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

$$
\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \quad \Delta H_{298}^{\ominus}+206.1 \mathrm{~kJ} \mathrm{~mol}^{1}
$$

Use these values:
the standard entropy of 1 mol of $\mathrm{H}_{2}(\mathrm{~g})$ is $(2 \times 65.3) \quad 130.6 \mathrm{~J} \mathrm{~mol}^{1} \mathrm{~K}^{1}$ the standard entropy of 1 mol of $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ is $188.7 \mathrm{~J} \mathrm{~mol}^{1} \mathrm{~K}^{1}$

You will also need to refer to the data booklet in the calculations which follow.
(a) Calculate the standard entropy change of the system, $\Delta S_{\text {system }}^{\ominus}$, for this reaction at 298 K .
(b) Calculate the standard entropy change of the surroundings, $\Delta S_{\text {surroundings }}^{\ominus}$, for this reaction at 298 K . Include a sign and units in your answer.
(c) Calculate the total entropy change, $\Delta S_{\text {total }}^{\ominus}$, for this reaction at 298 K .

Explain why this value shows that the reaction is not spontaneous at this temperature.
(d) The composition of an equilibrium mixture produced at 2.0 atmospheres pressure and at a much higher temperature is shown below.

$$
\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})
$$

$\begin{array}{lllll}\text { Amount in equilibrium } & 0.80 & 0.80 & 1.20 & 3.60\end{array}$ mixture / mol
*(i) Write the expression for the equilibrium constant, $K_{\mathrm{p}}$, of the reaction and calculate its value. Include units in your answer.
(ii) The total entropy change in J mol ${ }^{1} \mathrm{~K}{ }^{1}$ is related to the equilibrium constant by the equation

$$
\Delta S_{\text {total }}^{\ominus} \quad R \ln K_{\mathrm{p}} \quad \text { or } \quad \Delta S_{\text {total }}^{\ominus} \quad 2.3 R \log K_{\mathrm{p}}
$$

Calculate the total entropy change at the temperature of the reaction.
$\left[\begin{array}{ll}R & 8.31 \mathrm{~J} \mathrm{~mol}\end{array}{ }^{1} \mathrm{~K}^{1}\right]$
(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S_{\text {total. }}^{\ominus}$. Assume that $\Delta H$ is still $+206.1 \mathrm{~kJ} \mathrm{~mol}^{1}$ and that $\Delta S_{\text {system }}^{\ominus}+225 \mathrm{~J} \mathrm{~K}^{1} \mathrm{~mol}^{1}$. (This is not the same as the value for $\Delta S_{\text {system }}^{\ominus}$ calculated in (a) which is at 298 K .)
*(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.

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

$$
4 \mathrm{Fe}(\mathrm{~s})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})
$$

(a) Explain the meaning of spontaneous in a thermodynamic context.
(b) (i) Find the values of the standard molar entropies of iron and of iron(III) oxide from your data booklet.
(ii) The standard molar entropy at 298 K for oxygen molecules $\mathrm{O}_{2}$ is $+205 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$. Calculate the standard entropy change of the system for the reaction between iron and oxygen. Include a sign and units in your answer.
(iii) The standard enthalpy change for the reaction at $25^{\circ} \mathrm{C}$ is $-1648 \mathrm{~kJ} \mathrm{~mol}{ }^{-1}$. Calculate $\Delta S_{\text {surroundings }}$.
(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.
*(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.

