Answer any **four** questions.

1 Penicillin can be made in the laboratory by reacting 6-aminopenicilanic acid with a suitable acyl chloride. For a particular penicillin, the acyl chloride is the $CH_3CH_2CH{=}CHCH_2COCl$. Since the acyl chloride used can be easily made from the corresponding carboxylic acid, the chemist has decided to work with $CH_3CH_2CH{=}CHCH_2CO_2H$ because the acyl chloride is more reactive.

(a) (i) The acyl chloride, $CH_3CH_2CH{=}CHCH_2COCl$, can be obtained by reacting $CH_3CH_2CH{=}CHCH_2CO_2H$ with PCl_5. Write a balanced equation for the reaction.

[1]

(ii) Using relevant data from the Data Booklet and the bond energies given below, calculate the enthalpy change for the above reaction. [2]

	Bond Energies /kJ mol^{-1}
P-C*l*	322
P=O	423

(b) (i) The carboxylic acid, $CH_3CH_2CH{=}CHCH_2COOH$, can be converted into the hydroxyacid, $CH_3CH_2CH(OH)CH_2CH_2COOH$. Give the reagent and condition for the reaction. [1]

(ii) The hydroxyacid obtained can be distinguished from its starting material by using bromine. Name and describe the mechanism involved. [4]

(iii) Suggest another reagent and condition in which the hydroxyacid obtained can be distinguished from its starting material. [2]

(c) (i) In the course of preparing the hydroxyacid, an internal chiral ester was also detected. Draw the structure of this ester. Circle the chiral centre(s). [2]

(ii) State the number of sp^2 and sp^3 hybridised carbons in the ester. [2]

(iii) This ester may be made into a diol. Give the reagent and condition for the conversion and draw the structure of this diol. [2]

(d) (i) An experiment was carried out to determine the enthalpy change of combustion of this diol. Write a balanced equation including state symbols for the combustion of the diol under standard condition. [1]

(ii) A large beaker of water was placed on the stove and heated. The temperature rise was recorded. The cylinder was weighed before and after the experiment to determine the mass of diol used. The following results were obtained.

Mass of diol used = 3.4 g
Mass of water heated = 500 g
Temperature rise = 44 ^oC

Using relevant data from the Data Booklet and results given above, calculate the enthalpy change for the combustion of the diol. [3]

[Total: 20]

2 (a) The triodide ion, I_3^-, is known to exist as a stable species in aqueous solution. Draw a dot and cross diagram for I_3^- and hence deduce its shape.
[2]

(b) Solid CsI_3 is stable with respect to CsI and I_2 but LiI_3 is not stable with respect to LiI and I_2. Based on your knowledge of the relative stabilities of group II carbonates, rationalize the relative stability of CsI_3 and LiI_3. [3]

(c) (i) Given that the enthalpy of atomization of Ca is +176.4 kJ mol^{-1}, and using relevant ionization energy values from the *Data Booklet*, calculate the enthalpy change for the reaction: [2]

$$Ca(s) + Ca^{2+}(g) \rightarrow 2Ca^{+}(g)$$

(ii) What can you conclude about the relative stability of $Ca^+(g)$ with respect to Ca and Ca^{2+}? [1]

(d) The energetic relations between the aqueous ions of Ca and the solid Ca metal is given as follows:

$$Ca(s) + Ca^{2+}(aq) \rightarrow 2Ca^{+}(aq) \qquad \Delta H = +63 \text{ kJ mol}^{-1}$$

In the light of your answer to (c)(ii), account for the differences (if any) noted. [2]

(e) (i) Based on data, the standard electrode potentials of Ca, Sr and Ba are nearly the same, but the enthalpy changes associated with the reactions vary considerably.

	Mg	Ca	Sr	Ba
E^{θ} (M^{2+} / M) / V	-2.38	-2.87	-2.89	-2.90
ΔH / kJ mol^{-1} $M^{2+}(aq) + 2e \rightarrow M(s)$	-403.2	-256.2	-289.8	-365.4

.
Although there is found to be a good correlation between the ΔH for $M^{2+}(aq) + 2e \rightarrow M(s)$ and the corresponding E^{θ} (M^{2+}/M), the degree of similarity between the E^{θ} (M^{2+}/M) is greater whilst that for the ΔH is noticeably lower. What factor is responsible for the dissimilarity of the set ΔH values? [1]

(ii) For Mg, ΔH deviates so greatly, that no good correlation can be observed between ΔH and E^{θ}. Suggest a reason for this inconsistency between the two values for Mg. [2]

(iii) In the light of your answers to (e)(i) and (e)(ii), what energy term will give a more exact correlation with the E^{θ}? Why? [2]

(f) HF(aq) is the weakest acid compared with the other aqueous hydrogen halides. One factor relevant to its weakness is that the entropy change that accompanies its dissociation is the most negative. What other factor is relevant in explaining the weakness of HF(aq) as an acid? [1]

(g) (i) The enthalpy of vaporisation of the hydrogen halides is markedly different for one of the HX as compared with the others. Identify the hydrogen halide and suggest what phenomenon is responsible for this deviation. [2]

(ii) The values of entropies of vaporization (ΔS_b), that is the molar latent enthalpy of evaporation (ΔH_{vap}) divided by the boiling point (T_b/ K) is approximately constant for HC*l*, HBr and HI, but very different for HF. How would you expect the entropies of vaporization for HF to compare with the other three? Why? [2]

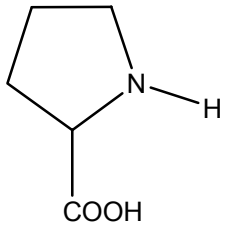
[Total: 20]

3 Glycine, H_2NCH_2COOH, is the smallest of the 20 amino acids commonly found in proteins.

(a) Propose a synthesis pathway to obtain glycine starting from chloromethane. State clearly all intermediates, reagents and conditions. [7]

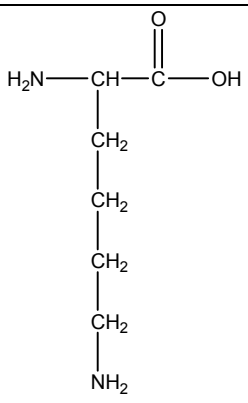
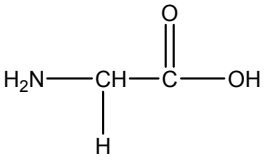
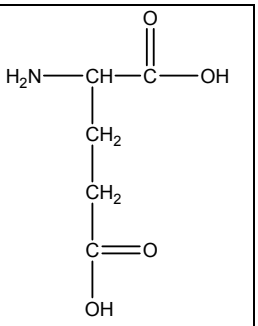
(b) Would you expect the amine group in glycine to have a bigger or smaller K_b than that in proline? Explain your answer briefly.
[2]

proline



(c) Glycine has many uses. For example it can serve as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. With the use of equations, show how glycine can acts as a buffer. [2]

(d) In a reaction, tripeptide **S** produces the following amino acids in equimolar amounts. The resulting solution was added to an excess of a buffer solution of pH 4.0 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino Acid	 Lys	 Gly	 Glu
pI	9.7	6.0	3.2

(i) Draw a possible structure of tripeptide **S**. [1]

(ii) What reagent and condition are needed break tripeptide **S** into its constituent amino acids? What is the name given to this type of reaction? [2]

(iii) Draw the predominant form of the three amino acids in the buffer solution and hence explain how they can be separated. [6]

[Total: 20]

4 (a) Hard water is water that has higher calcium and magnesium content. Using hard water results in sediments accumulating in electrical appliances such as water heaters and washing machines. This raises the electricity consumption rate and shortens the lifespan of the appliances. Hard water is treated through a softening process, where the metal ions are removed, before it is used for consumption.

A sample of hard water containing Mg^{2+} (aq) was collected. The presence of Mg^{2+} is to be tested by precipitating $MgCO_3$.

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

(ii) The solubility of $Mg(OH)_2$ in pure water at 25 ^oC is 9.08 x 10^{-3} g dm^{-3}. For a saturated aqueous solution of $Mg(OH)_2$ at 25 ^oC, calculate the concentrations of Mg^{2+} and OH^- and prove that the solubility product, K_{sp}, of $Mg(OH)_2$ is 1.5 x 10^{-11} mol^3 dm^{-9}. [2]

(iii) How would you expect the solubility of magnesium hydroxide in aqueous magnesium nitrate to compare with that in pure water? Discuss this effect using Le Chatelier's Principle. [2]

(iv) The concentration of Mg^{2+} in the water sample was found to be 3.2 x 10^{-4} mol dm^{-3}. A 50 cm^3 sample was used in this test. To this sample, 30 cm^3 of a 5.0 x 10^{-4} mol dm^{-3} aqueous sodium hydroxide was added. Using the K_{sp} value in (ii), deduce if a precipitate would appear when the two solutions were added. [2]

(b) Compound **A**, $C_9H_{10}NOCl$, is a basic compound. It reacts with 2,4-dinitrophenylhydrazine to form a orange precipitate **B**, but does not react with Tollens' reagent. **A** does not react with aqueous bromine. When **A** was heated with bromine and iron(III) bromide, it was found that **A** reacts with 2 moles of bromine. Compound **C**, $C_9H_{11}NO_2$, is formed when **A** is heated under reflux with aqueous sodium hydroxide. **C** reacts with acidified potassium dichromate to produce **D**. 0.10 mole of **D** reacts completely in the presence of 0.05 moles of sodium carbonate. Upon heating **A** with ethanol in a sealed tube, a single organic compound **E**, C_9H_9NO, is obtained.

Deduce the structures of compounds **A**, **B**, **C**, **D** and **E**, giving reasons for your answer. [13]

[Total 20]

5 (a) It is often stated that, compared to the (III) oxidation state of the adjacent elements, Mn(III) is a stronger oxidizing agent and that Fe(III) is a weaker oxidizing agent than expected. Show how relevant data from the data booklet can be used to illustrate this statement. What explanation can you offer for this? [4]

(b) Manganese(IV) oxide is used in the manufacture of 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 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. [2]

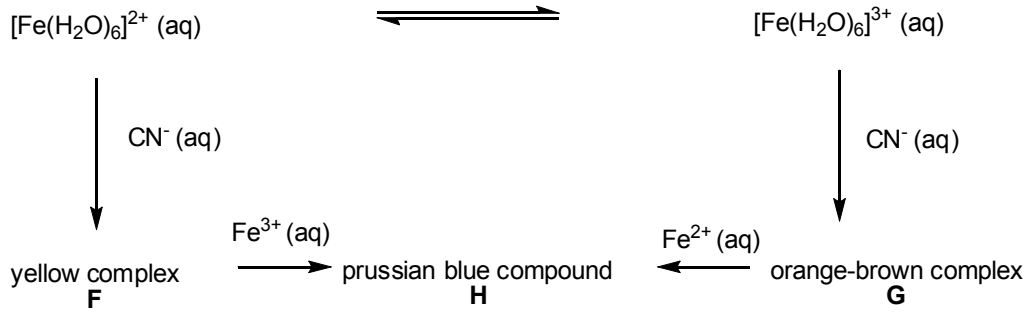
(ii) The voltage of this sodium-carbon dry cell is found to be 1.0 V. With reference to the data booklet, estimate approximately the E^o of the manganese half cell and state any assumptions you make. [2]

(c) Hadfield steel which is used in situation where very hard steel is required contains manganese and iron together with very little carbon.

When a 0.2 g sample of steel was dissolved in dilute acid and suitably oxidized, a purple solution containing iron(III) ions and manganate(VII) was formed. Titration of this solution required 24.5 cm^3 of 0.100 mol dm^{-3} iron(II) sulphate to discharge the colour.

Calculate the percentage of manganese in the Hadfield steel sample. [4]

(d) Aqueous Fe(II)/Fe(III) undergo the following reactions.

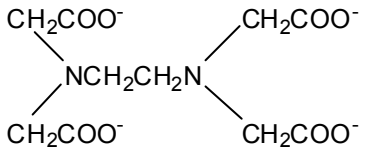


(i) Suggest the formulae of the anions of **F** and **G**. [2]

(ii) The anions of compounds **F** and **G** are complex ions. They are formed between a transition metal ion and ligands. What do you understand by the term ligand? Why do transition metal ions have strong tendency to form complex ions? [4]

(iii) Suggest a formula for the compound **H**. [1]

(iv) The deterioration in the air of some organic substances, such as cosmetics, is accelerated by iron(II) ions Suggest why the deterioration can be slowed down by a small quantity of EDTA. [1]



EDTA

[Total: 20]