2

Answer any **four** questions.

1 (a) Liquid bromine is added to propenyl ethanoate $CH_2=CHCH_2OCOCH_3$ in presence of concentrated ethanoic acid which acts as a solvent, slowly enough for the reaction to be followed by usual laboratory techniques. The following results were obtained at 25 ^oC. **[10]**

Experiment Number	[propenyl ethanoate]/mol dm^{-3}	$[Br_2]$/mol dm^{-3}	Rate/ mol dm^{-3} s^{-1}
1	4.0×10^{-2}	2.0×10^{-2}	1.29×10^{-3}
2	6.0×10^{-2}	2.0×10^{-2}	1.94×10^{-3}
3	4.0×10^{-2}	4.0×10^{-2}	5.16×10^{-3}

(i) Write the equation for the addition of bromine to propenyl ethanoate

(ii) Deduce the order of reaction with respect to propenyl ethanoate and bromine and hence write the rate equation for the reaction.

(iii) Estimate how long it would take for 1% of ester to react in Experiment Number 3.

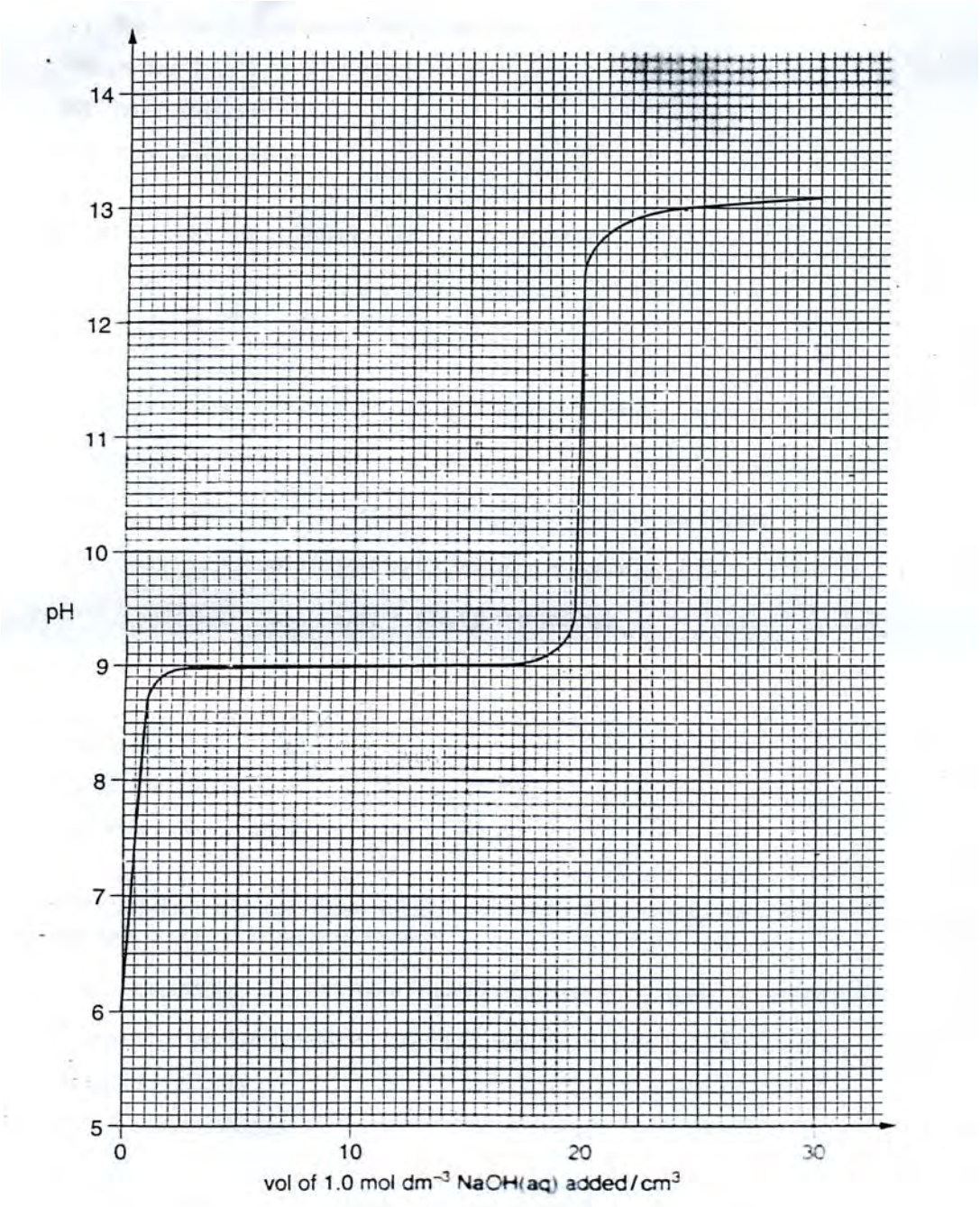
(iv) Experiment Number 1 was repeated with 2.0×10^{-2} mol dm^{-3} bromine under the same experimental condition, but using 4.0×10^{-2} mol dm^{-3} $CH_2=CHCHClOCOCH_3$ instead. Would you expect any change to the rate? Suggest a reason for this change if any.

(v) What would be the product if water were to be used as a solvent instead of concentrated ethanoic acid?

(vi) Would you expect the rate of reaction to be slower or faster if aqueous bromine were to react with propenyl ethanoate? Suggest a reason.

3

(b) In an experiment, 50.0 cm^3 of aqueous magnesium chloride were titrated with 1.00 mol dm^{-3} sodium hydroxide. The pH of the solution changed as shown in the diagram below. **[10]**



4

(i) Calculate the initial concentration of magnesium chloride.

(ii) When 10.0 cm^3 of NaOH have been added, calculate the

(a) hydroxide ion concentration
(b) hydrated magnesium ion concentration

Hence, calculate the solubility product of magnesium hydroxide.

(iii) Suggest how, if at all, the pH of a saturated solution of $Mg(OH)_2$ would change if the temperature were to be increased given that K_{sp} of $Mg(OH)_2$ decreases with increasing temperature.

(iv) By means of an equation, explain why initial pH of graph starts at 6.

[Total: 20 marks]

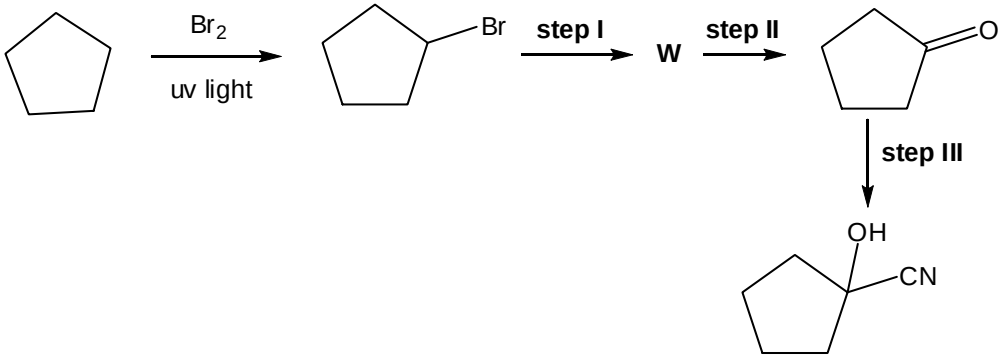
5

2 **(a)** A cycloalkane, C_5H_{10}, gives only two mono-brominated products (ignoring any stereoisomers) with Br_2 under uv light. **[3]**

(i) Give the structural formulae of the cycloalkane and the two mono-brominated products formed.

(ii) Suggest the ratio in which the two mono-brominated products will be formed.

(b) Cyclopentane is an isomer of the cycloalkane identified in **(a)(i)**. It can be used to synthesise a cyanohydrin. **[7]**



(i) Step **I** is a first order reaction. Write a balanced equation for the reaction, stating suitable reagents and conditions required. Hence, state the rate equation of the reaction.

(ii) State the reagents and conditions required in step **III**. Describe the mechanism involved.

(c) Aluminium is obtained from electrolysis of aluminium oxide which is mainly from the mining the mineral bauxite. Bauxite contains only 30 to 54% aluminium oxide and the rest being other solid impurities. Hence, bauxite must be purified prior to electrolysis. The Bayer process is the principal industrial means of refining bauxite to produce pure aluminium oxide. **[10]**

(i) In order to separate aluminium oxide from the other solid impurities in bauxite, it is digested by washing with a hot solution of sodium hydroxide under pressure followed by filtration in the Bayer process. Write a balanced equation with state symbols for the chemical reaction above.

(ii) In the subsequent step of the Bayer process, the above solution is cooled and treated by bubbling carbon dioxide into it, through which a solid is precipitated. When heated to a high temperature, this solid decomposes to aluminium oxide, giving off water vapour in the process. Identify the solid and write a balanced equation with state symbols for its formation.

(iii) The purified bauxite ore of aluminium oxide is continuously fed into the electrolysis process and cryolite is added to lower the melting point and dissolve the ore.
Write half-equations for the reactions at the cathode and anode during electrolysis.

6

(iv) Aluminium cannot be produced by the electrolysis of an aqueous aluminium salt. Instead, a molten aluminium salt could be used. In the Hall–Héroult process, aluminium oxide is dissolved in molten cryolite, Na_3AlF_6 and electrolysed.
Explain

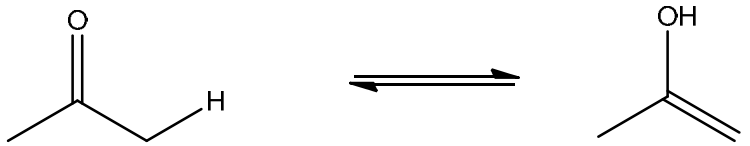
- why it is not feasible to obtain aluminium by the electrolysis of the aqueous aluminium salt;
- why cryolite is added in the electrolysis of aluminium oxide.

(v) A proposed aluminium plant is expected to consume 1.00×10^8 kg of bauxite per year. Assuming that the bauxite contains 54 % of aluminium oxide, calculate the mass of aluminium produced and the total amount of charge (in C) that flows through the electrolytic cell per year.

[Total: 20 marks]

7

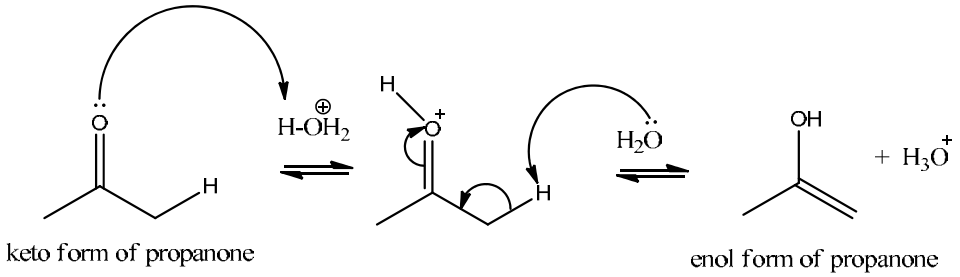
3 (a) For most aldehydes and ketones, the most stable structural isomer has a C=O bond and this is called the keto form. The enol form of the aldehyde or ketone is derived from the keto form by transfer of a hydrogen atom and it has a C=C bond with an OH substituent. This interconversion between the keto and enol forms is called keto-enol tautomerism. At normal room conditions the keto form is the predominant form at equilibrium suggesting that the keto form is the more stable form. **[2]**



keto form of propanone enol form of propanone

Using bond energy data from the data booklet, calculate the energy change for the above interconversion and hence explain why the equilibrium lies heavily towards the keto form.

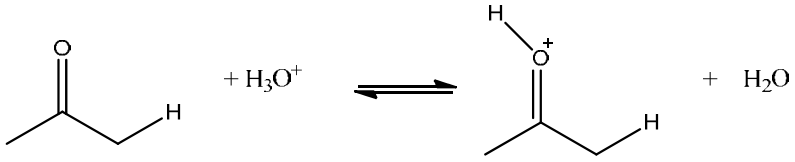
(b) The above conversions can be **catalysed by an acid** which involves protonation of oxygen atom of the C=O bond followed by loss of H^+ from the α-position as shown in the mechanism below **[7]**



keto form of propanone enol form of propanone

Equilibrium 1 **Equilibrium 2**

The first equilibrium step in the above mechanism can be written in a simplified form as given below:



…Equilibrium 1

(i) Given that all the equilibriums concerned are in a homogeneous system, write the K_a expressions for the acid dissociation of H_3O^+, and $(CH_3)_2C{=}OH^+$

(ii) Hence, by combining the two expressions, obtain the K_c expression for equilibrium 1.

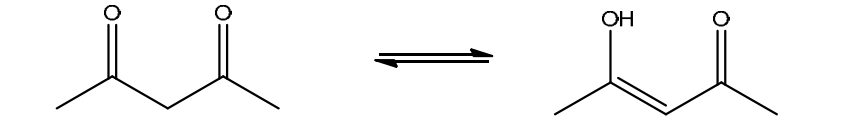
(iii) Given that the pKa of H_3O^+ is -1.7 and the pKa of $(CH_3)_2C{=}OH^+$ is -7.2, calculate the K_c for the above equilibrium.

8

(iv) Given that $\Delta G^o = -RT \ln K$, calculate the Gibbs Free energy change for the above equilibrium.

(v) Based on your answers to the values of ΔG^o and K_c, comment on the relative stability of the keto form versus the enol form.

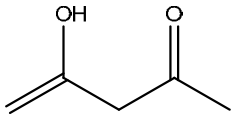
(c) It has been observed that the enol form of 1,3-dicarbonyl compounds are unusually stable and hence the equilibrium lies more towards the enol form as in the case of pentane-2,4-dione. It is also observed that the percentage of the enol form increases as the solvent used is changed from a polar solvent to a non polar solvent. **[5]**



keto form of pentane-2,4-dione enol form of pentane-2,4-dione

(i) By comparing the structures of the enol form of pentane-2,4-dione with its keto form , suggest a reason for the increased stability of the enol form in pentane-2,4-dione.

(ii) Another enol form of pentane-2,4-dione, as shown below can also be drawn.



another enol form of pentane-2,4-dione

Can this enol form likely to be formed also? Explain.

(iii) Explain why the keto form is favoured with polar solvents.

(d) A hydrocarbon, P, of molecular mass 132, contains 90.91% by mass of carbon. It does not react with cold aqueous potassium manganate (VII). However, P with hot acidified potassium manganate (VII) yields Q, with the molecular formula, $C_8H_6O_4$. One mole of Q reacts exactly with one mole of Na_2CO_3 giving off a colourless gas. Heating Q to about 250 ^oC yields a neutral compound, R, with a molecular formula of $C_8H_4O_3$. Reaction of R with one molar equivalent of ethanol forms a compound that is both an ester and an acid. Deduce with reasoning the structural formulae of P, Q and R. Write appropriate balanced equations where relevant. **[6]**

4 (a) (i) Write the **full** electronic configuration for Cu^+ and Cu^{2+} ions. **[1]**

(ii) Explain why $Cu^+(aq)$ is colourless whereas $Cu^{2+}(aq)$ is coloured. **[2]**

(iii) Describe what is seen when dilute $NH_3(aq)$ is added slowly to $CuSO_4(aq)$ until in excess. Write balanced equations for the reactions. **[4]**

(iv) Describe what is seen (including intermediate colour) when concentrated HCl(aq) is added to $CuSO_4(aq)$. Write balanced equation for the reaction. **[2]**

(v) Describe what is seen when KI(aq) is added to $CuSO_4(aq)$. Write balanced equation for the reaction. **[2]**

(vi) Copper(I) oxide is the brick-red precipitate formed when Fehling's solution oxidises an aldehyde. When dilute $H_2SO_4(aq)$ is added to this oxide, a brown solid and a blue solution is formed.

Explain this observation with appropriate E^θ values from the *Data Booklet*. Write balanced equation for the reaction of this oxide with the acid. State the **two types** of reactions occurring here. **[3]**

(b) Vanadium is the only element that has four successive oxidation states that are all stable in aqueous solution. **[5]**

Colours of vanadium ions are given as follows.

Specie	$V^{2+}(aq)$	$V^{3+}(aq)$	$VO^{2+}(aq)$	$VO_2^+(aq)$ or $VO_3^-(aq)$
Colour	Violet	Green	Blue	Yellow

By selecting appropriate E^θ values from the *Data Booklet*, describe and explain the series of colour changes when $(NH_4)_2Ce(NO_3)_6(aq)$ is added slowly to $VCl_2(aq)$. Write balanced equations for all reactions.

Reduction electrode potential for $Ce^{4+}(aq) / Ce^{3+}(aq)$ is +1.61V.

Colours of $Ce^{4+}(aq)$ and $Ce^{3+}(aq)$ are yellow and colourless respectively.

It is given that solid NH_4VO_3 dissolves in dilute $H_2SO_4(aq)$ to give a yellow solution.

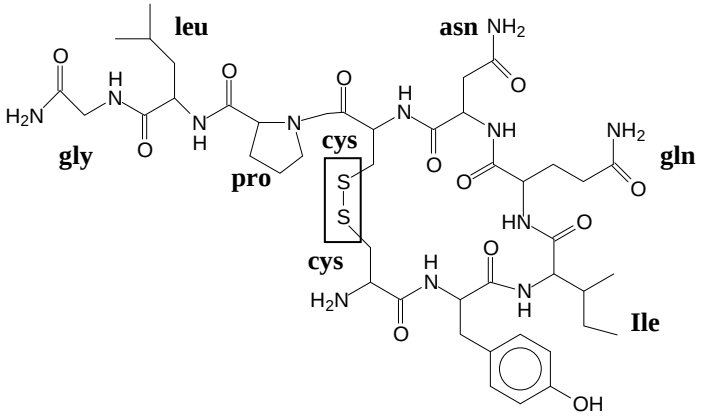
$$VO_3^- + 2H^+ \rightleftharpoons VO_2^+ + H_2O$$

(c) In the reaction between $S_2O_8^{2-}(aq)$ and $I^-(aq)$, $Fe^{3+}(aq)$ could be used as a homogeneous catalyst. If $[Fe(CN)_6]^{3-}(aq)$ is used instead of $Fe^{3+}(aq)$, **explain** whether $[Fe(CN)_6]^{3-}(aq)$ will still act as a catalyst. **[1]**

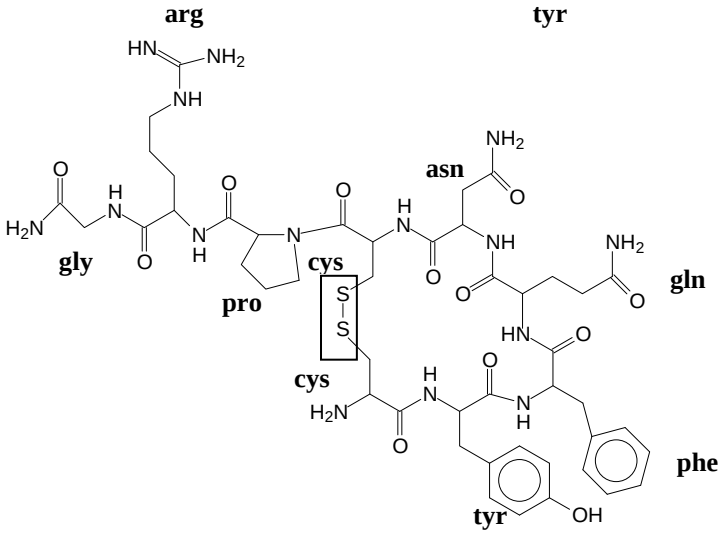
[Total: 20 marks]

10

5 (a) Oxytocin and vasopressin are two rather small polypeptides with strikingly similar structures. In spite of the similarity of their amino acid sequences, these two polypeptides have quite different physiological effects. Oxytocin occurs only in the female of a species and stimulates uterine contractions during childbirth. Vasopressin occurs in males and females; it causes contraction of peripheral blood vessels and an increase in blood pressure. Its major function, however, is as an *antidiuretic;* physiologists often refer to vasopressin as an *antidiuretic hormone.* **[7]**



oxytocin



vasopressin

(i) Apart from the peptide bond in oxytocin, state **two** other functional groups in oxytocin.

(ii) State the name of the linkage that is highlighted in the two structures above which is common in both polypeptides.

(iii) Oxytocin and vasopressin has different primary structures, where oxytocin has **leucine**, vasopressin has **arginine**, and where oxytocin has **isoleucine**, vasopressin has **phenylalanine**. State the type of interactions **arginine** and **phenylalanine** are able to form in maintaining the tertiary structure of proteins.

11

(iv) The melting points of leucine, along with two other compounds, are given in the table below.

Compound	**Mr**	**Melting Point/^{o}C**
Leucine	**131**	**293**
1,7-Heptanediamine	**130**	**25**
Heptanoic acid	**130**	**-7**

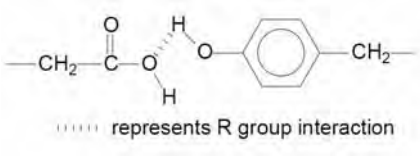
Explain the difference in melting points between
I Leucine and 1,7-Heptanediamine and,
II 1,7-Heptanediamine and Heptanoic acid .

(b) **Denaturation** is a process in which proteins lose the quaternary structure, tertiary structure and secondary structure which is present in their native state, by application of some external stress or compound such as a strong acid or base. **[2]**

A classic example of denaturing in proteins comes from egg whites, which are largely egg albumins in water. Fresh from the eggs, egg whites are transparent and liquid. Cooking the thermally unstable whites turns them opaque, forming an interconnected solid mass.

Considering the types of R group interactions that are affected during the denaturation of proteins, explain the following phenomena, highlighting the changes in the bonds that lead to denaturation.

I Casein is the predominant protein found in milk. The conversion of milk to cheese involves the addition of the Lactobacillus bacterium which produces lactic acid.
II Alcohol (ethanol) solutions are used as disinfectants on the skin as it can penetrate the bacterial cell wall and denature the proteins inside the cell. The part of the protein molecule which is affected by the ethanol added is as follows:



12

(c) Compound **A**, $C_8H_{10}O_2$, when treated with dilute nitric acid, gives compound **B**, $C_8H_9NO_4$. Compound **A** also reacts with aqueous bromine to form compound **C** with molecular formula, $C_8H_7O_2Br_3$ **[11]**

Treatment of compound **B** with tin in concentrated hydrochloric acid, followed by treatment with hot aqueous sodium hydroxide gives compound **D**, $C_8H_{10}NO_2Na$.

Compound **D** turns hot acidified potassium dichromate solution green and forms compound **E,** $C_8H_9NO_3$. 1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide.

Treatment of compound **E** with phosphorus pentachloride gives a compound **F**, $C_8H_7NO_2$.

Suggest structures for **A**–**F** and give an account of the chemistry involved.

[Total: 20 marks]