1 Ammonia is manufactured using the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K. Give your answer in J mol$^{\ 1}$ K$^{\ 1}$ and include a sign. You will need to refer to your data booklet.

[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules eg entropy for 1 mol of N_2 is 2 × 95.8 J mol$^{\ 1}$ K$^{\ 1}$.]

(2)

(ii) Using ideas about disorder, explain whether the sign of your answer to (a)(i) is as expected.

(2)

(b) At 700 K, the enthalpy change for this reaction, ΔH 110.2 kJ mol$^{\ 1}$.

(i) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K. Include a sign and units in your answer.

(2)

(ii) Calculate ΔS_{system} for this reaction at 700 K. At this temperature the total entropy change, ΔS_{total} 78.7 J K^{-1} mol^{-1}. Include a sign and units in your answer.

(1)

(iii) What does the value of ΔS_{total}, which is 78.7 J K^{-1} mol^{-1} at 700 K, indicate about the relative proportions of nitrogen, hydrogen and ammonia at equilibrium?

(1)

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(c) A mixture of nitrogen, hydrogen and ammonia is at equilibrium at 150 atm. The partial pressures of nitrogen and ammonia in the mixture are 21 atm and 36 atm respectively.

(i) Write an expression for the equilibrium constant, K_p, for the formation of ammonia, in terms of partial pressures for this reaction, and calculate its value at 700 K. Include units in your answer.

(4)

(ii) In the manufacture of ammonia, pressures of between 100 and 250 atm are used. State and explain **one** advantage, in terms of the yield of ammonia, of using a pressure above 100 atm.

(1)

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*(iii) In the manufacture of ammonia, a temperature of about 700 K is used.

For this exothermic reaction how does $\Delta S_{\text{surroundings}}$ change as temperature increases?

Explain how this change affects the value of ΔS_{total} and the equilibrium constant as temperature increases.

Hence explain the disadvantage of using a temperature higher than 700 K.

(4)

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(iv) Suggest **one** advantage of using a temperature higher than 700 K.

(1)

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(Total for Question 18 marks)

2 (a) Crystals of hydrated cobalt(II) chloride, $CoCl_2.6H_2O$, lose water when they are heated, forming anhydrous cobalt(II) chloride, $CoCl_2$.

$$CoCl_2.6H_2O(s) \rightarrow CoCl_2(s) + 6H_2O(l)$$

(i) Calculate the entropy change of the system, $\Delta S^{\ominus}_{system}$, at 298 K. Include a sign and units in your answer. You will need to refer to your data booklet.

(2)

(ii) Explain whether the sign of your answer to (a)(i) is as expected from the equation for the reaction.

(1)

(iii) The standard enthalpy change for the reaction, $\Delta H^{\ominus}$, is +88.1 kJ mol^{-1}. Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, at 298 K for this reaction. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, at 298 K for the reaction.

(1)

(v) Does your answer to (a)(iv) indicate whether hydrated cobalt(II) chloride can be stored at 298 K without decomposition? Explain your answer.

(1)

(b) A student attempted to measure the enthalpy change of solution of anhydrous cobalt(II) chloride by adding 2.00 g of cobalt(II) chloride to 50.0 cm^3 of water in a well-insulated container. A temperature rise of 1.5 °C was recorded.

The student used a balance which reads to 0.01g, a 50.0 cm^3 pipette, and a thermometer which can be read to 0.25 °C.

(i) Which measuring instrument should be changed to give a result which is closer to the accepted value? Justify your answer.

(2)

(ii) Suggest ONE **other** change the student could make to give a result which is closer to the accepted value. Justify your suggestion.

(2)

*(c) The lattice energies of magnesium chloride, $MgCl_2$, calcium chloride, $CaCl_2$, and strontium chloride, $SrCl_2$ are shown in the table below.

Chloride	Lattice energy / kJ mol^{-1}
$MgCl_2$	–2526
$CaCl_2$	–2258
$SrCl_2$	–2156

(i) Use data on ionic radii, from your data booklet, to explain the trend in these values. Estimate a value for the lattice energy of cobalt(II) chloride, giving ONE piece of data to justify your estimate.

(4)

(ii) Explain how lattice energy values, together with other data, can be used to predict the solubility of ionic compounds.

(3)

*(d) Cobalt forms another chloride, $CoCl_3$, but scientists predict that $MgCl_3$ cannot be made. Suggest a reason for this.

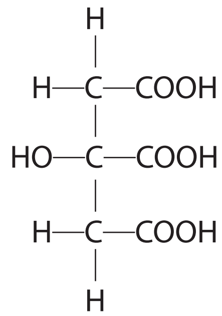
You should consider the enthalpy changes in the Born-Haber cycle, which provide evidence about why cobalt(III) chloride is known but magnesium(III) chloride is not.

(2)

(Total for Question = 20 marks)

3 Citric acid is found in lemon juice.

The structure and formula of citric acid are shown below.



$C_6H_8O_7$

(a) In the presence of a small amount of moisture, citric acid reacts with sodium hydrogencarbonate as shown in the equation below.

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

Use the structural formula of citric acid to explain why one mole of citric acid neutralizes three moles of sodium hydrogencarbonate.

(1)

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(b) You will need to refer to the data booklet in the calculations which follow.

You should also use the values given below.

compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Na_3C_6H_5O_7(s)$	200.5
$C_6H_8O_7(s)$	199.9

(i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the following reaction at 298 K. Include a sign and units in your answer.

(2)

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

*(ii) Explain how the sign of your answer to (b)(i) could be predicted from the equation for the reaction between citric acid and sodium hydrogencarbonate.

(2)

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(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction shown in (b)(i) is +70 kJ mol^{-1}, calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for this reaction at 298 K.

(1)

(v) What does the sign of $\Delta S^{\ominus}_{total}$ suggest about this reaction at 298 K?

(1)

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(Total for Question = 9 marks)

4 The hydrocarbon butane can be cracked to form propene and methane by passing it over a heated aluminium oxide catalyst at a temperature of 700 K. The equation for the reaction is

$$C_4H_{10}(g) \rightarrow C_3H_6(g) + CH_4(g) \qquad \Delta H \quad +71.9 \text{ kJ mol}^{-1}$$

(a) (i) Use page 20 of the data booklet to complete the table below.

(1)

Hydrocarbon	$S^{\ominus}$ / J mol^{-1} K^{-1}
$C_4H_{10}(g)$	+310.1
$C_3H_6(g)$	+266.9
$CH_4(g)$	

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction. Include a sign in your answer.

(2)

(iii) Was the sign for your answer as you expected? Fully justify your answer.

(2)

(iv) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K.

Include a sign and units in your answer.

Use this value and your answer to (ii) to explain why butane cracks into propene and methane at this temperature.

(3)

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(v) Calculate the minimum temperature needed for this reaction to be thermodynamically feasible.

(3)

(b) The aluminium oxide behaves as a heterogeneous catalyst. Explain both what is meant by the term **heterogeneous** and how, in terms of activation energy, the catalyst is able to speed up the reaction.

(3)

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(Total for Question 14 marks)