Predict how ΔG_{hyd} of Ca^{2+} will change with increasing temperature.

.....

[6]

- (c) (i) Use the data given in (b) to calculate the solubility, in mol dm^{-3} , of barium sulfate, BaSO_4 at 298 K.
[density of water = 1.00 g cm^{-3}]

- (ii) Write an expression for the solubility product, K_{sp} , of BaSO_4 and hence use your answer obtained in (c)(i) to calculate the value of the K_{sp} of BaSO_4 at 298 K, stating the units.

[3]
[Total: 12]

- 5 (a) Some data concerning particle **X**, **Y** and **Z** are given in the table below.

Particle	Electric charge	Mass number	Number of		
			protons	electrons	neutrons
X	0		16		16
Y	-1	81		36	
Z		70	31	28	

- (i) Complete the above table.

- (ii) State the electronic configuration of particle **Z**.

.....

- (iii) Draw and label the shapes of the **two** types of electron orbital found in particle **X**.

- (iv) In a particular experimental set-up, a beam of particle **Y** was deflected through an angle of $+2.0^\circ$. Assuming an identical set of experimental conditions, determine the angle of deflection of a beam of Ca^{2+} .

Angle of deflection = $^\circ$

[8]

- (b) **X** reacts with fluorine to form XF_2 which reacts readily with more fluorine to give XF_4 . When compared with Mg, MgF_2 does not react further with more fluorine to give MgF_4 . Explain why this is so.

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.....
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[2]

[Total: 10]

Section B

Answer **all** questions in this section on separate writing paper.

- 6 (a) A gaseous hydrocarbon **A** contains 85.7% of carbon by mass. When 10.0 cm^3 of **A** underwent complete combustion in 80.0 cm^3 of oxygen the remaining gases occupied 60.0 cm^3 . After shaking these gases with aqueous sodium hydroxide the final volume of gas remaining was 20.0 cm^3 .
(All volumes were measured at room temperature and pressure.)

- (i) Determine the empirical and molecular formulae of **A**.
- (ii) **A** exists as a pair of *cis-trans* isomers. Draw the structures of the *cis-trans* isomers of **A**, labelling your structures clearly.

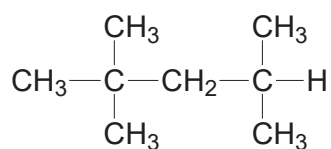
[6]

- (b) Bromoalkanes can be synthesised from alkanes and bromine via free-radical substitution.

- (i) Describe the mechanism of the reaction between ethane and bromine. In your answer, state the condition of the reaction and label each step in the mechanism appropriately.
- (ii) Free-radical substitution is not a good method to prepare bromoalkanes as organic by-products can be formed during the reaction.

When an alkane **B** is allowed to react with bromine in a free-radical substitution reaction, the following by-product is found in the reaction mixture.

Draw the structural formula of **B**.



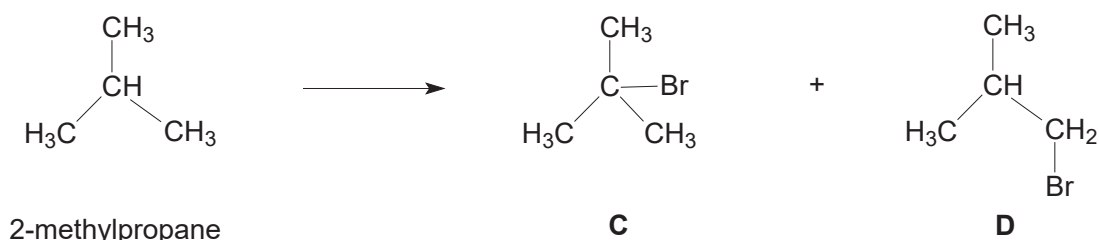
by-product

- (iii) During a free-radical substitution reaction, the rate of substitution of **each** hydrogen atom by a halogen atom is dependent on the type of hydrogen substituted – primary, secondary or tertiary.

The table below shows the relative rate of substitution by bromine.

Reaction	Type of hydrogen substituted	Relative rate
$\text{RCH}_3 \longrightarrow \text{RCH}_2\text{Br}$	primary	1
$\text{R}_2\text{CH}_2 \longrightarrow \text{R}_2\text{CHBr}$	secondary	7
$\text{R}_3\text{CH} \longrightarrow \text{R}_3\text{CBr}$	tertiary	21

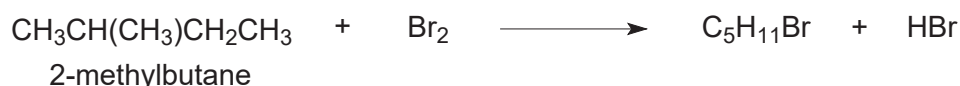
Bromination of 2-methylpropane produces compounds **C** and **D**.



Using the information from the table and by considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within 2-methylpropane, predict the relative ratio of the two possible products **C** and **D**. Explain your answer.

[7]

- (c) Bromination of 2-methylbutane yields a pair of stereoisomers in the product mixture.



- (i) Name the type of stereoisomerism shown and draw the displayed formulae of the isomers.
- (ii) Suggest a **physical** property in which the pair of stereoisomers are:
- I. similar with;
 - II. different from each other.
- (iii) 2,2-dimethylpropane, a structural isomer of 2-methylbutane, has a much lower boiling point than 2-methylbutane. Explain why this is so.

[7]

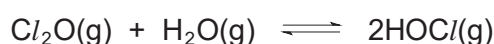
[Total: 20]

- 7 (a) Dichlorine monoxide, Cl_2O , and chlorine dioxide, ClO_2 , exist as gases at room temperature. Cl_2O explodes in high concentrations when exposed to heat or sparks while ClO_2 is a potent and useful oxidising agent.

- (i) Draw dot-and-cross diagrams to show the bonding in the molecules of Cl_2O and ClO_2 .
- (ii) Suggest a value for the bond angle in **each** of the above two molecules, giving reasons for your answer.

[4]

- (b) Dichlorine monoxide, Cl_2O , reacts with steam in a reaction vessel to produce hypochlorous acid, HOCl , until equilibrium is established.



The value of the equilibrium constant, K_p , is 0.815 at a temperature T.

- (i) If dichlorine monoxide and steam, both at a partial pressure of 0.323 atm, are injected into a reaction vessel and allowed to reach equilibrium at temperature T, what will be the equilibrium partial pressure of hypochlorous acid in the vessel?
- (ii) Use the appropriate bond energies given below to estimate a value for ΔH^\ominus for the above reaction.

Bond	Energy / kJ mol^{-1}
$\text{Cl}-\text{Cl}$	244
$\text{Cl}-\text{O}$	203
$\text{H}-\text{Cl}$	431
$\text{H}-\text{H}$	436
$\text{H}-\text{O}$	460

- (iii) State and explain the effect, if any, on the position of this equilibrium of:
- increasing the temperature,
 - decreasing the pressure.

[5]

- (c) NeutroPhase[®], containing 0.01%, by mass, of hypochlorous acid, HOCl , has been developed as a potent and safe wound care agent. Hypochlorous acid is known to be a highly effective antimicrobial solution produced by the human body to fight infection. At 25 °C, the $\text{p}K_a$ value of hypochlorous acid is 7.46.

- (i) State the relationship between the $\text{p}K_a$ of an acid and its dissociation constant, K_a .
- (ii) Write the equation, with state symbols, which represents the dissociation of hypochlorous acid.
- (iii) 10.0 cm^3 of hypochlorous acid solution was obtained from a 10 g sample of NeutroPhase[®]. Calculate the pH of the hypochlorous acid solution.

The hypochlorous acid solution in **(c)(iii)** was titrated against $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ NaOH using an indicator.

- (iv)** Suggest a suitable indicator for the titration, giving a reason for your choice.
- (v)** Calculate the volume of NaOH required for complete neutralisation of the hypochlorous acid solution.
- (vi)** Using your answers in **(c)(iii)** and **(c)(v)**, sketch the pH–volume added curve you would expect to obtain when 25 cm^3 of $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ NaOH was added to 10.0 cm^3 of hypochlorous acid solution in **(c)(iii)**.

Label clearly the various key points on the curve.

- (vii)** Indicate clearly, with an “X”, on your curve obtained in **(c)(vi)** the point at which the solution formed is most effective in resisting pH changes.

Write appropriate equations to illustrate how this solution resists pH changes.

[11]

[Total: 20]

Section A

1 (a) $\Delta H_r = - \frac{\text{heat released}}{n_{\text{malic acid}}}$

$$-96000 = - \frac{mc\Delta T}{n_{\text{malic acid}}}$$

$$-96000 = - \frac{50 \times 4.18 \times 8.0}{n_{\text{malic acid}}}$$

[1]

[1]: suitable volume chosen (25 – 100 cm³)

Note: sodium hydroxide is in excess

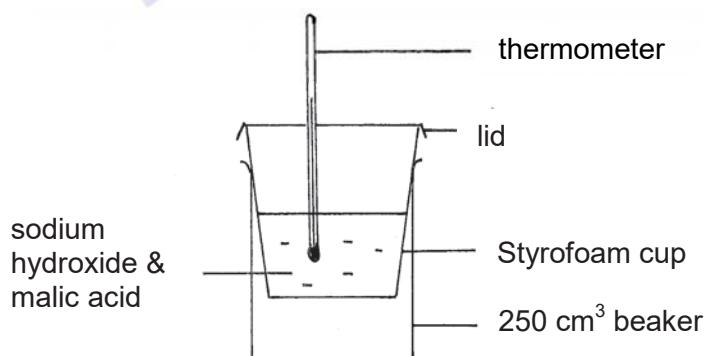
$$n_{\text{malic acid}} = 0.0174 \text{ mol}$$

$$\text{Mass of malic acid} = 0.0174 \times 134.0 = \underline{2.33 \text{ g}}$$

[1]

- (b)
1. Weigh accurately about 2.00 g of malic acid crystals in a weighing bottle, using a weighing balance.
 2. Using a 50 or 100 cm³ measuring cylinder, measure 50 cm³ of sodium hydroxide solution into a dry 200 cm³ Styrofoam cup. Support the Styrofoam cup in a 250 cm³ beaker.
 3. Stir the sodium hydroxide solution using a thermometer.
 4. Start the stopwatch.
 5. Record the temperature of the solution in the Styrofoam cup using a thermometer at 30 s interval until 2.5 min.
 6. At exactly the third minute (*accept 1 – 5 min*), transfer the malic acid into the Styrofoam cup. Do not measure the temperature at this time.
 7. Stir the solution gently and record the temperature of the solution at 3.5 min. Continue to stir and record the temperature at 30 s intervals until the solution returns to room temperature / temperature stays constant / for further 3 min.
 8. Reweigh the weighing bottle.

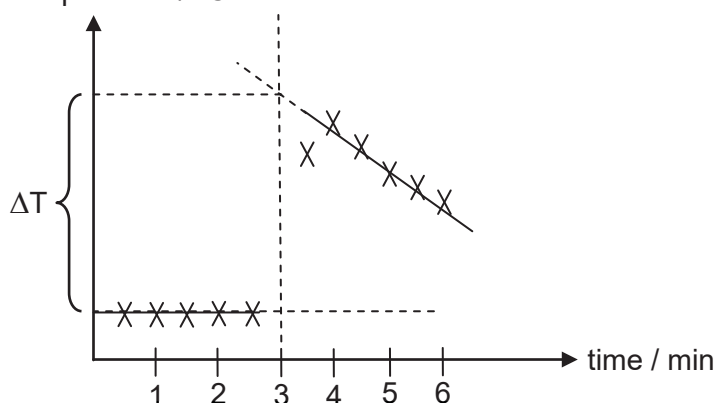
[4]



(c)

temperature / °C

[2]

[1]: show extrapolations to the 3rd min

[1]: correctly labelled temperature change of the reaction

Total: [8]

2 (a) (i)

$$p = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

[1]

$$= \frac{(1)(8.31)(298)}{(0.5 \times 10^{-3} - 5.68 \times 10^{-5})} - \frac{(1)^2(0.687)}{(0.5 \times 10^{-3})^2}$$

$$= 5.588 \times 10^6 - 2.748 \times 10^6$$

$$= \underline{2.84 \times 10^6 \text{ Pa}}$$

(ii) Using the ideal gas equation,

[1]

$$p = nRT/V$$

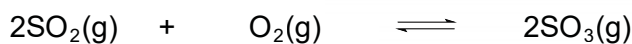
$$= \frac{(1)(8.31)(298)}{(0.5 \times 10^{-3})}$$

$$= \underline{4.95 \times 10^6 \text{ Pa}}$$

(iii) The actual pressure exerted is lower than the pressure calculated from the ideal gas equation as significant / strong intermolecular forces of attraction (permanent dipole–permanent dipole) exist between SO₂ molecules.

[1]

(b) (i)



Initial (mol):	4	2	0
Change (mol):	-0.98 x 4 = -3.92	-3.92/2	+3.92
Equilibrium (mol):	0.08	0.04	3.92
Eqm [] (mol dm ⁻³):	0.08/10.0 = 8 x 10 ⁻³	0.04/10.0 = 4 x 10 ⁻³	3.92/10.0 = 0.392

$$[\text{SO}_2]_{\text{eqm}} = \underline{8.00 \times 10^{-3} \text{ mol dm}^{-3}}$$

[1]

$$[\text{O}_2]_{\text{eqm}} = \underline{4.00 \times 10^{-3} \text{ mol dm}^{-3}}$$

[1]

$$[\text{SO}_3]_{\text{eqm}} = \underline{0.392 \text{ mol dm}^{-3}}$$

[1]

(ii) $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.392)^2}{(8 \times 10^{-3})^2(4 \times 10^{-3})} = 6.00 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$ [1]

(iii) Exothermic [1]

When temperature increases (from 500 °C to 700 °C),

- endothermic reaction is favoured
- since less SO₃ is formed when temperature is increased, the position of equilibrium has shifted to the left [1]
- ∴ reverse reaction is endothermic

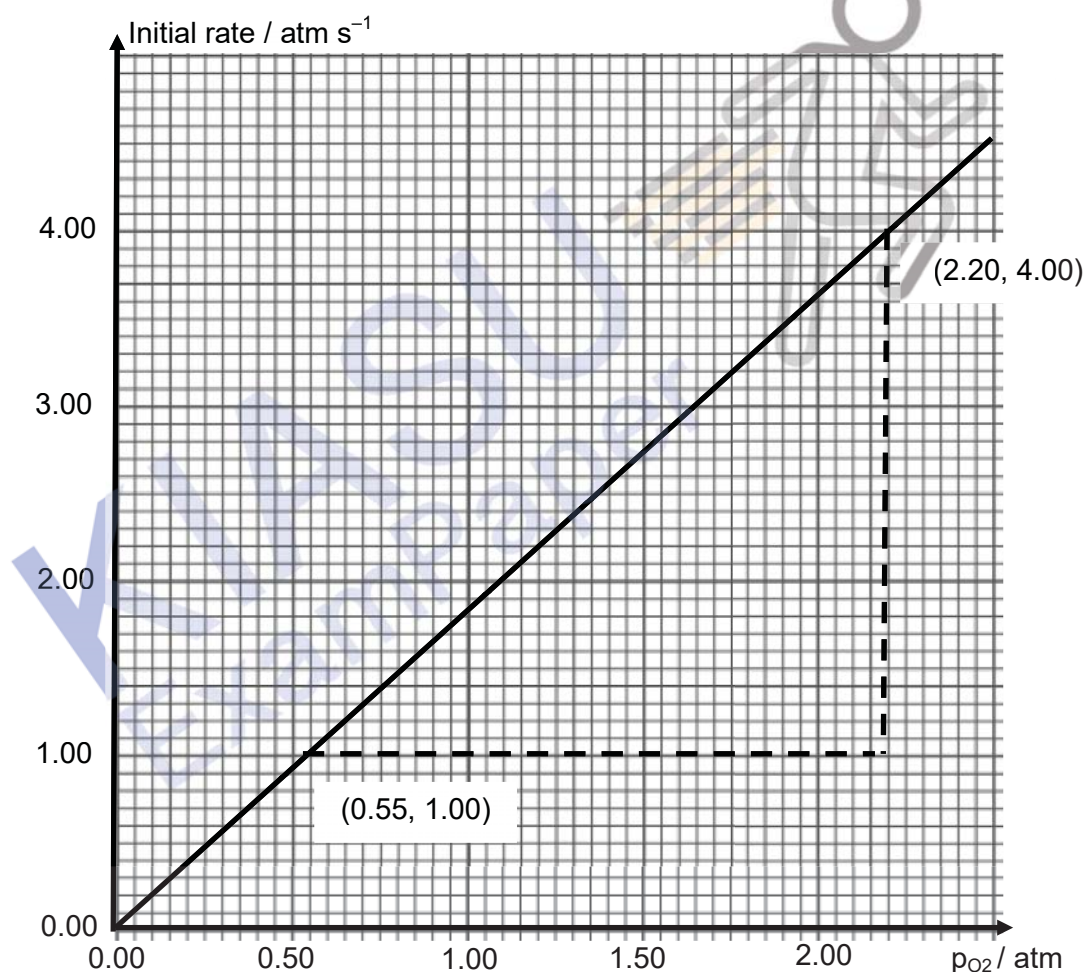
[Total: 9]

3 (a) (i)

$p_{\text{O}_2} / \text{atm}$	0.60	1.20	1.70	2.00	2.30
-------------------------------	------	------	------	------	------

[1]

(ii) [3]



(iii) Order one / first order with respect to oxygen. [1]

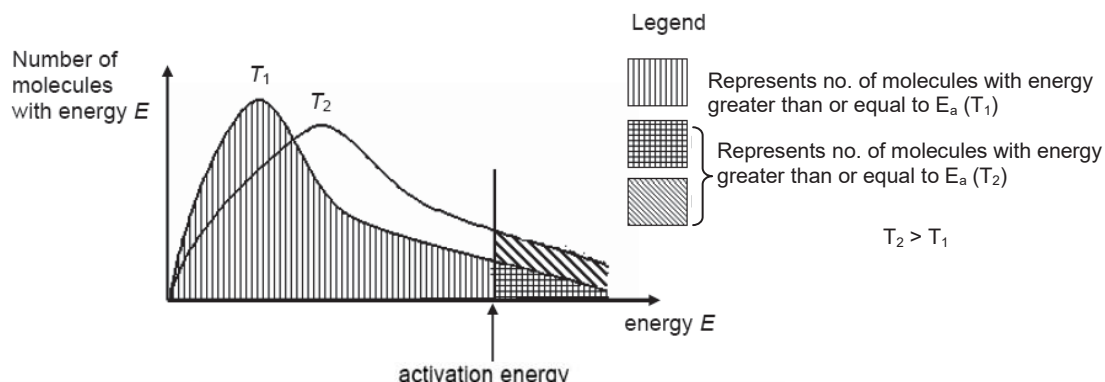
Since a straight line graph (through origin) is obtained, rate is directly proportional to p_{O_2} . [1]

(iv) rate constant for *pseudo* first order reaction, $k = \frac{(4.00 - 1.00)}{(2.20 - 0.55)} = 1.82$ [1]

$$t_{1/2} = \frac{\ln 2}{(1.82)} = 0.381 \text{ s}$$

[1]

(b)



[1]

As shown in the area under the curves, when temperature increases, the average kinetic energy of the molecules increases.

The number of molecules with energy greater than or equal to the activation energy, E_a , will increase.

[1]

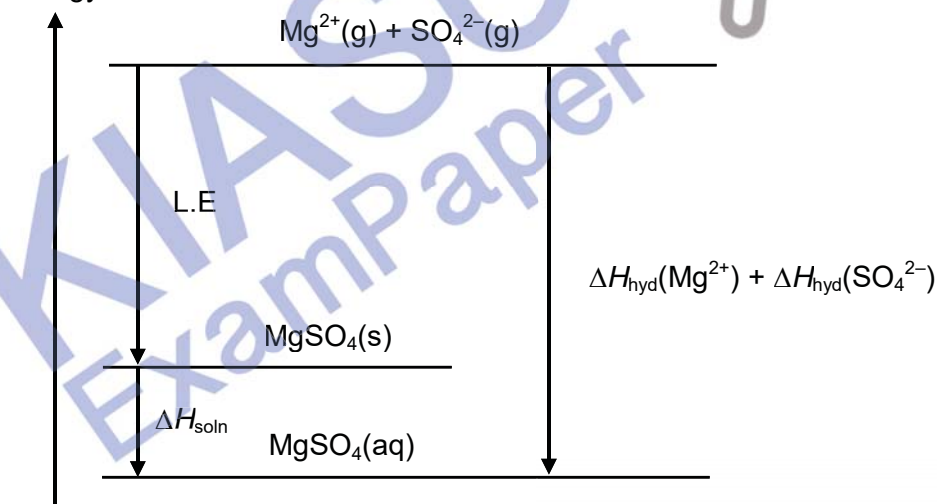
This results in an increase in the frequency of effective collisions. Hence, the rate increases.

[1]

[Total: 11]

4 (a) (i) energy

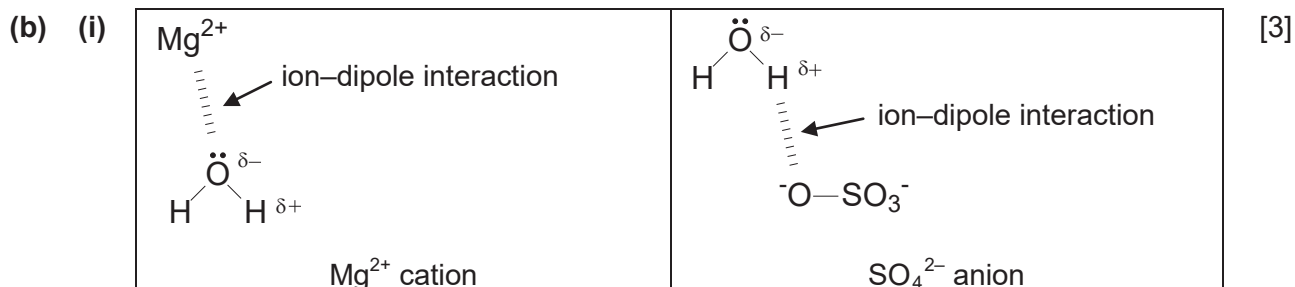
[2]



(ii) By Hess's law,

$$\begin{aligned} \Delta H_{\text{soln}} &= -\text{LE} + \Delta H_{\text{hyd}}(\text{Mg}^{2+}) + \Delta H_{\text{hyd}}(\text{SO}_4^{2-}) \\ &= -(-2959) + (-1890) + (-1160) \\ &= \underline{-91.0 \text{ kJ mol}^{-1}} \end{aligned}$$

[1]



(ii) Down Group II, ionic radius increases / charge density decreases.
Ion-dipole interactions become weaker and hence release less energy when formed. [1]

(iii) ΔG_{hyd} of Ca²⁺ = $\Delta H_{\text{hyd}} - T\Delta S_{\text{hyd}}$ [1]
 = $-1650 - (298)(-238/1000)$
 = $-1580 \text{ kJ mol}^{-1}$

(iv) As temperature increases, ΔG^\ominus becomes less negative / less spontaneous [1]

(c) (i) Solubility in mol dm⁻³ of BaSO₄ = $9.4 \times 10^{-7} / (100/1000) = \underline{9.40 \times 10^{-6} \text{ mol dm}^{-3}}$ [1]

(ii) $K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ [1]

K_{sp} of BaSO₄ = $(9.4 \times 10^{-6})^2 = \underline{8.84 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}}$ [1]

[Total: 12]

5 (a)

(i)	Particle	Electric charge	Mass number	Number of		
				protons	electrons	neutrons
	X	0	32	16	16	16
	Y	-1	81	35	36	46
	Z	+3	70	31	28	39

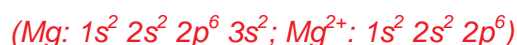
(ii) **Z**: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ [1]



(iv)

Particle	z/m ratio	angle of deflection
Y	1/81	+2.0°
Ca ²⁺	2/40.1	$-(81/1)(2/40.1) \times 2 = \underline{-8.1^\circ}$

(b) To form MgF₄, two more electrons must be removed from Mg²⁺.
 The two electrons must be removed from an inner quantum shell nearer to the nucleus which requires too much energy. Hence, MgF₂ will not react further with fluorine. [1]



X can expand its octet to form two more **X**-F bonds. [1]

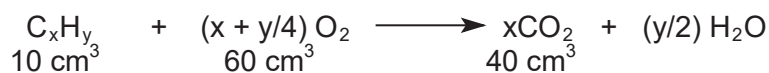
Section B

6 (a)

	C	H
% by mass	85.7	14.3
A_r	12.0	1.0
no. of moles	7.1416	14.3
simplest whole no. ratio	1	2

[2]

Empirical formula of A: CH_2



Volume of CO_2 produced = $60 - 20 = 40 \text{ cm}^3$

Volume of O_2 reacted = $80 - 20 = 60 \text{ cm}^3$

[1]

$$\frac{n(\text{A})}{n(\text{CO}_2)} = \frac{1}{x} = \frac{10}{40}$$

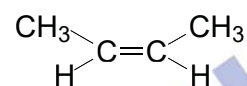
$$x = 4$$

$$\frac{n(\text{A})}{n(\text{O}_2)} = \frac{1}{4 + \frac{y}{4}} = \frac{10}{60}$$

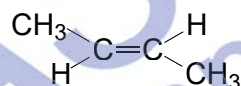
$$y = 8$$

Molecular formula of A: C_4H_8 .

[1]



cis-isomer



trans-isomer

[2]

(b) (i) Condition: high temperature or uv light

[1]

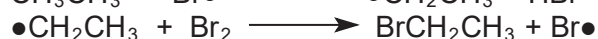
Mechanism:

[3]

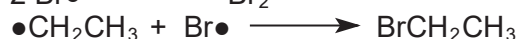
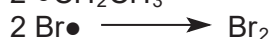
Initiation



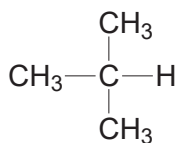
Propagation



Termination



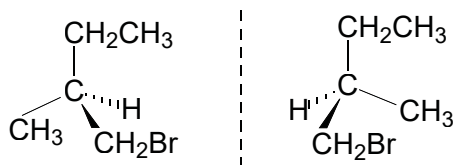
- (ii) Alkane B: [1]



- (iii) C/D = 2.3 : 1 or 7 : 3 or 21 : 9 [1]

Relative rate suggests 21 : 1, but there are 1 tertiary to 9 primary hydrogen atoms, hence this ratio becomes 21 : 9. [1]

- (c) (i) Optical isomerism [1]



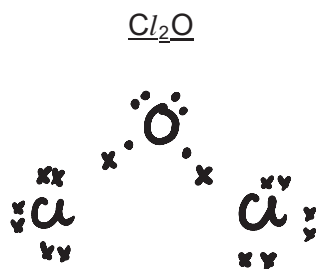
- (ii) I. Boiling point / melting point / density [1]
II. Optical activity / Direction of rotation of plane-polarised light [1]

- (iii) 2,2-dimethylpropane is more highly branched, thus it is more compact / spherical compared to 2-methylbutane. [1]

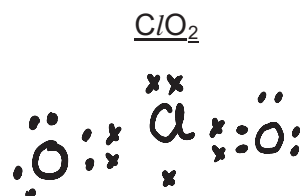
As a result, 2,2-dimethylpropane has a smaller surface area for instantaneous dipole-induced dipole attractions between molecules to operate. Hence, it has a much lower boiling point than 2-methylbutane. [1]

[Total: 20]

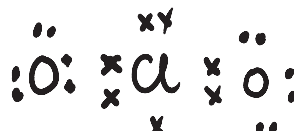
7 (a) (i)



[1]



OR

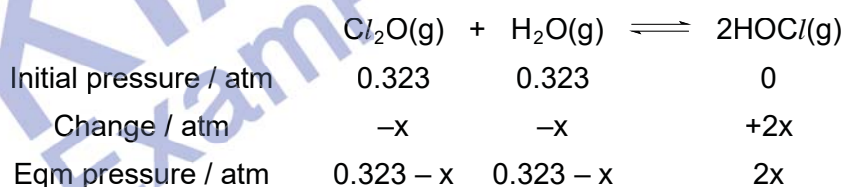


[1]

(ii)

	Bond angle	Reason
Cl ₂ O	Accept 105° < angle < 107.5° (actual 110.9°)	<ul style="list-style-type: none"> central oxygen atom is surrounded by 2 bond pairs and 2 lone pairs: the basic angle is therefore 109.5° lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion [1]: reason & bond angle angle will be reduced to a value much less than 109.5°
ClO ₂	Accept Cl–O–Cl < angle < 110°	<ul style="list-style-type: none"> A single unpaired electron exerts <u>less repulsion</u> than a lone pair ∴ bond angle should be <u>greater</u> than that for Cl₂O [1]: reason & bond angle

(b) (i)



$$K_p = \frac{(2x)^2}{(0.323 - x)(0.323 - x)} = 0.815$$

[1]

$$\therefore \frac{(2x)}{(0.323 - x)} = \sqrt{0.815} \quad x = 0.1004$$

Equilibrium partial pressure of hypochlorous acid = 2 x 0.1004 = 0.201 atm

[1]

(ii)

$$\begin{aligned} \Delta H^\ominus &= \Sigma \text{BE}(\text{Bonds broken}) - \Sigma \text{BE}(\text{Bonds formed}) \\ &= [2(203) + 2(460)] - 2[(203 + 460)] \\ &= \underline{0 \text{ kJ mol}^{-1}} \end{aligned}$$

[1] with units, ignore any sign

- (iii) Since $\Delta H^\ominus = 0 \text{ kJ mol}^{-1}$, the reaction takes place without any heat change / does not involve heat absorption or evolution
 \therefore Increase in temperature has no effect on position of equilibrium. [1]

No change in number of reactant and product molecules.
 \therefore Decrease in pressure has no effect on position of equilibrium. [1]

- (c) (i) $\text{p}K_a = -\log K_a$ [1]



OR



(iii)
 $n(\text{HOCl}) \text{ in } 10 \text{ g sample} = \frac{(\frac{0.01}{100} \times 10)}{52.5} \text{ mol} = 1.90 \times 10^{-5} \text{ mol}$

$[\text{HOCl}] = \frac{1000}{10.0} \times 1.90 \times 10^{-5} = 1.90 \times 10^{-3} \text{ mol dm}^{-3}$ [1]

$K_a = \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HOCl}]} \approx \frac{[\text{H}^+]^2}{[\text{HOCl}]_{\text{initial}}}$

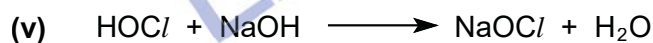
$10^{-7.46} = \frac{[\text{H}^+]^2}{1.90 \times 10^{-3}}$

$[\text{H}^+] = 8.12 \times 10^{-6} \text{ mol dm}^{-3}$

$\text{pH} = -\log(8.12 \times 10^{-6}) = \underline{5.09}$ [1]

- (iv) Phenolphthalein / Thymol blue
 The working pH range of indicator lies within the range of rapid pH changes at equivalence point.

[1] with reason



From part (iii),

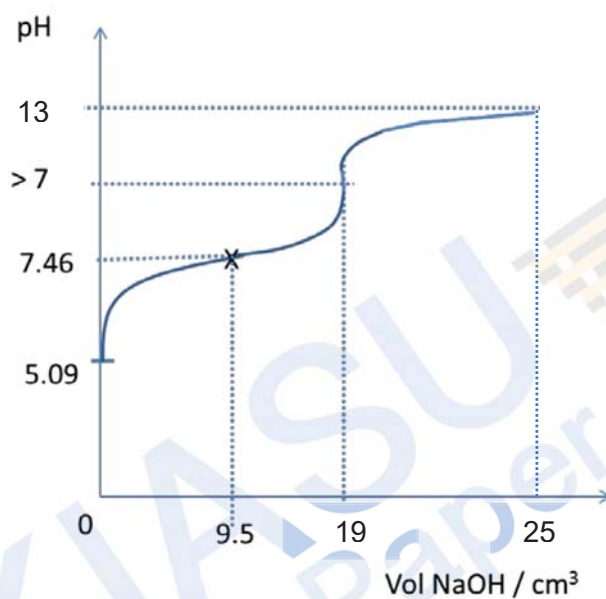
$n(\text{HOCl}) = 1.90 \times 10^{-5} \text{ mol}$

$n(\text{NaOH}) = n(\text{HOCl}) = 1.90 \times 10^{-5} \text{ mol}$

$\therefore \text{Volume of NaOH required} = 1.90 \times 10^{-5} / 1.00 \times 10^{-3}$
 $= 0.0190 \text{ dm}^3 = \underline{19.0 \text{ cm}^3}$ [1]

(vi)

[3]



(vii) Point at maximum buffer capacity: at 9.5 cm³ NaOH, pH at 7.46

[1]



[1]

[Total: 20]

Section A

Part 1: For each question, there are four possible answers, **A, B, C** and **D**. Choose the **one** you consider to be correct.

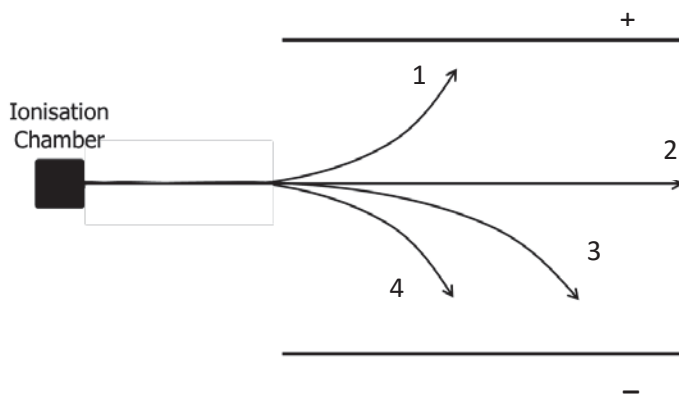
- 1 The successive ionisation energies (kJ mol^{-1}) of two elements are given below:

X	1012	1907	2914	4964	6274	21270	26430	29880	35910
Y	1251	2298	3822	5159	6542	9362	11110	33600	38860

Which of the following statements is **correct**?

- A** The formula of the compound formed between **X** and **Y** is X_3Y .
- B** The compound formed between **X** and **Y** is covalent.
- C** **X** has a giant molecular structure.
- D** **Y** has six valence electrons.
- 2 On decaying, americium-241 emits α -particles (${}^4\text{He}^{2+}$), while strontium-90 emits β -particles which can be considered as electrons.

A small amount of americium-241 and strontium-90 are placed in an ionisation chamber and the emitted particles are passed through an electric field.



What would be the path of the emitted particles in an electric field?

	α -particles	β -particles
A	3	1
B	4	1
C	1	2
D	1	3

- 3 Sulfur dichloride dioxide, SO_2Cl_2 , reacts with water to give a mixture of sulfuric acid and hydrochloric acid. How many moles of ammonia, NH_3 , would be needed to neutralise the solution formed by adding 1 mole of SO_2Cl_2 to an excess of water?

A 1 **B** 2 **C** 3 **D** 4

- 4 The mass percentage of magnesium in a mixture of magnesium chloride and magnesium nitrate was found to be 21.25%. What mass of magnesium chloride is present in 100 g of the mixture?

A 53.3 g **B** 46.7 g **C** 31.5 **D** 20.3 g

- 5 The nickel–cadmium rechargeable battery is based on the following overall reaction.



What is the oxidation number of nickel at the beginning and at the end of the reaction?

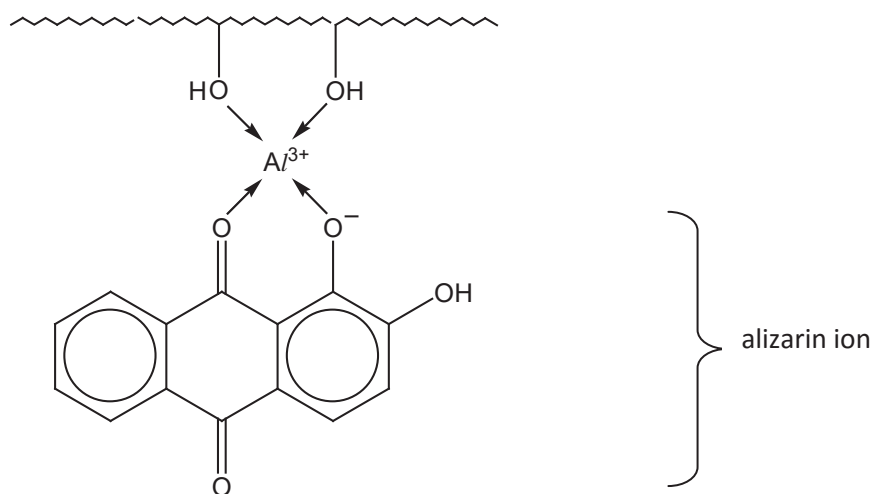
	Beginning	End
A	+1.5	+2
B	+2	+3
C	+3	+2
D	+3	+4

- 6 The mineral tellurite, TeO_2 ($M_r = 160.0$) is often used in the manufacture of optic fibres. It was found that 1.01 g of TeO_2 in an ore sample required exactly 60 cm^3 of $0.035 \text{ mol dm}^{-3}$ acidified $\text{K}_2\text{Cr}_2\text{O}_7$ for complete reaction. In this reaction, $\text{Cr}_2\text{O}_7^{2-}$ is converted into Cr^{3+} .

What is the oxidation state of Te in the final product?

A +6 **B** +5 **C** +3 **D** +2

- 7 The dye alizarin only sticks fast to cotton when a 'mordant' is used. If an aluminium compound is used as a mordant under alkaline conditions, aluminium ions become bonded to the hydroxyl groups of cotton. Alizarin can bond with the aluminium ions, giving the structure below which dyes the cotton red.



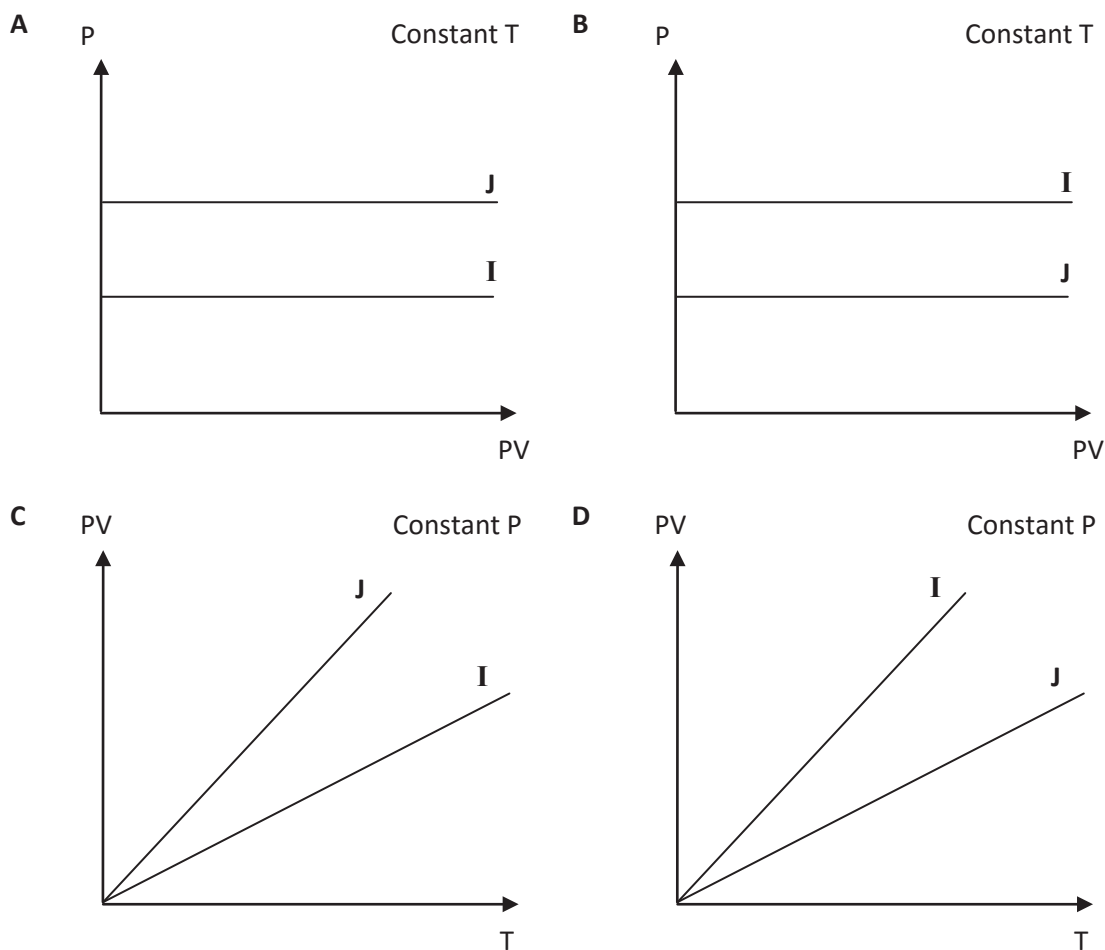
Which statement is **incorrect**?

- A All the carbon atoms in alizarin are sp^2 hybridised.
 - B The four oxygen atoms form coordinate bonds with the aluminium ion.
 - C In the absence of a mordant, alizarin can bind to cotton via hydrogen bonding.
 - D There is a decrease in the bond angles about the oxygen atoms of the cotton hydroxyl groups upon binding to aluminium ions.
- 8 The cylinder in a car engine has a volume of 0.500 dm^3 when the piston is at the bottom of its stroke. At this point the pressure is reduced to 95.0 kPa and the reduced pressure causes the fuel/air mixture to move the cylinder. At the top of its stroke, the position has compressed the gases to 25 cm^3 .

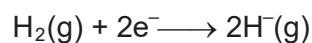
Assuming that the temperature in the cylinder remains constant, what is the pressure of the gases (in kPa) when the piston is at the top of its stroke?

- A 1900 B 132 C 4.75 D 1.90

- 9 Which graph correctly describes the behaviour of fixed masses of the ideal gases I and J, where I has a higher M_r than J?



- 10 Barium hydride, BaH_2 , is an ionic compound. The standard enthalpy changes for the following two reactions related to its constituent elements and ions are known.



What additional data is needed to determine the lattice energy of barium hydride?

- A The first ionisation energy of hydrogen.
- B The standard enthalpy change of atomisation of hydrogen.
- C The standard enthalpy change of atomisation of barium.
- D The standard enthalpy change of formation of barium hydride.

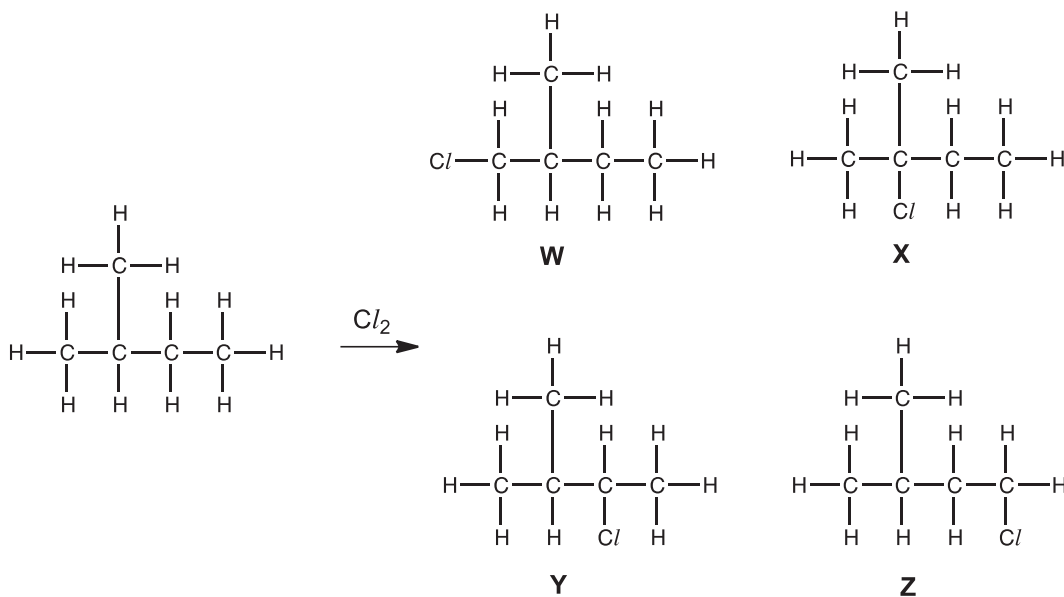
- 11 Instant 'hot packs' are often used by athletes to conveniently treat injuries. One type of 'hot packs' is composed of powdered calcium chloride and water separated by a thin plastic membrane. When the pack is squeezed, the membrane breaks and the calcium chloride dissolves in water.



Which line in the table gives the signs of ΔH , ΔS and ΔG for the overall process?

	ΔH	ΔS	ΔG
A	+	+	+
B	+	–	–
C	–	+	–
D	–	–	+

- 12 2-methylbutane undergoes a free radical substitution reaction with chlorine gas to produce four mono-chlorinated products as shown below.



Given also that the order of reactivity of primary, secondary and tertiary hydrogen atoms follows a 1:4:5 ratio, what is the ratio in which these products are formed?

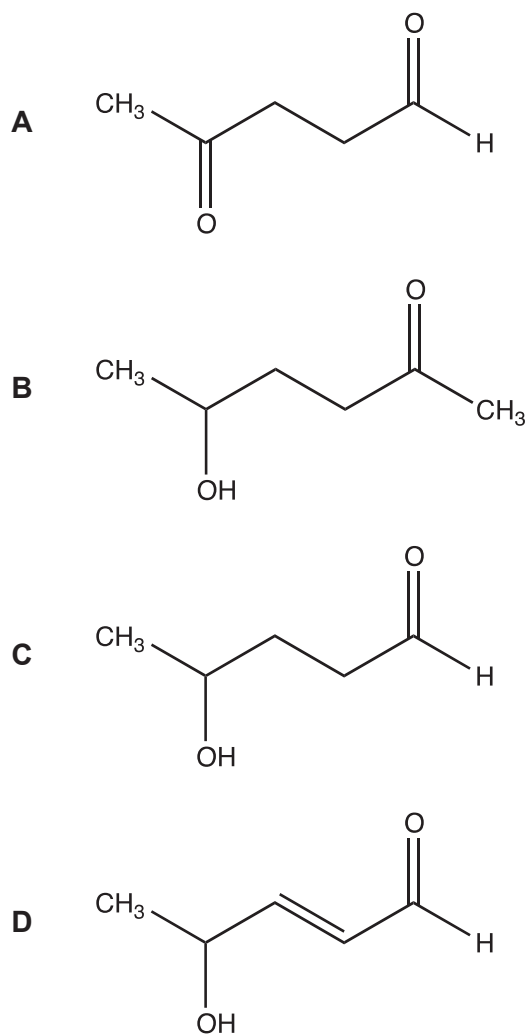
	W	X	Y	Z
A	6 :	1 :	2 :	3
B	1 :	5 :	4 :	1
C	6 :	5 :	8 :	3
D	7 :	6 :	6 :	4

13 **X** reacts with alkaline iodine to produce a yellow precipitate.

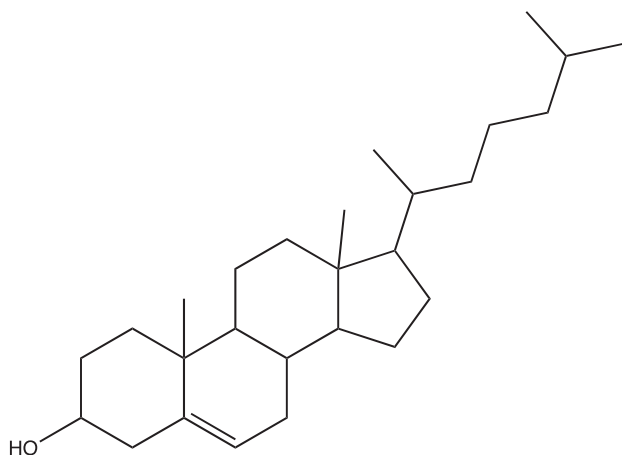
X reacts with Tollens' reagent to produce a silver mirror.

X produces carbon dioxide when heated with acidified KMnO_4 .

What is the structure of **X**?

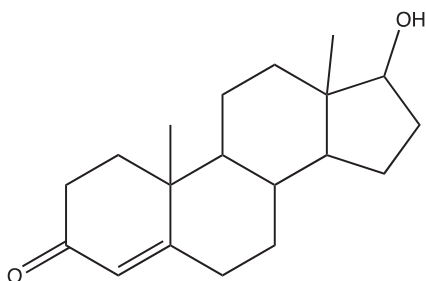


- 14 The structure of cholesterol is shown below.



How many chiral carbons does it contain?

- A 7
 - B 8
 - C 9
 - D 10
- 15 The structure of testosterone is shown below.



Which of the following statements is correct?

- A One mole of testosterone reacts with two moles of bromine.
- B One mole of testosterone reacts with excess sodium to produce half a mole of hydrogen gas.
- C Testosterone undergoes an electrophilic addition reaction with hydrogen cyanide.
- D A white fume is observed when testosterone reacts with phosphorus trichloride.

Part 2: For each of the questions in this section, one or more of the 3 numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct. (You may find it helpful to put a tick against the statements which you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

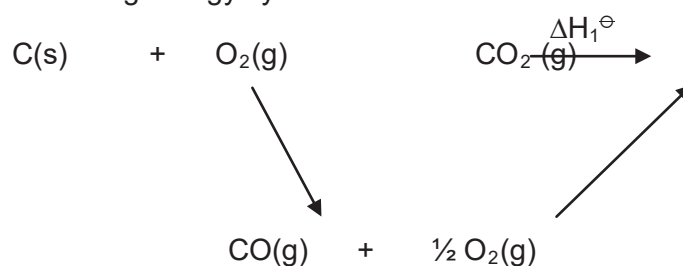
16 In which sequences are the molecules quoted in order of decreasing boiling points?

- 1 $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$, $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_3$
- 2 CO_2 , SO_2 , SiO_2 ,
- 3 AlBr_3 , AlCl_3 , AlF_3

17 In which of the following is the bond angle in species **I** greater than that in species **II**?

	I	II
1	BCl_3	NCl_3
2	NO_3^-	ClO_2^-
3	SF_6	SF_4^{2-}

18 Given the following energy cycle:

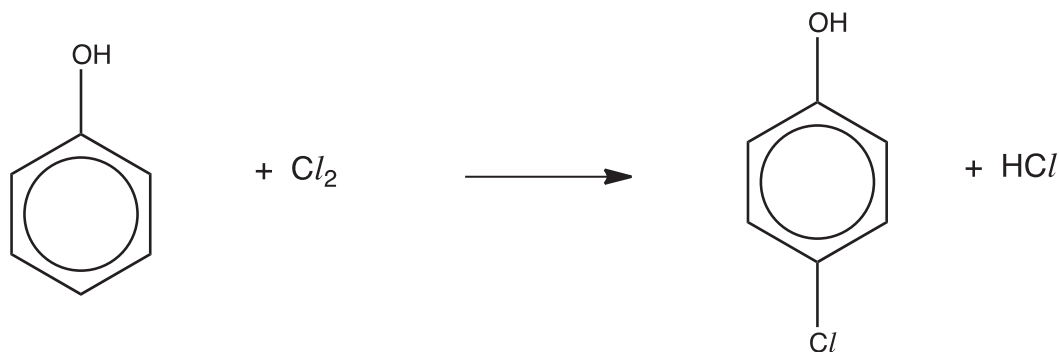


Which of the following have the same value as the standard enthalpy change, ΔH_1^\ominus ?

- 1 $\Delta H_f^\ominus(\text{CO}) + \Delta H_c^\ominus(\text{CO})$
- 2 $\Delta H_c^\ominus(\text{graphite}) - \Delta H_f^\ominus(\text{CO}_2)$
- 3 $\Delta H_c^\ominus(\text{graphite}) - \Delta H_c^\ominus(\text{CO})$

- 19** Chlorophenols are commonly used as pesticides, herbicides and disinfectants. They are organochloride of phenol that contains one or more covalently bonded chlorine atoms.

For example, 4-chlorophenol can be produced from the reaction between phenol and chlorine gas.



Which of the following statements correctly describe the intermediate complex formed in the reaction between phenol and chlorine gas?

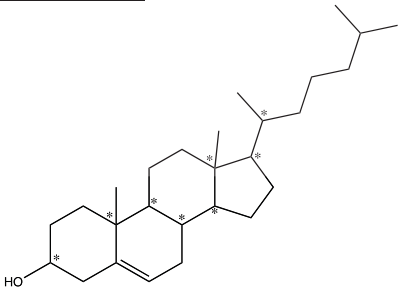

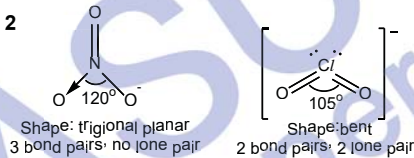
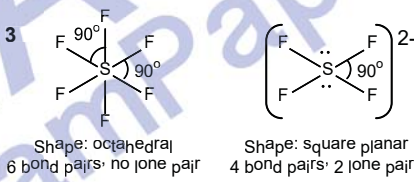
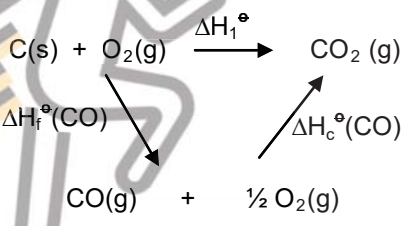
- 1 It contains a sp^3 hybridised carbon atom.
 - 2 It contains four π electrons.
 - 3 It is planar.
- 20** Which of the following reactions will produce a racemic mixture?

- 1 $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} + \text{HCN}$
- 2 $\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array} + \text{HBr}$
- 3 $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} + \text{Br}_2$

2013 Chemistry H2 Promotional Examination Section A Worked Solutions

1	2	3	4	5	6	7	8	9	10
B	A	D	A	C	A	D	A	C	D
11	12	13	14	15	16	17	18	19	20
C	C	D	B	B	D	B	D	B	B

<p>Question 1 Answer is B</p> <p>A. The formula of the compound formed between X & Y is XY₃ and NOT TX₃Y.</p> <p>B. X is group V element & Y is group VII element. Therefore compound formed between X and Y is covalent (both X and Y shared electrons & achieved octet structure).</p> <p>C. X exists as diatomic molecules.</p> <p>D. Y has 7 valence electrons.</p>	<p>Question 2 Answer is A</p> <p>Given that α-particles (${}^4\text{He}^{2+}$) and β-particles (${}_{-1}^0\text{e}$, electrons), α-particles will be deflected towards the negative plate and by a smaller magnitude (due to greater mass no.) than β-particles (towards positive plate).</p>	<p>Question 3 Answer is D</p> <p>$\text{SO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HCl}$ 1 mol of SO_2Cl_2 produces 1 mol of H_2SO_4 & 2 mol of HCl which ionize to give 4 mol of H^+. $\text{H}^+ \equiv \text{NH}_3$ Thus, 4 moles of NH_3 is required for neutralization.</p>
<p>Question 4 Answer is A</p> <p>Let mass of MgCl_2 be x g, hence mass of $\text{Mg}(\text{NO}_3)_2 = (100 - x)$ g $\frac{[(24.3/95.3)x + (24.3/148.3)(100 - x)] \times 100}{100} = 21.25$ $0.25x + 0.164(100 - x) = 21.25$ $0.091x = 4.85$ $x = 53.3$</p>	<p>Question 5 Answer is C</p> <p>Oxidation no. of Ni in $\text{NiO}(\text{OH})$, $x + 2(-2) + (+1) = 0$, $x = +3$</p> <p>Oxidation no. of Ni in $\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$, $x + 3(-2) + 4(+1) = 0$, $x = +2$</p>	<p>Question 6 Answer is A</p> <p>No. of moles of $\text{TeO}_2 = 1.01/160 = 6.31 \times 10^{-3} \text{ mol}$ No of moles of $\text{Cr}_2\text{O}_7^{2-} = 60/1000 \times 0.035 = 0.0021 \text{ mol}$ $3\text{TeO}_2 \equiv \text{Cr}_2\text{O}_7^{2-}$ $\text{Cr}_2\text{O}_7^{2-} \equiv 2\text{Cr}^{3+} \equiv 6\text{e}^-$ $3\text{TeO}_2 \equiv \text{Cr}_2\text{O}_7^{2-} \equiv 6\text{e}^-$ $\text{TeO}_2 \equiv 2\text{e}^-$ (ox state of Te in TeO_2 is +4) Hence, oxidation state of Te in final product = +4 + 2 = +6</p>
<p>Question 7 Answer is D</p> <p>There is an increase in the bond angles about the oxygen atoms of the cotton hydroxyl groups upon binding to aluminium ions (1 lone pair & 3 bond pairs: larger angle). An oxygen atom of the cotton hydroxyl group without binding to aluminium ion has 2 lone pairs & 2 bonding pairs: smaller angle).</p>	<p>Question 8 Answer is A</p> <p>$P_1V_1 = P_2V_2$ (Const temp) $(500 \text{ cm}^3)(95 \text{ kPa}) = P_2(25 \text{ cm}^3)$ $P_2 = 1900 \text{ kPa}$</p>	<p>Question 9 Answer is C</p> <p>For options A and B, $pV = nRT$ $pV = (m/M)RT = \text{constant}$ \Rightarrow Graph of P against pV should be a vertical line at a particular value of pV.</p> <p>For options C and D, $pV = nRT = (mR/M_r)T \Rightarrow pV \propto T/M_r$ On keeping T constant, $\Rightarrow pV \propto 1/M_r$ \Rightarrow Since the M_r of I is higher, the gradient of the line is gentler.</p>
<p>Question 10 Answer is D</p> <p>Using Born Haber Cycle:</p> <div style="text-align: center;"> $\begin{array}{ccc} \text{Ba(s)} + \text{H}_2(\text{g}) & \xrightarrow{\Delta H_f^\circ} & \text{BaH}_2(\text{s}) \\ \downarrow \Delta H_1^\circ & & \uparrow \Delta H_{\text{latt}}^\circ \\ \text{Ba}^{2+}(\text{g}) + 2\text{H}^\cdot(\text{g}) & & \end{array}$ </div> <p>Hence $\Delta H_f^\circ(\text{BaH}_2)$ is needed.</p>	<p>Question 11 Answer is C</p> <p>Hot packs \Rightarrow exothermic process, ΔH negative</p> <p>Calcium chloride solid dissolves in water, ions become mobile, more disordered state $\Rightarrow \Delta S$ is positive</p> <p>$\Delta G = \Delta H - T\Delta S$ Since ΔH is negative and ΔS is positive Therefore ΔG is negative.</p>	<p>Question 12 Answer is C</p> <p>To form W, there are 6 possible (primary) hydrogen to replace</p> <p>To form X, there is 1 possible (tertiary) hydrogen to replace</p> <p>To form Y, there are 2 possible (secondary) hydrogen to replace</p> <p>To form Z, there are 3 possible (primary) hydrogen to replace</p>

		<p>Hence the ratio of W:X:Y:Z after considering the reactivity of the different type of hydrogen atoms is</p> <p>6 x 1: 1 x 5: 2 x 4: 3 x 1 6: 5: 8: 3</p>
<p>Question 13 Answer is D</p> <p>X must be an aldehyde and possibly contain a carbon-carbon double bond so that carbon dioxide is given off upon oxidation.</p> <p>D upon oxidation produces $C_2H_2O_4$ which will be further oxidised.</p>	<p>Question 14 Answer is B</p> 	<p>Question 15 Answer is B</p> <p>A. One mole of testosterone reacts one mole of bromine B. $ROH + Na \rightarrow RO^-Na^+ + \frac{1}{2} H_2$ C. The ketone functional group undergoes an nucleophilic addition with HCN D. White fumes is observed when reacted with PCl_5</p>
<p>Question 16 Answer is D</p> <p>1. $CH_3(CH_2)_3CH_3$ – straight-chain $(CH_3)_2CHCH_2CH_3$ – less branching $CH_3C(CH_3)_2CH_3$ – more branching Boiling point decreases.</p> <p>2. CO_2 – simple molecular structure (non-polar molecule, id-id, Bpt: $-57^\circ C$) SO_2 – simple molecular structure (polar molecule, pd-pd; bpt: $-10^\circ C$) SiO_2 – giant molecular structure (covalent bond; bpt: $2250^\circ C$) Therefore, boiling point increases</p> <p>3. $AlBr_3$ – simple molecular structure with larger electron cloud (bpt: $265^\circ C$) $AlCl_3$ – simple molecular structure with smaller electron cloud (bpt: $120^\circ C$) AlF_3 – giant ionic lattice structure (bpt: $1291^\circ C$)</p>	<p>Question 17 Answer is B</p> <p>species I species II</p> <p>1:</p>  <p>Shape: trigonal planar 3 bond pairs, no lone pair Shape: trigonal pyramidal 3 bond pairs, 1 lone pair</p> <p>2</p>  <p>Shape: trigonal planar 3 bond pairs, no lone pair Shape: bent 2 bond pairs, 2 lone pairs</p> <p>3</p>  <p>Shape: octahedral 6 bond pairs, no lone pair Shape: square planar 4 bond pairs, 2 lone pairs</p>	<p>Question 18 Answer is D</p>  <p>Energy cycle shows option 1 is correct but not options 2 and 3. $\Delta H_f^\ominus(CO_2) = \Delta H_f^\ominus(CO) + \Delta H_c^\ominus(CO)$</p>
<p>Question 19 Answer is B</p> <p>1. The carbon atom which the Cl is attached to has a tetrahedral arrangement. 2. One pair of pi electrons is being used to form a bond between benzene and chlorine 3. The intermediate is not planar as it contains a sp^3 hybridised carbon atom</p>	<p>Question 20 Answer is B</p> <p>1. A nucleophilic addition reaction resulting in the formation of a chiral compound. The CN^- ion can attack the planar carbonyl carbon from top and bottom with equal probability. 2. An electrophilic addition reaction resulting in the formation of a chiral compound. The Br^- ion can attack the planar carbon carrying the positive charge from top and bottom with equal probability. 3. The product form is not chiral.</p>	

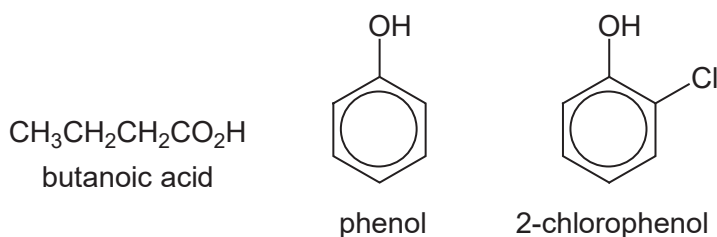
Section B

Answer **all** questions. Begin each answer on a separate sheet of paper.

1 This question is about carboxylic acids and its applications.

(a) Butanoic acid is responsible for the rancid odour of sour butter.

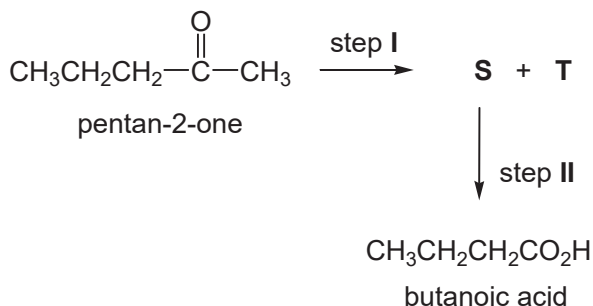
(i) The acidity of butanoic acid is compared against phenol and 2-chlorophenol. Arrange the three compounds in order of increasing acidity. Explain your answer.



(ii) Butanoic acid is used in the preparation of various esters. Low-molecular-weight esters of butanoic acid, such as methyl butanoate, have mostly pleasant aromas or tastes and are often used as food and perfume additives.

Suggest suitable reagents and conditions to form methyl butanoate from butanoic acid.

Butanoic acid can be made from pentan-2-one as shown below. In step I, compounds **S** and **T** are formed. **S** is subsequently converted to butanoic acid in step II.



(iii) Suggest reagents and conditions for steps I and II.

(iv) Predict from this synthesis, the structural formulae of **S** and **T**.

A student prepared a sample of butanoic acid via oxidation of butanal.

- (v) Suggest a simple chemical test to detect the presence of residual butanal in the sample. You should state the reagent and condition, and the observation if butanal is present in the sample.

Write a balanced equation for the chemical test suggested.

[12]

- (b) Long chain carboxylic acids, often referred to as fatty acids, are important components of biomolecules known as lipids.

Natural fatty acids may be saturated or unsaturated. Depending on the number of C=C bonds present (all are in the *cis* configuration), as well as their respective carbon chain lengths, these fatty acids have significantly different melting points.

Molecular Formula	Structural Formula	Common Name	Melting Point / °C
$C_{15}H_{29}CO_2H$	$CH_3(CH_2)_5CH=CH(CH_2)_7CO_2H$	palmitoleic acid	0
$C_{17}H_{33}CO_2H$	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$	oleic acid	13
$C_{17}H_{35}CO_2H$	$CH_3(CH_2)_{16}CO_2H$	stearic acid	69

- (i) With reference to the data above, explain the difference in melting points between:

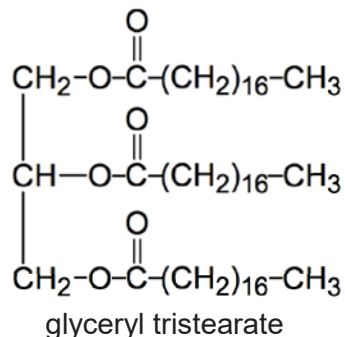
- (A) palmitoleic acid and oleic acid
(B) oleic acid and stearic acid

- (ii) Oleic acid is insoluble in water but soluble in organic solvents such as ethanol. Draw a well-labelled diagram to show the type(s) of interactions involved between oleic acid and ethanol.

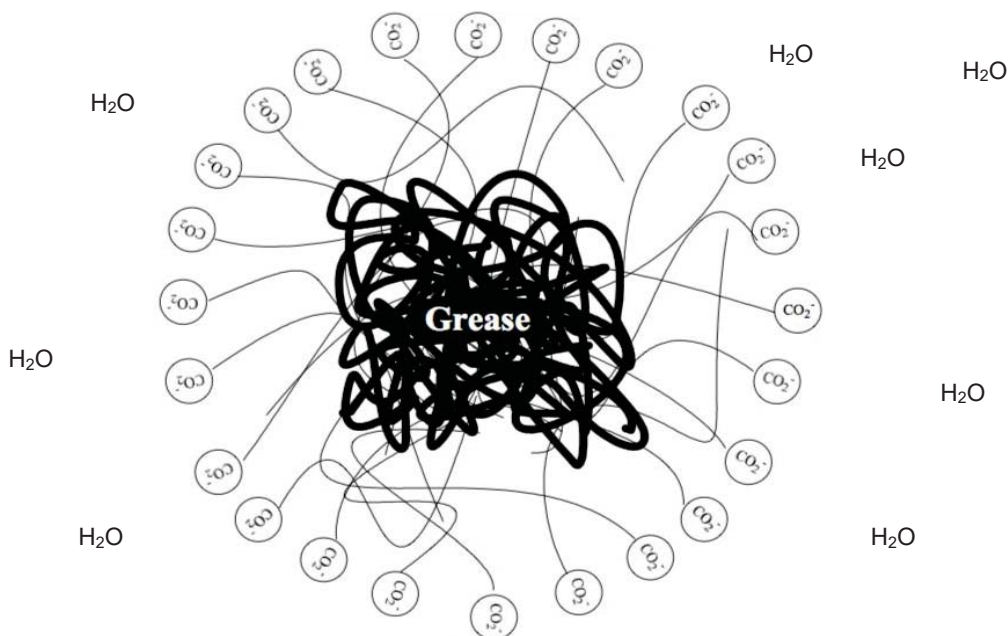
[4]

- (c) Fatty acids are generally stored in living organisms in the form of triglycerides. When triglycerides are hydrolysed with a base in a process known as *saponification*, long-chain carboxylate salts are produced. One industrial use of such carboxylate salts is in the manufacture of soap.

An example of a triglyceride is shown below:



- (i) Write a balanced equation for the saponification of glyceryl tristearate using sodium hydroxide.
- (ii) When soap molecules come into contact with grease or oil, they surround and isolate little particles of the grease forming *micelles* as shown in the diagram below.
- This gives an emulsion of soapy grease particles, which can then be easily washed away with water.



With reference to the diagram above and considering the type(s) of interactions between the carboxylate salts in soap with grease and water respectively, explain how soaps function in removing grease or oil stains.

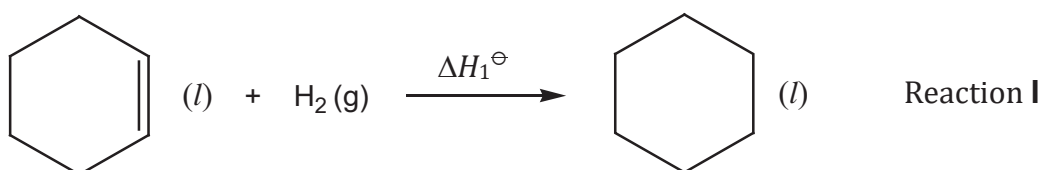
- (iii) Though soap is a generally good cleansing agent, it is not able to remove acidic food stains (such as kimchi stains), unlike its detergent counterpart.

Explain why soap does not function well in the presence of acidic food stains.

[4]

[Total: 20]

- 2 (a) Cyclohexane is often used as a non-polar solvent for the chemical industry and also as a standard in analytical laboratories. It may be obtained from cyclohexene as shown in Reaction I below.

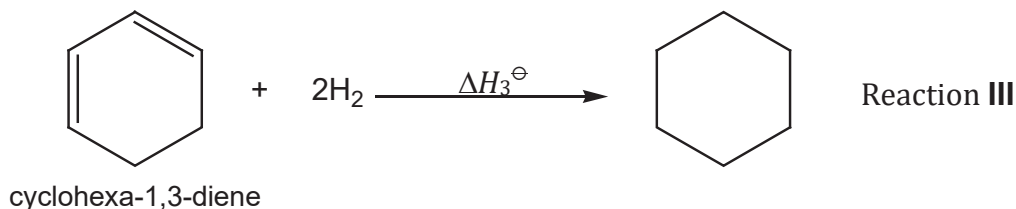
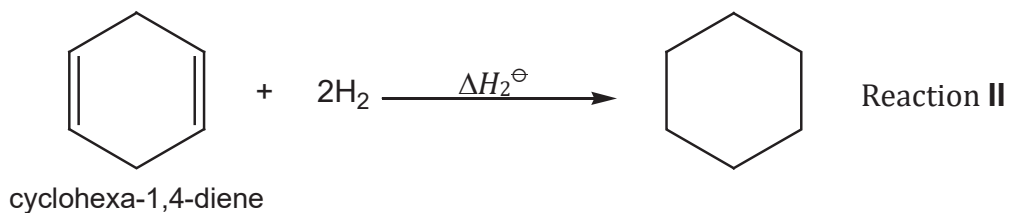


- (i) State the type of reaction above.
- (ii) Given the following standard enthalpy changes, use an energy cycle to calculate ΔH_1^\ominus .

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
Enthalpy change of combustion for cyclohexane	–3920
Enthalpy change of combustion for cyclohexene	–3754
Enthalpy change of formation for water	–286

- (iii) Given that the entropy change of Reaction I is $-143 \text{ JK}^{-1}\text{mol}^{-1}$. Calculate the ΔG^\ominus for the reaction and predict the spontaneity of the reaction at room conditions.

(iv) Cyclohexane may also be obtained from the two reactions below.

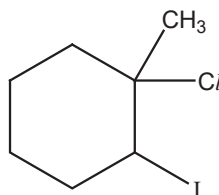


Explain why the value of ΔH_2^\ominus is approximately twice the value of ΔH_1^\ominus but the value of ΔH_3^\ominus is less than twice the value of ΔH_1^\ominus .

[8]

(b) 1-methylcyclohexene can also be obtained from cyclohexene.

(i) 1-methylcyclohexene reacts with iodine monochloride, ICl , to give the following product:



Name and describe, with the aid of equations, the mechanism of the reaction between 1-methylcyclohexene and ICl .

(ii) State the total number of optical isomers for the product obtained in (b)(i).

[4]

(c) Compound **A**, $\text{C}_9\text{H}_{10}\text{O}$, is a useful intermediate in the synthesis of pharmaceuticals and organic compounds. **A** forms an orange precipitate on reaction with 2,4-dinitrophenylhydrazine. **A** does not react with Tollens' reagent and aqueous alkaline iodine. On reaction of **A** with lithium tetrahydridoaluminate(III) in dry ether under room conditions, compound **B**, $\text{C}_9\text{H}_{12}\text{O}$, is formed. Heating **B** over Al_2O_3 produces the isomers **C** and **D**, C_9H_{10} .

Suggest structures for compounds **A** to **D** and explain the reactions involved.

[8]

[Total: 20]

Answers to 2013 JC1 H2 Promotional Examination

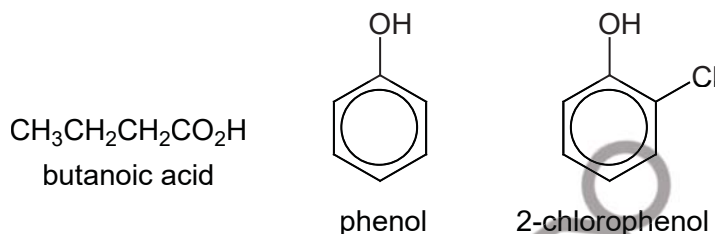
Section B:

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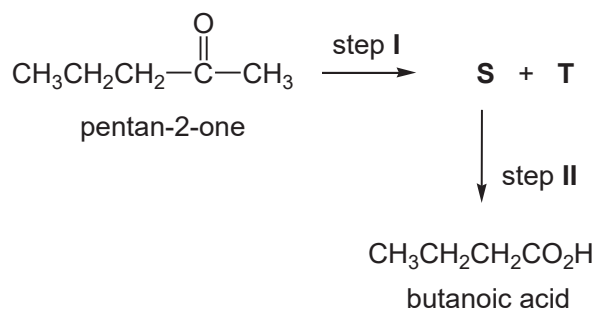
(i) The acidity of butanoic acid is compared against phenol and 2-chlorophenol. Arrange the three compounds in order of increasing acidity. Explain your answer.



- **Acid strength is dependent on stability of anion, since**
Stability of anion: phenoxide < 2-chlorophenoxide < butanoate
Order of acidity: phenol < 2-chlorophenol < butanoic acid
 - Butanoic acid is the strongest acid as there is delocalisation of negative charge (or electrons) over the two oxygen atoms in the carboxylate ion. The negative charge is dispersed, stabilizing the anion. Thus, protons leave the acid molecules more readily.
 - 2-chlorophenol is a stronger acid than phenol as Cl atom is electron withdrawing. The negative charge on the anion is further dispersed by delocalization of lone pair of electrons into the benzene ring, thereby stabilizing the ion. Thus, protons leave the 2-chlorophenol molecules more readily than in phenol.
- (ii) Butanoic acid is used in the preparation of various esters. Low-molecular-weight esters of butanoic acid, such as methyl butanoate, have mostly pleasant aromas or tastes and are often used as food and perfume additives.
- Suggest suitable reagents and conditions to form methyl butanoate from butanoic acid.

- **Reagent: methanol**
- **Condition: concentrated H_2SO_4 , reflux**

Butanoic acid can be made from pentan-2-one as shown below. In step I, compounds **S** and **T** are formed. **S** is subsequently converted to butanoic acid in step II.



(iii) Suggest reagents and conditions for steps I and II.

- **Step I: Alkaline aqueous iodine, heat**
- **Step II: Dilute HCl, room temperature**

(iv) Predict from this synthesis, the structural formulae of **S** and **T**.

- **S:** $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{O}^-$
- **T:** CHI_3

A student prepared a sample of butanoic acid via oxidation of butanal.

(v) Suggest a simple chemical test to detect the presence of residual butanal in the sample. You should state the reagent and condition, and the observation if butanal is present in the sample.

Write a balanced equation for the chemical test suggested.

1 mark for reagent and condition,
1 mark for observation,
1 mark for equation

Possible answers

Reagent and condition	Observation	Equations
2,4-DNPH, room temp	Bright orange ppt	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H} + \text{H}_2\text{NNH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{NNH}-\text{C}_6\text{H}_3(\text{NO}_2)_2)\text{H} + \text{H}_2\text{O}$
Tollens' reagent, heat	Silver mirror	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H} + 2\text{Ag}^+ + 3\text{OH}^- \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{O}^- + 2\text{Ag} + 2\text{H}_2\text{O}$
Fehling's solution, heat	Reddish brown ppt	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{O}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$
Acidic KMnO_4, heat	Purple KMnO_4 decolourises	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H} + [\text{O}] \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OH}$
Acidic $\text{K}_2\text{Cr}_2\text{O}_7$, heat	Orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green	

[12]

- (b) Long chain carboxylic acids, often referred to as fatty acids, are important components of biomolecules known as lipids.

Natural fatty acids may be saturated or unsaturated. Depending on the number of C=C bonds present (all are in the *cis* configuration), as well as their respective carbon chain lengths, these fatty acids have significantly different melting points.

Molecular Formula	Structural Formula	Common Name	Melting Point / °C
$C_{15}H_{29}CO_2H$	$CH_3(CH_2)_5CH=CH(CH_2)_7CO_2H$	palmitoleic acid	0
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- (i) With reference to the data above, explain the difference in melting points between:

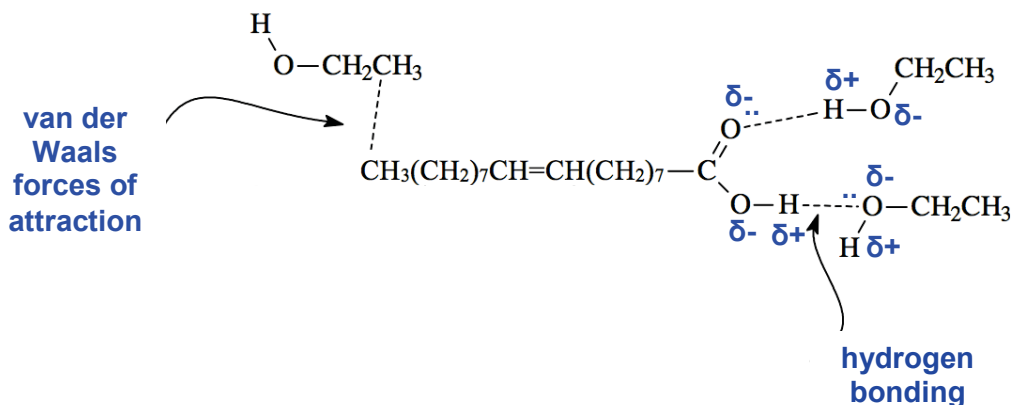
- (A) palmitoleic acid and oleic acid
(B) oleic acid and stearic acid

- Oleic acid has a larger electron cloud due to a higher M_r , as compared to palmitoleic acid. This gives rise to a greater extent of polarisation, which leads to stronger and more extensive van der Waals forces of attraction between oleic acid molecules. As more energy is required to overcome the stronger and more extensive intermolecular forces of attraction, a higher melting point is observed.
- The absence of double bonds in stearic acid allows close and uniform packing of the fatty acid molecules. On the other hand, the presence of a cis-double bond in oleic acid introduces a kink (or “bend”) in their shape, which makes it more difficult to pack oleic acid molecules so closely together in a uniform repeating array. This accounts for a lower melting point as a smaller amount of energy is required to overcome the less extensive intermolecular van der Waal’s forces of attraction.

- (ii) Oleic acid is insoluble in water but soluble in organic solvents such as ethanol.

Draw a well-labelled diagram to show the type(s) of interactions involved between oleic acid and ethanol.

••

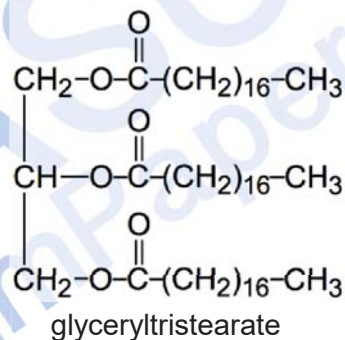


[Note: Need to show 1 H-bond and 1 VDW in diagram]

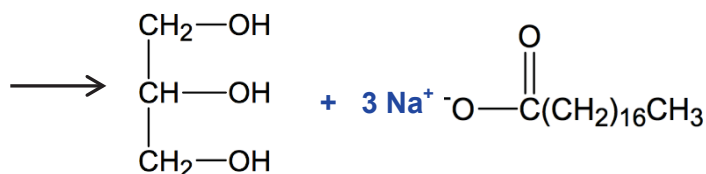
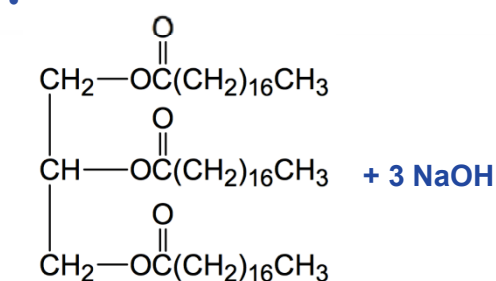
[4]

- (c) Fatty acids are generally stored in living organisms in the form of triglycerides. When triglycerides are hydrolysed with a base in a process known as *saponification*, long-chain carboxylate salts are produced. One industrial use of such carboxylate salts is in the manufacture of soap.

An example of a triglyceride is shown below:

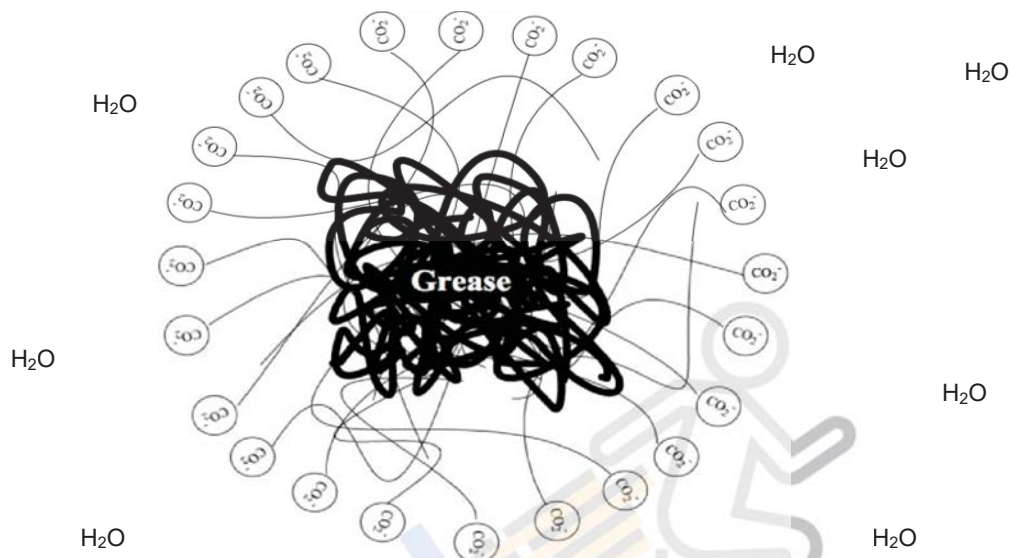


- (i) Write a balanced equation for the saponification of glyceryl tristearate using sodium hydroxide.



- (ii) When soap molecules come into contact with grease or oil, they surround and isolate little particles of the grease forming *micelles* as shown in the diagram below.

This gives an emulsion of soapy grease particles, which can then be easily washed away with water.



With reference to the diagram above and considering the type(s) of interactions between the carboxylate salts in soap with grease and water respectively, explain how soaps function in removing grease or oil stains.

- The long non-polar/hydrophobic hydrocarbon chain (the “tail”) of soap can interact with grease via van der Waals forces of attraction to form micelles.
- The polar/hydrophilic carboxylate anion (the “head”) of soap on the other hand is able to form strong ion-dipole interactions with polar water molecules (not hydrogen bonding). Soapy grease particles can thus be easily washed away with water.

[Note: Max 1 mark if answer just states the type of interactions]

- (iii) Though soap is a generally good cleansing agent, it is not able to remove acidic food stains (such as kimchi stains), unlike its detergent counterpart.

Explain why soap does not function well in the presence of acidic food stains.

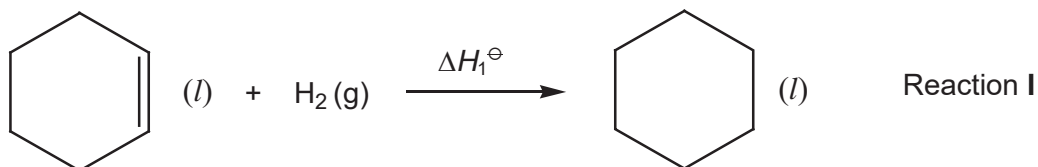
- In acidic food stains, the long-chain carboxylate anion end (the “head”) in soap will react with H^+ ions to form insoluble fatty acid molecules. This inhibits the formation of micelles to dissolve the acidic food stains.

OR

The H^+ ions present in acidic food stains protonate the long-chain carboxylate anion end (the “head”) in soap to give a carboxyl group which is unable to form ion-dipole interactions with water molecules.

[Note: $CH_3(CH_2)_{16}COO^-Na^+ (aq) + H^+ (aq) \rightarrow CH_3(CH_2)_{16}COOH(s) + Na^+ (aq)$][4]

- 2 (a) Cyclohexane is often used as a non-polar solvent for the chemical industry and also as a standard in analytical laboratories. It may be obtained from cyclohexene as shown in Reaction I below.

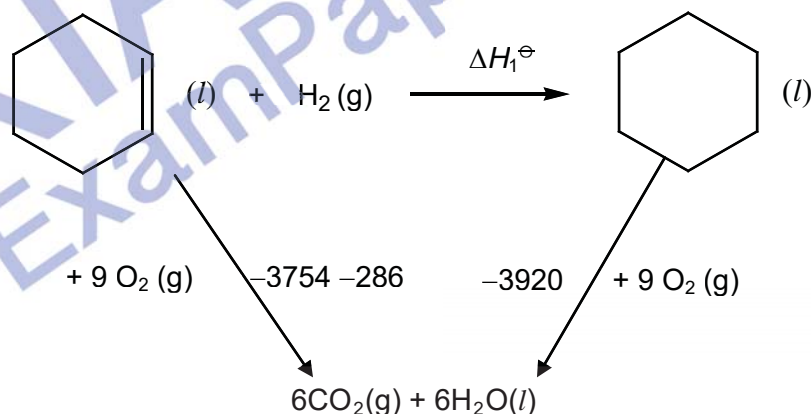


- (i) State the type of reaction above.

• **Reduction**

- (ii) Given the following standard enthalpy changes, use an energy cycle to calculate ΔH_1^\ominus .

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
Enthalpy change of combustion for cyclohexane	–3920
Enthalpy change of combustion for cyclohexene	–3754
Enthalpy change of formation for water	–286



(• correct cycle)

• $\Delta H_1^\ominus = -3754 - 286 - (-3920)$

• $= -120 \text{ kJ mol}^{-1}$

- (iii) Given that the entropy change of Reaction I is $-143 \text{ JK}^{-1}\text{mol}^{-1}$. Calculate the ΔG^\ominus for the reaction and predict the spontaneity of the reaction at room conditions.

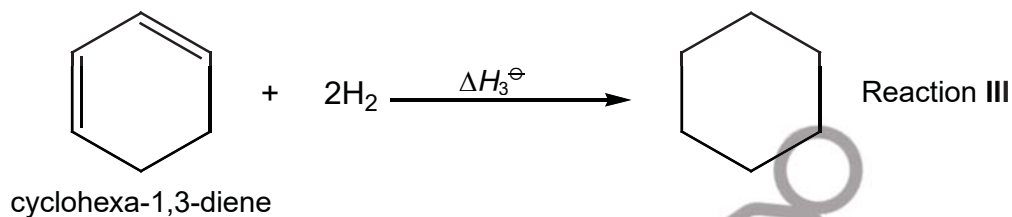
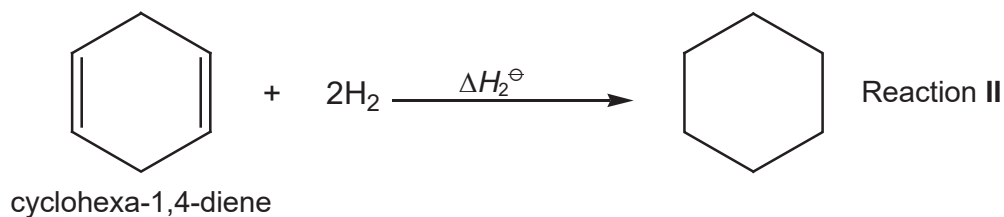
• $\Delta G^\ominus = \Delta H_1^\ominus - T\Delta S^\ominus$

$= -120 - (298)(-143 \times 10^{-3}) = -77.4 \text{ kJ mol}^{-1}$

• The reaction is spontaneous.

(mark awarded based on the outcome of ΔG^\ominus calculated)

- (iv) Cyclohexane may also be obtained from the two reactions below.



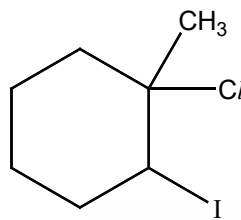
Explain why the value of ΔH_2^\ominus is approximately twice the value of ΔH_1^\ominus but the value of ΔH_3^\ominus is less than twice the value of ΔH_1^\ominus .

[8]

- Since there are two C=C bonds in cyclohexa-1,4-diene, energy given out in hydrogenating it is twice that given out in hydrogenating cyclohexene which has only one C=C bond.
- Energy given out in hydrogenating cyclohexa-1,3-diene is less than twice of that given out in hydrogenating cyclohexene because cyclohexa-1,3-diene is stabilised by delocalisation of pi electrons over 4 carbon bonds (alternate double bonds).

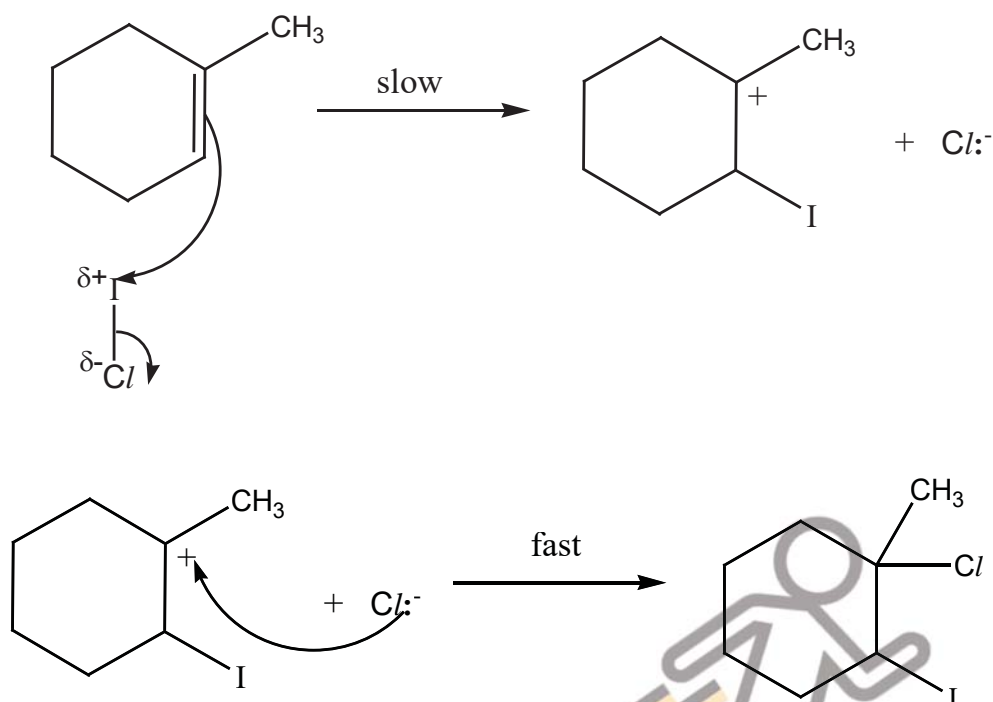
- (b) 1-methylcyclohexene can also be obtained from cyclohexene.

- (i) 1-methylcyclohexene reacts with iodine monochloride, ICl , to give the following product:



Name and describe, with the aid of equations, the mechanism of the reaction between 1-methylcyclohexene and ICl .

- **Electrophilic addition**



- for showing curly arrows and partial charges
- for the correct slow/fast step and intermediates

(ii) State the total number of optical isomers for the product obtained in (b)(i).

• 4

[4]

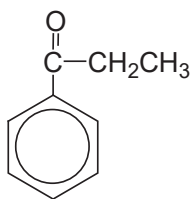
(c) Compound **A**, $C_9H_{10}O$, is a useful intermediate in the synthesis of pharmaceuticals and organic compounds. **A** forms an orange precipitate on reaction with 2,4-dinitrophenylhydrazine. **A** does not react with Tollens' reagent and aqueous alkaline iodine. On reaction of **A** with lithium tetrahydridoaluminate(III) in dry ether under room conditions, compound **B**, $C_9H_{12}O$, is formed. Heating **B** over Al_2O_3 produces the isomers **C** and **D**, C_9H_{10} . Suggest structures for compounds **A** to **D** and explain the reactions involved.

- **A** has high C:H ratio, hence benzene ring is present.
- **A** is a carbonyl compound as it forms an orange precipitate with 2,4-DNPH.
- **A** is a ketone since it does not react with Tollens' reagent.

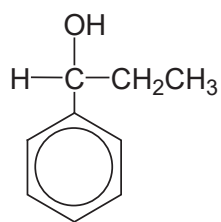
- **A** does not contain $\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$ or $\text{—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—OH}$ as it does not react with aqueous alkaline iodine.

- **B** is a secondary alcohol as it is formed from the reduction of **A** (a ketone).
- On heating **B** over Al_2O_3 , dehydration/elimination of **B** (an alcohol) occurs to form an alkene.
- **C** and **D** are cis-trans isomers of the alkene, C_9H_{10} .

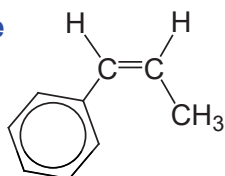
• A is



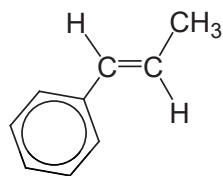
• B is



•• C and D are



and



[Total 11 , maximum 8]

[8]

[Total: 20]



Section C (Structured Questions)

Answer all the 5 structured questions in the spaces provided on the question paper.

1 Planning (P)

- (a) **FA 1** contains 10.0 g dm^{-3} of one of the dibasic acids **A – C** shown in the table below:

Acid	Structural formula	M_r	Concentration / mol dm^{-3}
A	$\text{HO}_2\text{C}(\text{CH}_2)_4\text{CH}(\text{C})\text{CO}_2\text{H}$	194.5	0.0514
B	$\text{HO}_2\text{C}(\text{CH}_2)_3\text{COCH}_2\text{CO}_2\text{H}$	174	0.0575
C	$\text{HO}_2\text{C}(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{H}$	158	0.0633

You are required to identify the dibasic acid present in **FA 1** by determining its M_r .

- Insert the missing data in the table above.
- A standard solution of aqueous potassium hydroxide solution is prepared using solid potassium hydroxide pellets so that it can be titrated against **FA 1**. Suggest an appropriate concentration of the standard aqueous solution of potassium hydroxide solution to be prepared. Explain your answer.

FA 1 \equiv 2 KOH

In a titration, for high accuracy the volume of titre = volume of pipetted volume

• Thus, $[\text{KOH}] = 2 \times [\text{FA 1}]$

• So $[\text{KOH}]$ ranges from 0.1028 to $0.1266 \text{ mol dm}^{-3}$

An appropriate $[\text{KOH}] = 0.10 \text{ mol dm}^{-3}$ or choose any other value 0.10 to 0.15 mol dm^{-3} (not 0.20 mol dm^{-3} as titre volume is too low).

- Outline, step by step, how you would prepare 250 cm^3 of an aqueous solution of potassium hydroxide with exactly the concentration you have suggested in (a)(ii) and finally the titration against **FA 1**.

Preparation of KOH Solution

To prepare 250 cm^3 standard solution of KOH of 0.10 mol dm^{-3} , about $0.025 \text{ mol} = 1.40 \text{ g}$ of solid KOH must be used.

1. Weigh accurately about **1.40 g** of KOH into a **dry weighing bottle**.
2. Pour the weighed solid into a clean small beaker. **Rinse** the weighing bottle with deionized water and **pour the washings** into the beaker. Dissolve the solid in the beaker.
3. **Transfer the solution and all washings** into a **250 cm^3 volumetric flask**. Top up the solution with distilled water to the 250 cm^3 mark. Stopper **and shake well** to obtain a

homogenous solution.

Titration Procedure

- 1. **Pipette 25.0 cm³** of FA 1 solution into a 250 ml conical flask. Add 5 drops of **thymol blue**. (or 1-2 drops of **phenolphthalein**)
- 2. Titrate FA 1 against the standard KOH solution until a colour change from **yellow to green** is obtained (or colorless to pink for phenolphthalein).
- 3. **Repeat the titration** until **consistent results** (within +/- 0.10 cm³) are obtained. [4m]

** Allow solution in burette and conical flask to be reversed; colour change of indicator must be changed accordingly.*

(iv) 25.0 cm³ of **FA 1** solution required **v** cm³ of **cmol dm⁻³** KOH solution prepared in (a)(iii).

Outline how you would process the results to determine the **M_r** of the acid present in 10.0 g dm⁻³ **FA 1** solution.

FA 1 \equiv **2 KOH**

No of moles of KOH used = **cv** $\times 10^{-3}$ mol

No of moles of FA 1 in 25.0 cm³ = $\frac{1}{2}$ (**cv** $\times 10^{-3}$) mol

• Concentration of FA 1 = $[\frac{1}{2} (\text{cv} \times 10^{-3}) / 0.025] = \text{cv}/50 \text{ mol dm}^{-3}$

10/M_r of acid = **cv/50**

• **M_r of acid** = $\frac{500}{\text{cv}}$ [8 + 1 bonus]

[8]

- (b) **FA 2** is a solution containing 1 mol dm⁻³ of either acid **C**, **HO₂C(CH₂)₂CH=CHCH₂CO₂H** or acid **D**, **CH₃(CH₂)₃CO₂H**. In an attempt to identify the acid present in **FA 2**, a student decided to mix different volumes of **FA 2** and aqueous KOH in two separate experiments. The temperature rise for each experiment was measured.

- (i) Given the concentration of aqueous KOH used in the experiments is 1 mol dm⁻³, complete the following table.

Experiment	Vol of KOH / cm ³	Vol of FA 2 / cm ³	Temperature rise / °C
1	25	50	T ₁
2	50	25	T ₂

2m

Note: 1. The same total volume of reaction mixture in both experiments.
2. Volume of base in one experiment is doubled the other base volume.
Similarly the same applies for the acid.

- (ii) Explain how the student can make use of the data collected in (b)(i) to identify the acid

present in **FA 2**.

- If $T_1 = T_2$, the monobasic acid, D is present.

In both experiments the same amount of water will be formed, releasing the same amount of heat (temperature rise).

- If $T_1 = \frac{1}{2} T_2$, the dibasic acid, C is present.

Experiment 1 will result in half the amount of water formed, releasing in half the amount of heat evolved (temperature rise).

OR

- A dibasic acid reacts with aq KOH in 1:2 mole ratio

Experiment 1 will result in half the amount of water formed (0.025 mol of water formed in experiment 1 but 0.05 mol in experiment 2), releasing half the amount of heat evolved (temperature rise).

- A monobasic acid reacts with aq KOH in 1:1 mole ratio.

In both experiments, same amount of water will be formed (0.025 mol of water is formed), releasing same amount of energy (temperature rise).

2m

[4]

[Total: 12]

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2 (a) Acrylamide is a compound that is found in fried foods such as French fries and potato chips

and beverages such as prune juice. There is growing concern on the occurrence of acrylamide in food as it is believed to be carcinogenic.

- (i) Acrylamide contains 50.7% by mass of carbon, 7.0% by mass of hydrogen, 19.8% by mass of nitrogen and the rest is made up of oxygen. Given that the relative molecular mass of acrylamide is 71.0, determine the molecular formula of acrylamide.

	C	H	N	O
% by mass	50.7	7.0	19.8	100-50.7-7-19.8 = 22.5
A_r	12	1	14	16
No of moles	4.225	7	1.414	1.406
Ratio	3	5	1	1

- 1 mark for working

Let the molecular formula of acrylamide be $C_{3n}H_{5n}N_nO_n$.

$$M_r \text{ of acrylamide} = n(3 \times 12.0 + 5 \times 1.0 + 14.0 + 16.0) = 71.0$$

- $n = 1$

Hence, the molecular formula of acrylamide is C_3H_5NO .

- (ii) Some studies have shown that a person can safely ingest acrylamide up to 0.25 mg per kg body weight in a day without any observed adverse effects to his nervous system. In an experiment, it was found that 1 kg of prune juice contains 1.20×10^{-7} mol of acrylamide. Calculate the maximum volume of prune juice a 60 kg man can drink per day. You may assume that the prune juice has the same density as water.

- Max mass of acrylamide the man can take in per day = $0.25 \times 10^{-3} \times 60$
= 0.0150 g

- Mass of acrylamide in 1 kg of prune juice = $1.2 \times 10^{-7} \times 71.0$
= 8.52×10^{-6} g per kg of prune juice

$$\text{Max mass of prune juice the man can drink per day} = 0.0150 \div (8.520 \times 10^{-6})$$

$$= 1760 \text{ kg (3 sf)}$$

- Max vol of prune juice the man can drink per day = $1760 \div 1$
= 1760 dm^3 (3 sf)

[5]

- (b) A container holds a gaseous mixture of nitrogen and propane. The pressure in the container at 200°C is 4.5 atm. At -40°C , the propane completely condenses and the pressure drops

to 1.5 atm. Calculate the mole fraction of nitrogen in the original gaseous mixture.

Let the no. of moles of nitrogen and propane be n_1 and n_2 respectively. Since R and volume of container V are constant,

$$\frac{P}{T} = \frac{nR}{V}$$

- At 200 °C, $\frac{4.5}{473} = (n_1 + n_2) R/V = 9.513 \times 10^{-3}$ -----(1)

- At -40°C, $\frac{1.5}{233} = n_1 R/V = 6.437 \times 10^{-3}$ -----(2)

- (2)/(1),

$$\text{mole fraction of nitrogen} = \frac{n_1}{n_1 + n_2} = \frac{6.437 \times 10^{-3}}{9.513 \times 10^{-3}} = 0.677(3 \text{ sf})$$

Alternative method:

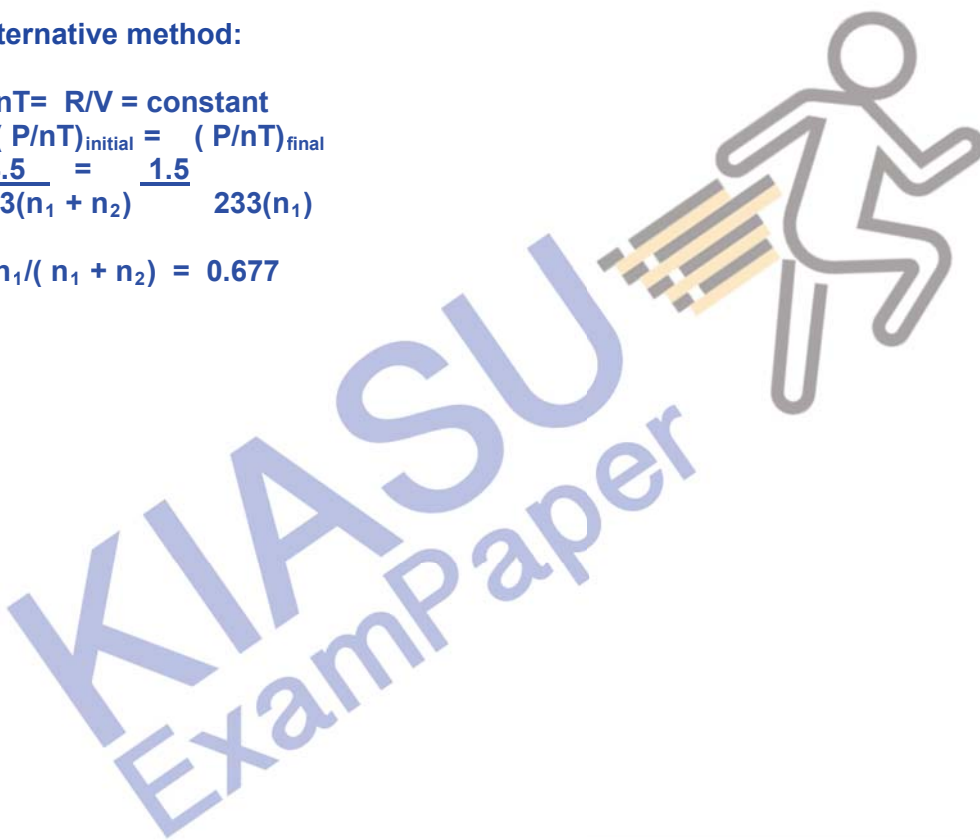
$$P/nT = R/V = \text{constant}$$

- $(P/nT)_{\text{initial}} = (P/nT)_{\text{final}}$

- $\frac{4.5}{473(n_1 + n_2)} = \frac{1.5}{233(n_1)}$

- $n_1/(n_1 + n_2) = 0.677$

[3]
[Total: 8]



3 This question is on the chemistry of Group III elements and their compounds.

- (a) Aluminium chloride, AlCl_3 , is used as a halogen carrier in the chlorination of benzene to generate the electrophile, Cl^+ .



- (i) Give the name of the type of bond present in AlCl_4^- . Explain how this bond is formed.

• Type of bond: **Dative bond/ Co-ordinate bond**

• Explanation: **Al atom has a vacant orbital in its valence shell (or AlCl_3 is electron deficient) so it can accept a lone pair of electrons from Cl_2 , achieving the octet structure.**

- (ii) Draw the dot-and-cross diagram for the AlCl_4^- ion. State the shape of the ion and the bond angle present.

Species	Dot-and-cross diagram	Shape and bond angle
AlCl_4^-		Shape: Tetrahedral Bond angle: 109.5°

[1 m for each correct dot-and-cross diagram and 1m for each correct name of shape and bond angle]

- (iii) Like aluminium, phosphorus also forms a trichloride, PCl_3 . State the shape of the molecule and explain whether the molecule is polar or non-polar.

• Shape of PCl_3 : **Trigonal pyramidal**

• PCl_3 is **polar** as the P-Cl bond is polar and **the net dipole moment is non-zero.**

[6]

- (b) Although boron and gallium are from Group III of the Periodic Table, their fluorine compounds, BF_3 and GaF_3 have very different physical properties.

- (i) Given that the melting point of BF_3 is -126.8°C and that of GaF_3 is 800°C , account for the difference in their melting points.

• **BF_3 has a simple molecular structure with weak van der Waals' forces between its molecules.**

• **GaF_3 has a giant ionic structure with strong ionic bonds between its oppositely charged ions. More energy is required to overcome the strong ionic bonds, thus a much higher melting point is observed for GaF_3 .**

(ii) State the electronic configuration of Ga^{3+} .

• **Electronic configuration of Ga^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$**

(iii) Explain why Ga^{3+} has a larger ionic radius than Ge^{4+} .

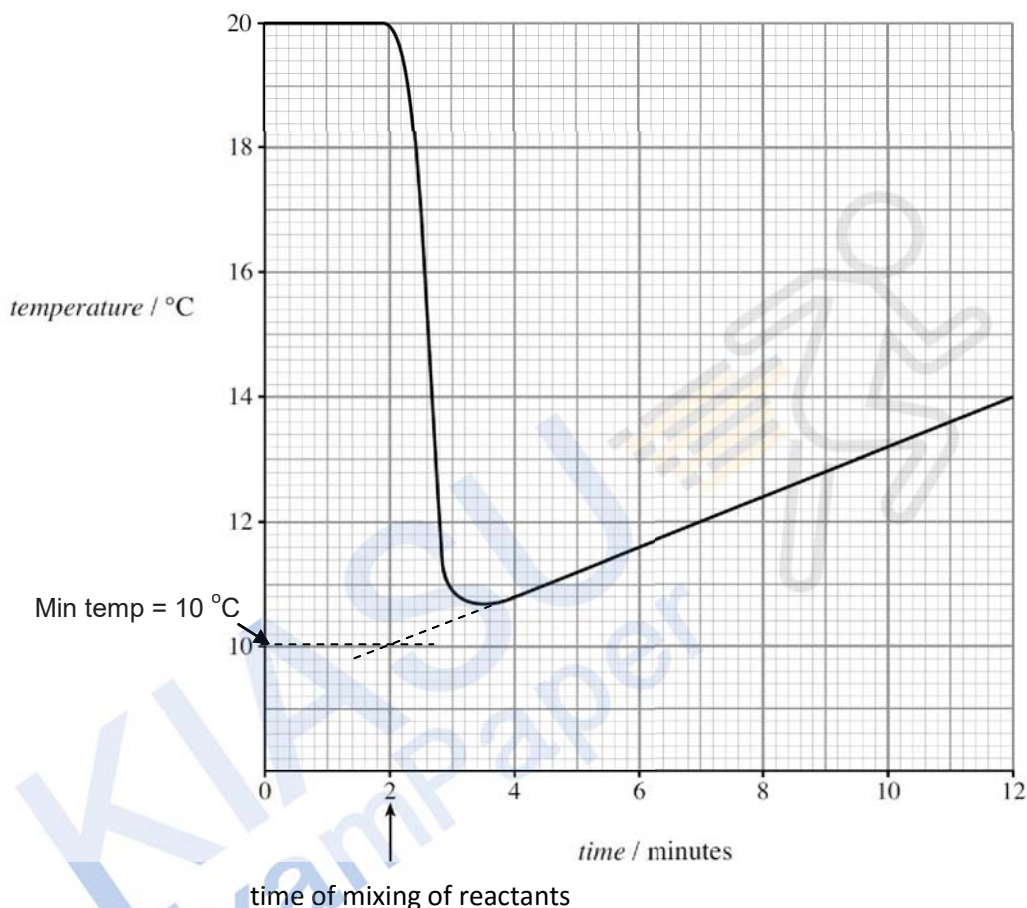
• **Ge^{4+} and Ga^{3+} are isoelectronic (same screening effect) but the nuclear charge of Ge^{4+} is larger than that of Ga^{3+} as Ge^{4+} has more protons, hence electrons are more strongly attracted in Ge^{4+} .**

[4]
[Total: 10]



- 4 (a) Ammonium chloride can be used in cold packs to treat minor injuries such as sprains.

An experiment was carried out to determine the enthalpy change of solution of ammonium chloride in water. The initial temperature of 50 cm³ of water was recorded every 30 seconds for 1.5 minutes. At exactly 2 minutes, 9.20 g of solid ammonium chloride was added to the water and the temperature of the resultant solution was monitored at various time intervals. The following graph was obtained.



- (i) With reference to ammonium chloride, define *standard enthalpy change of solution*.
- The standard enthalpy change of solution of ammonium chloride is the enthalpy change when one mole of ammonium chloride is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 atm.
- (ii) Calculate the enthalpy change of solution of ammonium chloride based on the data from the above experiment.

Specific heat capacity of water = 4.2 J g⁻¹ K⁻¹

[4]

- Extrapolate from the graph to get minimum temperature = 10 °C
- Amount of heat absorbed = $50 \times 4.2 \times (20 - 10) \div 1000 = 2.10 \text{ kJ}$

no of moles of ammonium nitrate = $9.2/53.5 = 0.172 \text{ mol}$

- $\therefore \Delta H_{\text{soln}} = + 2.10 / 0.172$
 $= + 12.2 \text{ kJ mol}^{-1} \text{ (to 3 sf)}$

- (b) The following data relate to the energy changes which occur when lithium chloride and ammonium chloride dissolve in water.

	Lithium chloride	Ammonium chloride
Hydration energy of cation / kJ mol^{-1}	-519	-290
Lattice energy / kJ mol^{-1}	-846	-669
Enthalpy change of solution / kJ mol^{-1}	-37	x

- (i) Calculate the enthalpy change of hydration of Cl^- ion.

$\Delta H_{\text{soln}} = -\text{Lattice Energy} + \Delta H_{\text{hyd}}$

- For LiCl : $-37 = 846 + (-519) + \Delta H_{\text{hyd}}(\text{Cl}^-)$
- $\Delta H_{\text{hyd}}(\text{Cl}^-) = -364 \text{ kJ mol}^{-1}$

- (ii) Using the data above and your answer in **(i)**, calculate **x**, the enthalpy change of solution of NH_4Cl .

- For NH_4Cl : $x = 669 - 290 - 364 = +15 \text{ kJ mol}^{-1}$

- (iii) Compare your answer in **(b)(ii)** and **(a)(ii)** and suggest one possible reason for any difference.

- The enthalpy change of solution of ammonium chloride calculated in **(a)(ii)** is less endothermic than that in **(b)(ii)**

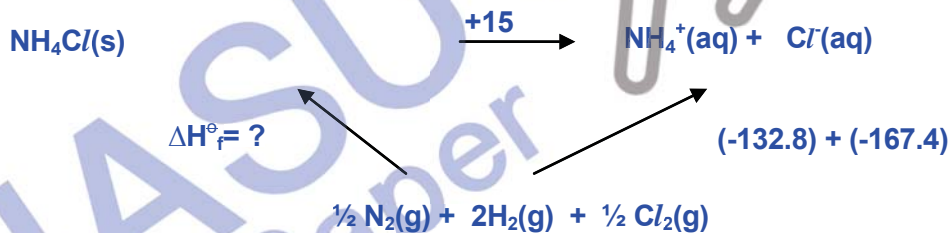
Possible reasons:

- The temperature readings may not be accurate as the thermometer may not be sensitive enough OR
- There is little or no stirring, hence the temperature of the solution is not homogeneous OR
- Specific heat capacity of water varies with temperature

(iv) Using your answer from (b)(ii) and the following information,

	$\Delta H_f / \text{kJ mol}^{-1}$
$\text{NH}_4^+ (\text{aq})$	-132.8
$\text{Cl}^- (\text{aq})$	-167.4

Construct an energy cycle to determine the standard enthalpy change of formation of solid ammonium chloride.



Hess' Law, $\Delta H_f(\text{NH}_4\text{Cl}) + 15 = (-132.8) + (-167.4)$

- $\Delta H_f(\text{NH}_4\text{Cl}) = -315.2 \text{ kJ mol}^{-1}$

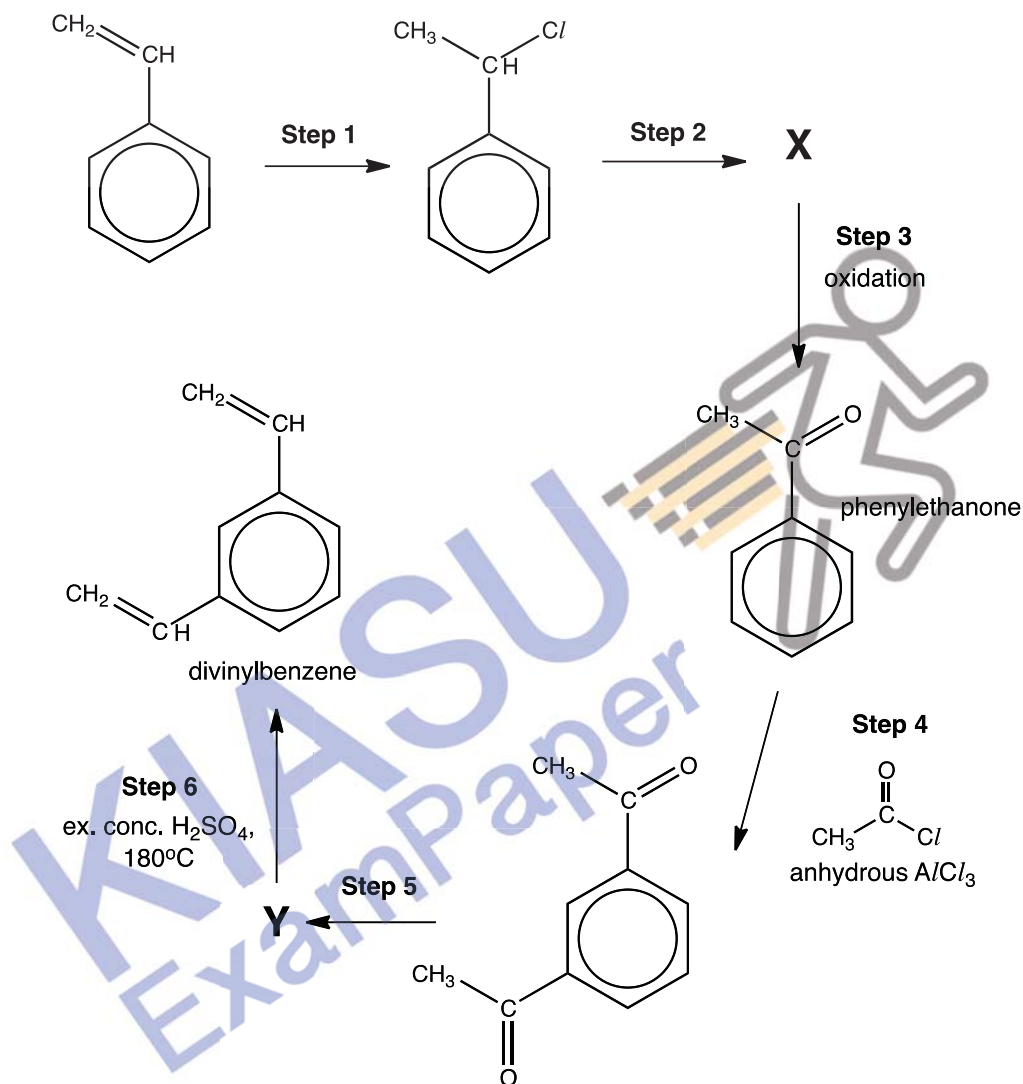
[1m for correct energy cycle]

[7]

[Total: 11]

- 5 Divinylbenzene is an extremely versatile cross-linking agent that also improves polymer properties. As a result, it has been used to manufacture adhesives, plastics, ceramics and ion exchange resins.

Industrially, it is manufactured by the thermal dehydrogenation of diethylbenzene. In the laboratory, divinylbenzene could be produced via the reaction scheme shown below.



- (a) (i) Suggest reagents and conditions for the following steps:

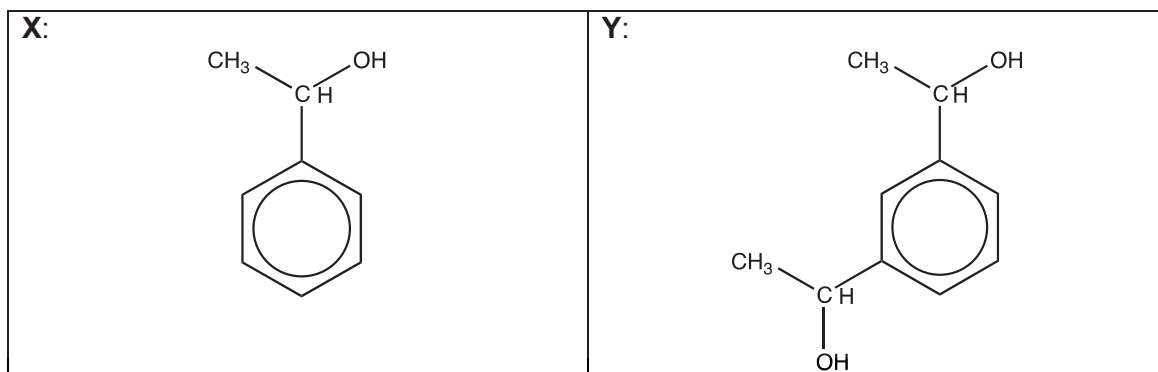
Step 1: HCl (g), rt

Step 2: NaOH(aq) , heat under reflux

Step 3: $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$, heat

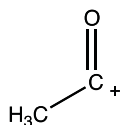
Step 5: LiAlH_4 dry ether &rt

(ii) Suggest structural formulae for the following compounds:



[6]

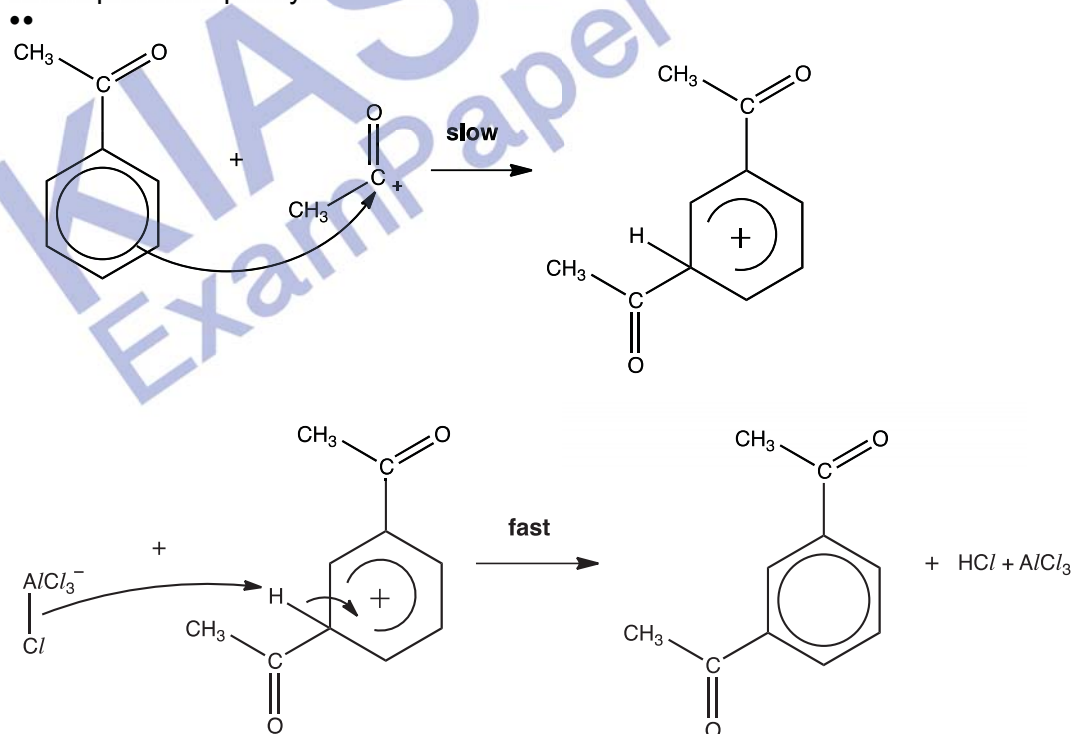
(b) In **Step 4**, the electrophile in the reaction is as shown below.



(i) Explain the meaning of the term *electrophile*.

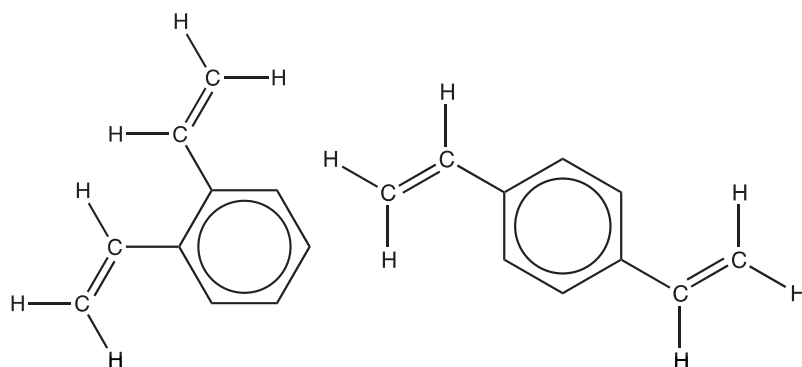
•It is an electron pair acceptor.

(ii) Describe, with the aid of equations, the mechanism of the reaction between the electrophile and phenylethanone.



[3]

(c) Divinylbenzene has two other positional isomers. Draw their structural formulae.



[2]
[Total: 11]

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