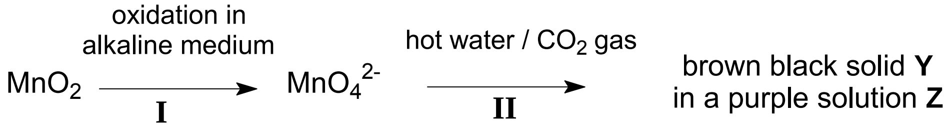
Answer any **four** questions.

1 **(a)** One property of manganese that typifies it as a transition element is its ability to exhibit variable oxidation states. What features of manganese allow it to do so?

[2]

(b) Manganese commonly occurs as the ore pyrolusite, which is mainly manganese(IV) oxide. This is the most usual starting material for the production of compounds of manganese in other oxidation states.

Manganese(IV) oxide undergoes a 2-step reaction to produce compounds **Y** and **Z**.



$$MnO_2 \xrightarrow[\textbf{I}]{\text{oxidation in alkaline medium}} MnO_4^{2-} \xrightarrow[\textbf{II}]{\text{hot water / } CO_2 \text{ gas}} \text{brown black solid } \textbf{Y} \text{ in a purple solution } \textbf{Z}$$

(i) The brown black solid **Y** contains 63.8% by mass of manganese and 36.2% by mass oxygen. Using these information, determine the empirical formula of **Y**.

(ii) Suggest the identity of **Z** and state the type of reaction that occurs at step **II**. Construct a balanced equation for the reaction.

(iii) With reference to your answer in **(b)(ii)**, explain the role of bubbling carbon dioxide gas into the hot solution of MnO_4^{2-}.

[7]

(c) Half a million tonnes of manganese(IV) oxide are used each year in dry cell batteries. A particular dry cell, consisting of a sodium anode and a graphite cathode immersed in a polymer electrolyte, has been developed to detect gases like fluorine and chlorine. The graphite cathode is coated with solid manganese(IV) oxide which will be converted to MnO(OH) solid and hydroxide ions during discharge.

(i) Write the ion-electron equations for the reaction which occurs at the anode and cathode respectively.

(ii) The voltage of this sodium-carbon dry cell is found to be 1.0 V. With reference to the *Data Booklet*, estimate approximately the $E^{\ominus}$ of the manganese half cell, explaining how you arrive at your answer and stating any assumptions you make.

[4]

(d) Manganese(IV) oxide catalyses the decomposition of hydrogen peroxide.

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

The volume of oxygen gas liberated from a sample of hydrogen peroxide contaminated with some manganese(IV) oxide was measured every minute. The results are tabulated below.

Time / min	0	1	2	3	4	5	6	7
Total volume of O_2 / cm^3	0	23.0	36.5	46.0	51.0	54.5	57.0	58.5

(i) Use a graphical method to deduce the order of reaction with respect to hydrogen peroxide. Explain your answers as fully as you can.

(ii) Calculate the rate constant for the reaction, stating its units.

(iii) What effect will the presence of the manganese(IV) oxide catalyst have on the rate constant for this reaction? Explain your answer.

[7]

[Total: 20]

2 **(a)** The lattice energy of calcium chloride is –2255 kJ mol^{-1}.

(i) Use the following values of enthalpy change of hydration to construct a Born-Haber energy cycle and use it to calculate the enthalpy change of solution, ΔH_{sol} for calcium chloride.

	ΔH_{hyd} / kJ mol^{-1}
Ca^{2+}	–1650
Cl^{-}	–381

(ii) How would you expect the temperature to change when calcium chloride is dissolved in water?

(iii) By quoting suitable data from the *Data Booklet*, suggest, with reasons, how the enthalpy change of hydration of Ca^{2+} might compare to that of Cu^{2+}.

[6]

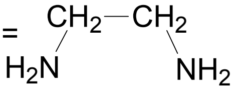
(b) Copper(II) ion forms many complexes. When copper(II) ion coordinates with polydentate ligands, the complex formed has greater stability than one which is formed with comparable monodentate ligands. This is known as the *chelate effect*.

Consider the following complex formation reactions:

$$\text{I} \qquad [Cu(H_2O)_6]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(en)(H_2O)_4]^{2+}(aq) + 2H_2O(l)$$

$$\text{II} \qquad [Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+}(aq) + 2H_2O(l)$$

where ethylenediamine (en) =



$H_2N-CH_2-CH_2-NH_2$

The standard enthalpy changes of reaction, $\Delta H_r^\ominus$, and the standard entropy changes of reaction, $\Delta S_r^\ominus$, for the ligand exchange reactions I and II are as follows.

reaction	$\Delta H_r^\ominus$ / kJ mol^{-1}	$\Delta S_r^\ominus$ / J K^{-1} mol^{-1}
I	– 54.0	+23.0
II	– 46.0	– 8.4

(i) How do the similar values of $\Delta H_r^\ominus$ for reaction I and II relate to the changes that occur at the molecular level?

(ii) Explain why $\Delta S_r^\ominus$ for reaction I is so different from reaction II.

(iii) Calculate the standard free energy changes, $\Delta G_r^\ominus$, for reaction I and II and hence explain why ethylenediamine complex exhibits the chelate effect.

(iv) "*The chelate effect is an entropy effect.*"

With reference to the Gibbs free energy equation and your answers in (**b)(i)**, **(ii)** and **(iii)**, comment qualitatively on the statement.

[8]

(c) Another polydentate ligand which can form complexes with transition metal ions is the deprotonated anion of compound **X**.

HS–C(CN)=C(CN)–SH

compound **X**

Compound **X** occurs in *two* isomeric forms.

(i) Draw the displayed formulae of the two isomers of **X**.

(ii) State the type of hybridisation present in the **two** differently bonded carbon atoms in **X**?

The deprotonated anionic **X**, however, occurs in only one form when acting as a polydentate ligand.

(iii) Suggest a structural formula of the deprotonated anionic **X**.

(iv) Which isomeric form of the deprotonated anionic **X** acts as a polydentate ligand? Explain why the other isomer cannot be used to form complexes.

(v) What type of bond is formed between the anionic ligand **X** and the transition metal ions in complexes?

[6]

[Total: 20]

3 **(a)** Describe the reactions, if any, of the chlorides of sodium to silicon with water, relating any differences to their bonding. Give equations for any reactions and sketch a graph to show the pH values of the resulting solutions.

[5]

(b) When aqueous sodium hydroxide is added to an aqueous solution of $AlCl_3$, a white precipitate is formed which dissolves in excess sodium hydroxide.

(i) Write an equation for the formation of the white precipitate.

(ii) State what you would observe when the above procedure is repeated using aqueous $MgCl_2$. Explain the difference(s) in the observations.

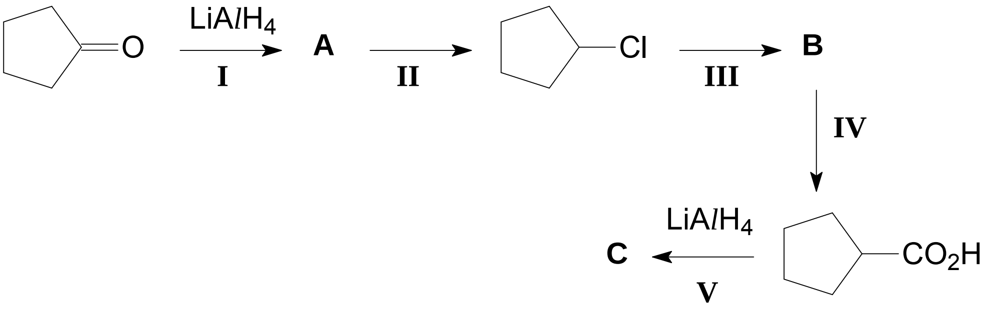
[3]

(c) Lithium aluminium hydride, $LiAlH_4$, is prepared from the reaction between $AlCl_3$ and lithium hydride, LiH.

$$AlCl_3 + 4LiH \longrightarrow LiAlH_4 + 3LiCl$$

$LiAlH_4$ and sodium borohydride, $NaBH_4$, are commonly used to reduce the carbonyl group of an aldehyde or a ketone, but not alkenes. Both compounds carry out the reduction by transferring a hydride ion, H^-, to the carbonyl carbon. However, $LiAlH_4$ is a more powerful reducing agent than $NaBH_4$ as it can also reduce carboxylic acids and esters.

In the following conversion, $LiAlH_4$ is used to reduce a ketone and carboxylic acid.



(i) By considering the bonding in $LiAlH_4$ and $NaBH_4$, suggest a reason why $LiAlH_4$ is a more powerful reducing agent.

(ii) What is the role of the H^- ion in the reduction process? Suggest a reason why $LiAlH_4$ and $NaBH_4$ cannot reduce alkenes.

(iii) Write the structural formulae of **A, B** and **C**.

(iv) State the reagents and conditions needed for reactions **II** to **IV**.

[8]

(d) An ester is reduced by $LiAlH_4$ to two alcohols.

(i) Draw the structures of the two alcohols formed when ethyl benzoate is treated with $LiAlH_4$.

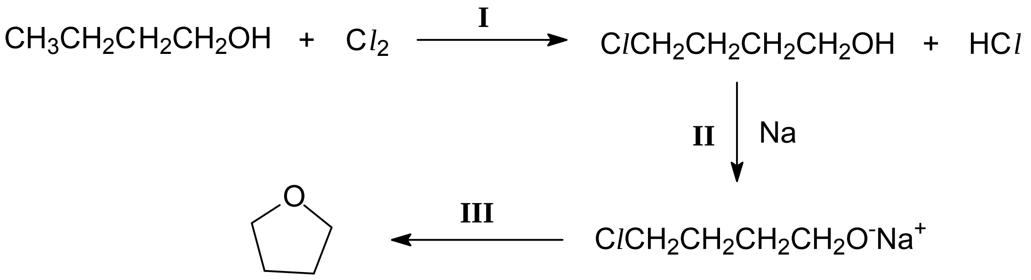
(ii) Suggest a chemical test that could be used to distinguish the two alcohols in **(d)(i)** from each other. You should state what you would observe for each alcohol in the test.

[4]

[Total: 20]

4 **(a)** The common industrial solvent, tetrahydrofuran (THF), is widely used to degrease metal parts.

It can be synthesised from butan-1-ol as shown below.



Tetrahydrofuran
(THF)

(i) What *types of reaction* are steps **I**, **II** and **III**?

(ii) Use the bond energies given in the *Data Booklet* to calculate a value for the enthalpy change of reaction for step **I**.

(iii) The accurate experimental enthalpy change of reaction for step **I** is found to be -144 kJ mol^{-1}. Suggest a reason for the discrepancy between this value and your answer in **(a)(ii)**.

(iv) Suggest a mechanism for step **III**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

(v) Comment on the yield of THF in this synthesis. Briefly explain your reasoning.

[10]

(b) This question is about the neutral compound **D**, C_8H_7ON.

On heating **D** with dilute hydrochloric acid, only compound **E** ($C_8H_9O_2N$) is obtained.

E is soluble in dilute sulphuric acid, aqueous sodium carbonate and aqueous sodium hydroxide. **E** also reacts with lithium aluminium hydride to give **F** ($C_8H_{11}ON$). **F** is no longer soluble in sodium carbonate and aqueous sodium hydroxide but is still soluble in dilute sulphuric acid.

On passing **F** over hot Al_2O_3, **G** (C_8H_9N) is produced. Heating **G** with alkaline potassium manganate(VII) gives **H** ($C_7H_6NO_2Na$) together with the evolution of a gas.

H can also be synthesised by treating 2-nitrobenzoic acid with tin and concentrated hydrochloric acid followed by NaOH(aq).

Deduce the structures of compounds **D**, **E**, **F**, **G** and **H**, and explain the reactions involved.

[10]

[Total: 20]

5 **(a)** Proteins are long-chain molecules made by linking together amino acids. There are 22 different amino acids found widely in nature and proteins contain several thousand amino acid units.

(i) Given that the general formula of an α-amino acid is $H_2NCHRCO_2H$ where R is its side chain (R groups), draw a displayed formula of a unit of a protein chain containing two such amino acids using the general formula.

Show how this unit could be linked by hydrogen bonds to similar amino acid units in a α-helix structure.

(ii) Suggest reagents and conditions that could be used to hydrolyse a protein into its amino acids.

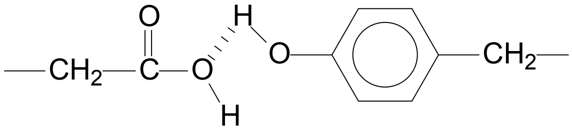
[4]

(b) **(i)** What do you understand by the term *denaturation* of proteins?

(ii) Considering the types of R group interactions that are affected during the denaturation of proteins, explain the following phenomena with the aid of relevant equations and diagrams where appropriate.

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:



ııııı represents R group interaction

[5]

(c) Glycine and alanine are two important α-amino acids. Glycine is found in sweeteners while alanine can be found in high concentrations in meats.

(i) Given that the R groups of the α-amino acids, glycine and alanine, are hydrogen and methyl groups respectively, comment and explain the difference in their optical activity.

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

Compound	M_r	Melting Point/^oC
glycine	75	262
1-aminobutane	73	- 49
propanoic acid	74	- 21

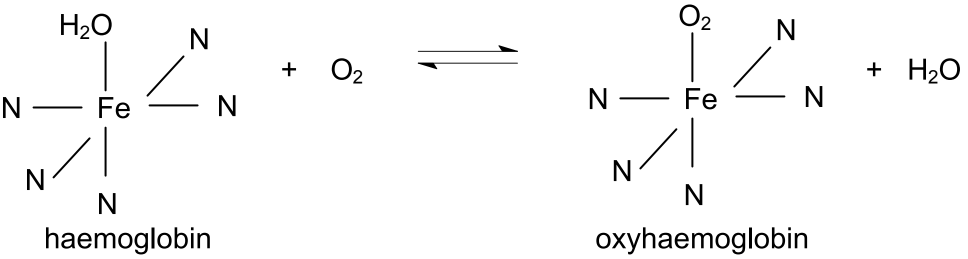
Explain the difference in melting points between

I glycine and 1-aminobutane and,

II 1-aminobutane and propanoic acid.

[5]

(d) Haemoglobin is an oxygen-binding protein. The iron atom in the haemoglobin molecule is surrounded by six ligand atoms, one of which is an oxygen atom from a water molecule. This molecule is replaced by an oxygen molecule in oxyhaemoglobin as shown:



(i) The iron atom in haemoglobin contains six 3d electrons. Deduce the oxidation state of iron in haemoglobin.

(ii) What change of oxidation number of iron, if any, occurs when haemoglobin is converted into oxyhaemoglobin? Explain your answer.

[2]

(e) Another oxygen-binding protein, hemocyanin, found in octopus and horseshoe crabs contains copper atom in its structure. Oxygenation causes a colour change in hemocyanin from the colourless Cu(I) deoxygenated form to the blue Cu(II) oxygenated form.

With reference to the electronic configurations of copper in the two complexes, explain the difference in their colours.

[4]

[Total: 20]