NATIONAL JUNIOR COLLEGE
SH2 TIMED PRACTICE
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/01**
Paper 1 Multiple Choice **27 June 2024**
1 hour

Additional Materials: Optical Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

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 separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

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.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

Instructions on how to fill in the Optical Mark Sheet
Shade the index number in a 5 digit format on the optical mark sheet:
2nd digit and the last 4 digits of the Registration Number.

Example:

Student	Examples of Registration No.	Shade:
	2305648	**35648**

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

1	2	3	4		6	7	8	9	10
A	**C**	**A**	**D**		**B**	**C**	**D**	**A**	**D**
11	12	13	14	15	16	17	18	19	20
B	**B**	**D**	**B**	**C**	**C**	**C**	**C**	**A**	**B**
21	22	23		25		27	28	29	30
D	**C**	**C**		**C**		**D**	**D**	**B**	**D**

1 Which statement about one mole of a metal is always correct?

A It contains the same number of atoms as 0.5 mol of hydrogen gas.

B It contains the same number of atoms as $\frac{1}{12}$ mol of ^{12}C.

C It has the same mass as 1 mol of hydrogen atoms.

D It can be oxidized by a reaction with an acid.

Ans: A

Option A is correct
1 mol of M = 6.02×10^{23} atom
½ mol of H_2 = 1 mol of H atom = 6.02×10^{23} atom

Option B is wrong
1 mol of M = 6.02×10^{23} atom
$\frac{1}{12}$ mol of $^{12}C = \frac{1}{12} \times 6.02 \times 10^{23}$

Option C is wrong
Mass of 1 mol of H atom = 1 g
Mass of 1 mol of M = 1 × A_r of metal

Option D is wrong
Not all metal can be oxidized by an acid (H^+)
$Cu^{2+} + 2e \rightleftharpoons \underline{\mathbf{Cu}}$ E = +0.34V
$\underline{\mathbf{2H^+}} + 2e \rightleftharpoons H_2$ E = 0.00V

$E^{\ominus}_{cell} = E^{\ominus}_{[R]} - E^{\ominus}_{[O]}$
$E^{\ominus}_{cell} = E^{\ominus}(H^+/H_2) - E^{\ominus}(Cu^{2+}/Cu)$
$= 0.00 - (+0.34)$
$= -0.34$ V
Reaction between H^+ and Cu is not feasible.

2 10 cm^3 of a gaseous hydrocarbon was reacted with an excess of oxygen. A contraction of 30 cm^3 occurred. On treating the cooled resulting mixture with excess barium hydroxide, a further contraction of 40 cm^3 occurred. All volumes were measured at room temperature and pressure.

What is the formula of the hydrocarbon?

A C_2H_4 **B** C_2H_6 **C** C_4H_8 **D** C_4H_{10}

Ans: C

$$C_xH_y(g) + \left(x + \frac{y}{4}\right) O_2(g) \longrightarrow x\,CO_2(g) + \frac{y}{2} H_2O(l)$$

	$C_xH_y(g)$		$\left(x + \frac{y}{4}\right) O_2(g)$		$x\,CO_2(g)$		$\frac{y}{2} H_2O(l)$
Reacting vol / cm^3	10		60		40		
Mole ratio	1		6		4		

$Ba(OH)_2$ reacts with acidic gas CO_2.
Vol of CO_2 = 40 cm^3 (from 2nd contraction)
$\therefore x = 4$,

Initial vol – Final vol = 30 cm^3 (1st contraction)
(Vol of hydrocarbon + Total Vol of O_2) – (Vol of unreacted O_2 + Vol of CO_2) = 30 cm^3
(10 + Total vol of O_2) – (Vol of unreacted O_2 + 40) = 30 cm^3
Total vol of O_2 – Vol of unreacted O_2 = 60 cm^3
Vol of O_2 reacted = 60 cm^3

$$x + \frac{y}{4} = 6$$

$$4 + \frac{y}{4} = 6$$

$\Rightarrow y = 8$
$\therefore$ The molecular formula of the hydrocarbon is C_4H_8.

3 The following reaction occurs when chlorine is added to water.

$$Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + HCl(aq)$$

Which statement about this reaction is correct?

A Chlorine is both oxidised and reduced.

B Chlorine is oxidised but **not** reduced.

C Hydrgen is both oxidised and reduced.

D Hydrogen is oxidised but **not** reduced.

Ans: A

$Cl_2(g)$ to $HOCl$ (aq) : oxidation
(0) (+1)

$Cl_2(g)$ to $Cl^-(aq)$: reduction
(0) (-1)

4 **X** is either nitrogen or sulfur and forms pollutant oxide **Y** in a car engine.

Further oxidation of **Y** to **Z** occurs in the atmosphere. In this further oxidation, 1 mol of **Y** reacts with 0.5 mol of gaseous oxygen molecules.

Which statements about **X**, **Y** and **Z** can be correct?

1 The oxidation number of **X** increases by two from **Y** to **Z**.

2 **Y** has an unpaired electron in its molecules.

3 **Y** is a polar molecule.

A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

Ans: D

Y can be:

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

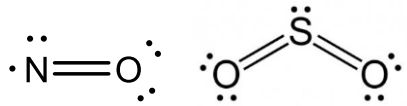
(O.N. of N increases from +2 to +4)

or

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

(O.N. of S increases from +4 to +6)

Statement 1 is correct.

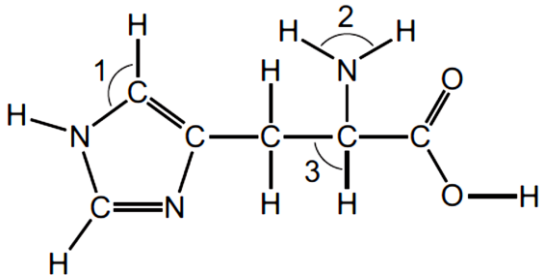


Statement 2 is correct for NO

Both are polar molecule with net dipole moment.

Statement 3 is correct

6 Histidine is an amino acid.



Histidine

What are the approximate bond angles 1, 2 and 3?

	1	2	3
A	109.5°	107°	90°
B	120°	107°	109.5°
C	120°	120°	90°
D	120°	120°	109.5°

Angle 1: 3 bond pairs (120°)
Angle 2: 3 bond pairs + 1 lone pair (107°)
Angle 3: 4 bond pairs (109.5°)

7 Ammonium ions, NH_4^+, are formed when ammonia gas reacts with hydrogen chloride gas.

Which statement about the changes that occurs in this reaction is correct?

A The dipole moment of an ammonium ion is greater than the dipole moment of an ammonia molecule.

B The H–N–H bond angle decreases when an ammonium ion is formed.

C The hybridisation of nitrogen does not change.

D There is electron transfer from nitrogen to chlorine.

Ans: C

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

Option A is wrong. There is no dipole moment in an ion as they are charged particles.
Option B is wrong. The H-N-H bond angles increases from 107° (trigonal pyramidal) to 109.5° (tetrahedral).
Option C is correct. The hybridisation of nitrogen remains as sp^3 with 4 electron regions around N.
Option D is wrong. There is no change in oxidation number in the reaction.

8 Ethylene glycol, $HOCH_2CH_2OH$, is used as a de-icer. It allows ice to melt at temperatures below 0 °C.

Which statements are correct?

1 Ethylene glycol changes the extensive network of hydrogen bonds in ice.

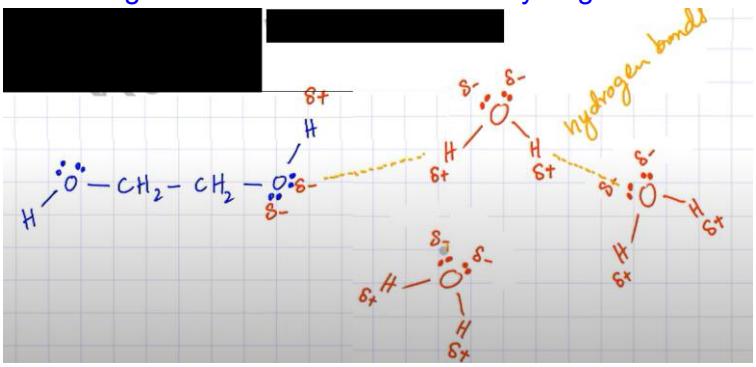
2 Ethylene glycol molecules form hydrogen bonds with other ethylene glycol molecules.

3 Ethylene glycol molecules will dissolve in the water formed from the ice.

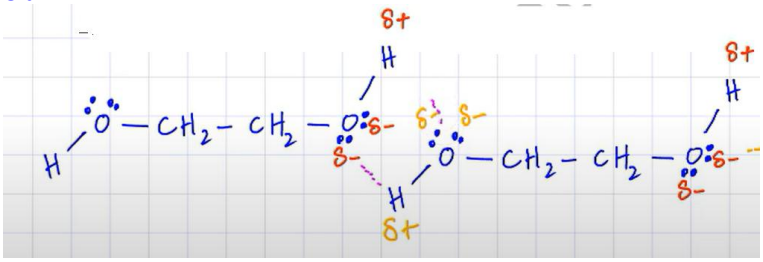
A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

Ans: D

Statement 1 is correct. Ethylene glycol molecules form hydrogen bonds with H_2O molecule and changes the extensive network of hydrogen bond in ice.



Statement 2 is correct. Ethylene glycol molecule form hydrogen bonds with other ethylene glycol molecule.



Statement 3 is correct. Ethylene glycol molecules form significant hydrogen bonds with water molecule which will make it soluble in water.

9 When an evacuated tube of volume 400 cm^3 is filled with gas at 300 K and 101 kPa, the mass of the tube increases by 0.65 g. Assume the gas behaves as an ideal gas.

What is the identity of the gas?

A Argon

B Helium

C Krypton

D Neon

Ans: A

pV = nRT

$(101 \times 10^3)(400 \times 10^{-6}) = (\frac{0.65}{Mr})(8.31)(300)$

$M_r = 40$

10 Two identical bulbs at the same temperature contain ideal gases **A** and **B** separately. The density of gas **A** is twice that of gas **B** and the molecular mass of gas **A** is half that of gas **B**.

What is the ratio of the pressure of gas **A** to that of gas **B**?

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

Ans: D

For gas A,

$P_AV = nRT$,

Density, $\rho = \frac{m}{V}$

$P_A = \rho_A \times \frac{RT}{M_A}$ ----- eqn 1

For gas B,

$P_B = \rho_B \times \frac{RT}{M_B}$ ----- eqn 2

$\frac{eqn\ 1}{eqn\ 2}$

$\frac{P_A}{P_B} = \frac{\rho_A}{\rho_B} \times \frac{M_B}{M_A}$

[$\rho_A = 2 \times \rho_B$ and $M_A = ½ \times M_B$]

$\frac{P_A}{P_B} = 2 \times 2 = 4$

11 When 60 cm^3 of **1** mol dm^{-3} of sulfuric acid and 40 cm^3 of **2** mol dm^{-3} sodium hydroxide were mixed in a styrofoam cup, the temperature rose by 6.5 °C.

Calculate the standard enthalpy change of neutralisation in kJ mol^{-1}. Assume that the specific heat capacity of the solution is 4.18 J g^{-1} K^{-1}.

A –22.6 **B** –34.0 **C** –45.3 **D** –57.0

Ans: B

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

Amount of sulfuric acid = $\frac{60}{1000} \times 1 = 0.06$ mol

Amount of sodium hydroxide = $\frac{40}{1000} \times 2 = 0.08$ mol (limiting reactant)

Amount of sodium hydroxide = amount of water = 0.08 mol

$\Delta H_{neutralisation} = -\frac{(100)(4.18)(6.5)}{0.08} = = -34000$ J $mol^{-1} = -34.0$ kJ mol^{-1}

12 Nitric acid is made industrially by the oxidation of ammonia. The overall equation for the process is shown.

equation 1: $NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(l)$

The process happens in three stages. The equations and enthalpy changes for these stages are given.

Stage 1:	$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$	$\Delta H = -904$ kJ mol^{-1}
Stage 2:	$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$\Delta H = -114$ kJ mol^{-1}
Stage 3:	$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$	$\Delta H = -348$ kJ mol^{-1}

What is the enthalpy change of the process shown in equation 1?

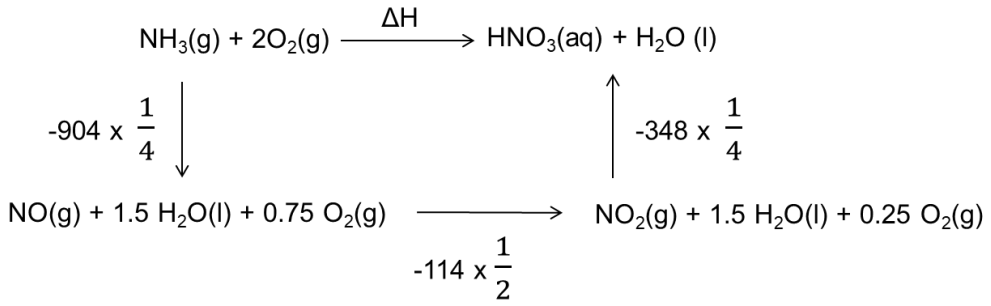
A -1480 kJ mol^{-1}

B -370 kJ mol^{-1}

C -341.5 kJ mol^{-1}

D $+82.0$ kJ mol^{-1}

Ans : B



$\Delta H = \frac{1}{4}(-904\text{kJ mol}^{-1}) + \frac{1}{2}(-114\text{kJ mol}^{-1}) + \frac{1}{4}(-348\text{kJ mol}^{-1})$

$= -370\text{kJ mol}^{-1}$

13 Hydrogen can be made from steam according to the following equation:

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

The Gibbs free energy change of reaction at two different temperatures are shown

$\Delta G_1 = +78$ kJ mol^{-1} at 378 K
$\Delta G_2 = -58$ kJ mol^{-1} at 1300 K

Which row of the table gives the correct sign of ΔH and ΔS for this reaction?

	ΔH	ΔS
A	–	–
B	–	+
C	+	–
D	+	+

Ans: D

Δn of gas = 2-1 = +1
ΔS is positive.
$\Delta G = \Delta H - T\Delta S$
As temperature increases to 1300 K, ΔG is negative and reaction is spontaneous.

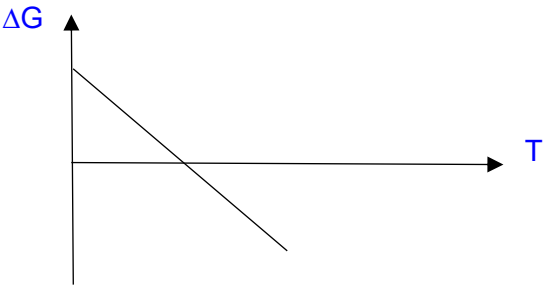
When the temperature is lower at 378 K, ΔG is positive and reaction is non-spontaneous.

Since ΔS is positive, this indicate that ΔH is positive as only low temperature can allow ΔG to become positive.

Alternatively, using $\Delta G = \Delta H - T\Delta S$ where

- ΔG (y-axis)
- ΔH (y intercept)
- T (x-axis)
- $-\Delta S$ (gradient)

Since ΔS is positive (which leads to a negative gradient) and ΔG changes from positive to negative with increasing temperature, ΔH is positive.



14 A student carried out two experiments using MnO_2 as a catalyst to decompose hydrogen peroxide. The equation for this reaction is shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The student's results are recorded in the table.

Experiment	Mass of MnO_2	Conditions	Vol of H_2O_2	Final vol of O_2	Time taken
1	0.25 g	r.t.p	10.0 cm^3	48 cm^3	200 s
2	0.25 g	r.t.p	10.0 cm^3	48 cm^3	500 s

Which statements are correct?

1 The activation energy was the same for both experiments.

2 The concentration of the hydrogen peroxide solution used was 0.4 mol dm^{-3}.

3 The MnO_2 used in experiment 1 was in a larger piece than the MnO_2 used in experiment 2.

A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

Ans: B

Statement 1 is correct. Activation energy is constant for the same reaction with the same catalyst.

Statement 2 is correct.
At r.t.p, amount of $O_2 = \frac{48}{24000} = 0.002$ mol
Amount of $H_2O_2 = 2 \times 0.02 = 0.004$ mol
Concentration of $H_2O_2 = \frac{0.004}{10/1000} = 0.4$ mol dm^{-3}

Statement 3 is wrong.
Larger pieces of MnO_2 will reduce surface area of the solid catalyst and rate would be smaller. This would increase the time take for the reaction in experiment 1.

15 When an equimolar mixture of H_2 and I_2 react, the mole fraction of HI in the final mixture is x at 500 °C

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What is the equilibrium constant, K_p, for the reaction at 500 °C?

A $\frac{x^2}{(1-x)^2}$

B $\frac{x^2}{(1-2x)^2}$

C $\frac{4x^2}{(1-x)^2}$

D $\frac{4x^2}{(1-2x)^2}$

Ans: C

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Mole fraction:	$\frac{1-x}{2}$		$\frac{1-x}{2}$		x

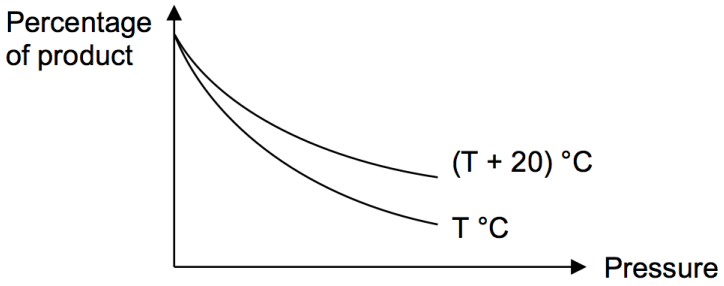
$P_{HI} = x \times P_T$

$P_{H2} = P_{I2} = \frac{1-x}{2} \times P_T$

$$K_p = \frac{(x(P_T))^2}{(\frac{1-x}{2})(P_T)(\frac{1-x}{2})(P_T)}$$

$$= \frac{4x^2}{(1-x)^2}$$

16 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



A $4Fe\,(s) + 3O_2\,(g) \rightleftharpoons 2Fe_2O_3\,(s)$ $\Delta H = -1644$ kJ mol^{-1}

B $2C\,(s) + O_2\,(g) \rightleftharpoons 2CO\,(g)$ $\Delta H = -222$ kJ mol^{-1}

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol^{-1}

D $CO(g) + CI_2(g) \rightleftharpoons COCI_2(s)$ $\Delta H = +86$ kJ mol^{-1}

Ans: C

From observation of data, when temperature increases, percentage of products increase.
⇒ By Le Chatelier's Principle, when temperature increases, system will partially absorb some heat by favouring endothermic reaction. Since % of products increase, equilibrium position shifts right. Hence forward reaction is endothermic.
Either **C** or **D**.

From observation of data, when pressure increases, percentage of products decrease.
⇒ By Le Chatelier's Principle, when pressure increases, system will partially decrease pressure by decreasing number of gas particles. Since % of products decrease, equilibrium position shifts left. Hence, no. of gas particles for reactants less than no. of gas particles of products.

17 At body temperature of 37 °C, K_w has a value of 2.4×10^{-14}.

What is the concentration of OH^- if the pH of blood is 7.4 under these conditions?

A 3.98×10^{-8} mol dm^{-3}

B 2.51×10^{-7} mol dm^{-3}

C 6.03×10^{-7} mol dm^{-3}

D 7.00×10^{-7} mol dm^{-3}

Ans: C

pH = 7.4

$[H^+] = 10^{-7.4} = 3.981 \times 10^{-8}$

$K_w = [H^+][OH^-] = 2.4 \times 10^{-14}$

$[OH^-] = \frac{2.4 \times 10^{-14}}{3.981 \times 10^{-8}} = 6.03 \times 10^{-7}$

18 CaF_2 has a K_{sp} value of 3.9×10^{-11} at 25 °C. A sample of solid CaF_2 is dissolved in water to form a saturated solution.

What is the concentration of F^- ions in a saturated solution of CaF_2 at 25 °C?

A 2.1×10^{-4} mol dm^{-3}

B 3.4×10^{-4} mol dm^{-3}

C 4.3×10^{-4} mol dm^{-3}

D 6.8×10^{-4} mol dm^{-3}

Ans: C

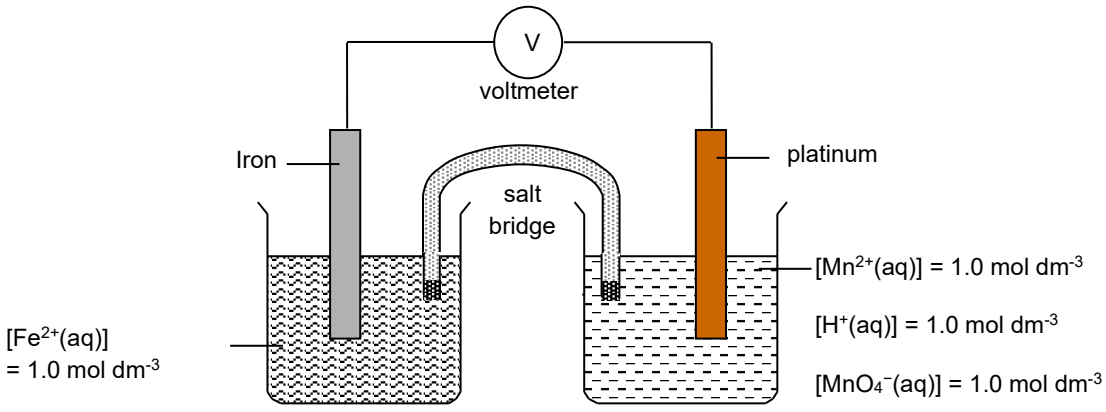
Let s be the solubility of CaF_2.

	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$2F^-(aq)$
Initial conc/ mol dm^{-3}					
Change in conc/ mol dm^{-3}	$-s$		$+s$		$+2s$
Eqm conc/ mol dm^{-3}			s		$2s$

$$K_{sp} = [Ca^{2+}][F^-]^2$$
$$3.9 \times 10^{-11} = (s)(2s)^2 = 4s^3$$
$$s = \sqrt[3]{9.75 \times 10^{-12}}$$
$$= 2.136 \times 10^{-4} \text{ mol dm}^{-3}$$
$$[F^-] = 2s = 2 \times 2.136 \times 10^{-4}$$
$$= 4.27 \times 10^{-4} \text{ mol dm}^{-3}$$

19 *The use of the Data Booklet is relevant to this question.*

A cell is set up by connecting a Fe^{2+}/Fe half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.



Which option is a correct description of the effect on the e.m.f (potential difference) of the cell when the corresponding change is made?

	Change	Effect on e.m.f of cell
A	Addition of NH_3 (aq) into oxidation half-cell	Increases
B	Addition of 1 mol dm^{-3} H_2SO_4 (aq) into reduction half-cell	Decreases
C	Addition of NaOH (aq) into reduction half-cell	Increases
D	Replace Iron with an alloy of Iron and zinc	Remains the same

Ans: A

$Fe^{2+} + 2\ e^- \rightleftharpoons Fe$ $\quad E^\ominus = -0.44V$
$MnO_4^- + 8H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad E^\ominus = +1.52\ V$
MnO_4^- / Mn^{2+} is the reduction half-cell as it has a more positive $E^\ominus$ value.
Fe^{2+} / Fe is the oxidation half-cell as it has a less positive $E^\ominus$ value.

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]}$
$= E^\ominus(MnO_4^-/Mn^{2+}) - E^\ominus(Fe^{2+}/Fe)$

Option A is correct.
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Adding NH_3, would result in the concentration of Fe^{2+} to be lowered.
$Fe^{2+} + 2\ e^- \rightleftharpoons Fe$
Position of equilibrium will shift to the left, favouring oxidation reaction. $E(Fe^{2+}/Fe)$ will be less positive. $E_{cell} = E^\ominus(MnO_4^-/Mn^{2+}) - E(Fe^{2+}/Fe)$. E_{cell} will increase.

Option B is wrong.
MnO_4^- + $8H^+$ + 5 e^- ⇌ Mn^{2+} + $4H_2O$
1 mol dm^{-3} of H_2SO_4 contains 2 mol dm^{-3} H^+, this would increase $[H^+]$ in the half cell.
Position of equilibrium will shift to the right, favouring reduction reaction. $E(MnO_4^-/Mn^{2+})$ will be more positive. Since $E_{cell} = E(MnO_4^-/Mn^{2+}) - E^{\ominus}(Fe^{2+}/Fe)$. E_{cell} will increase.

Option C is wrong.
MnO_4^- + $8H^+$ + 5 e^- ⇌ Mn^{2+} + $4H_2O$
Addition of NaOH decreases $[H^+]$ in the half cell.
Position of equilibrium will shift to the left, favouring oxidation reaction. $E(MnO_4^-/Mn^{2+})$ will be less positive. Since $E_{cell} = E(MnO_4^-/Mn^{2+}) - E^{\ominus}(Fe^{2+}/Fe)$. E_{cell} will decrease.

Option D is wrong.
Zn^{2+} + $2e^-$ ⇌ **Zn** $E^{\ominus} = -0.76V$
Fe^{2+} + 2 e^- ⇌ Fe $E^{\ominus} = -0.44V$
Zn would react with Fe^{2+}, as the redox reaction is spontaneous ($E_{cell} = -0.44 - (-0.76) = +0.32V$)
This would result in $[Fe^{2+}]$ to be lowered.
Fe^{2+} + 2 e^- ⇌ Fe
Position of equilibrium will shift to the left, favouring oxidation reaction. $E(Fe^{2+}/Fe)$ will be less positive. $E_{cell} = E^{\ominus}(MnO_4^-/Mn^{2+}) - E(Fe^{2+}/Fe)$. E_{cell} will increase.

20 *The use of the Data Booklet is relevant to this question.*

Two separate students accidentally spilled chemicals on their clothes in the laboratory which resulted in brown MnO_2 stains and I_2 stains. Their teacher suggested the use of H_2O_2 for removal of these stains.

Which statement is true regarding the removal of the stains?

A Only I_2 will be successfully removed.

B Only MnO_2 will be successfully removed.

C Both MnO_2 and I_2 will be successfully removed.

D Both stains cannot be removed

Ans: B

Both I_2 and MnO_2 needs to be reduced for the stain to be removed.

$\underline{\mathbf{I_2}} + 2\ e^- \rightleftharpoons 2\ I^-$ $\quad E^\ominus = +0.54$ V

$\underline{\mathbf{MnO_2}} + 4\ H^+ + 2\ e^- \rightleftharpoons Mn^{2+} + 2\ H_2O$ $\quad E^\ominus = +1.23$ V

$O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons \underline{\mathbf{H_2O_2}}$ $\quad E^\ominus = +0.68$ V

H_2O_2 needs to be oxidised.

Reaction of I_2 and H_2O_2.

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]}$

$E^\ominus_{cell} = E^\ominus(I_2/I^-) - E^\ominus(O_2/H_2O_2)$

$= +0.54 - (+0.68)$

$= -0.14$ V

Reaction is not feasible. I_2 stain will not be removed.

Reaction of MnO_2 and H_2O_2

$E^\ominus_{cell} = E^\ominus_{[R]} - E^\ominus_{[O]}$

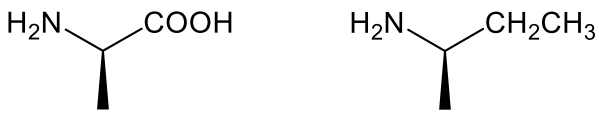
$E^\ominus_{cell} = E^\ominus(MnO_2/Mn^{2+}) - E^\ominus(O_2/H_2O_2)$

$= +1.23 - (+0.68)$

$= +0.55$ V

Reaction is feasible. MnO_2 will be successfully removed.

21 The melting point of 2-aminopropanoic acid and butan-2-amine are as shown.



	2-aminopropanoic acid	butan-2-amine
Melting Point	258 °C	−105 °C

Which statement best explains the difference in melting point?

A 2-aminopropanoic acid molecules are held by more extensive hydrogen bonds than butan-2-amine.

B 2-aminopropanoic acid has a higher M_r than butan-2-amine.

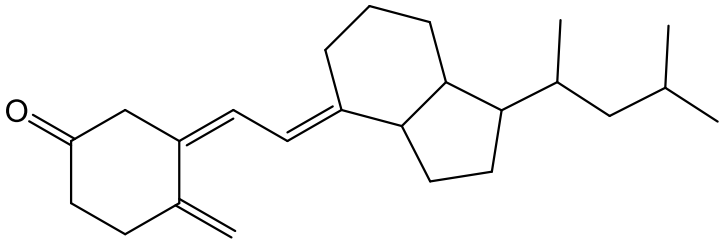
C Weak covalent bonds are broken to melt butan-2-amine

D 2-aminopropanoic acid adopts a giant ionic lattice structure in crystalline state.

Ans: D

In crystalline form, 2-aminopropanoic acid exists as **zwitterions** which are held by **strong ionic bonds**. Large amount of energy is required to overcome the strong ionic bonds between the zwitterions, hence it has a higher melting point.

22 Compound **Y** can be reduced using $NaBH_4$ to form compound **Z**.



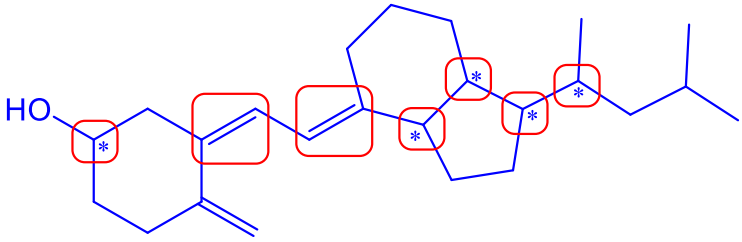
Compound **Y**

How many stereoisomers does compound **Z** have?

A 2^5 **B** 2^6 **C** 2^7 **D** 2^8

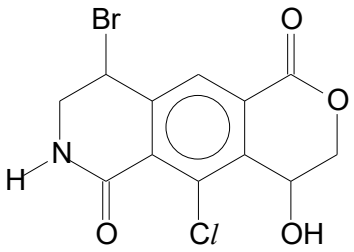
Ans: C

$NaBH_4$ can reduce carbonyl C=O but no reaction with electron rich C=C.



7 stereocentres. Total number of stereoisomers = 2^7

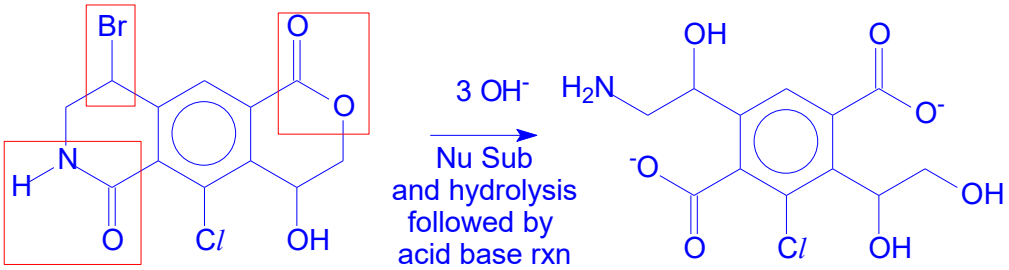
23 How many moles of NaOH(aq) will react with 1 mole of compound **E** when it is heated under reflux with an excess of NaOH(aq)?



compound **E**

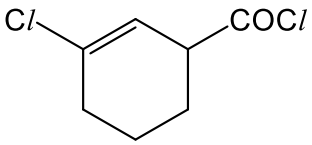
A 1 **B** 2 **C** 3 **D** 4

Ans: C



1 mol of **E** reacts with 3 mol of NaOH.
Nucleophilic sub of C–Br with OH^-
Alkaline hydrolysis of ester
Alkaline hydrolysis of amide
Chlorobenzene cannot undergo nucleophilic sub.
Alcohol is neutral and would not react with NaOH.

25 What is the mass of precipitate produced when excess ethanolic silver nitrate is added to 0.5 mol of compound **G**?



compound **G**

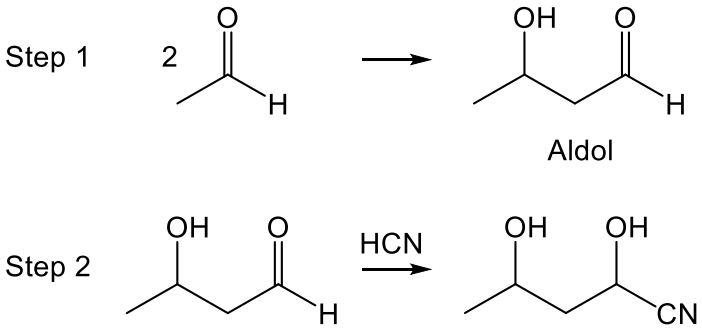
A 17.8 g **B** 35.5 g **C** 71.7 g **D** 143.4 g

Ans: C

Only acyl chloride will react with water in the acidified silver nitrate. The resultant chloride ions will produce a white precipitate with silver ions.
0.5 mol of Z would produce 0.5 mol of Cl^- and hence giving 0.5 mol of AgCl solid
Mass of AgCl produced = 0.5 × (35.5 + 107.9) = 71.7 g

27 Two aldehydes can combine to form an aldol. A base is required to generate the nucleophile for the reaction in step 1.

Aldol can be further reacted to form highly functionalised molecules.

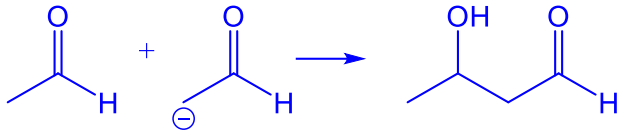


Which of the following best describes steps 1 and 2?

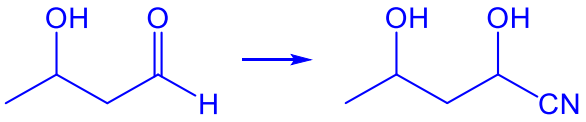
	Step 1	Step 2
A	Substitution	Reduction
B	Addition	Reduction
C	Substitution	Addition
D	Addition	Addition

Ans: D

In Step 1, after generation of nucleophile, nucleophilic addition occur on C=O to generate the aldol.

Step 1 

In Step 2, a HCN is added onto the C=O of carbonyl carbon. Nucleophilic addition occurred.

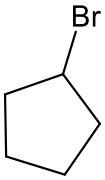
Step 2 

28 A mixture of product is formed from when cyclopentane is heated with liquid bromine.

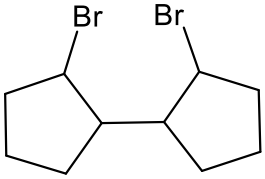
Which molecule could not be formed?

A HBr

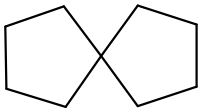
B



C

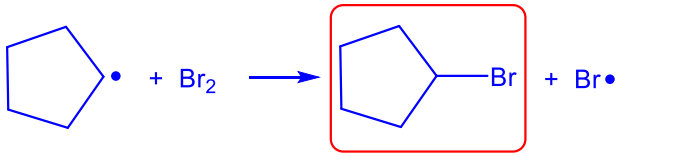


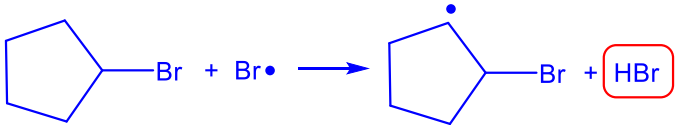
D



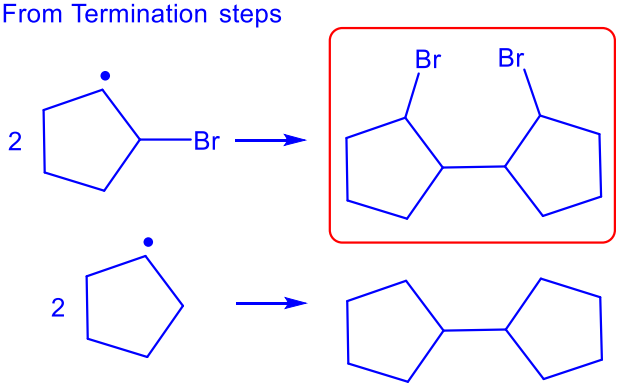
Ans: D

From Propagation steps





From Termination steps



29 Benzene can react with ethanoyl chloride, CH_3COCl, in the presence of anhydrous $AlCl_3$.

Which statements are true for above reaction?

1 The organic product gives an orange precipitate with 2,4-DNPH solution.

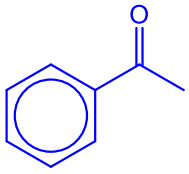
2 The organic product gives a yellow precipitate when warm with alkaline iodine.

3 The reaction intermediate has 5 delocalised pi electrons.

A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

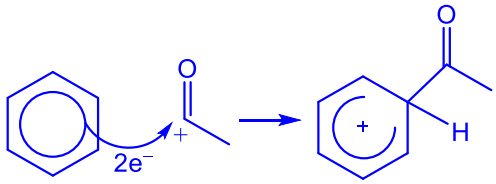
Ans: B

Statements 1 and 2 are correct.

Organic Product from the reaction: 

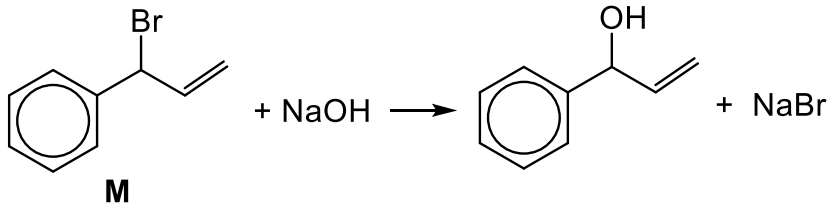
The methyl ketone will give positive test with 2,4-DNPH and alkaline iodine.

Statement 3 is wrong.



2 electrons are transferred from the 6 delocalised pi electron cloud to form a bond with the electrophile. Hence, 4 electrons are left in the arenium pi electron cloud.

30 Compound **M** reacts with sodium hydroxide to form 2 isomeric alcohols.

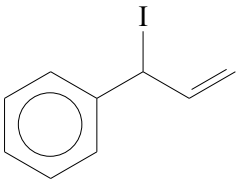


M

Which statement do not describe the above reaction?

A The resultant mixture is not optically active.

B The reaction intermediate is planar in structure.

C The rate of reaction increases when  is used.

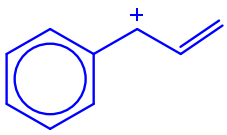
D Increasing the concentration of OH^- used will result in shorter reaction time.

Ans: D

2 Isomeric products indicate S_N1 reaction.
Hence, rate law is rate = k[M]. Changing $[OH^-]$ will not affect the react of reaction.
Statement D is wrong.

Statement C is correct. C–I bond is weaker than C–Br bond, the rate of reaction increases.

Statement B is correct.

Intermediate of reaction: 
All carbons in the intermediate are sp2 hybridised. Hence, the whole molecule is planar in structure.

Statement A is correct. A racemic mixture is formed for S_N1 reaction, which is optically inactive.

NATIONAL JUNIOR COLLEGE
SH2 MID YEAR TIMED PRACTICE
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/02
Paper 2 Structured Questions
24 June 2024
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

For Examiner's Use	
1	**/15**
2	**/15**
3	**/17**
4	**/15**
5	**/13**
Paper 2 Total	**/75**

This document consists of **21** printed pages.

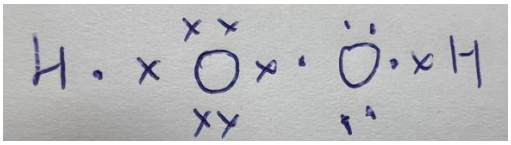
1 **(a)** 1.20 g of an unknown alcohol, RCH_2OH was diluted with water to give a 250 cm^3 solution. 25.0 cm^3 of the solution was pipetted out and added to 25.0 cm^3 of 0.16 mol dm^{-3} acidified $KMnO_4$ in a hot water bath. $KMnO_4$ reacts with RCH_2OH as shown in the following equation:

$$4\ MnO_4^- + 5\ RCH_2OH + 12\ H^+ \rightarrow 4\ Mn^{2+} + 5\ RCOOH + 11\ H_2O$$

The unreacted $KMnO_4$ in the resultant solution requires 24.00 cm^3 of 0.200 mol dm^{-3} of H_2O_2 for complete reaction.

$$5\ H_2O_2 + 2\ MnO_4^- + 6\ H^+ \rightarrow 2\ Mn^{2+} + 8\ H_2O + 5\ O_2$$

(i) Draw the dot-and-cross diagram for H_2O_2.



[1]

(ii) Calculate the amount of $KMnO_4$ reacted with H_2O_2 and the amount of $KMnO_4$ that reacted with the alcohol from the 25.0 cm^3 of solution.

No. of moles of H_2O_2 titrated = $\frac{24.00}{1000} \times 0.200 = 4.80 \times 10^{-3}$

No. of moles of $KMnO_4$ that reacted with the H_2O_2

= $\frac{2}{5} \times 4.80 \times 10^{-3} = 1.92 \times 10^{-3}$ **[1]**

Total no. of moles of $KMnO_4$ present in 25.0cm^3 of 0.16 mol dm^{-3} acidified $KMnO_4$ = $\frac{25.0}{1000} \times 0.16 = 4.00 \times 10^{-3}$

No. of moles of $KMnO_4$ that reacted with the alcohol

= $4.00 \times 10^{-3} - 1.92 \times 10^{-3}$

= 2.08×10^{-3} **[1]**

[2]

(iii) Calculate the amount of alcohol in 250 cm^3 solution and the M_r of the alcohol.

No. of moles of alcohol that reacted with $KMnO_4 = \frac{5}{4} \times 2.08 \times 10^{-3}$

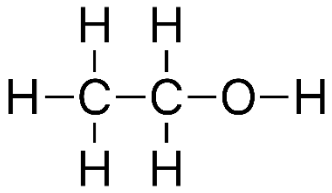
$= 2.60 \times 10^{-3}$ **[1]**

No. of moles of alcohol in 250 $cm^3 = \frac{250}{25} \times 2.60 \times 10^{-3} = 2.60 \times 10^{-2}$

M_r of alcohol = $1.20 \div 2.60 \times 10^{-2} = 46.2$ **[1]**

[2]

(iv) Using your answer to **(iii)**, determine the structure of the alcohol.



[1]

(b) A double salt is a salt that contains more than one cation or more than one anion in its ionic lattice. To identify the ions that make up a double salt, its individual ions are passed through the same electric field and their angle of deflection are recorded in Table 1.

The angle of deflection of Na^+ in an electric field can be used as a reference to determine the mass of the ions. When passed through an electric field, a beam of Na^+ give an angle of deflection of +3.00°.

Charged particle	Angle of deflection
X^{2+}	+5.68°
Y^-	−1.94°
Z^+	+1.76°

(i) Determine the mass of each of the ions and suggest their identity.

Angle of deflection $\propto \frac{charge}{mass}$, using Na^+ as reference,

$3.00 = k \times \frac{+1}{23.0}$

$k = +69.0$

For X^{2+},

$+5.68 = +69 \times \frac{+2}{mass\ of\ X}$

mass of X = 24.3

X is Mg.

For Y^-,

$-1.94 = +69 \times \frac{-1}{mass\ of\ Y}$

mass of Y = 35.6

Y is C*l*.

For Z^+,

$+1.76 = +69 \times \frac{+1}{mass\ of\ Z}$

mass of Z = 39.2

Z is K.

2 marks for 3 correct identities

1 mark 2 correct identities

[2]

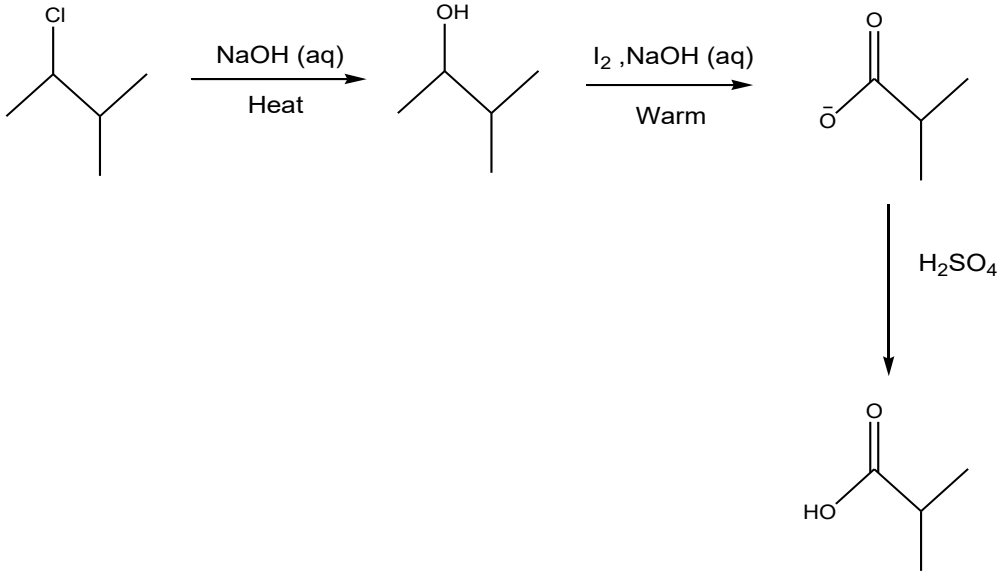
(ii) Hence, suggest the formula of the salt.

$KMgCl_3$ or $KCl.MgCl_2$

[1]

(c) **(i)** Suggest a synthetic route for the conversion of 2-chloro-3-methylbutane to 2-methylpropanoic acid.

You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.



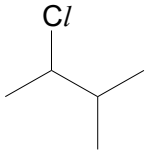
1 mark for structure of each intermediate
2 marks for 3 correct reagents and conditions
1 mark for 2 correct reagents and conditions
0 mark for 1 correct reagents and conditions

To accept if the first 2 steps are combined.

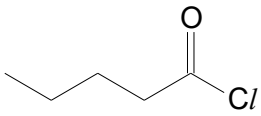
-1 mark if student eliminate to get alkene followed by oxidation since there are two possible alkene that can be obtained.

[4]

(ii) 2-chloro-3-methylbutane and pentanoyl chloride can both undergo hydroylsis. State and explain how the rate of hydrolysis differs.



2-chloro-3-methylbutane



pentanoyl chloride

The acyl carbon of the pentanoyl chloride is attached to electronegative O and Cl **[1/2]** resulting in a more electron deficient carbon centre **[1/2]** than that of the 2-chloro-3-methylbutane as the C is only attached to a Cl. Hence, the pentanoyl chloride is more susceptible to nucleophilic attack **[1/2]** and the rate of reaction is faster. **[1/2]**

[2]

[Total: 15]

2 Interhalogens are compounds that are made up of two or more different halogens. They are generally used as non-watery solvents.

IC*l* and IBr are two such examples.

(a) Explain why IBr has a higher boiling point than IC*l* by making reference to their structure and bonding.

Both are simple covalent molecules. **[1/2]** compounds experience weak forces of attraction between their respective molecules **[1/2]**. IBr has a significantly larger and more polarizable electron cloud/ its dipoles are more easily induced than IC*l* **[1/2]**, thus it has significantly stronger id-id than IC*l* **[1/2]**. Thus greater amount of energy required to overcome intermolecular force in IBr than IC*l*, thus boiling point of IBr is higher than IC*l*.

[2]

(b) IC*l* reacts with water in which water is acting as the nucleophile.

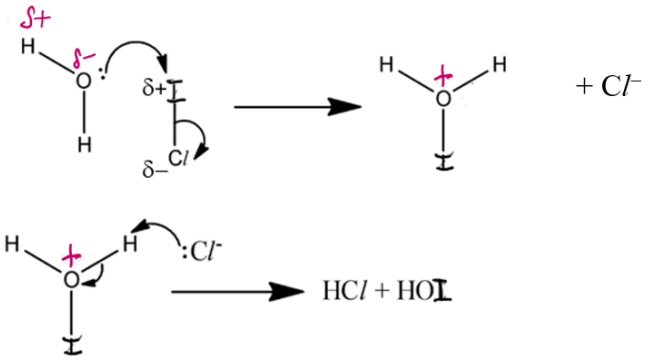
$$ICl + H_2O \rightarrow HX + HOY$$

(i) Considering electronegativities of the halogens, identify **X** and **Y**.

C*l* is more electronegative than I. electron rich O of H_2O would react with $\delta+$ I in I–C*l*.
X is chlorine while **Y** is iodine

[1]

(ii) Hence propose a two-step mechanism for this reaction. Show relevant lone pairs of electrons, dipoles and curly arrows.



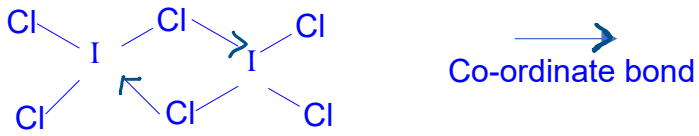
Dipoles on O–H and I–Cl
Lone pair electron on O and Cl^-
Balanced equation (atoms and charge)

Correct use of curly arrows
½ for each

[2]

(c) ICl_3 exists as a planar dimer I_2Cl_6 in solid state.

(i) Draw the structure of the dimer. Label the co-ordinate bonds on your structure.



[1]

(ii) The molten form of ICl_3 is able to conduct electricity because it undergoes auto-ionisation to form an ionic compound **X** with molar mass of 466.8 g mol^{-1}

The cation formed is bent while the anion formed is square planar.

Deduce the formulae of the cation and the anion in compound **X**.

Compound X is I_2Cl_6 (M_r = 466.8)

ICl_4^- [1] (4 b.p. regions + 2 l.p. regions around I, square planar)
and ICl_2^+ [1] (2 b.p. regions + 2 l.p. regions around I, bent)

[2]

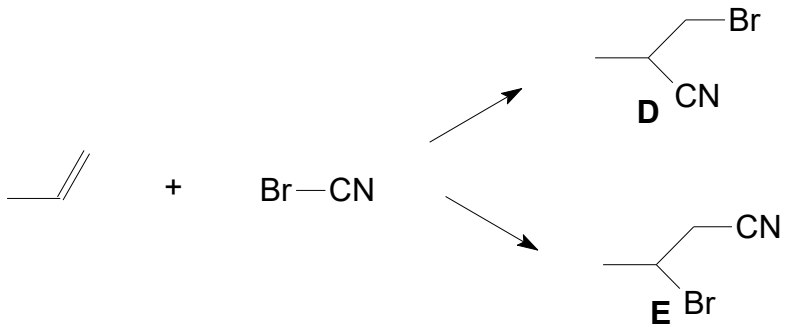
(d) Cyanogen bromide, BrCN, undergoes substitution with phenol and addition reaction with propene.

(i) Benzene can only react with BrCN in the presence of a suitable catalyst. Suggest why there is a difference in the condition required for benzene and phenol to react with BrCN.

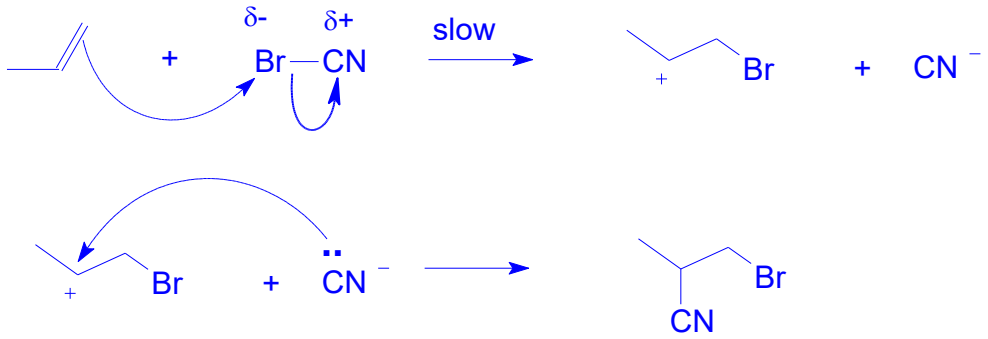
In phenol, the delocalisation of the lone pair of electrons on oxygen **[½]** into the benzene ring **increases** the electron density in the ring significantly **[½]**. This makes phenol **more reactive** than benzene towards an **electrophile [½], thus catalyst which is used to generate a strong electrophile [½]** is no longer required for phenol.

[2]

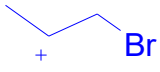
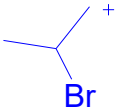
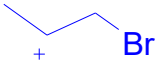
(ii) When propene is reacted with BrCN, compound **D** is produced as the major product.



Describe the reaction mechanism for the formation of **D**. Show relevant lone pairs of electrons, dipoles and curly arrows. Hence explain the preferential production of compound **D**.



Dipoles on Br–C
Lone pair electron on C of CN^-
Balanced equation (atoms and charge)
Correct use of curly arrows
Indicate slow step in step 1
Minus ½ for each mistake

The carbocation  has 2 electron donating alkyl group attached to disperse its positive charge, thus it is a more stable **[0.5]** carbocation intermediate than  with only 1 alkyl group attached.  is formed at preferentially **[0.5]**, which reacts with CN^- to form **D**.

[3]

(iii) When separate samples of 4-bromophenol and compound **D** was heated with ethanolic $AgNO_3$, they give different observations. State and explain the difference in observation.

D gives cream precipitate of AgBr while no ppt is observed with 4-bromophenol. 1 or 0

C-Br bond in 4-bromophenol exhibits partial double bond character (due to the lateral overlap of p orbital of Br with the pi electron cloud of benzene), resistant to substitution thus will not give free halide ion to produce AgX ppt. 1 or 0

[2]

[Total : 15]

3 Methanol is the simplest alcohol, and is a volatile, colourless and flammable liquid. Methanol is mainly used as an antifreeze, solvent or fuel.

(a) Define the term *standard enthalpy change of combustion of methanol* in words.

The amount of heat released when 1 mol of methanol undergoes complete combustion in excess oxygen under standard conditions of 298K and 1 bar.

[1]

(b) **(i)** Using appropriate data from the *Data Booklet*, calculate the ΔH_r of the following reaction.

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \text{ -------- } \Delta H_r$$

$\Delta H_r = \sum BE(reactants) - \sum BE(products)$
$= [6\times410 + 2\times360 + 2 \times 460 + 3 \times 496] - [4 \times 805 + 8 \times 460]$ **[1]**
$= 5588 - 6900$
$= -1312$
$= -1310$ kJ mol^{-1} (3s.f.) **[1]**

[2]

(ii) Hence determine the standard enthalpy change of combustion of methanol.

Answer in (b)(i) is for combustion of 2 mol of methanol.

ΔH_c (CH_3OH) = −656 kJ mol^{-1} (3s.f.)

[1]

(c) The theoretical standard enthalpy change of combustion of methanol is −715 kJ mol^{-1}. Give a reason to explain the discrepancy between this value and your answer in **(b)(ii)**.

Bond energy values are for breaking and forming of covalent bonds in gaseous state. Under standard conditions, CH_3OH and H_2O are in liquid state. The enthalpy for the conversion of liquid to gas is not accounted for during calculation in (b)

[1]

(d) In a laboratory, methanol can also be oxidised using suitable chemicals.

Give the appropriate reagents and conditions required for the following conversion.

I: Methanol → Methanal

Reagents and conditions: ……..
$K_2Cr_2O_7$, H_2SO_4(aq), heat with distillation

II: Methanol → Methanoic acid

Reagents and conditions: ……...
$K_2Cr_2O_7$, H_2SO_4(aq), heat with reflux

III: Methanol → Carbon dioxide

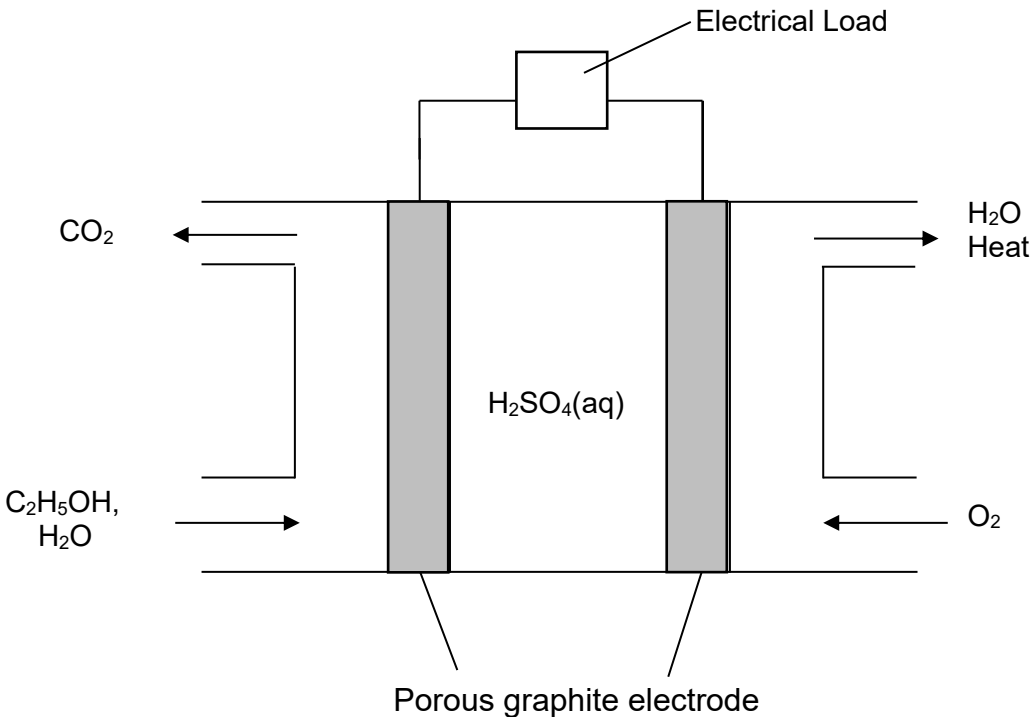
Reagents and conditions: ……...
$KMnO_4$, H_2SO_4(aq), heat/ excess O_2, heat

Note: Methanol is oxidised to methanoic acid, which undergoes further oxidation by strong oxidising agent $KMnO_4$ to give CO_2.

[3]

A fuel cell is an electrochemical cell that converts a fuel into electrical energy. The direct oxidation of alcohols in a fuel cell is one of the methods used.

(e) The diagram below illustrates the functional parts of a fuel cell.



(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the fuel cell, and hence an overall equation for the cell reaction.

Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ **[0.5]**

Cathode: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$ **[0.5]**

Overall: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ **[1]**

Must be full arrow. Minus 0.5 max if reversible arrow is used.

[2]

(ii) Indicate on the diagram, the direction of electron flow, and the polarity of each electrode.

Direction of electron : ethanol half-cell (anode) to oxygen half cell (cathode) (answer on the diagram) **[1]**

Ethanol half-cell graphite anode (-) negative terminal of battery (that releases e^- to wire)

Oxygen half-cell graphite cathode (+) positive terminal of battery (that accepts e^- from wire) **[1]**

[2]

(iii) The fuel cell has a standard cell potential, $E^{\ominus}_{cell}$, of 1.61 V. By using suitable data from the *Data Booklet*, calculate the $E^{\ominus}$ value for the CO_2/C_2H_5OH half-cell.

$E^{\ominus}_{cell} = E^{\ominus}_{O2/H2O} - E^{\ominus}_{CO2/C2H5OH}$

$1.61 = 1.23 - E^{\ominus}_{CO2/C2H5OH}$

$E^{\ominus}_{CO2/C2H5OH} = -0.38$ V

[1]

(iv) Determine the standard Gibbs free energy change ($\Delta G^{\ominus}$) for the overall cell reaction, state the polarity of each electrode and indicate on the diagram the direction of electron flow.

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$\Delta G^{\ominus} = -(12)(9.65 \times 10^4)(1.61) = -1.86 \times 10^6$ J mol^{-1} $= -1860$ kJ mol^{-1} **[1]**

[1]

(v) Discuss the effect on the cell potential of the above cell if the ethanol used has a concentration of 0.5 mol dm^{-3}.

$2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_5OH + 3H_2O$ **[0.5]**

When concentration of ethanol is decreased to 0.5 mol dm^{-3}, by *Le Chatelier's* Principle, the system will partially increase the [ethanol] by favoring the forwards reduction reaction. Therefore, $E(CO_2/C_2H_5OH)$ becomes more positive. **[0.5]**

Since $E_{cell} = E^{\ominus}_{O2/H2O} - E_{CO2/C2H5OH}$,
E_{cell} becomes less positive. **[1]**

[2]

(vi) Name an advantage that a fuel cell has over a conventional battery in which the reactive materials are stored within the cell.

To replace used electrolyte with fresh electrolyte so that the battery does not run out of power.
(Other acceptable answers: Storage of chemicals in conventional battery led to loss of power/ environment aspect due to battery being thrown away etc.)

[1]

[Total : 17]

4 **(a)** Methanoic acid, HCOOH, ionise according to the following equation.

$HCOOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HCOO^-\ (aq)$ $\quad K_a = 1.8 \times 10^{-4}$

(i) Write the expression of the acid dissociation constant, K_a.

$K_a = \frac{[H_3O^+]\,[HCOO^-]}{[HCOOH]}$ **[1]**

[1]

(ii) Calculate the pH of a 0.25 mol dm^{-3} solution of HCOOH.

Method 1:

$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$

$1.8 \times 10^{-4} = \frac{[H_3O^+]^2}{0.25}$

$[H_3O^+] = 0.006708$ **[1]**

$pH = -\lg([H_3O^+])$
$= -\lg(0.006708)$
$= 2.17$ **[1]**

if no 2d.p. minus 0.5m

Method 2:

For weak acid,

$[H^+] = \sqrt{K_a \times [weak\ acid]}$
$= \sqrt{1.8 \times 10^{-4} \times 0.25}$
$= 0.006708$ **[1]**

$pH = -\lg([H_3O^+])$
$= -\lg(0.006708)$
$= 2.17$ **[1]**

if no 2d.p. minus 0.5m

[2]

(iii) Calculate the volume of 0.50 mol dm^{-3} aqueous sodium hydroxide added to 10.0 cm^3 of 0.25 mol dm^{-3} aqueous methanoic acid to produce a solution of pH 4.

NaOH reacts with HCOOH to form a salt.

Let volume of NaOH required be x cm^3.

Initial amount of NaOH = $\frac{x}{1000}$ × 0.5 = 0.0005x mol

Initial amount of HCOOH = $\frac{10}{1000}$ x 0.25 = 0.0025 mol

[**1**] for initial amt of HCOOH

	NaOH	+ HCOOH	→	$HCOO^-Na^+$	+ H_2O
Initial / mol	0.0005x	0.0025		0	–
Change / mol	–0.0005x	–0.0005x		+0.0005x	–
Final / mol	0	0.0025 – 0.0005 x		0.0005x	–

$pH = pK_a + lg\left(\frac{[HCOO^-]}{[HCOOH]}\right)$

$4 = -lg\,(1.8 \times 10^{-4}) + lg\left(\frac{[HCOO^-]}{[HCOOH]}\right)$

$\frac{[HCOO^-]}{[HCOOH]}$ = 1.8 **[1] for the ratio of [salt] : [acid]**

$$\frac{\frac{0.0005\,x}{V}}{\frac{0.0025-0.0005\,x}{V}} = 1.8$$

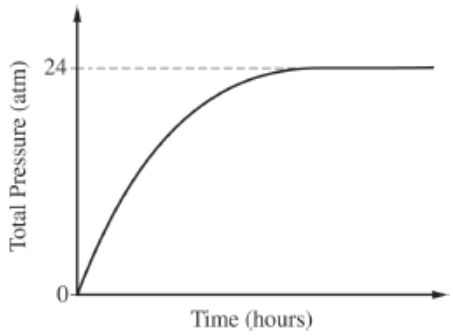
$0.0005\,x = 0.0045 - 0.0009\,x$

x = 3.21 cm^3 **[1]**

[3]

(b) When a catalyst is added to a solution of HCOOH(aq), the following reaction occurs.

$$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$$



The gas produced was collected in a 4.3 dm^3 vessel maintained at 25 °C and the total pressure is monitored, as shown in the graph above.

Calculate the number of moles of CO_2 produced in the reaction.
[Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.]

PV = nRT
(24 x 101325) x(4.3 x 10^{-3}) = n x 8.31 x (25 +273)
n_{total} = 4.223 mol **[1]**

Since equal molar of H_2 and CO_2 is formed,
Amount of CO_2 = ½ × 4.223 = 2.11 mol **[1]**

[2]

(c) Suggest how would the actual pressure of CO_2 differ from that of an ideal gas.
Pressure of CO_2 is **lower than that of an ideal gas.** **[1]**

CO_2 is not an ideal gas.

There is presence of **intermolecular forces of attraction between the CO_2 molecules**, result in the **lowering the force of collision of particles with the wall of container**. **[1]**

[2]

(d) A gaseous chemical equilibrium is established in a 2 dm^3 container at 500 K for the following reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

The initial amount of NOC*l* is 0.3 mol. At equilibrium, 0.05 mol of Cl_2 is present.

(i) Calculate the K_C for the reaction, stating the units.

	2NOCl	⇌	2NO	+ Cl_2
Initial / mol	0.3		0	0
Change / mol	-0.10		+0.10	+0.05
Eqm / mol	0.20		0.10	0.05
Eqm conc / mol dm^{-3}	0.10		0.05	0.025

Note: K_c is in terms of concentration

$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$

$= \frac{[0.05]^2[0.025]}{[0.10]^2}$

= 0.00625 mol dm^{-3}

1m of eqm mol or conc
1m for correct final ans value
1m for correct units

[3]

(ii) If the volume of the container is increased while keeping the temperature constant, explain how the position of equilibrium would be affected.

If the volume of the container is increased while keeping the temperature constant, the total pressure will decrease.**[0.5]** According to Le Chatelier's Principle, the system will **partially increase** the total pressure**[0.5]**. the position of equilibrium will **shift right [0.5] to increase the total number of moles of gas particles [0.5]** until a new equilibrium is reached.

[2]

[Total : 15]

5 Most of the 20 different common amino acids found in humans have the same general structure.

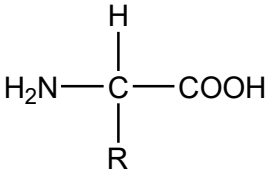
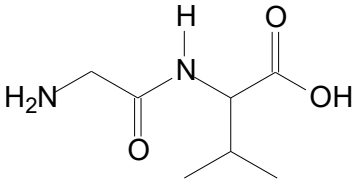


Table 5.1 shows the structural formulae of some amino acids and their respective taste.

Table 5.1

Abbreviation	Amino acid	Formula of –R group	Taste
ala	alanine	$-CH_3$	sweet
asp	aspartic acid	$-CH_2CO_2H$	sour
gly	glycine	$-H$	sweet
phe	phenylalanine	$-CH_2C_6H_5$	bitter
ser	serine	$-CH_2OH$	sweet
val	valine	$-CH(CH_3)_2$	bitter

(a) **(i)** Draw the structure of the dipeptide gly-val.



N-terminal on the left.

[1]

(ii) The sequence of amino acids in a polypeptide may be determined by partial hydrolysis of the chain into smaller pieces, often tripeptides. Following such a partial hydrolysis, the following tripeptides were obtained from a given polypeptide.

ala-gly-asp phe-val-ser ser-ala-gly val-ser-ala

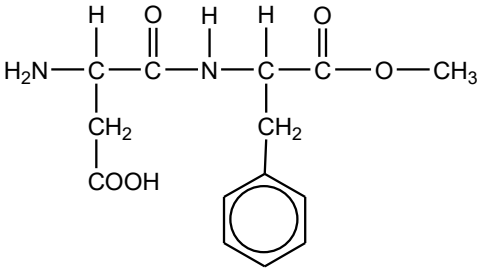
Suggest the amino acid sequence of the **shortest** polypeptide that would give the above tripeptides.

phe-val-ser-ala-gly-asp

[1]

(b) *Use of the data in Table 5.1 is relevant to parts of this question.*

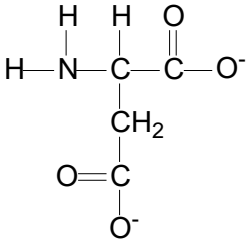
Aspartame, an artificial sweetener, is used in soft drinks and in sugar-free foods for people with diabetes.

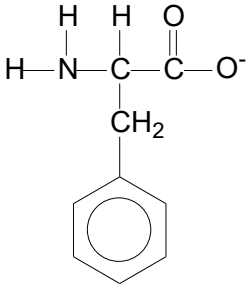


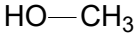
aspartame

Alkaline hydrolysis of aspartame produces three products.

(i) Suggest the three products obtained from the alkaline hydrolysis of aspartame.







1m for 3 organic products
1m for correct ionised form of amino acids in alkaline medium

[2]

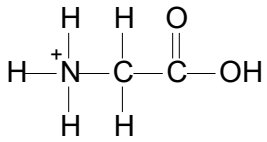
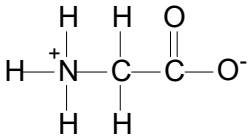
(ii) Hence suggest why aspartame is not used to sweeten foods that are to be boiled.

Under high temperature, aspartame will undergo hydrolysis to give the amino acids aspartic acid and phenylalanine, which has a sour and bitter taste respectively.

[1]

(c) Glycine, $H_2NCH_2CO_2H$, is the simplest amino acid. There are two pK_a values associated with glycine: 2.34 and 9.60.

Suggest the major species present in solutions of glycine at the following pH values.

pH 1	pH 6
	

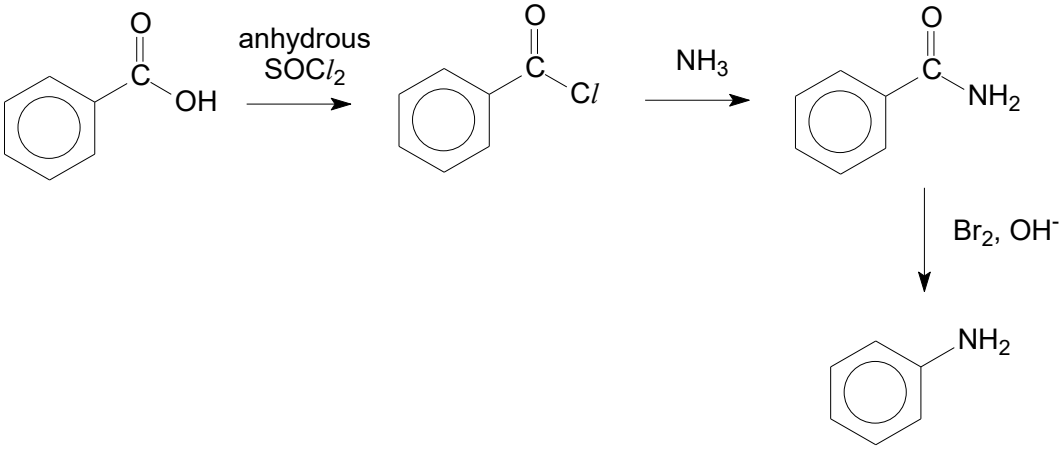
[2]

(d) Hoffmann degradation whereby treating a primary amide with aqueous alkaline bromine produces a primary amine.

$$R\text{–}CONH_2 \xrightarrow{Br_2 + OH^-} R\text{–}NH_2$$

The Hoffmann degradation can be used as the last step in the synthesis of phenylamine from benzoic acid.

Suggest 3-stage synthesis of phenylamine from benzoic acid.
You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.



1 m for each intermediate compound
2 m for correct reagents for all 3 steps
1 m for correct reagents for 2 steps

[4]

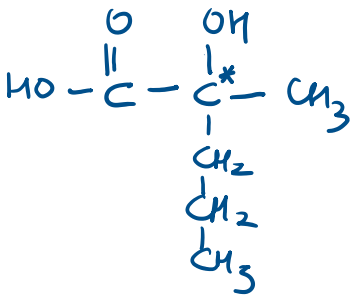
(e) Compound **R**, $C_6H_{12}O_3$, is optically active.

Three chemical tests are carried out on portions of **R** and the results are described in Table 5.2.

Table 5.2

Reagents	Observations
Excess Sodium metal	Effervescence. 1 mol of R produces 1 mol of gas
Hot acidified $K_2Cr_2O_7$	Orange solution remains
Na_2CO_3 (aq)	Effervescence

Draw the structure of **R**.



1 m for identifying –COOH and tertiary alcohol
1 m for correct final structure with chiral C

[2]

[Total : 13]

NATIONAL JUNIOR COLLEGE
SH2 MID YEAR TIMED PRACTICE
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/03**

Paper 3 Free Response **27 June 2024**

1 hour

Candidates answer on Question Paper.

Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use	
1	**/20**
2	**/20**
Paper 3 Total	**/40**

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

1 (a) Propene and lactic acid are commonly used as feedstock for polymers. **Fig 1.1** shows the synthesis of lactic acid from propene.

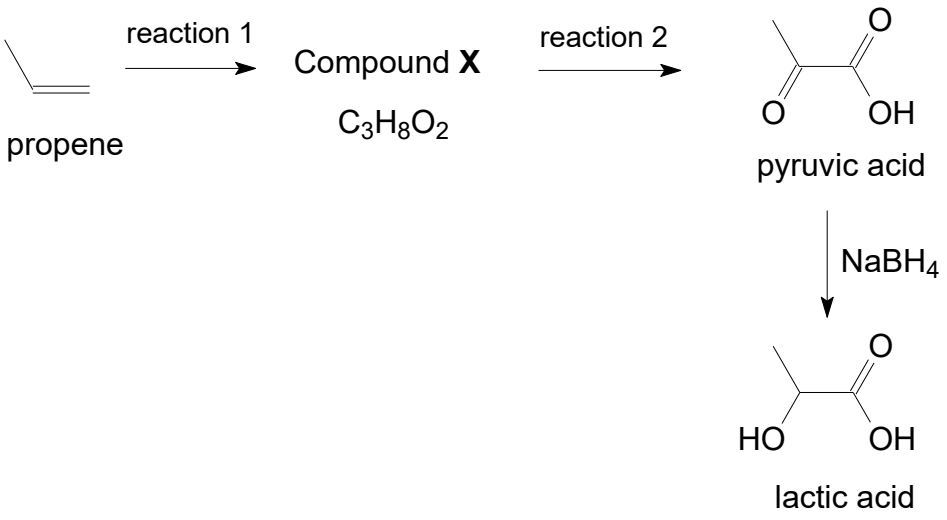


Fig 1.1

(i) Suggest the displayed formula of compound **X**.

[1]

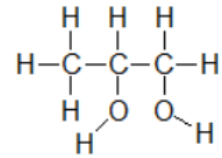
(ii) Suggest reagents and conditions for reaction 1 and 2.

[2]

(iii) Explain why sodium borohydride can reduce the carbonyl C=O bond in pyruvic acid but not C=C bond in propene.

[1]

(i)



(ii) Reaction 1: cold dil H_2SO_4, $KMnO_4$ or cold dil NaOH, $KMnO_4$

Reaction 2: $K_2Cr_2O_7$/ dil H_2SO_4, heat with reflux or $KMnO_4$/ dil H_2SO_4, heat

(iii) C in C=O is electron deficient [½] due to presence of electronegative O hence it is susceptible to nucleophilic attack by nucleophiles like BH_4^- / H^- [½]

C=C is electron rich [½] hence does not react with nucleophiles like BH_4^- / H^- [½]

.....

.....

.....

(b) Compound **Y,** $C_6H_8O_4$, is formed when lactic acid reacts in the presence of hot concentrated H_2SO_4. **Y** is a cyclic compound that does not react with sodium carbonate.

(i) Deduce the structure of compound **Y**.

[1]

(ii) Explain why compound **Y** have low solubility in methanol.

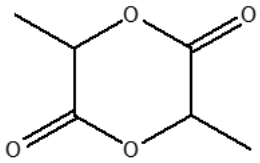
[2]

.....

.....

.....

.....



(i) **Y**:

Accept anhydride and ether in same molecule.

(ii) The energy released from the **Hydrogen bonds** formed between Y and methanol are insufficient to overcome the **strong idid/pdpd** interactions between Y molecules and the **hydrogen bonds** between methanol molecules, hence it is insoluble in methanol.

[1] for energy released being insufficient

[1] for correct types of bonds

(c) Compound **Z**, $C_5H_8O_2$, can be derived from further reactions between lactic acid molecules.

One mole of compound **Z** reacts with 2 moles of 2,4-dinitrophenylhydrazaine. It forms 1 mole of CHI_3 upon reaction with aqueous alkaline iodine and does not give silver mirror with Tollen's reagent.

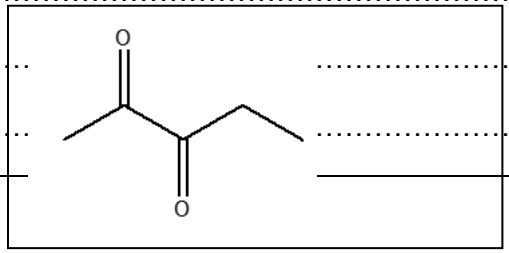
Deduce the structure of compound **Z**.

[1]

.....

.....

.....



……

……

(d) Hydrogen halides usually react with alkenes via an electrophilic addition mechanism. However, in the presence of organic peroxides, RO─OR, hydrogen halide reacts with alkenes via a different mechanism, free radical addition.

The *first 4 steps*, **A** to **D**, of the reaction between HBr and propene, in the presence of RO─OR take place as follow:

A Homolytic fission of RO−OR to produce two RO• radicals.

B RO• reacts with one HBr molecule to produce Br• radical.

C the bromine radical formed in step **B** react with propene to form $CH_3\dot{C}HCH_2Br$ radical

D $CH_3\dot{C}HCH_2Br$ radical react with HBr molecule to form $CH_3CH_2CH_2Br$ as one of the organic products of the free radical addition reaction.

(i) Outline the mechanism for steps **C** and **D** of the free radical addition mechanism, using curly arrows to indicate the movement of electrons.

[2]

(ii) The reaction starts when the reactants are exposed to bright light. Suggest a reason why the reaction continues at a high rate after the brief exposure to the bright light has stopped.

[1]

(iii) Explain why HC*l* does not react with alkenes via free radical addition under the same conditions, unlike HBr.

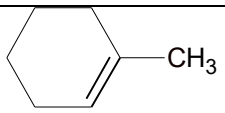
[1]

In the *final* stage of the free-radical addition reaction, two other organic products are obtained via the termination steps shown below.

$CH_3\dot{C}H{-}CH_2Br + \bullet Br \longrightarrow CH_3CHBrCH_2Br$

$CH_3\dot{C}H{-}CH_2Br + CH_3\dot{C}H{-}CH_2Br \longrightarrow$ $CH_3CH(CH_2Br)CH_3CHCH_2Br$

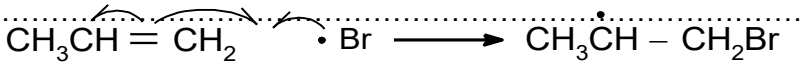
(iv) Suggest the structural formula of **two** organic products formed when 1-methylcyclohexene undergoes free radical addition with HBr in the presence of peroxide radicals.

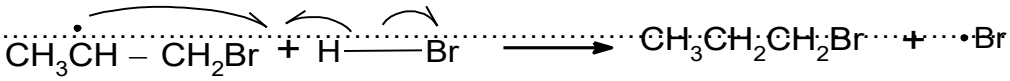


1-methylcyclohexene

[2]

(i)





[1] for each step

(ii) Reason 1: The brief exposure to bright lights produces peroxide and Br radicals that initiate the chain reactions of the propagation steps to produce more radicals [1] for reaction to proceed.

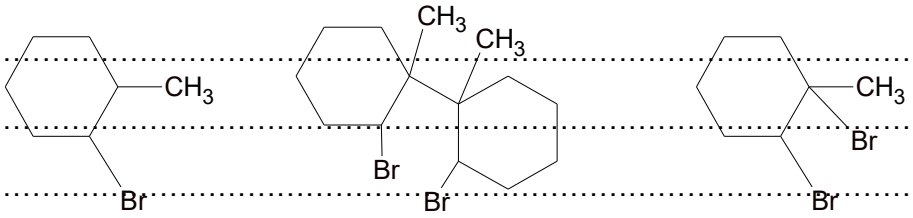
Or Reason 2: The exothermic reaction (due to breaking of the weaker pi bond and formation of stronger C—Br sigma bond) result in an increase in temperature [1], hence rate of reaction increases.

(iii) The HC*l* bond is stronger than the HBr bond, hence the propagation step involving the breaking of the HC*l* bond is very slow/requires a high activation energy. [1]

Or

The HC*l* bond is stronger than the HBr bond, hence the propagation step involving the breaking of the HC*l* bond is endothermic, and the reaction not favoured.

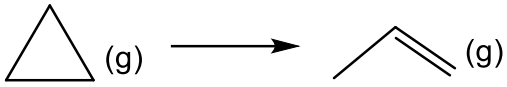
(iv) Either two of the three products below: [1] for each product



(1) (2) (3)

(1) Is formed as the anti-markonikov product, observed in step D of the reaction between propene and HBr, where $CH_3CH_2CH_2Br$ and not $CH_3CHBrCH_3$ is

(e) Propene can be formed from the isomerization of an explosive and colorless gas, cyclopropane, as shown in the equation below, at 298K.



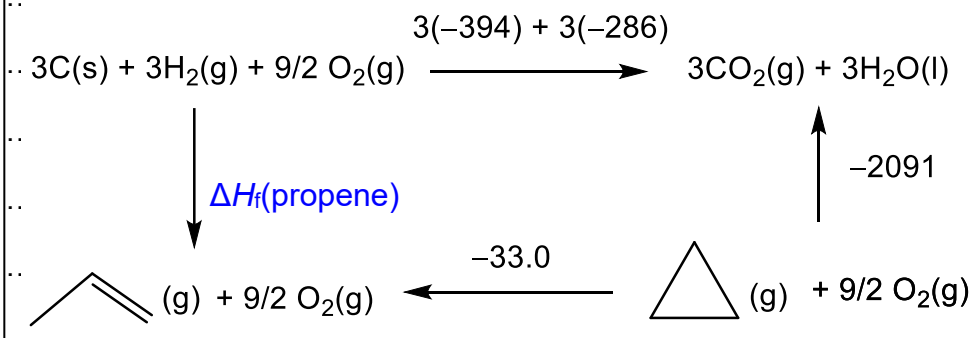
$\Delta H_{isomerisation} = -33.0$ kJ mol^{-1}

Table 1

	$\Delta H^{\ominus}$/ kJ mol^{-1}
standard enthalpy change of formation of $CO_2(g)$	−394
standard enthalpy change of formation of $H_2O(l)$	−286
standard enthalpy change of combustion of cyclopropane	−2091

Using the data given above and in **Table 1**, construct a suitable energy cycle and calculate the enthalpy change of formation of propene at 298 K.

[3]



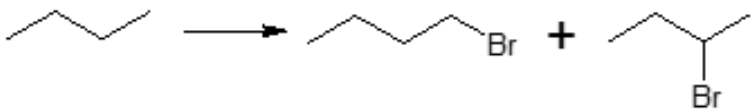
ΔH_f(propene)
= 3(−394) + 3(−286) – (−2091) + (−33.0) = **+18.0** kJ mol^{-1}

[2] for energy cycle **including** [1] for balanced atoms and [1] for correct direction of arrows for the relevant enthalpy changes.

[1] for application of hess law based on values in cycle.

0 if cycle is open

(f) The monobromination of butane forms two different bromobutanes as shown in **Fig 1.2**



1-bromobutane 2-bromobutane

Fig 1.2

(i) State the expected theoretical ratio in which these two products would form if the monobromination of butane occurs randomly.

[1]

(ii) When the monobromination is practically carried out, the experimental ratio of 1-bromobutane to 2-bromobutane is 2:98. Suggest an explanation for this observed ratio.

[2]

(i) Ratio of 1-bromobutane : 2-bromobutane = 3:2 [1]

(ii) The radical forming 1 bromobutane is a primary radical while the radical forming 2-bromobutane is a secondary radical. There are more electron-donating alkyl group [½] which reduces the electron-deficiency [½] of the secondary radical, making it more stable [½]. Therefore,it is more preferentially formed [½], resulting in the ratio of 1-bromobutane to 2-bromobutane is 2:98

[Total: 20]

2 **(a)** The kinetics of urea synthesis, $CO(NH_2)_2$, are investigated by using different concentrations of CO_2 and NH_3 in the presence of Fe_2O_3 catalyst at high temperature and pressure in a 10 dm^3 vessel, as shown in Table 2.1.

$$CO_2\,(g) + 2NH_3\,(g) \rightarrow CO(NH_2)_2\,(g) + H_2O\,(g) \qquad \text{reaction 1}$$

Table 2.1

experiment	initial $[CO_2]$ / mol dm^{-3}	initial $[NH_3]$ / mol dm^{-3}
A	0.03	2.00
B	0.03	1.00

Fig. **2.1** shows how $[CO(NH_2)_2]$ in the reaction mixture varies with time for experiments A and B.

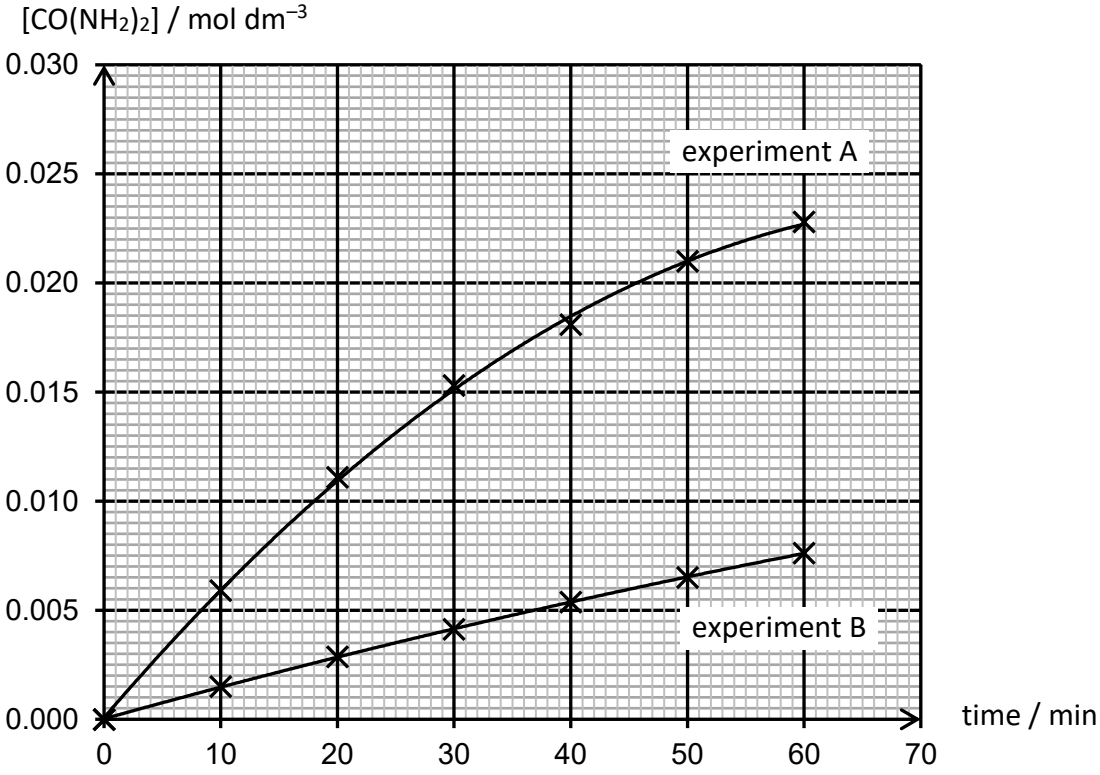


Fig. 2.1

(i) Using Table 2.1, calculate the concentration of urea, $CO(NH_2)_2$ at the end of the reaction using Experiment **A**.

[1]

(ii) Using the graphs in Fig. 2.1, show that the reaction is first order with respect to CO_2 and second order with respect NH_3.

You are required to show clearly all working, including any construction lines on Fig. 2.1.

[3]

		(iii)	Using the graph of experiment A, calculate a value for the rate constant, *k*, of the urea synthesis reaction, and state its units. [2]
		(iv)	With the aid of a Boltzmann distribution curve, explain how Fe_2O_3 catalyst increases the rate of the reaction. [2]

(i) $CO_2 + 2NH_3 \rightarrow CO(NH_2)_2 + H_2O$

Amount of CO_2 = 10 × 0.03 = 0.3 mol

Amount of NH_3 = 10 × 2 = 20 mol

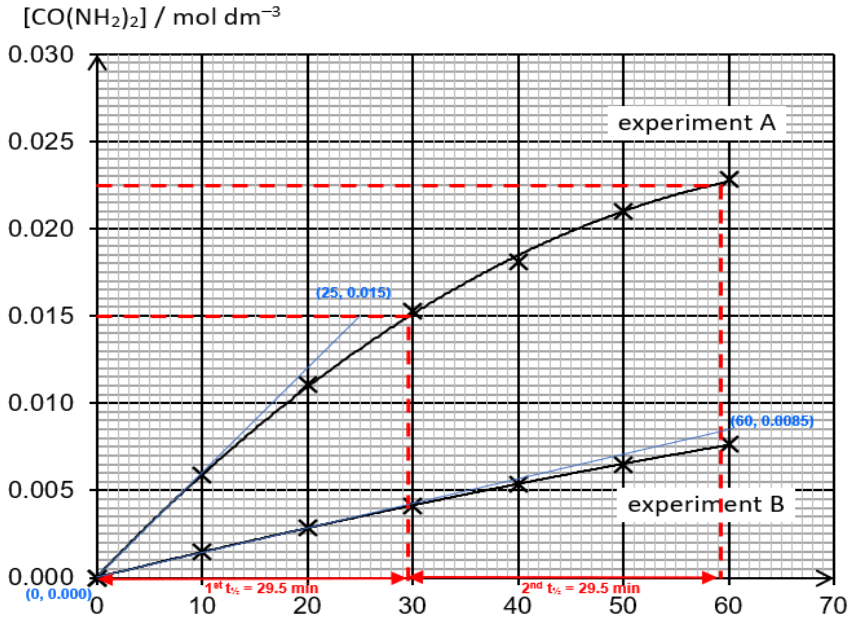
CO_2 is the limiting reagent since amount of NH_3 is in large excess.

Amount of $CO(NH_2)_2$ = 0.3 mol

$[CO(NH_2)_2]$ when the reaction goes to completion = 0.3/10

= 0.03 mol dm^{-3} **[1]**

(ii)



From the graph of expt A,

1st $t_{1/2}$ (from 0.0 → 0.015 mol dm^{-3}) = 29.5 min;

2nd $t_{1/2}$ (from 0.015 → 0.0225 mol dm^{-3}) = 29.5 min

⇒ $t_{1/2}$ is constant **[1]**

(Must show all construction lines and label at least two $t_{½}$ on the graph.

Note: Since NH_3 is in large excess, $[NH_3]$ remains effectively constant during the reaction. Hence the reaction is a pseudo order reaction where rate is dependent on concentration of CO_2.

rate = $k'[CO_2]^x$, where $k' = k[NH_3]^y$

∴ reaction is first order with respect to CO_2.

For expt A,

initial rate = $\frac{0 - 0.015}{0 - 25}$ = 6.000×10^{-4} mol dm^{-3} min^{-1} **[½]**

For expt B,

initial rate = $\frac{0 - 0.0085}{0 - 60}$ = 1.417×10^{-4} mol dm^{-3} min^{-1} **[½]**

(On the graph, label coordinates used to obtain the initial rates.)

Comparing expt A and expt B,

$$\frac{\text{initial rate}_{expt\ A}}{\text{initial rate}_{expt\ B}} = \frac{k[CO_2]_{expt\ A}[NH_3]^y_{expt\ A}}{k[CO_2]_{expt\ B}[NH_3]^y_{expt\ B}}$$

$$\frac{6.000 \times 10^{-4}}{1.417 \times 10^{-4}} = \frac{k(0.015)(2)^y}{k(0.015)(1)^y}$$

$$4.234 = (2)^y$$

$$y = \frac{\log(4.234)}{\log(2)}$$

$y = 2.08 \approx 2$ **[1]**

∴ reaction is second order with respect to NH_3.

(iii) From expt A,

rate = $k\,[CO_2]\,[NH_3]^2$

$6.000 \times 10^{-4} = k(0.03)(2.0)^2$

∴ k = 0.005**[1]** mol^{-2} dm^6 min^{-1}**[1]**

OR

Since NH_3 is in large excess, $[NH_3]$ remains effectively constant during the reaction. Hence the reaction follows pseudo first-order kinetics.

rate = $k'[CO_2]$, where $k' = k[NH_3]^2$

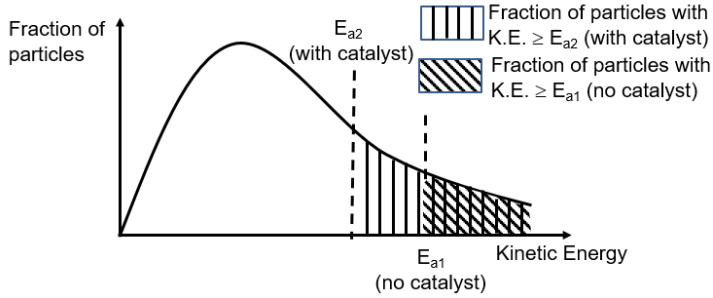
$t_{½} = \frac{\ln 2}{k'}$

$t_{½} = \frac{\ln 2}{k\,[NH_3]^2}$

From expt A, $29.5 = \frac{\ln 2}{k\,(2.0)^2}$

k = 0.00587 **[1]** mol^{-2} dm^6 min^{-1} **[1]**

(iv)



[1] for diagram

Fe_2O_3 catalyst provides an alternative reaction pathway with lower activation energy (E_{a2}). **[½]**
The fraction of molecules with K.E. ≥ E_a increases as shown in the Boltzmann distribution. The frequency of effective collisions increases hence rate of reaction increases. **[½]**

(b) The synthesis of urea involves the formation of compound **Y.**

Under suitable conditions, CO_2 reacts with NH_3 to form compound **Y** as the only product.

$$CO_2 + 2NH_3 \rightarrow \mathbf{Y}$$

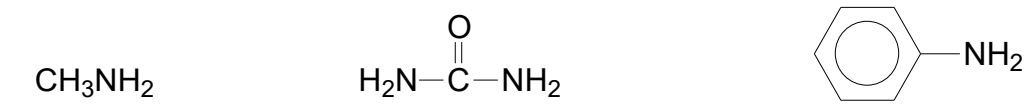
Compound **Y**, a white solid, is made up of a cation and an anion in 1:1 mole ratio. The cation liberates NH_3 when compound **Y** is heated with aqueous NaOH.

Suggest the identity of the cation and anion of compound **Y**. [2]

Compound Y has a molecular formula of $CH_6N_2O_2$
cation: NH_4^+ **[1]**
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

anion: $CH_2NO_2^-$ or $H_2NCO_2^-$ **[1]**

(c) Arrange the following compounds in order of increasing base strength. Explain your answer. [3]



		Order of increasing K_b: urea < phenylamine < methylamine **[½]** Urea is neutral as lone pair of electrons on N atom delocalised to the electron withdrawing C=O group, making it unavailable to accept a proton. **[1]** Phenylamine is less basic than methylamine as lone pair of electrons on N atom delocalised into benzene ring, making it less available to accept a proton. **[1]** Lone pair of electrons on N atom of methylamine, primary aliphatic amine, is more available to accept a proton due to presence of electron donating methyl group which increases the electron density of N atom. **[½]**

(d) Oxalic acid, $C_2H_2O_4$, commonly found in vegetables such as spinach and rhubarb, is known to contribute to the formation of calcium oxalate kidney stones, CaC_2O_4 , in the human body.

The solubility product, K_{sp}, of CaC_2O_4 is 2.7×10^{-9} mol^2 dm^{-6} at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of CaC_2O_4. [1]

(ii) Explain how the addition of solid calcium nitrate, $Ca(NO_3)_2$ at 298 K will affect the solubility and solubility product of CaC_2O_4. [2]

(iii) The value of solubility product, K_{sp}, of $Ag_2C_2O_4$ is 5.40×10^{-12}.

Determine whether precipitation will be observed when 1.80×10^{-7} mol of solid $AgNO_3$ was added to 25.0 cm^3 of 3.50×10^{-3} mol dm^{-3} $K_2C_2O_4$. [2]

(iv) Describe and explain how the solubility of $Ag_2C_2O_4$ is affected by the addition of excess aqueous NH_3. [2]

(i) $CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$ (I)

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$ [1]

(ii) $Ca(NO_3)_2(s) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$

Addition of common ion Ca^{2+} will cause $[Ca^{2+}]$ to increase **[½]**. By Le Chatelier's Principle, the position of equilibrium (I) will shift left to partially offset the increase in $[Ca^{2+}]$, reducing the solubility of CaC_2O_4. **[½]**

Solubility product of CaC_2O_4 is not affected **[½]** as the temperature remains constant. **[½]**

(iii) $[Ag^+] = 1.80 \times 10^{-7} \div (25.0 \times 10^{-3})$

$= 7.20 \times 10^{-6}$ mol dm^{-3} **[½]**

Ionic product $= [Ag^+]^2[C_2O_4^{2-}]$

$= (7.20 \times 10^{-6})^2 (3.50 \times 10^{-3})$ **(ecf)**

$= 1.81 \times 10^{-13}$ mol^3 dm^{-9} **[½]**

Since ionic product < K_{sp}, precipitation of $Ag_2C_2O_4$ will not be observed. **(ecf) [1]**

(iv) $Ag_2C_2O_4(s) \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$ -- (1) **[½]**

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ -- (2) **[½]**

On addition of excess aqueous NH_3, the formation of $[Ag(NH_3)_2]^+$ results in a decrease in $[Ag^+]$ **[½]**. By Le Chatelier's Principle, the position of equilibrium (1) shifts right to partially offset the decrease in $[Ag^+]$ **[½]**, increasing the solubility of $Ag_2C_2O_4$.