1 Hydrogen can be manufactured by reacting methane with steam, as shown in the equation below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^{\ominus}_{298} \quad +206.1\,\text{kJ mol}^{\ 1}$$

Use these values:

the standard entropy of 1 mol of $H_2(g)$ is (2×65.3) 130.6 J mol ^{1} K ^{1}
the standard entropy of 1 mol of $H_2O(g)$ is 188.7 J mol ^{1} K ^{1}

You will also need to refer to the data booklet in the calculations which follow.

(a) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$, for this reaction at 298 K.

(2)

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

(2)

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

Explain why this value shows that the reaction is not spontaneous at this temperature.

(2)

(d) The composition of an equilibrium mixture produced at 2.0 atmospheres pressure and at a much higher temperature is shown below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

	$CH_4(g)$	$H_2O(g)$	$CO(g)$	$3H_2(g)$
Amount in equilibrium mixture / mol	0.80	0.80	1.20	3.60

*(i) Write the expression for the equilibrium constant, K_p, of the reaction and calculate its value. Include units in your answer.

(6)

(ii) The total entropy change in J mol ^{1} K ^{1} is related to the equilibrium constant by the equation

$$\Delta S^{\ominus}_{\text{total}} \quad R\ln K_p \qquad \text{or} \qquad \Delta S^{\ominus}_{\text{total}} \quad 2.3R\log K_p$$

Calculate the total entropy change at the temperature of the reaction.

[R 8.31 J mol ^{1} K ^{1}]

(1)

(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S^{\ominus}_{\text{total}}$. Assume that ΔH is still +206.1 kJ mol $^{\ 1}$ and that $\Delta S^{\ominus}_{\text{system}}$ +225 J K $^{\ 1}$ mol $^{\ 1}$. (This is not the same as the value for $\Delta S^{\ominus}_{\text{system}}$ calculated in (a) which is at 298 K.)

(2)

*(e) Use the magnitude and signs of the entropy changes to explain the effect of a temperature increase on the equilibrium constant of this endothermic reaction.

(2)

(Total for Question   17 marks)

25 The oxidation of iron metal in the presence of oxygen is spontaneous.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

(a) Explain the meaning of **spontaneous** in a thermodynamic context.

(1)

(b) (i) Find the values of the standard molar entropies of iron and of iron(III) oxide from your data booklet.

(1)

(ii) The standard molar entropy at 298 K for oxygen molecules O_2 is +205 J mol^{-1} K^{-1}.

Calculate the standard entropy change of the system for the reaction between iron and oxygen. Include a sign and units in your answer.

(2)

(iii) The standard enthalpy change for the reaction at 25 °C is –1648 kJ mol^{-1}.

Calculate $\Delta S_{\text{surroundings}}$.

(1)

(iv) Use your answers to (b)(ii) and (iii) to calculate the total standard entropy change for the reaction. Include a sign and units in your answer.

(2)

*(v) The reaction is thermodynamically spontaneous.

Use your answers to (b)(ii), (iii) and (iv) to explain, in terms of the physical states of the substances in the reaction and the movement of the molecules in the surroundings, why this is so.

(3)

(Total for Question = 10 marks)