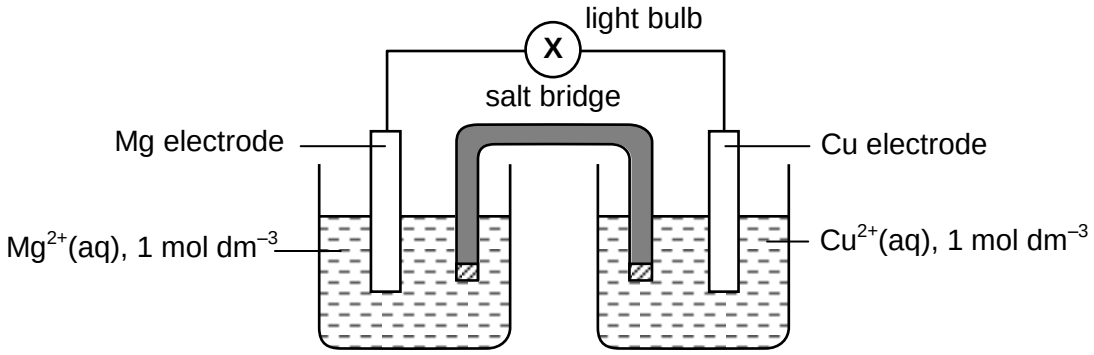
2014 Preliminary Examination H2 Chemistry Paper 3

Answer any 4 questions.

1 (a) *Use of the Data Booklet is relevant in this question.*

The following cell has been used to light up a light bulb.



(i) Suggest, with a reason, how the cell potential changes when the current has passed through for a while.

Anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

OR $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$

As $[Mg^{2+}]$ increases, $E(Mg^{2+}/Mg)$ will be less negative.

As $[Cu^{2+}]$ decreases, $E(Cu^{2+}/Cu)$ will be less positive.

The cell potential will become less positive.

The electrode potential of the cell is related to the equilibrium constant by the following equation,

$$E^{\ominus} = \frac{RT}{zF} \ln K_c$$

where T is the temperature measured in Kelvin, z is the number of moles of electrons transferred during the redox reaction and F is the Faraday constant.

(ii) By using relevant data from the *Data Booklet*, determine the equilibrium constant K_c for the reaction between Cu^{2+} and Mg.

$E_{cell} = E_{red} - E_{ox}$

$= (+0.34) - (-2.38)$

$= +2.72$ V

$$\ln K_c = \frac{2 \times 96500 \times 2.72}{8.31 \times 298} \quad \text{(ecf)}$$

$= 212$

$K_c = 1.16 \times 10^{92}$ (ecf)

(iii) Hence, determine the ratio $[Mg^{2+}]:[Cu^{2+}]$, when there is no current flowing in this cell.

When there is no current flowing in the electric cell, it has reached equilibrium.
$[Mg^{2+}]:[Cu^{2+}] = K_c = 1.18 \times 10^{92}$

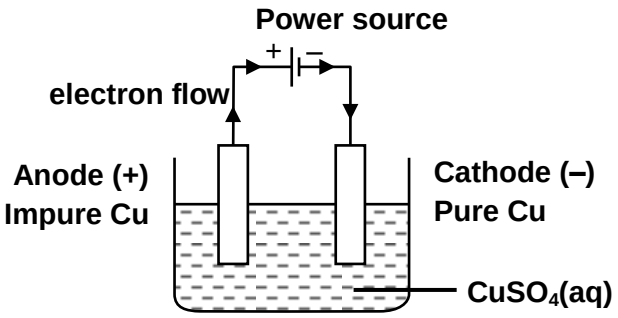
(iv) Suggest the significance of the magnitude of your answer in **(a)(iii)**.

Almost all the Cu^{2+} has been consumed.
OR Reaction goes to completion when the equilibrium has been reached.

[5]

(b) Copper minerals often contain suifides of magnesium and silver as impurity. After minerals are reduced with carbon, the solid impure copper is purified by electrolysis.

(i) Describe the electrode reactions that take place during the electrolysis and explain in detail how each of the two impurity metals is removed from copper.



Two electrodes + Electrolyte
OR diagram above

At the anode, oxidation takes place and Cu dissolves.
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Mg with $E^\ominus$ which is less positive than that of Cu dissolves as ions.
Ag with $E^\ominus$ which is more positive than that of Cu remains undissolved and drop to the bottom of the vessel as 'anode sludge'.
At the cathode, reduction of copper ions occurs due to more positive $E^\ominus$ (Cu^{2+}/Cu) compared to $E^\ominus$ (H_2O/H_2) and $E^\ominus$ (Mg^{2+}/Mg)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Hence, only pure Cu is formed at the cathode.

An impure copper rod is purified by electrolysis using a constant current. After 1 hour, mass of one electrode decreased by 19.0 g while mass of the other electrode increased by 17.8 g. The electrolyte was further analysed and found that the amount of Cu^{2+} ions is reduced by 0.020 mol.

(ii) Calculate the current used for this process.

Amount of Cu formed = $\frac{17.8}{63.5}$

= 0.280 mol

Amount of electron transferred = 0.280 x 2

= 0.560 mol (ecf)

Charge transferred = 0.560 x 96500

= 54100 C (ecf)

Current = $\frac{54100}{3600}$

= 15.0 A (ecf)

(iii) Determine the percentage composition by mass of the three elements.

Amount of Mg oxidised = amount of Cu^{2+} changed

= 0.020 mol

Mass of Mg = 0.020 x 24.3

= 0.486 g

Percentage composition by mass of Mg = $\frac{0.486}{19.0} \times 100\%$

= 2.56%

Amount of Cu oxidised = 0.280 – 0.020

= 0.260 mol

Mass of Cu = 16.51 g

Percentage composition by mass of Cu = $\frac{16.51}{19.0} \times 100\%$

= 86.9 %

Percentage composition by mass of Ag = 10.54 %

(iv) Suggest how magnesium can be recovered as magnesium oxide near the end of the electrolytic process. Write balanced equations for any reactions involving magnesium that might occur.

Filter the electrolyte to remove the metallic silver.

Add aqueous ammonia until excess.

Filter the mixture to obtain the residue which is magnesium hydroxide.

Heat the solid until no more change in mass.

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$

$Mg(OH)_2 \rightarrow MgO + H_2O$

[Accept reaction of $Mg(OH)_2$ with HNO_3 and followed by thermal decomposition of $Mg(NO_3)_2$].

[11]

(c) The methods of synthesis shown below are faulty.
In each case

- Explain why this is so.
- Suggest how the synthesis from the initial reactant to the final product could be satisfactorily achieved.

(i) $CH_3CH(OH)CO_2C_2H_5 \xrightarrow[\text{Heat}]{\text{dil HC}l} CH_2{=}CHCO_2C_2H_5$

(ii) $CH_3CH(OH)CN \xrightarrow[\text{Heat}]{\text{dil NaOH}} CH_3CH(OH)CH_2NH_2 \xrightarrow{CH_3COCl} CH_3CH(OCOCH_3)CH_2NH_2$

[4]

(c) (i) When HC*l* is used:

Dehydration will not occur with dilute HC*l.*
Ester will be hydrolysed to give alcohol and carboxylic acid.
Correct reaction reagent and condition: Al_2O_3 catalyst with heating.
(Conc. H_2SO_4 is not a good choice as it may lead to hydrolysis of ester.)

(ii)

NaOH causes hydrolysis of CN instead of reduction.
Amine is a stronger nucleophile as nitrogen is less electronegative, thus it will react with CH_3COCl first to give amide instead.

OR Both alcohol and amine will react with CH_3COCl, when excess amount of CH_3COCl is used.
React with CH_3COCl at room temperature and
followed by reduction with H_2 with Pt catalyst at room temperature.

[4]

[Total: 20]

2 (a) (i) When CHI_2CHO was warmed with alkaline aqueous iodine, two organic products are formed. Construct an equation for this reaction.

$CHI_2CHO + I_2 + 2OH^- \rightarrow CHI_3 + HCO_2^- + I^- + H_2O$

(ii) There are suggestions on using CF_3CH_2F to replace CFCs. One problem however is that CF_3CH_2F can be converted to CF_3CO_2H, which is toxic when ingested. When CF_3CH_2F eventually reaches the atmosphere, it is thought that CF_3CH_2F is initially attacked by •OH radicals.

A student suggested the following equation to represent the above reaction:

$CF_3CH_2F + {\bullet}OH \rightarrow CF_3\dot{C}H_2 + HOF$

By considering the

- bonds broken and
- bonds formed

in the above reaction, explain why the above reaction will **not** occur.

Bond broken: C-F bond is very strong / high bond energy
due to the <u>extensive overlap</u> between the <u>C and F atomic orbitals</u>.
Bond formed: O-F bond is very weak / low bond energy
O and F atoms are <u>small</u> / strongly <u>electronegative</u>, and the <u>electron pairs</u> will be <u>close</u> to each other and <u>repel</u> strongly.

(iii) In light of your answers to **(a)(ii)**, suggest a more appropriate equation for the reaction between CF_3CH_2F and •OH.

$$CF_3CH_2F + \bullet OH \rightarrow CF_3\dot{C}HF + H_2O$$

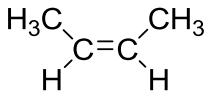
(iv) Ethanedioic acid, $HO_2C\text{-}CO_2H$ is a dibasic acid, with $pK_{a1} = 1.3$ and $pK_{a2} = 4.3$.
Methanoic acid is a monobasic acid with $pK_a = 3.7$.

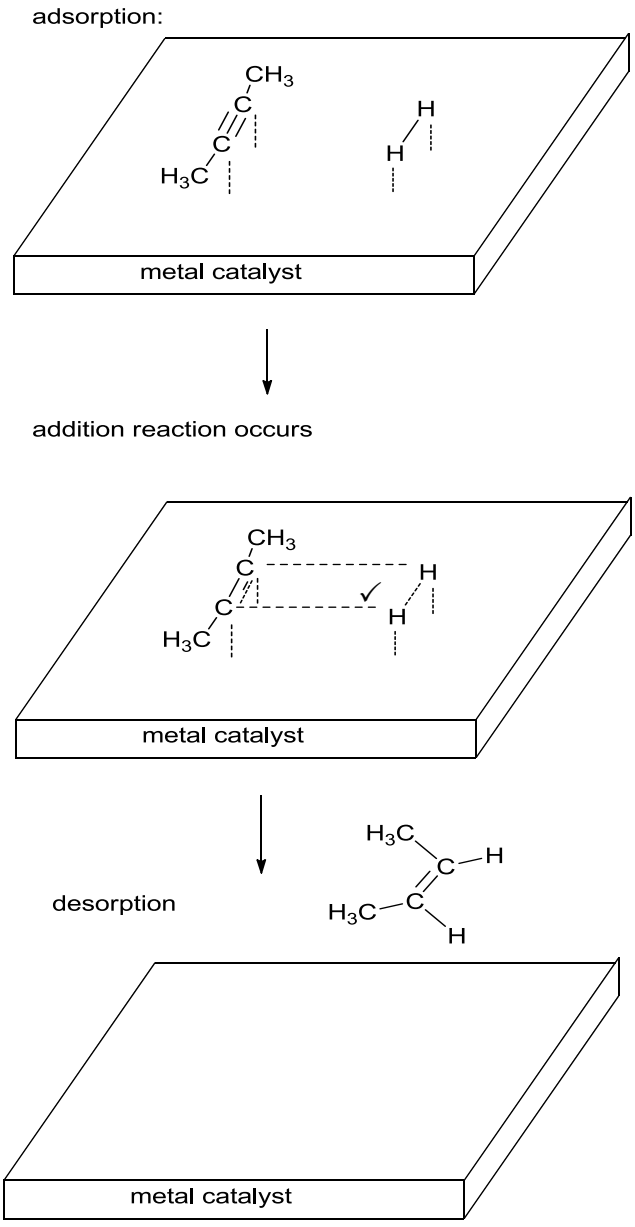
Account for the lower pK_{a1} value of ethanedioic acid as compared to the pK_a of methanoic acid.

<u>Lower pK_{a1}</u> value implies <u>stronger acid</u>.
<u>$HO_2C\text{-}CO_2^-$</u> is <u>more stable</u> than HCO_2^-.
<u>CO_2H</u> group exerts an <u>electron withdrawing inductive effect</u>
leading to <u>better charge dispersal</u> in <u>$HO_2C\text{-}CO_2^-$</u> compared to HCO_2^-.
Hence, greater tendency for $HO_2C\text{-}CO_2H$ to dissociate
OR equilibrium position of $HO_2C\text{-}CO_2H \rightleftharpoons HO_2C\text{-}CO_2^- + H^+$ lies more to the right.
<u>$HO_2C\text{-}CO_2^-$</u> can also be stabilised by <u>intramolecular hydrogen bonding</u>.
OR equivalent diagram

[6]

(b) But-2-yne, $H_3CC{\equiv}CCH_3$ may undergo the addition of hydrogen at the surface of a metal catalyst to produce an alkene **X**. Draw relevant diagrams to illustrate how the metal catalyses this reaction. Give the structure of **X**.

X is  *(cis isomer shown)*



Adsorption of reactants on surface of catalyst

Bonds weakened in reactants and less energy is required to form the activated complex.

After reaction, products desorb from the surface and diffuse away.

(award this mark even if the correct isomer is not shown)

[3]

(c) (i) Describe briefly how gaseous HC*l* can be made in the laboratory from NaC*l* and concentrated H_2SO_4.

Add conc H_2SO_4 to <u>solid</u> NaC*l* with <u>heating</u>.
<u>Collect</u> the gas produced in a <u>gas syringe</u> / <u>gas jar</u>.
OR equivalent diagram

(ii) Explain with relevant equations, if HBr and HI can be prepared in a similar method as in **(c)(i)**.

No for both HBr and HI
HBr and HI are strong reducing agents and will further react with conc H_2SO_4.
$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$
$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

(iii) Silver chloride is soluble in aqueous ammonia while silver bromide is soluble in concentrated aqueous ammonia. Explain these observations.

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$
The K_{sp} value of AgC*l* is larger than K_{sp} value of AgBr.
AgC*l* is soluble in aqueous NH_3 due to complex formation from $Ag^+(aq)$, enabling the ionic product $[Ag^+][Cl^-]$ to be less than the K_{sp} of AgC*l*.
For AgBr, due to the lower K_{sp} value, concentrated NH_3 has to be used to lower the $[Ag^+(aq)]$ sufficiently so that the ionic product $[Ag^+][Br^-]$ is less than its K_{sp} value.

[6]

(d) **A** is one of the elements from Na to P in the third period of the Periodic Table. When **A** is boiled with aqueous sodium hydroxide, a colourless gas, **B** is formed together with a sodium salt, **C**. Gas **B** is weakly basic and reacts with hydrogen iodide to form a solid compound, **D**, which contains 19.1% of **A**, 2.5% of hydrogen and 78.4% of iodine by mass. The sodium salt **C** contains 26.1% of sodium, 2.27% of hydrogen, 35.2% of **A** and 36.4% of oxygen by mass. **A** also forms two chlorides which dissolve readily in water to produce strongly acidic solutions of pH 2.

Identify the element **A** and the compounds **B**, **C** and **D**. Write equations for all the reactions involved.

A is phosphorus.
Phosphorus has two chlorides: PCl_3 and PCl_5.
$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
OR $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

Element	P	H	I
Mass (g)	19.1	2.5	78.4
No. of moles	$\frac{19.1}{31.0} = 0.616$	$\frac{2.5}{1.0} = 2.5$	$\frac{78.4}{127} = 0.617$
Ratio	$\frac{0.616}{0.616} = 1$	$\frac{2.5}{0.616} = 4$	$\frac{0.617}{0.616} = 1$

D is PH_4I.
B is PH_3.
$PH_3 + HI \rightarrow PH_4I$

Element	Na	H	P	O
Mass (g)	26.1	2.27	35.2	36.4
No. of moles	$\frac{26.1}{23.0} = 1.13$	$\frac{2.27}{1.0} = 2.27$	$\frac{35.2}{31.0} = 1.14$	$\frac{36.4}{16.0} = 2.275$
Ratio	$\frac{1.13}{1.13} = 1$	$\frac{2.27}{1.13} = 2$	$\frac{1.14}{1.13} = 1$	$\frac{2.275}{1.13} = 2$

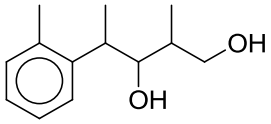
C is NaH_2PO_2.

$P_4 + 3H_2O + 3NaOH \rightarrow PH_3 + 3NaH_2PO_2$ (accept 4P instead of P_4)

[5]

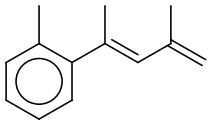
[Total: 20]

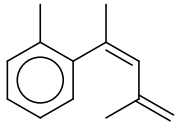
3 Alcohols are very useful in organic synthesis and can be used to produce a wide variety of compounds. The structural formula of one such alcohol is shown below.



compound **A** ($C_{13}H_{20}O_2$)

(a) When compound **A** is heated with an excess of concentrated sulfuric acid, a mixture of two isomeric hydrocarbons, **P** and **Q** are produced. Draw the structures of **P** and **Q**.

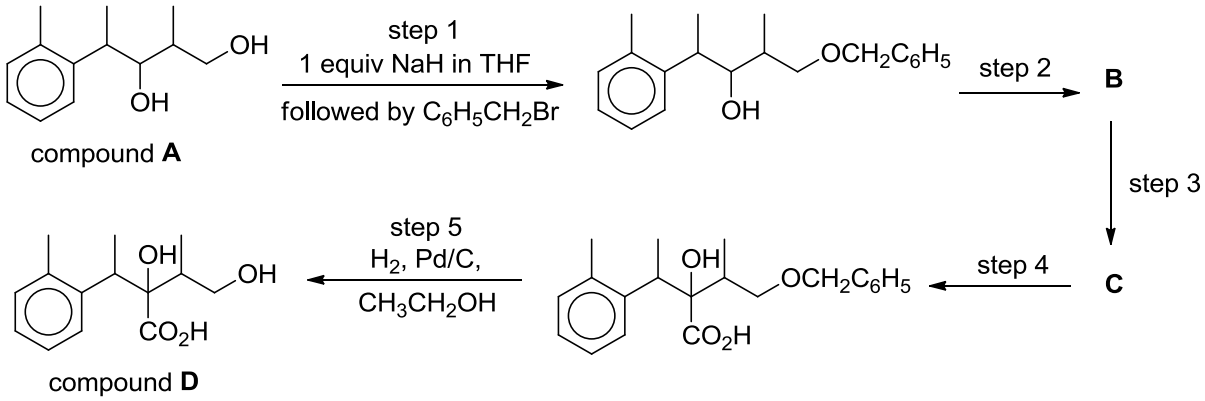
P: 

Q: 

Structures for **P** and **Q** can be interchanged.

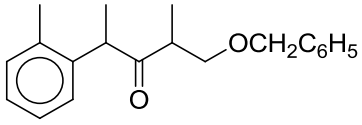
[2]

(b) Compound **D** can be formed from compound **A** via a five-step synthesis.



(i) State the reagents and conditions required for steps 2 to 4 and the structural formulae of the two intermediates **B** and **C**.

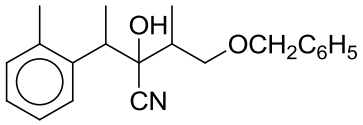
Step 2:
Reagents: $K_2Cr_2O_7$ / dil H_2SO_4 [Do not accept $KMnO_4$ /dil H_2SO_4]
Conditions: Reflux

B: 

Step 3:
Reagents: HCN / NaCN cat.
Conditions: Room temperature

[Note: If use $KMnO_4$ to form B, ecf for steps 3 and 4]

C:



Step 4:
Reagents: Dil. H_2SO_4
Conditions: Reflux

(ii) Step 1 involves the 'protection' of one of the alcohol groups to convert it into an ether, which is inert. Suggest a reason why this step is necessary.

Protection is necessary to prevent the primary alcohol from being oxidised in step 2.

(iii) Suggest the type of reaction in step 5.
Reduction

[6]

(c) Nitrosyl bromide, NOBr, is a red gas and can be formed by the reversible reaction of nitric oxide with bromine.

(i) Explain why nitrosyl bromide has a boiling point of 14 ^oC whereas nitrosyl chloride, NO*Cl* boils at −5 ^oC.

NOBr has more electrons compared to NO*Cl*.
Hence, there are stronger dispersion forces between NOBr molecules.
Thus NOBr has a higher boiling point.

NOBr decomposes to NO and Br_2 as shown below.

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

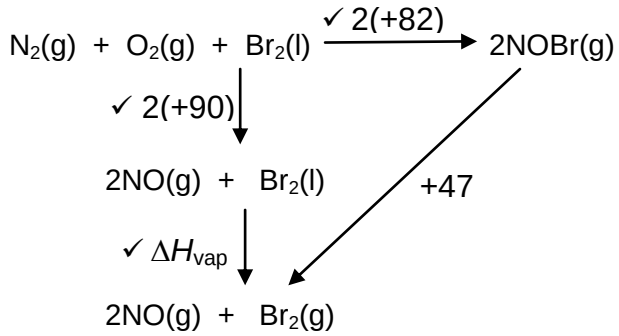
(ii) Given that the bond energy of N−Br is 120 kJ mol^{-1}, use the data from the *Data Booklet* to calculate the enthalpy change of decomposition of nitrosyl bromide, NOBr.

$\Delta H_{decomposition}$ = ½ [2 BE(N−Br) – BE(Br−Br)]
= ½ [2 (120) – 193]
= +23.5 kJ mol^{-1}

(iii) Standard enthalpy changes of formation of nitrosyl bromide and nitrogen monoxide are given below.

compound	ΔH_f / kJ mol^{-1}
NOBr(g)	+82
NO(g)	+90

With the aid of an energy cycle, use your answer in **(c)(ii)** and data above to calculate the enthalpy change of vaporisation of bromine.



Complete state symbols

ΔH_{vap} = –2(90) + 2(82) + 47 (ecf)
= +31 kJ mol^{-1} (ecf)

(iv) Predict and explain the sign of entropy change for the decomposition of nitrosyl bromide.

Entropy change is positive as number of moles of gaseous particles increases from 2 mol to 3 mol, which increase the disorderliness of the system.

[6]

(d) A calorimeter containing 300 cm^3 of water at 25 °C was calibrated as follows.

(i) 10 kJ of heat energy from a heating coil was used to increase the temperature of water by 7.5 °C. Calculate the heat capacity of the empty calorimeter.

Heat used to heat water = 300 x 4.18 x 7.5
= 9405 J
Heat used to heat calorimeter = 10000 – 9405
= 595 J
Heat capacity of calorimeter = $\frac{595}{7.5}$
= 79 J K^{-1}

(ii) A solution containing 0.040 mol $Ag^+(aq)$ was mixed with a second solution containing 0.050 mol $Br^-(aq)$ in this calorimeter, causing AgBr(s) to precipitate. The temperature increased by 2.4 ^oC. Calculate the equilibrium concentrations of $Ag^+(aq)$ and $Br^-(aq)$ present in the final voiume of 320 cm^3.
[K_{sp} of AgBr = 5 x 10^{-13} mol^2 dm^{-6}]

Let x be the no. of moles of Ag^+ that do not precipitate.

	$Ag^+(aq)$	$Br^-(aq)$	⇌	AgBr(s)
Initial / mol	0.040	0.050		0
Change / mol	–0.040	–0.040		0.040
Final / mol	x	0.010 + x		0.040 – x

$K_{sp} = [Ag^+][Br^-]$

$= (\frac{x}{0.32})(\frac{0.010 + x}{0.32})$

Since K_{sp} is small, x is small and 0.010 + x ≈ 0.010

$[Br^-] = \frac{0.010}{0.32}$

$= 0.031$ mol dm^{-3}

$[Ag^+] = \frac{5 \times 10^{-13}}{0.031}$

$= 1.6 \times 10^{-11}$ mol dm^{-3}

(iii) Hence, calculate the enthalpy change of solution of AgBr(s).
[You may assume that the density of all solutions is 1 g cm^{-3}.]

Heat evolved = (320 x 4.18 x 2.4) + (79 x 2.4)
= 3400 J

Since precipitation is exothermic, **<u>enthalpy change of solution is endothermic</u>**.

ΔH_{sol} of AgBr = $+\frac{3400}{0.040}$
= +85000 J mol^{-1}
= +85 kJ mol^{-1} (ecf)

[6]

[Total: 20]

4 (a) Sulfuryl dichloride, SO_2Cl_2, is a compound of industrial, environmental and scientific interest, widely used as a chlorinating or sulfonating agent. At room temperature, SO_2Cl_2 is a colourless liquid with a pungent odour.

An empty container is filled with SO_2Cl_2. Its decomposition to SO_2 and Cl_2 is followed by monitoring the change in total pressure at 375 K. The following data are obtained.

time/ hour	0	1	3	6	10	14	18
P_{total} / atm	1.000	1.076	1.211	1.378	1.547	1.670	1.760
$P_{SO_2Cl_2}$ / atm	1.000	**p**	**q**	0.622	**r**	0.330	0.240

(i) Determine the values of **p**, **q** and **r**. Show your working clearly.

	$SO_2Cl_2(g)$	$\rightarrow SO_2(g)$	+ $Cl_2(g)$
Initial partial pressure / atm	1	0	0
Change in partial pressure / atm	-x	+x	+x
Final pressure / atm	1– x	x	x

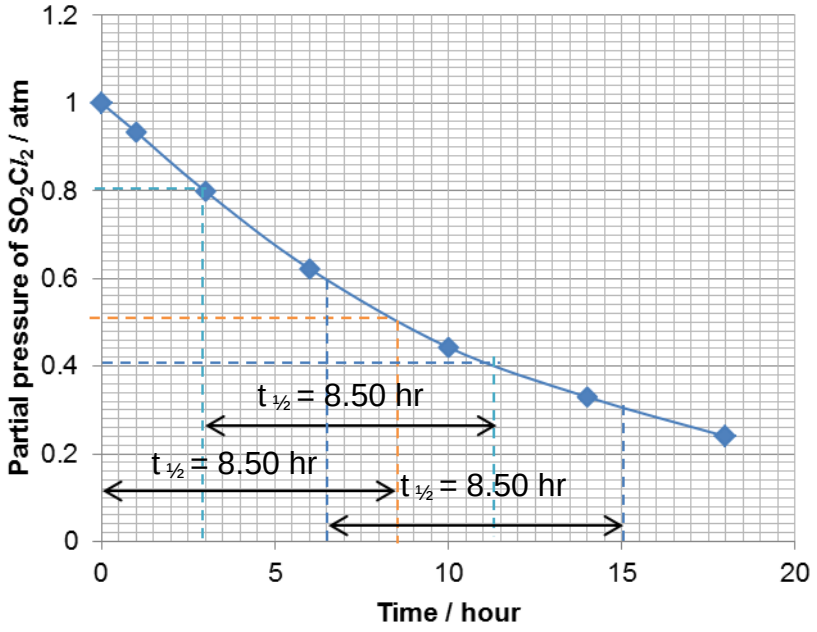
$P_{total} = 1 - x + x + x = (1 + x)$ atm

$P_{SO_2Cl_2} = (1 - x)$ atm

p = 0.924 atm, **q** = 0.789 atm, **r** = 0.453 atm

Note: 1m for 3 correct values [0.5m for 2 correct values]

(ii) Hence, by plotting a suitable graph, show that the decomposition of SO_2Cl_2 is a first order reaction.



x-axis with units
y-axis with units
correct shape
shows three $t_{1/2}$
shows two constant $t_{1/2}$
two correct $t_{1/2}$ values

(iii) Calculate the rate constant, stating its unit.

$$k = \frac{\ln 2}{t_{1/2}}$$
$$= 0.0815\ h^{-1}$$

(iv) Calculate the concentration of SO_2Cl_2, in mol dm^{-3} after 18 hours.
You may assume ideal gas conditions.

$$PV = nRT$$
$$P_{SO_2Cl_2} = (n/V)RT$$
$$[SO_2Cl_2] = P_{SO_2Cl_2} / RT$$
$$= \frac{0.24 \times 1.01 \times 10^5}{8.31 \times 375} \quad \text{(ecf)}$$
$$= 7.78\ \text{mol}\ m^{-3}$$
$$= 7.78 \times 10^{-3}\ \text{mol}\ dm^{-3}$$

(v) In another experiment, the decomposition reaction is repeated at 375 K with initial total pressure of 2 atm of SO_2Cl_2.

Use the graph drawn in **(a)(ii)** to estimate the time taken for partial pressure of SO_2Cl_2 to fall by 20% in this experiment. Explain your answer.

For a **first order reaction**, time taken for 20% fall in partial pressure (concentration) is **independent of initial partial pressure (concentration).**
Partial pressure in **(a)(ii)** with 20% decrease = 0.80 atm.
Time taken for partial pressure to fall by 20% in **(a)(ii)** = 3 hr

(vi) There will be a negligible amount of SO_2Cl_2 (g) in the reaction vessel after a long period of time. Therefore, the content of the vessel might be considered to be a mixture of SO_2 and Cl_2 gases.

A possible way to separate SO_2 and Cl_2 from each other is to pass the mixture over solid CaO which will convert all the SO_2 to $CaSO_3$, a strong electrolyte. Calculate the pH of a 0.020 mol dm^{-3} $CaSO_3$ solution.
[For H_2SO_3 $K_{a1} = 1.7\times10^{-2}$ mol dm^{-3} and $K_{a2} = 6.4\times10^{-8}$ mol dm^{-3}.]

$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$

$K_b = 10^{-14} / 6.4\times10^{-8}$

$= 1.56 \times 10^{-7}$ mol dm^{-3}

$K_b = \dfrac{[HSO_3^-][OH^-]}{[SO_3^{2-}]} = \dfrac{x^2}{0.02}$ (since $[HSO_3^-] = [OH^-]$ and $x << 0.02$)

$[OH^-] = 5.59 \times 10^{-5}$ mol dm^{-3}

pH $= 14 - pOH$

$= 14 + \lg(5.59 \times 10^{-5})$

$= 9.75$

[12]

(b) Compound **G** has a sweet smell. When heated with an excess of acidified concentrated manganate(VII) ions, it forms initially three products **H**, **J** and **K**.

$$\underset{C_{13}H_{20}O_2}{\mathbf{G}} \xrightarrow{MnO_4^- / H^+} \underset{C_6H_8O_3}{\mathbf{H}} + \underset{C_5H_{10}O_2}{\mathbf{J}} + \underset{C_2H_2O_4}{\mathbf{K}}$$

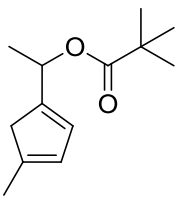
- When compound **G** was mixed with liquid bromine at room temperature, $C_{13}H_{20}O_2Br_4$ was obtained.

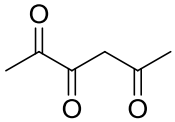
- Compound **J** evolves CO_2 with $NaHCO_3$. **J** also reacts with $LiAlH_4$ to give a compound which does not react with concentrated sulfuric acid.

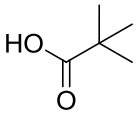
- Compound **H** gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent. **H** has no reaction with Tollens' reagent. When 1 mol of **H** reacts with an excess of alkaline aqueous iodine, 2 mol of yellow precipitate are produced.

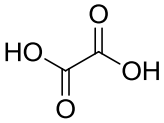
Use the information above to deduce the structures for compounds **G**, **H**, **J** and **K**.

G undergoes acid hydrolysis to give a carboxylic acid and an alcohol.
G is an ester.
G undergoes oxidative cleavage with MnO_4^-/H^+ to give **H**, **J** and CO_2.
G undergoes electrophilic addition with Br_2.
G is an alkene and contains two C=C bonds due to the addition of four Br atoms.
J undergoes neutralisation with $NaHCO_3$. Thus **J** is a carboxylic acid.
J undergoes reduction with $LiAlH_4$ to give a primary alcohol.
Primary alcohol cannot undergo elimination with conc H_2SO_4 as it has no H on the beta-C (C atom next to C with –OH group has no available H atom).
H undergoes condensation with 2,4-DNPH to give an orange ppt. Thus **H** is a ketone compound. Aldehyde group is absent since there is no reaction with Tollen's reagent.
H undergoes oxidative cleavage with I_2/OH^- to give CHI_3, the yellow ppt.
H contains two CH_3CO structural units.


G


H


J

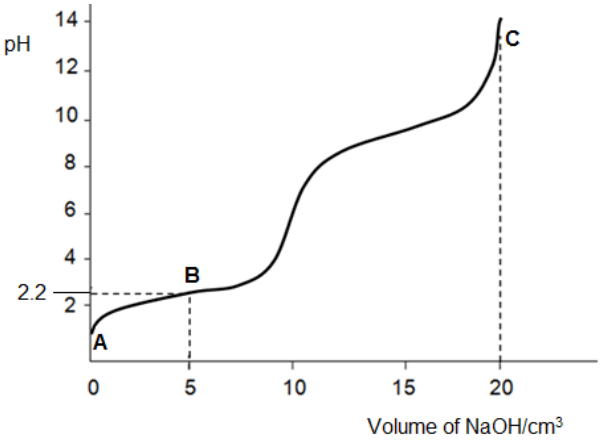

K

[8]

[Total: 20]

5 Amino acids are critical to life, and they serve as building blocks of proteins.

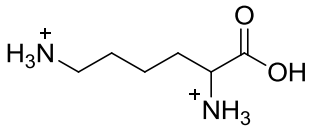
(a) Lysine is an alpha amino acid which shows both acidic and basic properties. The R group of lysine is $-(CH_2)_4NH_2$. In acidic solution, lysine is completely protonated. 10.0 cm^3 of completely protonated lysine is titrated with 1.00 mol dm^{-3} sodium hydroxide solution. Its titration curve is shown below.

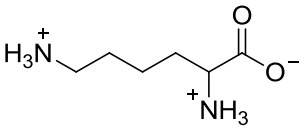


(i) Calculate the first dissociation constant K_{a1} of fully protonated lysine.

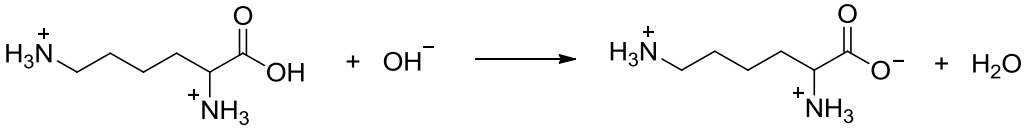
$pK_{a1} = 2.2$
$K_{a1} = 10^{-2.20}$
$= 6.31 \times 10^{-3}$ mol dm^{-3}

(ii) Identify the two species at point **B**. Write an equation to show how the species present at point **B** can resist change in pH when a small amount of base is added.



and


When base is added,



(iii) Calculate the pH when 10.0 cm^3 of 0.0200 mol dm^{-3} sodium hydroxide is added to the solution at point **B**. (You may represent the fully protonated lysine as HA.)

Number of moles of HA at point **A**= $1.00 \times \frac{10}{1000} = 1.00 \times 10^{-2}$ mol

At point **B**, $n_{HA} = n_{A^-}$

$= \frac{1.00 \times 10^{-2}}{2}$
$= 5.00 \times 10^{-3}$ mol

No of moles of NaOH added = $0.0200 \times \frac{10.0}{1000}$
$= 2.00 \times 10^{-4}$ mol

$HA + OH^- \rightarrow A^- + H_2O$

n_{HA} present after NaOH is added $= (5.00 \times 10^{-3}) - (2.00 \times 10^{-4})$
$= 4.80 \times 10^{-3}$ mol

n_{A^-} present after NaOH is added $= (5.00 \times 10^{-3}) + (2.00 \times 10^{-4})$
$= 5.20 \times 10^{-3}$ mol

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

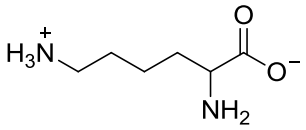
$$6.31 \times 10^{-3} = \frac{[H^+] \times 5.20 \times 10^{-3}}{4.80 \times 10^{-3}}$$

$[H^+] = 5.82 \times 10^{-3}$ mol dm^{-3}

pH = 2.24

(iv) State the predominant species at point **C**. Explain why it has a high melting point.

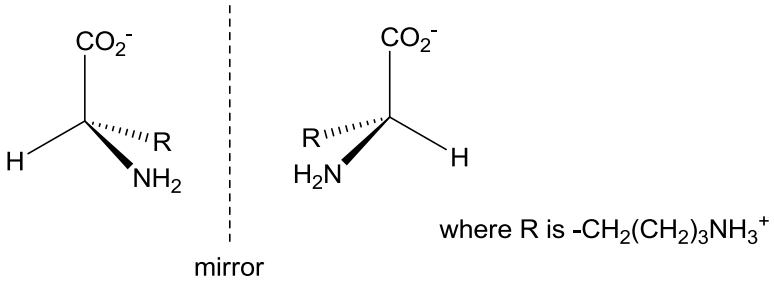
The predominant species at point **C** is a zwitterion, as given by the structure below.



A large amount of energy is required to overcome the **strong ionic bonds**.

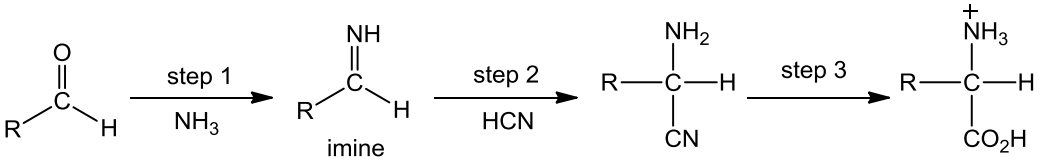
(v) State the type of isomerism in the species at point **C** and draw its isomers.

Optical isomerism



[8]

(b) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker.



(i) Name the type of reaction in step 1.

Condensation

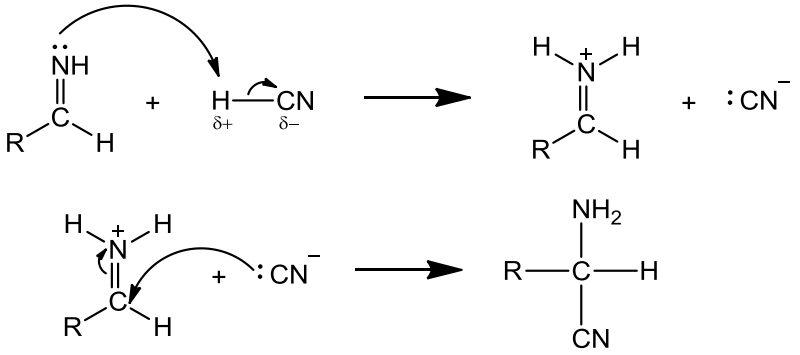
(ii) Suggest suitable reagents and conditions for step 3.

H_2SO_4(aq), reflux

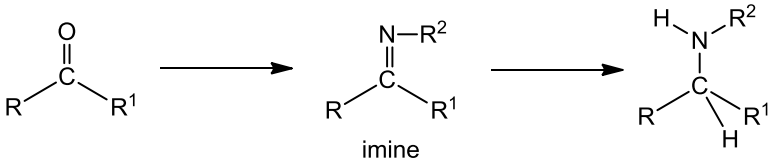
(iii) In step 2, the reaction proceeds via two stages:

(I) acid-base reaction between the N atom in imine and HCN
(II) nucleophilic attack on C by CN^-

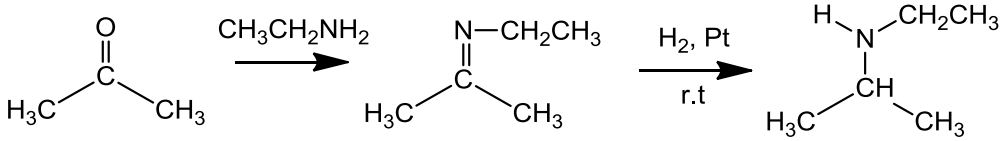
Write the mechanism for step 2, showing clearly the movement of electrons and partial charges.



(iv) An imine intermediate is also formed in preparing secondary amines from ketones.



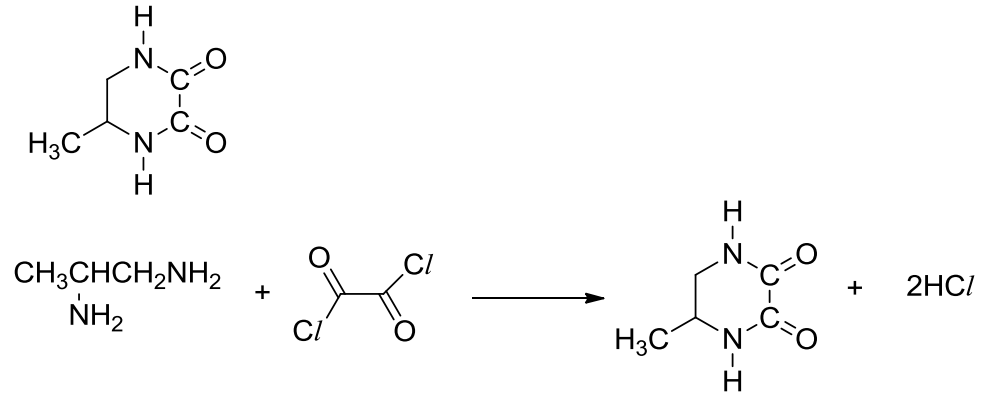
With reference to the Adolf Strecker synthesis, suggest the synthetic route by giving the reagents, conditions and intermediates for the preparation of $(CH_3)_2CHNH(CH_2CH_3)$.



Note: Can accept LiAlH$_4$ in dry ether, r.t. as reducing agent in second step

(v) Another amine **X**, $CH_3CH(NH_2)CH_2NH_2$ reacts with ethanedioyl dichloride $(COCl)_2$ to produce compound **Y** with molecular formula $C_5H_8N_2O_2$. Suggest the structure for compound **Y** and write the equation between **X** and ethanedioyl dichloride.

Suggest the structure for compound **Y** and write the equation between **X** and ethanedioyl dichloride.



[8]

[8]

(c) A polypeptide **H** was analysed and found to contain the following amino acids.

amino acid	aspartic acid	glycine	serine	tyrosine	valine
abbreviation	asp	gly	ser	tyr	val
number of residues	1	1	2	1	1

Analysis gave the following results:

- The N-terminus was shown to be ser.
- On reaction with the enzyme chymotrypsin, which hydrolyses at the carboxylic acid end of tyr, **H** gave two tripeptides.
- On reaction with a special reagent which digests at the carboxylic end of val, **H** gave two peptides. One of these two was a dipeptide of sequence gly-ser.

Determine the amino acid sequence of polypeptide **H**. Briefly justify your answer.
[You should use the same 3–letter abbreviations as shown above to write out the amino acid sequence].

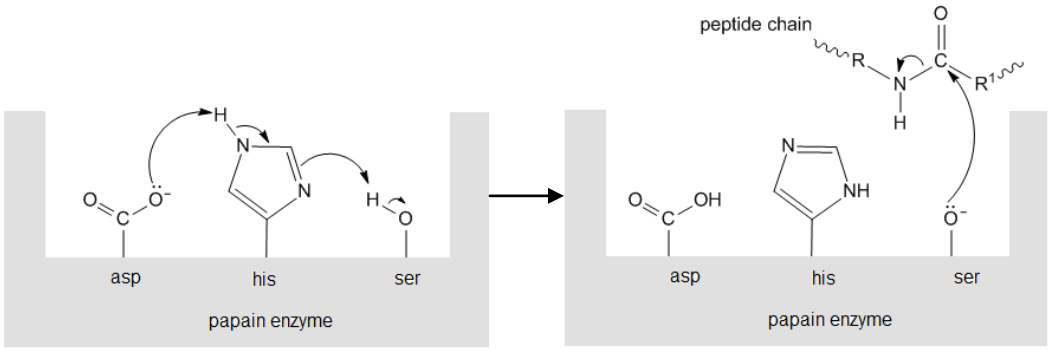
ser–asp–tyr–val–gly–ser

[Any 2 valid points from below]

H has 6 amino acids OR first amino acid on left is ser
Enzyme hydrolyses at carboxylic acid end of tyr gives 2 tripeptides, hence third amino acid from left is tyr.
Reagent digests at carboxylic end of val gave a tetrapeptide ending with val.
OR Tripeptide val–gly–ser is present.

[2]

(d) Papain, an enzyme in fresh papaya juice is used as a meat tenderiser. The three main amino acids involved in the catalytic activity of papain are his, asp and ser. Part of the mechanism of the action of papain is illustrated in the figures below.



(I) (II)

With reference to figures (I) and (II) above, explain why the action of this enzyme would be inhibited if the pH was too low.

When pH is low, $[H^+]$ is high.

CO_2^- of asp is <u>protonated</u> to form $-CO_2H$.

Proton on his cannot be abstracted.

O^- of ser in figure II cannot be formed.

$-OH$ is a weaker nucleophile than O^-. Hence, absence of O^- on ser prevent attack on peptide to occur.

[2]

[Total: 20]