CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

Wednesday 27 August 2014
2 hours

Additional Materials: Data Booklet
Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions. Write your answers on the answer paper provided.

You are reminded of the need for good English and clear presentation in your answers.

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

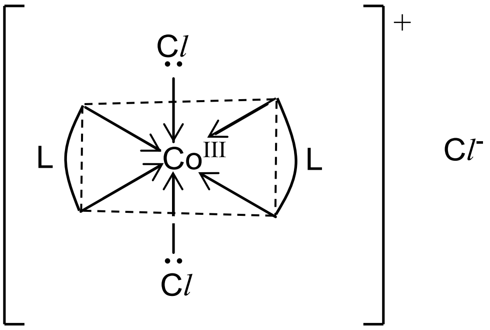
At the end of the examination, fasten all your work securely together.

Answers

[Turn over

Answer any **four** questions.

1 **(a)** When an aqueous solution of Co^{2+} is reacted with hydrochloric acid and ethane-1,2-diamine (en) under oxidising conditions, a green mixed-ligand cobalt(III) complex, $[Co(en)_2Cl_2]^+Cl^-$, with the following structure is formed:



, where L = en

(i) State the coordination number of the above complex.

6

(ii) Explain why the above complex is green in colour.

Co^{3+}: [Ar] $3d^6$

In the presence of ligands, the incompletely filled (or partially filled) 3d-orbitals become non-degenerate or split into 2 different energy levels. Hence d-d* electronic transition takes place as radiation in the red region of the visible spectrum is absorbed. The light energy not absorbed is thus seen as the colour of the complex, which is green.

(iii) When 0.03 mol of aqueous silver nitrate is added to 0.01 mol of the above aqueous complex, a white precipitate weighing 1.44 g is formed.

Identify and calculate the amount of precipitate formed. With reference to the structure of the above complex, explain the above observations fully.

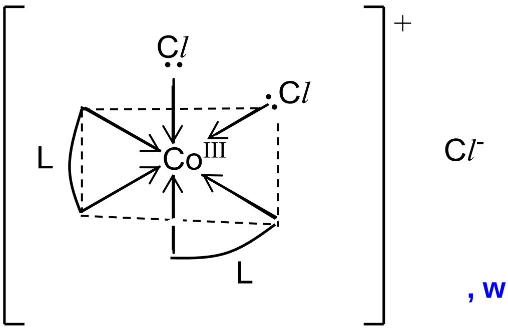
The white precipitate is AgC*l*.

No. of mol of AgC*l* $= \frac{1.44}{108+35.5} = 0.0100$ **mol**

AgC*l* $\equiv [Co(en)_2Cl_2]^+Cl^-$

Although $[Co(en)_2Cl_2]^+Cl^-$ has three chloride ions, only one of them is free to be precipitated out by Ag^+, as the other two are covalently bonded to Co^{3+}.

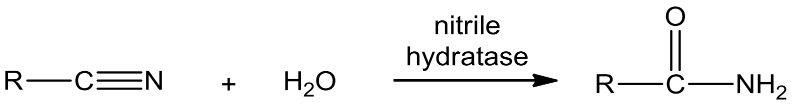
(iv) The formula $[Co(en)_2Cl_2]^+Cl^-$ may refer to a structure that is different from what is shown above.
Draw this other structure of $[Co(en)_2Cl_2]^+Cl^-$ and state its relationship with the above structure.



, where L = en

[9]

(b) Cobalt is also found in nitrile hydratase, a bacterial enzyme which catalyses the conversion of nitriles to their corresponding amides:

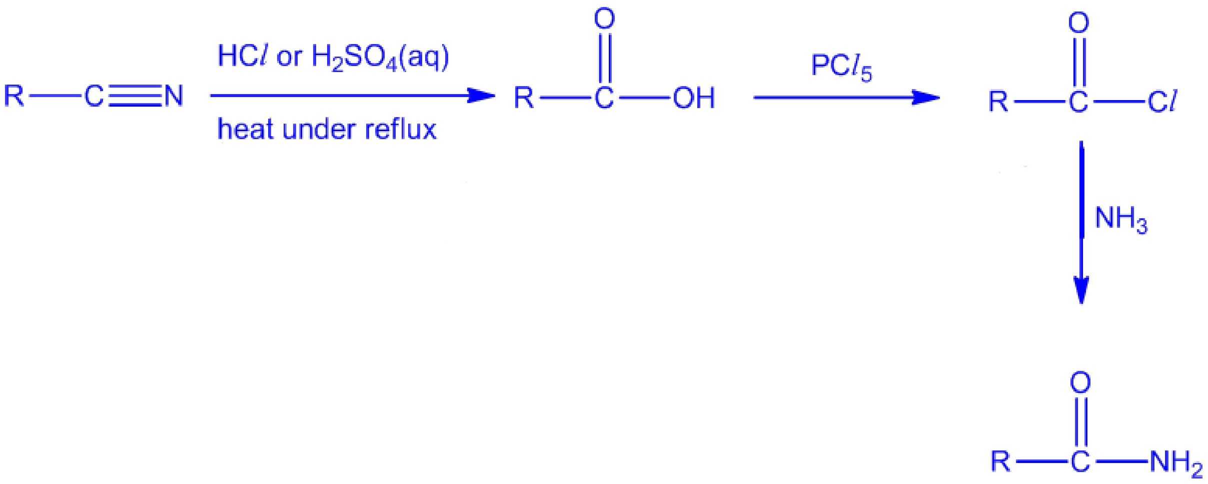


$$R{-}C{\equiv}N + H_2O \xrightarrow{\text{nitrile hydratase}} R{-}\overset{\overset{\large O}{\|}}{C}{-}NH_2$$

Nitrile hydratase has a quaternary structure with four subunits. Each pair of subunits binds a cobalt atom, which serves as a catalytic centre for the above reaction.

(i) Identify the type of reaction performed by nitrile hydratase, and propose a three-step synthesis pathway to perform the same conversion, stating clearly all intermediates, reagents and conditions.

Hydration/Addition of water/nucleophilic addition



** cannot be alcoholic or aqueous NH_3*

(ii) One way to obtain nitriles is to synthesize them from chloroalkanes. State the reagents and conditions required to carry out this synthesis.

KCN in ethanol, heat under reflux

(iii) Haemoglobin, like nitrile hydratase, has a quaternary structure.

With reference to the **haemoglobin** (Hb) molecule, describe and explain what is meant by the terms *secondary, tertiary* and *quaternary* structures of proteins. You should state the type of bonding or interaction involved in each case.

Secondary structure: α-helix
In the α-helix, the polypeptide chain coils in a helical manner, with hydrogen-bonding between the hydrogen of N-H of one peptide bond with the oxygen of C=O of another peptide bond holding the helix together.

Tertiary structure: The polypeptide chain bends and folds to give its overall 3-dimensional shape due to the R-group interactions between the R groups of the different amino acids in the polypeptide. These R-group interactions are: hydrogen bonding, ionic bonds, van der Waals forces, disulfide linkages .

Quaternary structure: There are four subunits of haemoglobin, each with its own haem group. Two are α subunits and the other two are β subunits . The subunits are brought together by van der Waals forces or similar R group interactions as tertiary structure of the subunits.

[11]

[Total: 20]

2 Most commercial chlorine is produced by the electrolysis of a concentrated aqueous sodium chloride solution in a *chloralkali cell*. An example of a *chloralkali cell* is the membrane cell as shown below.

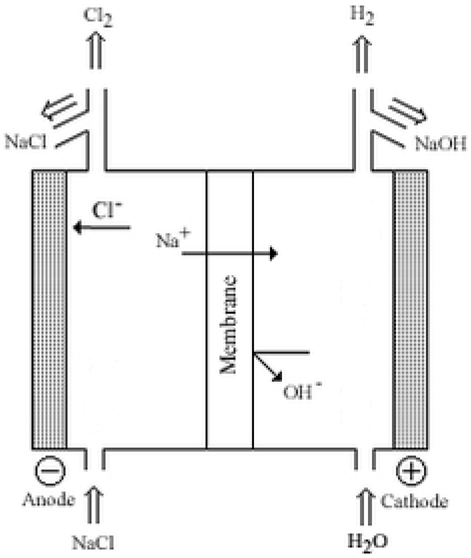


Diagram of a membrane cell

(a) **(i)** Write the ion-electron half-equations, with state symbols, for the reactions taking place at the anode and cathode.

Anode (oxidation): $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$

Cathode (reduction): $2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

(ii) Hence, deduce the overall reaction for the electrolysis of concentrated aqueous sodium chloride solution.

$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH$

OR

$2\ Cl^- + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ OH^-$

(iii) In the membrane cell, current was passed through the concentrated aqueous sodium chloride for 20 minutes. At room temperature and pressure, 450 dm^3 of chlorine gas was liberated at the anode.

Calculate the current used in the electrolysis.

Anode (oxidation): $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$

No. of moles of electrons involved = $\frac{450}{24}$ x 2

= 37.5 mol

Quantity of charge = 37.5 x 96500
= 3.62×10^6 C

Current used = $\frac{Q}{t} = \frac{3.62x10^6}{20x60}$
= 3.02×10^3 A

(iv) The anode and cathode compartments are separated by a polymeric ion-exchange membrane. The membrane can exchange cations, and only permits Na^+ ions to migrate from the anode to the cathode compartment.

With the aid of a balanced equation, state the reaction that occurs when the membrane is removed and the products are allowed to mix at the high temperature of the cell.

[7]

When the membrane is removed, the chlorine produced can undergo disproportionation with the OH^- ions.

Equation:

$3\ Cl_2 + 6\ NaOH \rightarrow 5\ NaCl + NaClO_3 + 3\ H_2O$

OR

$3\ Cl_2 + 6\ OH^- \rightarrow 5\ Cl^- + ClO_3^- + 3\ H_2O$

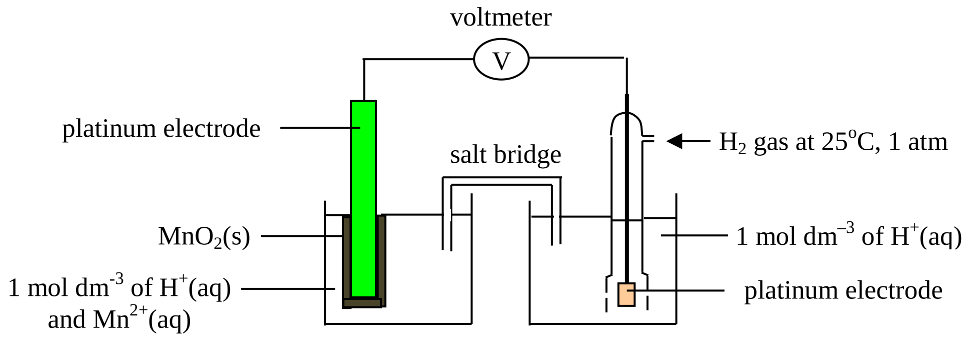
In the laboratory, chlorine can also be prepared by reacting concentrated hydrochloric acid with manganese(IV) oxide. The half-equation involving manganese(IV) oxide is shown below:

$$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons Mn^{2+}(aq) + 2\ H_2O(l) \qquad E^\ominus = +1.23\ V$$

(b) **(i)** Define the term *standard electrode potential*, $E^\ominus$.

***Standard electrode potential*, *$E^\ominus$*, is defined as the potential difference between a standard hydrogen electrode and a metal (the electrode) which is immersed in a solution containing metal ions at 1 mol dm^{-3} concentration at 25 °C and 1 atmospheric pressure.**

(ii) Describe with the aid of a labelled diagram, the set-up used to measure the standard electrode potential of manganese(IV) oxide and the reactions occurring at each electrode.



Reactions

Anode (oxidation): $H_2(g) \rightleftharpoons 2\ H^+(aq) + 2\ e^-$
Cathode (reduction): $MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons Mn^{2+}(aq) + 2\ H_2O(l)$

(iii) By selecting an appropriate E^θ value from the *Data Booklet*, explain why the reaction between hydrochloric acid and manganese(IV) oxide would **not** be expected to occur.

Oxidation half-equation: $2\ Cl^-(aq) \rightleftharpoons Cl_2(g) + 2\ e^-$ $E^\theta = -1.36$ V

$E^\theta_{overall} = E^\theta_{red} - E^\theta_{oxid} = +1.23 - 1.36$
$= -0.13$ V < 0 (hence unfeasible reaction)

(iv) Suggest a possible reason why the reaction does in fact occur.
This is the reaction is carried out using concentrated hydrochloric acid which is not under standard conditions .

[6]

(c) The composition of a mixture of **two** solid sodium halides was investigated in two separate experiments.

Experiment 1

When a large excess of chlorine gas was bubbled through a concentrated solution of the mixture, orange brown fumes and a black precipitate were produced.

Experiment 2

0.545 g of the solid mixture was dissolved in water and a large excess of silver nitrate solution was added. The mass of the mixture of silver halide precipitates formed was 0.902 g. After washing the mixture of precipitates with an excess of concentrated ammonia, the mass of the final precipitate was reduced to 0.564 g.

(i) With reference to **Experiment 1**, identify the two halides present in the mixture and explain why the reactions occur.

The halides present are <u>Br^-</u> (orange brown fumes of bromine) and <u>I^-</u> (black precipitate of iodine).

Chlorine gas is a <u>stronger oxidising agent</u>, and hence <u>displaces</u> the less reactive halogens from the mixture. (Or chlorine oxidises bromide to bromine and iodide to iodine)

(ii) *Use of the Data Booklet is required for this question.*

The atomisation of the reddish brown liquid produced in **Experiment 1** involves the vaporisation of the liquid, followed by the breaking of covalent bonds.

By constructing an energy cycle, calculate the standard enthalpy change of vaporisation of the reddish brown liquid.
[Given: $\Delta H^{\ominus}_{at}$ (reddish brown liquid) = +112 kJ mol^{-1}]

The reddish brown liquid is Br_2.

$$\begin{tikzcd}
\frac{1}{2}\ Br_2(l) \arrow[rr, "\frac{1}{2}\ \Delta H_{vap}(Br_2(l))"] \arrow[dr, "\Delta H_{at}(Br_2(l))"'] & & \frac{1}{2}\ Br_2(g) \arrow[dl, "\Delta H_{at}(Br_2(g))"] \\
& Br(g) &
\end{tikzcd}$$

By Hess' Law,

$$\frac{1}{2}\Delta H^{\ominus}_{vap}(Br_2(l)) + \tfrac{1}{2}(+193) = +112$$

$$\Delta H^{\ominus}_{vap}(Br_2(l)) = +31.0 \text{ kJ mol}^{-1}$$

(iii) Using data given in **Experiment 2**, calculate the mass of each halide ion present in the mixture.

[7]

AgI precipitate is <u>insoluble</u> in concentrated ammonia while AgBr precipitate is <u>soluble</u> in it.

Mass of AgI = 0.564 g

Mass of AgBr = 0.902 – 0.564
= 0.338 g

Amount of I^- = $\dfrac{0.564}{108+127}$

= 2.40×10^{-3} mol

Mass of I^- = 2.40×10^{-3} x (127)
= <u>0.305 g</u>

Amount of Br^- = $\dfrac{0.338}{108+79.9}$

= 1.80×10^{-3} mol

Mass of Br^- = 1.80×10^{-3} x (79.9)
= <u>0.144 g</u>

[Total: 20]

3 **(a)** *Use of the Data Booklet is relevant to this question.*

Lead(II) carbonate and zinc carbonate decompose on heating in the same way as calcium carbonate.

(i) Write an ionic equation for the thermal decomposition of the carbonate anions.

$CO_3^{2-} \rightarrow CO_2 + O^{2-}$

(ii) By listing the ionic radii of Zn^{2+}, Ca^{2+} and Pb^{2+}, suggest and explain the order of decomposition temperature of these three carbonates.

Zn^{2+} 0.074nm Ca^{2+} 0.099nm Pb^{2+} 0.120nm

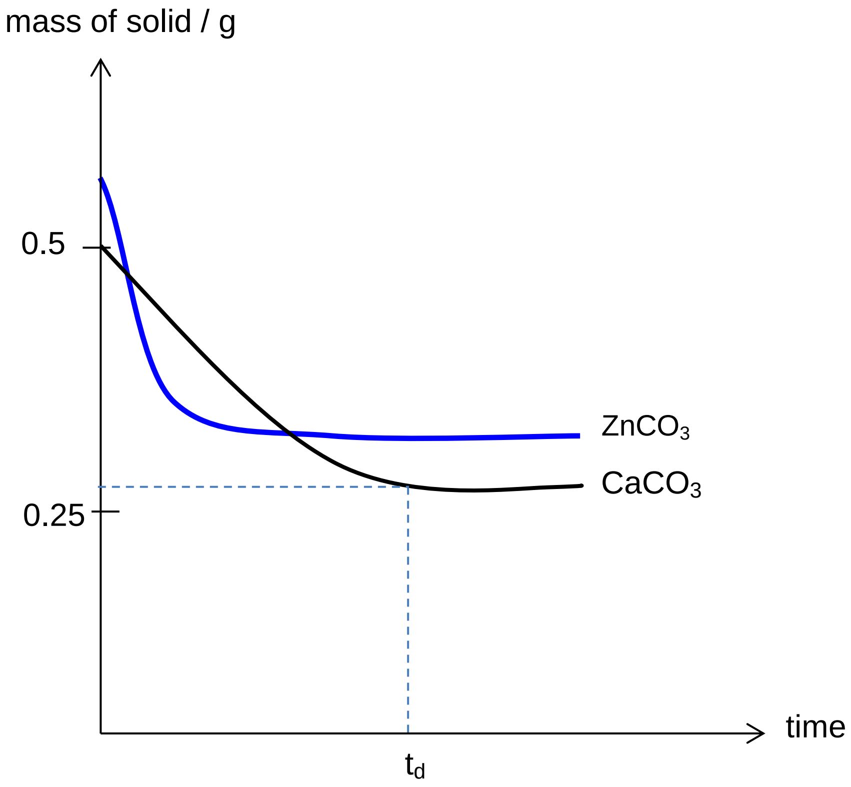
Ionic size $Zn^{2+} < Ca^{2+} < Pb^{2+}$

Zn^{2+} has the highest charge density as it has the smallest ionic radius and thus polarises the C-O bond most and the C-O bond is the weakest. Hence $ZnCO_3$ would have the lowest decomposition temperature.

Decomposition temperature $ZnCO_3 < CaCO_3 < PbCO_3$

(iii) The graph below shows the decomposition of $CaCO_3$. Copy the graph and on the same axes, sketch the graph when the same number of moles of $ZnCO_3$ was heated under the same conditions.

t_d is the time taken for the complete decomposition of $CaCO_3$.



[6]

(b) Methanoic acid occurs naturally in ants. Ants secrete methanoic acid for attack and defense purposes. To treat ant stings, bicarbonate of soda (sodium hydrogencarbonate) is often used.

(i) Write the equation for the reaction between sodium hydrogencarbonate and methanoic acid.

$NaHCO_3 + HCO_2H \rightarrow HCO_2^-Na^+ + CO_2 + H_2O$

When an ant bites, it injects a solution containing 50% by volume of methanoic acid. A typical ant may inject around 6.0×10^{-3} cm^3 of this solution.

(ii) Given that the density of methanoic acid is 1.2 g cm^{-3}, calculate the number of moles of methanoic acid a 'typical ant' injects.

$$1.2 = \frac{\text{mass of methanoic acid}}{6.0 \times 10^{-3} \times 0.5}$$

Mass of methanoic acid = $1.2 \times 6.0 \times 10^{-3} \times 0.5 = 0.0036$ g
Amount of methanoic acid = $0.0036 / 46 = 7.83 \times 10^{-5}$ mol

(iii) As soon as the methanoic acid is injected, it dissolves immediately in 1.0 cm^3 of water in the body to produce an aqueous solution of methanoic acid. The pH of the methanoic acid solution produced is 2.43.
Calculate the acid dissociation constant, K_a for methanoic acid.
$[H^+] = 10^{-2.43} = 0.003715$ mol dm^{-3}

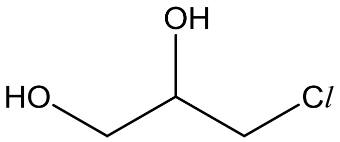
$$Ka = \frac{[H^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{0.003715^2}{(7.83 \times 10^{-5}) \div (\frac{1}{1000})}$$

$= 1.76 \times 10^{-4}$ mol dm^{-3} (or 1.85×10^{-4} mol dm^{-3} if no assumption was made)

Assumption: *$[HCO_2H]eqm = [HCO_2H]initial$ in the calculation as HCO_2H is a weak acid and only partially dissociates.*

(c) 3-monochloro-1,2-propanediol (3-MCPD) is used as a raw material for the synthesis of several drugs such as guaifenesin and atorvastatin.



3-MCPD

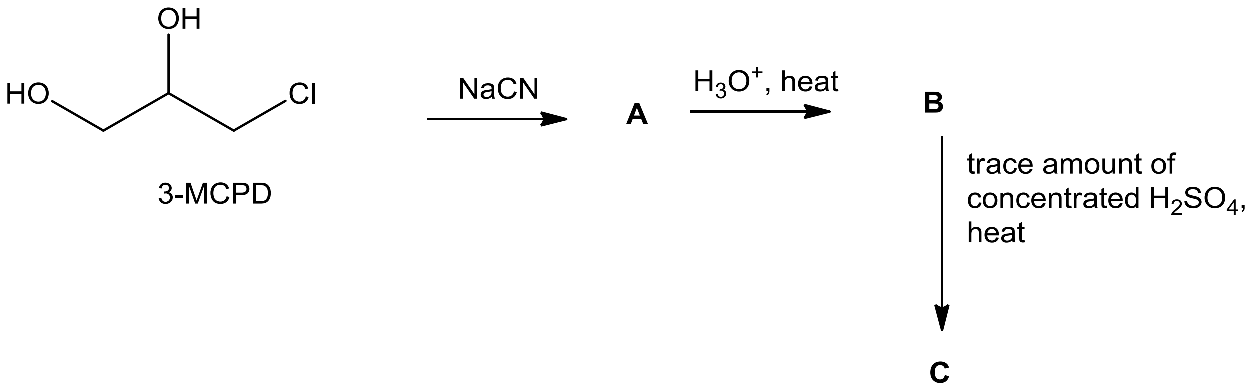
(i) State and explain how the acidities of 3-MCPD and methanoic acid would compare with each other.

Methanoic acid is a stronger acid than 3-MCPD.

The negative charge of the methanoate ion is dispersed over two O atoms and thus the conjugate base is stabilised(or resonance stabilised) and less likely to accept back the H^+.

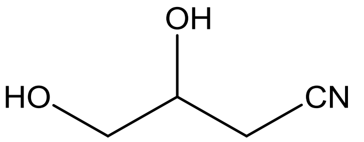
Alternative answer: The O–H bond in methanoic acid is more polarised as it is closer to another electronegative/electron-withdrawing O atom. The O-H bond is weaker and easier to break. Thus, methanoic acid is a stronger acid than 3-MCPD.

The following shows a reaction scheme involving 3-MCPD.

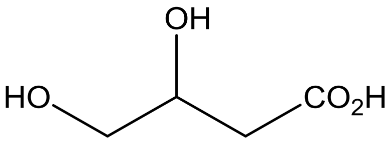


(ii) Suggest the structures of compounds **A** – **C**.

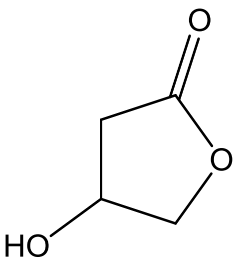
A



B



C

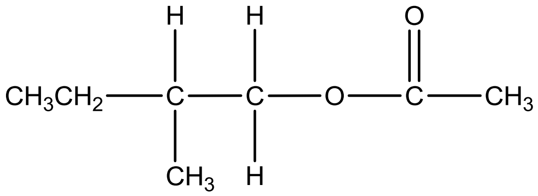


[5]

(d) An organic compound **E** is used as a flavouring and has the molecular formula $C_7H_{14}O_2$. **E** reacts with hot aqueous sodium hydroxide to form sodium ethanoate and compound **F**, $C_5H_{12}O$, which contains a chiral carbon. Compound **F** can be oxidised to $C_5H_{10}O_2$ by heating under reflux with acidified potassium dichromate(VI). Draw the structures of **E** and **F** and explain the reactions involved.

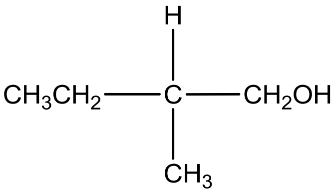
[4]

E:



$CH_3CH_2CH(CH_3)CH_2OCOCH_3$

F:



$CH_3CH_2CH(CH_3)CH_2OH$

E is an <u>ester</u> and undergoes <u>alkaline hydrolysis</u> to give carboxylate salt and an alcohol.

F undergoes oxidation with acidified $K_2Cr_2O_7$ to give a carboxylic acid => F is a <u>primary alcohol</u>

[Total: 20]

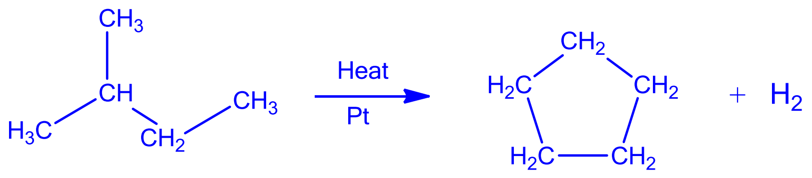
4 Methylbutane is an extremely volatile and flammable liquid at room temperature and pressure. When mixed with other compounds, methylbutane is often used in applications such as gasoline additives and cosmetics.

	pentane	methylbutane	cyclopentane	hydrogen
M_r	72	72	70	2
boiling point / ^oC	36.0	27.7	49.2	-252.9
standard molar entropy / J K^{-1} mol^{-1}	263	260	205	131

(a) **(i)** Explain the difference in boiling points between methylbutane and pentane.

The boiling point in methylbutane is lower compared to pentane due to branching in the molecule leading to lesser surface area of contact between methylbutane molecules and hence less extensive/weaker van der Waal/instantaneous dipole-induced dipole/London forces of attraction . Hence, less energy is required to overcome the forces of attraction leading to lower boiling point for methylbutane compared to pentane which is straight-chain molecule.

(ii) Methylbutane can undergo a process of catalytic reforming at 500 ^oC in the presence of platinum catalyst to form cyclopentane. By displaying the structural formula, show a balanced equation for the reaction and use bond energy values from the *Data Booklet* to calculate the enthalpy change for this reaction.



bonds broken (endothermic)		**bonds formed (exothermic)**	
4 C-C	**4(+350)**	**5 C-C**	**5(-350)**
12 C-H	**12(+410)**	**10 C-H**	**10(-410)**
		1 H-H	**(-436)**

$\Delta H = +6320 - 6286 = +34\ kJ\ mol^{-1}$

(iii) Calculate the standard entropy change, ΔS, for the reaction in **(ii)** and explain the significance of the sign of ΔS at the conditions where the reaction is taking place.

$\Delta S_{rxn} = \Sigma\, \Delta S_{products} - \Sigma\, \Delta S_{reactants}$

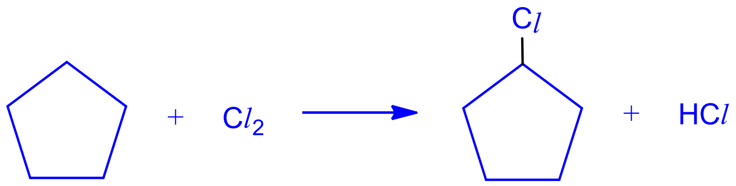
ΔS_{rxn} = (205 + 131) – (260) = <u>+76 J K^{-1} mol^{-1}</u>

ΔS_{rxn} is positive, indicating that the system becomes more disordered / less ordered because there is an <u>increase in number of gaseous particles from 1 mol to 2 mol</u> at conditions (high temperature) where the reaction is taking place.

[6]

(b) Cyclopentane is a highly flammable alicyclic hydrocarbon and occurs as a colourless liquid with a petrol-like odour. When yellow-green chlorine gas is passed through excess cyclopentane in ultraviolet light, the mixture slowly becomes pale yellow and steamy white fumes appear above the liquid.

(i) Explain these observations and write a balanced equation, showing the structural formulae for relevant compounds in the overall reaction.



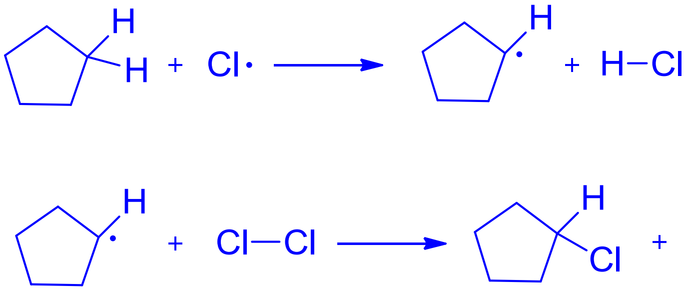
Cyclopentane undergoes free radical substitution reaction with Cl_2. Yellow-green Cl_2 dissolves in liquid cyclopentane to form a pale yellow solution and <u>steamy white fumes of HCl gas</u> is formed.

(ii) Name and describe the mechanism involved in the reaction.

Free radical substitution mechanism, with Cl• as the free radical.

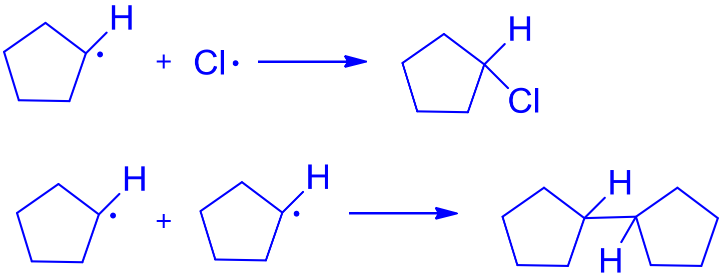
Initiation:

Propagation:



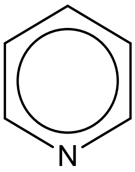
Termination:

$Cl\cdot + Cl\cdot \rightarrow Cl-Cl$



[6]

(c) Pyridine is a heterocyclic aromatic compound structurally and chemically similar to benzene. It is used as a precursor to agrochemicals and pharmaceuticals and is an important solvent for many organic compounds. Pyridine is a colourless liquid that is miscible in water and boils at 115.2 °C and freezes at −41.6 °C.



pyridine

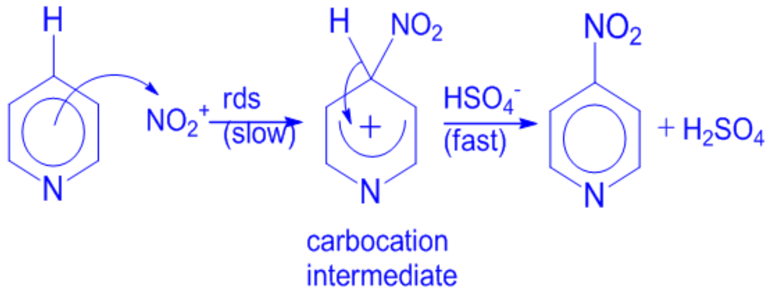
(i) Explain why pyridine is miscible in water.

Pyridine contains a nitrogen atom with a lone pair of electrons that is able to form hydrogen bond with the electron deficient hydrogen atoms in water molecules.

(ii) Name and describe the mechanism that pyridine undergoes with a mixture of concentrated nitric acid and concentrated sulfuric acid.

electrophilic substitution reaction

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$



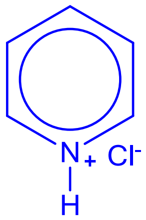
(iii) Explain why pyridine does not undergo the reaction in **(ii)** as readily as benzene.

Electronegative nitrogen atom in pyridine withdraws electron away from the ring and hence deactivates the ring towards electrophilic attack, making it less susceptible to undergo electrophilic substitution.

(iv) Excess pyridine reacts with chlorocyclopentane to form cyclopentene and another compound **A** with M_r 115.5, which is ionic in nature.

I. Suggest the structure of **A**.
II. State the role of pyridine in the reaction.
III. Name the type of reaction that has occurred to form cyclopentene.

I.



II. Base

III. Elimination/dehydrohalogenation

[8]

[Total: 20]

5 The mechanism of the Haber Process for the manufacture of ammonia is imperfectly understood. A complete understanding of this process might lead to the development of catalysts which could operate at room temperature and pressure instead of the existing industrial conditions of 450 – 500 °C and 250 – 300 atm.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = \text{negative}$$

(a) Explain clearly the reasons why the Haber Process is operated at the stated conditions of temperature and pressure.

The production of NH_3 is <u>exothermic</u>. Therefore, low temperature is needed to increase the yield of NH_3. However, if too low a temperature is used, the rate of production of NH_3 would be too slow to be economical. Therefore, a <u>relatively high temperature</u> of 450 – 500 °C is needed to <u>increase the rate</u> of reaction though the yield is reduced.

High pressure pushes the <u>position of equilibrium to the right</u> as production of NH_3 results in reduction in volume (4 volumes → 2 volumes). Therefore, the yield of NH_3 is increased. Also, at high pressure, the rate of production of NH_3 is increased. However, only <u>moderately high pressure</u> of 250 – 300 atm is used because if too high a pressure is used, the cost of constructing and maintaining equipment and structures would be too expensive.

[2]

(b) Another contributing factor to the cost of producing ammonia is the cost incurred in the synthesis of hydrogen. Natural gas is a common starting material for the production of hydrogen and the overall reaction is summarised by the equation:

$$CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$$

$$[\Delta H_f \text{ / kJ mol}^{-1}\text{: } CH_4 = -75 \text{ ; } H_2O(g) = -242 \text{ ; } CO_2 = -394]$$

By making use of the enthalpy change of formation data given, calculate the enthalpy change for the above reaction and hence explain why the cost of the synthesis of hydrogen is high.

	$CH_4(g)$	+	$2H_2O(g)$	→	$CO_2(g)$	+	$4H_2(g)$
ΔH_f/kJ mol^{-1}:	**-75**		**2(-242)**		**-394**		**0**

$$\Delta H_r = -394 - [-75 + 2(-242)]$$
$$= +165 \text{ kJ mol}^{-1}$$

The production of H_2 from natural gas (CH_4) is endothermic (+165 kJ mol^{-1}). Therefore, the cost factor to consider is the heat energy required to produce H_2.

[2]

(c) The rate of catalytic decomposition of ammonia on tungsten to nitrogen and hydrogen has been studied at 1400 K. From an initial pressure of ammonia at 40 kPa, the total pressure, **p**

of the reaction mixture, rose as the decomposition takes place over a period of time, as follows.

Time, t/s	0	250	500	750
Total pressure, **p**/kPa	40	50	60	70
Partial pressure of NH_3, p_{NH3}/kPa				

(i) Show that the partial pressure of NH_3, p_{NH3} at time, t is given by the expression, $p_{NH3} = (80 - \mathbf{p})$ kPa and hence insert the values of p_{NH3} in the empty spaces above. Copy these values on your writing paper.

	$2NH_3(g)$	$\rightleftharpoons$	$N_2(g)$ +	$3H_2(g)$
Initial pressure/kPa:	**40**		**0**	**0**
Pressure at time, t/kPa:	**40 – 2p’**		**p’**	**3p’**

Total pressure at time, t = (40 – 2p’) + p’ + 3p’

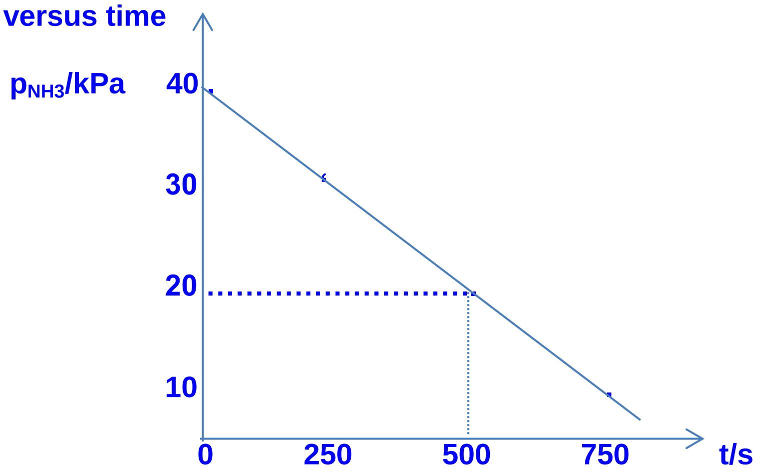
$$p = 40 + 2p'$$
$$2p' = p - 40$$

$$p_{NH3} = 40 - 2p'$$
$$= 40 - (p - 40)$$
$$= 80 - p$$

Partial pressure of NH_3, p_{NH3}/kPa	**40**	**30**	**20**	**10**

(ii) From the values of p_{NH3}, derived above, determine graphically or otherwise, the order of reaction with respect to ammonia. Explain how you arrived at your answer.

Plot p_{NH3} versus time



The plot/sketch of the partial pressures of NH_3 against time gives a straight line, indicating that the rate of decomposition of NH_3 is constant and therefore the reaction is zero order.

(alternative ans: constant decrease in pressure of NH_3 for a fixed time interval, thus rate of decomposition of NH_3 is constant)

(iii) Hence, calculate the rate constant for the reaction, stating the units.

Rate = $k[NH_3]^o = k$
Rate constant = rate = gradient of straight line

From graph/sketch/calculation, rate constant, $k = \frac{20}{500} = 0.04$ kPa s^{-1}

(iv) Explain why the pressure would not be exactly 80 kPa after 1000 s.

A total pressure of 80 kPa means that all the NH_3 molecules would have decomposed to form N_2 and H_2. But the reaction is reversible, so some NH_3 will be reformed. Therefore decomposition of NH_3 cannot be complete and so the total pressure would not be exactly 80 kPa after 1000 s.

[8]

(d) ***Citral***, a constituent of lemon-grass oil, is a naturally occurring compound. It gives a silver mirror with Tollens' reagent.

When 0.100 g of ***citral*** is catalytically hydrogenated at 0 °C and 1 atm, 44.2 cm^3 of hydrogen react to give $(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CH_2OH$, with a relative molecular mass of 158.

Oxidation of ***citral*** with hot acidified potassium manganate(VII) gives initially three compounds, **F**, $C_2H_2O_4$, **G**, C_3H_6O, and **H**, $C_5H_8O_3$.

Suggest structures for **citral** and compounds **F**, **G** and **H** from the information given above. Explain your reasoning.

[High marks can be scored for appropriate chemistry in this part of the question without a complete structure for ***citral***]

[8]

Citral **gives a positive test with Tollens' reagent suggests that it contains an aldehyde group, –CHO.**

The amount of H_2 used will indicate the degree of unsaturation (the number of C=C double bonds) and the reduction of –CHO to $–CH_2OH$.

Amount of H_2 used = $\frac{44.2}{22400}$ = 1.97×10^{-3} mol

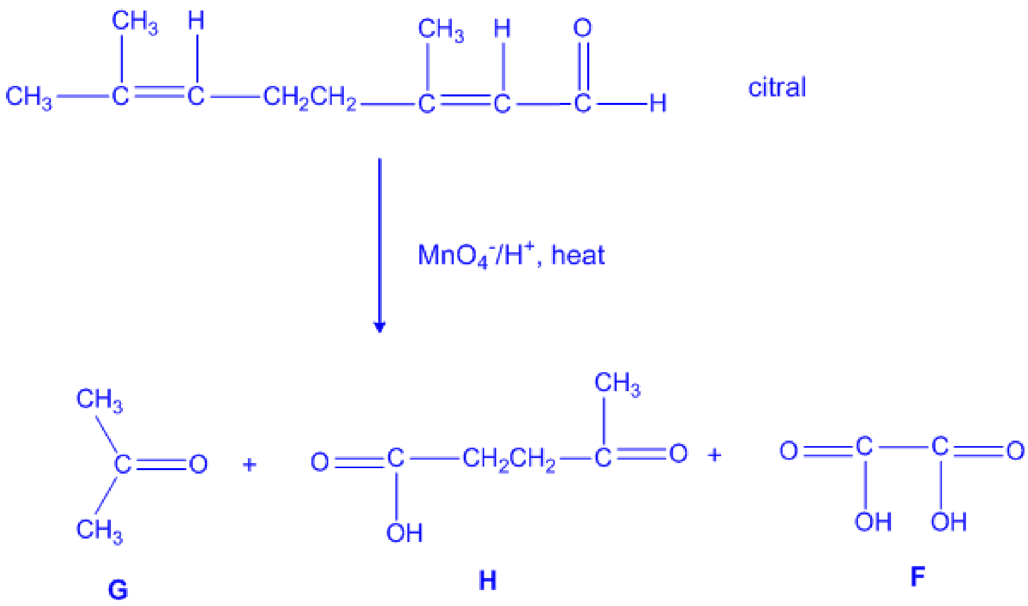
Let the number of mol of H_2 used to react with 1 mol of *citral* be n mol.

Citral	+	n H_2	→	$(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CH_2OH$
0.100 g		1.97×10^{-3} mol		$M_r = 158$
$= \frac{0.100}{158-2n}$ mol				

$$n = 1.97 \times 10^{-3} \div \frac{0.100}{158-2n} = 3$$

Therefore citral has 2 C=C groups and 1 –CHO group.

Vigorous oxidation of *citral* by MnO_4^-/H^+ gives $C_2H_2O_4$, C_3H_6O and $C_5H_8O_3$, hence *citral* is likely to be:



[Total: 20]