14

Entropy and Gibbs energy

Answers to worked examples

WE 14.1 Predicting the sign of an entropy change (on p. 658 in *Chemistry*^{3})

What will be the sign of the value of ΔS for:

(a) crystallization of salt from a solution;

(b) condensation of a vapour to a liquid;

(c) dissolving sugar in water?

Strategy

Consider whether the individual processes lead to increase in disorder, which would correspond to a positive value for ΔS, or a decrease in disorder, in which case ΔS will be negative.

Solution

(a) Crystallisation of salt from a solution: In solution, the ions can move around freely whereas in a crystal they are fixed in the solid. There is thus an increase in order so that ΔS is negative.

(b) Condensation of a vapour to a liquid: Although molecules can move around in a liquid, they are less free to do so than in a gas which is highly disordered. There is therefore a decrease in order, and ΔS is negative.

(c) Dissolving sugar in water: The position of sugar molecules are fixed relative to each other in a solid but the molecules can move around in solution: There is an increase in disorder, so that ΔS is positive.

WE 14.2 Entropy change of vaporization (on p. 662 in *Chemistry*^{3})

Calculate the entropy change when 1.00 mol of water at 0°C freezes to form ice. For water, $\Delta_{\text{fus}}H^{\ominus} = +6.02\ \text{kJ mol}^{-1}$.

Strategy

Use Equation 14.6, which relates the entropy change for a system to the enthalpy change and the temperature.

Solution

Using Equation 14.6, and remembering that the temperature should be expressed in units of kelvin, where 0°C = 273 K

$$\Delta_{\text{fus}}S^{\ominus}_{298} = \frac{\Delta_{\text{fus}}H^{\ominus}_{298}}{T} = \frac{+6.02 \times 10^3\,\text{J mol}^{-1}}{273\ \text{K}} = +22.1\ \text{J K}^{-1}\text{mol}^{-1}$$

This is for fusion, i.e. melting. Freezing is the opposite process, for which

$$\Delta S^{\ominus}_{298} = -\Delta_{\text{fus}}S^{\ominus}_{298} = -22.1\ \text{J K}^{-1}\text{mol}^{-1}$$

WE 14.3 Calculating entropy changes on heating (on p. 663 in *Chemistry*^{3})

Calculate the entropy change when 3.00 mol of nitrogen gas are heated from 25°C to 50°C at constant pressure. (C_p for N_2 (g) is 29.13 $\text{J K}^{-1}\ \text{mol}^{-1}$)

Strategy

Rearrange Equation 14.7, remembering that temperatures must be in kelvin.

Solution

From Equation 14.7

$$S_{T_\text{f}} = S_{T_\text{i}} + C_p \ln(T_\text{f}/T_\text{i})$$

then the molar entropy change

$$\Delta S_\text{m} = S_{T_\text{f}} - S_{T_\text{i}} = C_{p,\text{m}} \ln(T_\text{f}/T_\text{i})$$

Remembering that the temperatures must be in units of kelvin, so that

$$T_\text{i} = (273 + 25)\ \text{K} = 298\ \text{K}$$
$$T_\text{f} = (273 + 50)\ \text{K} = 323\ \text{K}$$

then the entropy change for an amount n mol is

$$\Delta S = n\Delta S_\text{m} = nC_{p,\text{m}} \ln(T_\text{f}/T_\text{i})$$

$$= 3.0\ \text{mol} \times 29.13\ \text{J K}^{-1}\text{mol}^{-1} \times \ln(323\ \text{K}/298\ \text{K})$$
$$= +7.04\ \text{J K}^{-1}$$

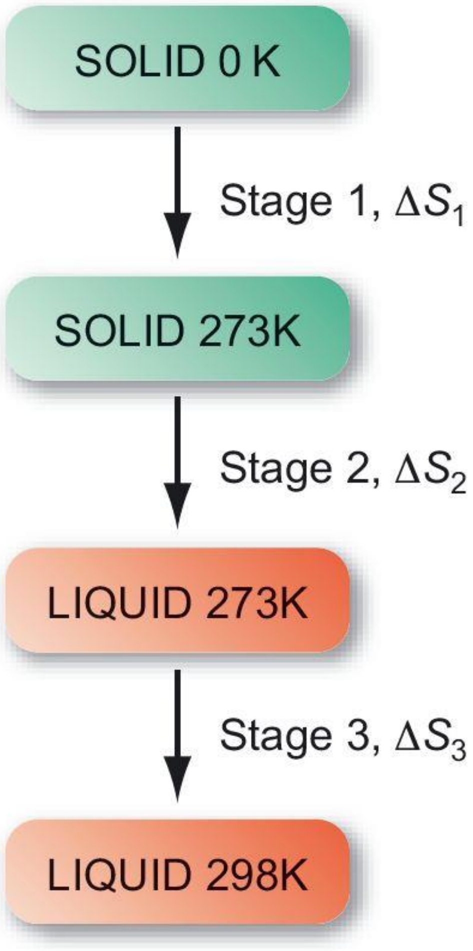
WE 14.4 Finding a standard entropy (on p. 667 in *Chemistry*^{3})

Draw a diagram, similar to Figure 1 in this example, to identify the stages involved in finding $S^{\ominus}_{298}$ (H_2O).

Strategy

Starting with Figure 1 in the worked example, decide what phase changes occur when $H_2O(s)$ at 0 K is converted to $H_2O(l)$ at 298 K, and what temperatures they occur at.

Solution



WE 14.5 Entropy changes for reactions at 298 K (on p. 669 in *Chemistry*³)

Calculate the standard entropy changes at 298 K for the following reactions:

(a) $CaCO_3\,(s) \rightarrow CO_2\,(g) + CaO\,(s)$

(b) $N_2O_4\,(g) \rightarrow 2\,NO_2\,(g)$

Strategy

Use Equation 14.11 to determine the entropy change from the entropies of the individual products and reactants.

Solution

Using Equation 14.11

$$\Delta_r S^{\ominus}_{298} = \sum \nu_i\, S^{\ominus}_{298}\,(\text{products}) - \sum \nu_i\, S^{\ominus}_{298}\,(\text{reactants})$$

where the terms in ν_i represent the stoichiometric coefficients of the products and reactants, then

(a)

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= S^{\ominus}_{298}\big(CO_2(g)\big) + S^{\ominus}_{298}\big(CaO(s)\big) - S^{\ominus}_{298}\big(CaCO_3(s)\big)\\ &= 213.7\ \text{J K}^{-1}\text{mol}^{-1} + 39.8\ \text{J K}^{-1}\text{mol}^{-1} - 92.9\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +160.6\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

(b)

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= 2 \times S^{\ominus}_{298}\big(NO_2(g)\big) - S^{\ominus}_{298}\big(N_2O_4(g)\big)\\ &= 2 \times 240.1\ \text{J K}^{-1}\text{mol}^{-1} - 304.3\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +175.9\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Note that it is good practice, as with enthalpy changes, to quote the sign of the change, even if it is positive.

WE 14.6 Entropy changes for reactions at other temperatures (on p. 671 in *Chemistry*³)

Calculate the standard entropy changes of reaction at 100°C (373 K) for the following reactions:

(a) $CaCO_3\,(s) \rightarrow CO_2\,(g) + CaO\,(s)$ $\Delta_r S^{\ominus}_{298} = +160.6\ \text{J K}^{-1}\ \text{mol}^{-1}$

(b) $N_2O_4\,(g) \rightarrow 2\,NO_2\,(g)$ $\Delta_r S^{\ominus}_{298} = +175.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

Strategy

Calculate the change in the heat capacity for the reaction using Equation 13.11 and the data in Appendix 7. Use this value, along with Equation 14.12 to determine the entropy change on reaction at the new temperature.

Solution

(a) From Equation 13.11

$$\begin{aligned}\Delta_r C_p^{\ominus} &= \sum \nu_i C_p^{\ominus}\,(\text{products}) - \sum \nu_i C_p^{\ominus}\,(\text{reactants})\\ &= \{C_p^{\ominus}(CO_2(g)) + C_p^{\ominus}(CaCO_3(s))\} - C_p^{\ominus}(CaO(s))\\ &= \{42.8\ \text{J K}^{-1}\text{mol}^{-1} + 37.1\ \text{J K}^{-1}\text{mol}^{-1}\} - 81.9\ \text{J K}^{-1}\text{mol}^{-1}\\ &= -2.0\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Using Equation 14.12

$$\Delta S_{T_2}^{\ominus} = \Delta S_{T_1}^{\ominus} + \Delta C_p^{\ominus} \ln(T_2/T_1)$$

then

$$\begin{aligned}\Delta S_{373}^{\ominus} &= \Delta S_{298}^{\ominus} + \Delta C_p^{\ominus} \ln(373\ \text{K}/298\ \text{K})\\ &= +160.6\ \text{J K}^{-1}\text{mol}^{-1} - 2.0\ \text{J K}^{-1}\text{mol}^{-1} \ln(373\ \text{K}/298\ \text{K})\\ &= +160.2\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

(b) From Equation 13.11

$$\begin{aligned}\Delta_r C_p^{\ominus} &= \sum \nu_i C_p^{\ominus}\,(\text{products}) - \sum \nu_i C_p^{\ominus}\,(\text{reactants})\\ &= 2 \times C_p^{\ominus}(NO_2(g)) - C_p^{\ominus}(N_2O_4(g))\\ &= 2 \times 37.2\ \text{J K}^{-1}\text{mol}^{-1} - 77.3\ \text{J K}^{-1}\text{mol}^{-1}\\ &= -2.9\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Using Equation 14.12

$$\Delta S_{T_2}^{\ominus} = \Delta S_{T_1}^{\ominus} + \Delta C_p^{\ominus} \ln(T_2/T_1)$$

then

$$\begin{aligned}\Delta S_{373}^{\ominus} &= \Delta S_{298}^{\ominus} + \Delta C_p^{\ominus} \ln(373\ \text{K}/298\ \text{K})\\ &= +175.9\ \text{J K}^{-1}\text{mol}^{-1} - 2.9\ \text{J K}^{-1}\text{mol}^{-1} \ln(373\ \text{K}/273\ \text{K})\\ &= +175.0\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

WE 14.7 Gibbs energy change and spontaneity (on p. 676 in *Chemistry*^{3})

For the melting of sodium chloride, NaCl, $\Delta_{\text{fus}}H^{\ominus}$ = +30.2 kJ mol^{-1} and $\Delta_{\text{fus}}S^{\ominus}$ = +28.1 J K^{-1} mol^{-1}. Estimate the melting point of NaCl.

Strategy

Use Equation 14.16, remembering that at the melting point, solid and liquid are in equilibrium so that $\Delta_{\text{fus}}G^{\ominus} = 0$.

Solution

Using Equation 14.16, since at the melting point

$$\Delta_{\text{fus}}G^{\ominus} = \Delta_{\text{fus}}H^{\ominus} - T_{\text{m}}\Delta_{\text{fus}}S^{\ominus} = 0$$

we may rearrange

$$T_{\text{m}} = \frac{\Delta_{\text{fus}}H^{\ominus}}{\Delta_{\text{fus}}S} = \frac{+30.2 \times 10^{3}\,\text{J mol}^{-1}}{+28.1\ \text{J K}^{-1}\text{mol}^{-1}} = 1075\ \text{K}$$

WE 14.8 Calculating the Gibbs energy change of reaction at 298 K (on p. 678 in *Chemistry*^{3})

Calculate the standard Gibbs energy change at 298 K for the reaction

$$4\ \text{HCl (g)} + \text{O}_2\ \text{(g)} \rightarrow 2\ \text{Cl}_2\ \text{(g)} + 2\ \text{H}_2\text{O (l)}$$

(Use Appendix 7 (p.1350) to find values of $\Delta_{\text{f}}H^{\ominus}_{298}$ and standard entropies for reactants and products.)

Strategy

Use the data in Appendix 7, along with Equations 13.6 and 14.11 to determine the enthalpy and entropy of reaction. Then use Equation 14.16 to determine the Gibbs energy of reaction from these values.

Solution

Using Equation 13.6

$$\Delta_{\text{r}}H^{\ominus}_{298} = \sum \nu_i\ \Delta_{\text{f}}H^{\ominus}_{298}\ \text{(products)} - \sum \nu_i\ \Delta_{\text{f}}H^{\ominus}_{298}\ \text{(reactants)}$$

$$\begin{aligned}
&= \{2 \times \Delta_f H^{\ominus}_{298}(\mathrm{Cl_2(g)}) + 2 \times \Delta_f H^{\ominus}_{298}(\mathrm{H_2O(l)})\}\\
&\qquad - \{4 \times \Delta_f H^{\ominus}_{298}(\mathrm{HCl(g)}) + \Delta_f H^{\ominus}_{298}(\mathrm{O_2(g)})\}\\
&= \{2 \times 0 + 2 \times -285.8\ \mathrm{kJ\ mol^{-1}}\} - \{4 \times -92.3\ \mathrm{kJ\ mol^{-1}} + 0\}\\
&= -202.4\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Using Equation 14.11

$$\begin{aligned}
\Delta_r S^{\ominus}_{298} &= \sum \nu_i\, S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\, S^{\ominus}_{298}\ (\text{reactants})\\
&= \{2 \times S^{\ominus}_{298}(\mathrm{Cl_2(g)}) + 2 \times S^{\ominus}_{298}(\mathrm{H_2O(l)})\} - \{4 \times S^{\ominus}_{298}(\mathrm{HCl(g)}) + S^{\ominus}_{298}(\mathrm{O_2(g)})\}\\
&= \{2 \times 223.1\ \mathrm{J\ K^{-1}mol^{-1}} + 2 \times 69.9\ \mathrm{J\ K^{-1}mol^{-1}}\}\\
&\qquad - \{4 \times 186.9\ \mathrm{J\ K^{-1}mol^{-1}} + 205.1\ \mathrm{J\ K^{-1}mol^{-1}}\}\\
&= -366.7\ \mathrm{J\ K^{-1}mol^{-1}}
\end{aligned}$$

Using Equation 14.16 to calculate $\Delta_r G^{\ominus}{}_{298}$,

$$\begin{aligned}
\Delta_r G^{\ominus} &= \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}\\
&= -202.4 \times 10^3\ \mathrm{J\ mol^{-1}} - (298\ \mathrm{K} \times -366.7\ \mathrm{J\ K^{-1}mol^{-1}})\\
&= -93.1\ \times 10^3\ \mathrm{J\ mol^{-1}} = -93.1\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

WE 14.9 Using Gibbs energy changes of formation to calculate Gibbs energy change of reaction (on p. 681 in *Chemistry*^{3})

Calculate the standard Gibbs energy change for the oxidation of ammonia at 298 K.

$$5\ \mathrm{O_2\ (g)} + 4\ \mathrm{NH_3\ (g)} \rightarrow 6\ \mathrm{H_2O\ (l)} + 4\ \mathrm{NO\ (g)}$$

Strategy

Use Equation 14.18, substituting the data for the Gibbs energy change of formation from Appendix 7.

Solution

Using Equation 14.18

$$\begin{aligned}
\Delta_r G^{\ominus}_{298} &= \sum \nu_i\, \Delta_f G^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\, \Delta_f G^{\ominus}_{298}\ (\text{reactants})\\
&= \{6 \times \Delta_f G^{\ominus}_{298}(\mathrm{H_2O(l)}) + 4 \times \Delta_f G^{\ominus}_{298}(\mathrm{NO(g)})\}\\
&\qquad - \{5 \times \Delta_f G^{\ominus}_{298}(\mathrm{O_2(g)}) + 4 \times \Delta_f G^{\ominus}_{298}(\mathrm{NH_3(g)})\}
\end{aligned}$$

$$
\begin{aligned}
&= \{6 \times -237.1\ \text{kJ mol}^{-1} + 4 \times 86.6\ \text{kJ mol}^{-1}\} \\
&\qquad - \{5 \times 0 + 4 \times -16.5\ \text{kJ mol}^{-1}\} \\
&= -1010\ \text{kJ mol}^{-1}
\end{aligned}
$$

WE 14.10 Calculating the Gibbs energy change of reaction at other temperatures (on p. 681 in *Chemistry*³)

Calculate the standard Gibbs energy change for the oxidation of ammonia at 650 K.

Compare your answer with the value calculated for 298 K in the question at the end of Worked Example 14.9.

$$5\ O_2\ (g) + 4\ NH_3\ (g) \rightarrow 6\ H_2O\ (l) + 4\ NO\ (g)$$

Strategy

Calculate the standard enthalpy and entropy of reaction at 298 K using Equations 13.6 and 14.11. Also determine the change in the heat capacity on reaction using Equation 13.11. Hence use Equations 13.10 and 14.12 to determine the standard enthalpy and entropy of reaction at 650 K. Finally, use Equation 14.16 to determine the change in the Gibbs energy at 650 K.

Solution

Using Equation 13.6,

$$
\begin{aligned}
\Delta_r H^{\ominus}_{298} &= \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants}) \\
&= \{6 \times \Delta_f H^{\ominus}_{298}\big(H_2O(l)\big) + 4 \times \Delta_f H^{\ominus}_{298}\big(NO(g)\big) +\} \\
&\qquad - \{5 \times \Delta_f H^{\ominus}_{298}\big(O_2(g)\big) + 4 \times \Delta_f H^{\ominus}_{298}\big(NH_3(g)\big)\} \\
&= \{6 \times -285.8\ \text{kJ mol}^{-1} + 4 \times 90.3\ \text{kJ mol}^{-1}\} \\
&\qquad - \{5 \times 0 + 4 \times -46.1\ \text{kJ mol}^{-1}\} \\
&= -1169.2\ \text{kJ mol}^{-1}
\end{aligned}
$$

Then, using Equation 14.11,

$$\Delta_r S^{\ominus}_{298} = \sum \nu_i\ S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ S^{\ominus}_{298}\ (\text{reactants})$$

$$\begin{aligned}
&= \{6\times S^{\ominus}_{298}(\mathrm{H_2O(l)}) + 4\times S^{\ominus}_{298}(\mathrm{NO(g)}) +\} \\
&\qquad - \{5\times S^{\ominus}_{298}(\mathrm{O_2(g)}) + 4\times S^{\ominus}_{298}(\mathrm{NH_3(g)})\} \\
&= \{6\times 69.9\ \mathrm{J\ K^{-1}\ mol^{-1}} + 4\times 210.8\ \mathrm{J\ K^{-1}\ mol^{-1}}\} \\
&\qquad - \{5\times 205.1\ \mathrm{J\ K^{-1}\ mol^{-1}} + 4\times 192.5\ \mathrm{J\ K^{-1}\ mol^{-1}}\} \\
&= -532.9\ \mathrm{J\ K^{-1}\ mol^{-1}}
\end{aligned}$$

Using Equation 13.11,

$$\begin{aligned}
\Delta_\mathrm{r}C^{\ominus}_p &= \sum \nu_i\, C^{\ominus}_p\,(\text{products}) - \sum \nu_i\, C^{\ominus}_p\,(\text{reactants}) \\
&= \{6\times C^{\ominus}_p(\mathrm{H_2O(l)}) + 4\times C^{\ominus}_p(\mathrm{NO(g)}) +\} \\
&\qquad - \{5\times C^{\ominus}_p(\mathrm{O_2(g)}) + 4\times C^{\ominus}_p(\mathrm{NH_3(g)})\} \\
&= \{6\times 75.3\ \mathrm{J\ K^{-1}\ mol^{-1}} + 4\times 29.8\ \mathrm{J\ K^{-1}\ mol^{-1}}\} \\
&\qquad - \{5\times 29.4\ \mathrm{J\ K^{-1}\ mol^{-1}} + 4\times 35.1\ \mathrm{J\ K^{-1}\ mol^{-1}}\} \\
&= +283.6\ \mathrm{J\ K^{-1}\ mol^{-1}}
\end{aligned}$$

Then, from Equation 13.10

$$\Delta_\mathrm{r}H^{\ominus}_{T_2} = \Delta_\mathrm{r}H^{\ominus}_{T_1} + \Delta C^{\ominus}_p(T_2 - T_1)$$

so that

$$\begin{aligned}
\Delta_\mathrm{r}H^{\ominus}_{650} &= \Delta_\mathrm{r}H^{\ominus}_{298} + \Delta C^{\ominus}_p(650\ \mathrm{K} - 298\ \mathrm{K}) \\
&= -1169.2\ \times 10^3\ \mathrm{J\ mol^{-1}} + 283.6\ \mathrm{J\ K^{-1}mol^{-1}} \times 352\ \mathrm{K} \\
&= -1069\times 10^3\mathrm{J\ mol^{-1}} = -1069\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Using Equation 14.12

$$\Delta S^{\ominus}_{T_2} = \Delta S^{\ominus}_{T_1} + \Delta C^{\ominus}_p \ln(T_2/T_1)$$

then

$$\begin{aligned}
\Delta S^{\ominus}_{650} &= \Delta S^{\ominus}_{298} + \Delta C^{\ominus}_p \ln(650\ \mathrm{K}/298\ \mathrm{K}) \\
&= -532.9\ \mathrm{J\ K^{-1}\ mol^{-1}} + 283.6\ \mathrm{J\ K^{-1}mol^{-1}} \ln(650\ \mathrm{K}/298\ \mathrm{K}) \\
&= -311.7\ \mathrm{J\ K^{-1}mol^{-1}}
\end{aligned}$$

Combining the values for the enthalpy and entropy changes at 650 K using Equation 14.16,

$$\begin{aligned}
\Delta_\mathrm{r}G^{\ominus}_{650} &= \Delta_\mathrm{r}H^{\ominus}_{650} - T\Delta_\mathrm{r}S^{\ominus}_{650} \\
&= -1069.4\times 10^3\mathrm{J\ mol^{-1}} - 650\ \mathrm{K} \times -311.7\ \mathrm{J\ K^{-1}mol^{-1}}
\end{aligned}$$

$$= -866.8 \times 10^3 \text{ J mol}^{-1} = -866.8 \text{ kJ mol}^{-1}$$

Comparing the value with that calculated in the previous Worked Example at a temperature of 298 K, $\Delta_r G^{\ominus}_{298} = -1010.2 \text{ kJ mol}^{-1}$, it can be seen that the standard Gibbs energy of reaction increases, that is, it becomes less negative, as the temperature increases. The reaction therefore must become less spontaneous at higher temperatures.

Answers to boxes

Box 14.4 What happens when proteins don't fold correctly? (on p. 673 in *Chemistry*^{3})

The thermodynamics of protein folding can be considered using the relationship in Equation 14.3:

$$\Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$$

(a) The folding of a protein leads to a highly ordered structure. What is the sign of the value of ΔS(system) for the process?

(b) Folding is a spontaneous process under physiological conditions. What does this tell you about the value of ΔS(total)? What implications does this have for the value of ΔS(surroundings)? Explain how this happens.

(c) Suggest why the formation of the misfolded form of PrP cannot take place spontaneously from the normal form of the protein.

Strategy

(a) Consider whether the entropy of a folded protein is greater than that of an unfolded protein. (b) Use the Second Law of Thermodynamics to predict the sign of ΔS(total), and therefore ΔS(surroundings). (c) Predict the sign of the total entropy change and use the Second Law of Thermodynamics.

Solution

(a) The folded protein is more highly ordered than the unfolded protein. The entropy of the protein must therefore decrease on folding so that $\Delta S(\text{system}) < 0$.

(b) The value of ΔS(total) must be positive for the process to obey the Second Law. Thus, if

$$\Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) > 0$$

yet

$$\Delta S(\text{system}) < 0$$

then

$$\Delta S(\text{surroundings}) > 0$$

and the magnitudes of the entropy changes for the surroundings and system,

$$|\Delta S(\text{surroundings})| > |\Delta S(\text{system})|$$

Thus, ΔS(system) must be less negative than ΔS(surroundings) is positive. Heat is released when hydrogen bonds or other non-covalent interactions form. Proteins are large molecules so lots of non-covalent interactions form, making the heat change large.

(c) The folding of PrP is endothermic, so that

$$\Delta_r H > 0$$

Thus,

$$\Delta S(\text{surroundings}) = -\frac{\Delta_r H}{T} < 0$$

The entropy change for the system

$$\Delta S(\text{system}) = \Delta_r S < 0$$

and so the total entropy change

$$\Delta S_{\text{total}} = \Delta S(\text{system}) + \Delta S(\text{surroundings}) < 0$$

For a reaction to be spontaneous, the total entropy change must be positive.

Box 14.6 Thermodynamics of addition polymerization (on p. 679 in *Chemistry*^{3})

At 298 K, $\Delta_{\text{pol}}H$ (the enthalpy change of polymerization) for styrene is -68.5 kJ mol^{-1}. The value of $\Delta_{\text{pol}}H$ for α-methyl styrene is –35.1 kJ mol^{-1}. $\Delta_{\text{pol}}S_{298}$ = -105 J K^{-1} mol^{-1} for both reactions.

(a) Calculate the Gibbs energy change of polymerization at 298 K for both monomers. Estimate the ceiling temperature at which $\Delta_{\text{pol}}G = 0$ in each case.

(b) What are the implications of the ceiling temperatures for these monomers?

Strategy

Use Equation 14.16 to determine the Gibbs energy of reaction from the enthalpy and entropy of reaction. Assume that the enthalpy and entropy of reaction do not vary with temperature and hence determine the temperature at which the Gibbs energy change is zero.

Solution

(a) For styrene,

$$\begin{aligned}\Delta_{\text{pol}}G^{\ominus}_{298} &= \Delta_{\text{pol}}H^{\ominus}_{298} - T\Delta_{\text{pol}}S^{\ominus}_{298}\\ &= -68.5 \times 10^3\ \text{J mol}^{-1} - (298 \times -105\ \text{J K}^{-1}\text{mol}^{-1})\\ &= -37.2 \times 10^3\ \text{J mol}^{-1} = -37.2\ \text{kJ mol}^{-1}\end{aligned}$$

When

$$\Delta_{\text{pol}}G^{\ominus}_{298} = \Delta_{\text{pol}}H^{\ominus}_{298} - T\Delta_{\text{pol}}S^{\ominus}_{298} = 0$$

rearranging,

$$T = \Delta_{\text{pol}}H^{\ominus}_{298}/\Delta_{\text{pol}}S^{\ominus}_{298} = -68.5 \times 10^3\ \text{J mol}^{-1}/-105\ \text{J K}^{-1}\text{mol}^{-1} = 652\ \text{K}$$

For α-methyl styrene:

$$\begin{aligned}\Delta_{\text{pol}}G^{\ominus}_{298} &= \Delta_{\text{pol}}H^{\ominus}_{298} - T\Delta_{\text{pol}}S^{\ominus}_{298}\\ &= -35.1 \times 10^3\ \text{J mol}^{-1} - (298\ \text{K} \times -105\ \text{J K}^{-1}\text{mol}^{-1})\\ &= -3.8 \times 10^3\ \text{J mol}^{-1} = -3.8\ \text{kJ mol}^{-1}\end{aligned}$$

When

$$\Delta_{\text{pol}}G^{\ominus}_{298} = \Delta_{\text{pol}}H^{\ominus}_{298} - T\Delta_{\text{pol}}S^{\ominus}_{298} = 0$$

rearranging,

$$T = \Delta_{\text{pol}}H^{\ominus}_{298}/\Delta_{\text{pol}}S^{\ominus}_{298} = -35.1 \times 10^3\ \text{J mol}^{-1}/-105\ \text{J K}^{-1}\text{mol}^{-1} = 334\ \text{K}$$

(b) The calculations show that that polystyrene is thermodynamically stable relative to its monomer up to 652 K (379°C). With α-methyl styrene, the monomer is thermodynamically stable above 334 K (61°C) so that the polymer will not form from monomers above this temperature. Since polymers are often made by heating, this means that care must be taken during the synthesis. It also has implications for the highest temperature at which the polymer can be used.

Box 14.7 Obtaining silicon for use in silicon chips (on p. 682 in *Chemistry*³)

Use the thermodynamic data in the following table to answer the following questions.

(a) Explain, in terms of entropy, why it is so difficult to prepare ultra-high purity silicon crystals.

Strategy

Consider the degree of disorder and hence the magnitude and sign of the entropy change.

Solution

Ultra-high purity silicon crystals have a very high degree of order. The entropy change for turning impure silicon to ultra-high purity silicon is thus large and negative.

(b) Silicon could be extracted using the reaction:

$$SiO_2\,(s) \rightarrow Si\,(s) + O_2\,(g) \qquad \text{(Reaction 1)}$$

What are the standard enthalpy change and the standard entropy change at 298 K for this reaction? Comment on the value of $\Delta_r S^{\ominus}{}_{298}$ that you obtain.

Strategy

Use Equation 13.6 to determine the enthalpy change and Equation 14.12 to determine the entropy change for the Reaction 1 using the enthalpies of formation and entropies in the table.

Solution

Using Equation 13.6

$$\begin{aligned}\Delta_r H^{\ominus}_{298} &= \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants})\\ &= \{\Delta_f H^{\ominus}_{298}(\text{Si(s)}) + \Delta_f H^{\ominus}_{298}(\text{O}_2(\text{g}))\} - \Delta_f H^{\ominus}_{298}(\text{SiO}_2(\text{s}))\\ &= 0 + 0 - (-910.9\ \text{kJ mol}^{-1})\\ &= +910.9\ \text{kJ mol}^{-1}\end{aligned}$$

and Equation 14.11

$$\Delta_r S^{\ominus}_{298} = \sum \nu_i\ S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ S^{\ominus}_{298}\ (\text{reactants})$$

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= \{S^{\ominus}_{298}(\text{Si(s)}) + S^{\ominus}_{298}(\text{O}_2(\text{g}))\} - S^{\ominus}_{298}(\text{SiO}_2(\text{s}))\\ &= 18.8\ \text{J K}^{-1}\text{mol}^{-1} + 205.1\ \text{J K}^{-1}\text{mol}^{-1} - 41.8\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +182.1\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

(c) Calculate the value of $\Delta_r G^\ominus{}_{298}$ for the reaction. Why does elemental silicon not exist in the Earth's crust?

Strategy

Use the values for the standard enthalpy and entropy change from part (b) and Equation 14.16.

Solution

Using Equation 14.16

$$\begin{aligned}\Delta_r G^\ominus_{298} &= \Delta_r H^\ominus_{298} - T\Delta_r S^\ominus_{298}\\ &= +910.9\times 10^3\,\text{J mol}^{-1} - 298\ \text{K}\times +182.1\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +856.6\times 10^3\,\text{J mol}^{-1} = +856.6\ \text{kJ mol}^{-1}\end{aligned}$$

Elemental silicon does not exist in the Earth's crust because $\Delta G^\ominus{}_{298}$ for the conversion of silicon(IV) oxide to silicon through reaction 1 has a large positive value, so the process does not occur spontaneously. The oxide is therefore thermodynamically much more stable.

(d) Estimate the temperature at which $\Delta_r G^\ominus = 0$. What is the significance of this for preparing elemental silicon using this reaction?

Strategy

Rearrange Equation 14.16 and solve for the temperature at which $\Delta_r G^\ominus = 0$.

Solution

From Equation 14.16

$$\Delta_r G^\ominus_{298} = \Delta_r H^\ominus_{298} - T\Delta_r S^\ominus_{298} = 0$$

then, rearranging,

$$T = \Delta_r H^\ominus_{298}/\Delta_r S^\ominus_{298} = +910.9\times 10^3\,\text{J mol}^{-1}/+182.1\ \text{J K}^{-1}\text{mol}^{-1} = 5002\ \text{K}$$

Achieving such a high temperature would need very large energy input and it would be unrealistic and uneconomic to operate under these conditions.

(e) Calculate the value of $\Delta_r G^\ominus{}_{298}$ for this reaction and comment on the value you obtain.

$SiO_2\,(s) + 2\,C\,(s) \rightarrow Si\,(s) + 2\,CO\,(g)$ (Reaction 2)

Strategy

Use Equation 14.6 to determine the enthalpy change and Equation 14.12 to determine the entropy change for Reaction 2 using the enthalpies of formation and entropies in the table. Use the values and Equation 14.16 to determine the standard Gibbs energy change.

Solution

Using Equation 13.6

$$\begin{aligned}\Delta_r H^\ominus_{298} &= \sum \nu_i\ \Delta_f H^\ominus_{298}\,(\text{products}) - \sum \nu_i\ \Delta_f H^\ominus_{298}\,(\text{reactants})\\ &= \{\Delta_f H^\ominus_{298}(\text{Si(s)}) + 2\times \Delta_f H^\ominus_{298}(\text{CO(g)})\}\\ &\qquad - \{\Delta_f H^\ominus_{298}(\text{SiO}_2\text{(s)}) + 2\times \Delta_f H^\ominus_{298}(\text{C(s)})\}\\ &= \{0 + 2\times -110.5\ \text{kJ mol}^{-1}\} - \{(-910.9\ \text{kJ mol}^{-1}) + 2\times 0\}\\ &= +689.9\ \text{kJ mol}^{-1}\end{aligned}$$

and Equation 14.11

$$\Delta_r S^\ominus_{298} = \sum \nu_i\ S^\ominus_{298}\,(\text{products}) - \sum \nu_i\ S^\ominus_{298}\,(\text{reactants})$$

$$\begin{aligned}\Delta_r S^\ominus_{298} &= \{S^\ominus_{298}(\text{Si(s)}) + 2\times S^\ominus_{298}(\text{CO(g)})\} - \{S^\ominus_{298}(\text{SiO}_2\text{(s)}) + 2\times S^\ominus_{298}(\text{C(s)})\}\\ &= \{18.8\ \text{J K}^{-1}\text{mol}^{-1} + 2\times 197.7\ \text{J K}^{-1}\text{mol}^{-1}\}\\ &\qquad - \{41.8\ \text{J K}^{-1}\text{mol}^{-1} + 2\times 5.7\ \ \text{J K}^{-1}\text{mol}^{-1}\}\\ &= +361\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Using Equation 14.16

$$\begin{aligned}\Delta_r G^\ominus_{298} &= \Delta_r H^\ominus_{298} - T\Delta_r S^\ominus_{298}\\ &= +689.9\times 10^3\,\text{J mol}^{-1} - 298\ \text{K}\times +361\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +582.3\times 10^3\,\text{J mol}^{-1} = \ +582.3\ \text{kJ mol}^{-1}\end{aligned}$$

$\Delta_r G^\ominus{}_{298}$ is thus still positive, so the reaction is not spontaneous, but it is significantly less positive than for Reaction 1.

(f) Estimate the temperature at which $\Delta_r G^\ominus = 0$ for this reaction. Comment on your answer.

Strategy

Rearrange Equation 14.16 and solve for the temperature at which $\Delta_r G^\ominus = 0$.

Solution

From Equation 14.16

$$\Delta_r G^{\ominus}_{298} = \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298} = 0$$

then, rearranging,

$$T = \Delta_r H^{\ominus}_{298}/\Delta_r S^{\ominus}_{298} = +689.9 \times 10^3 \text{J mol}^{-1}/{+361}\ \text{J K}^{-1}\text{mol}^{-1} = 1911\ \text{K}$$

The temperature at which the reaction becomes spontaneous is thus lower than for reaction 1, but still very high.

(g) Repeat the calculations of $\Delta_r G^{\ominus}{}_{298}$ and the temperature at which $\Delta_r G^{\ominus} = 0$ for this reaction

$$SiO_2\,(s) + C\,(s) \rightarrow Si\,(s) + CO_2\,(g) \qquad \text{(Reaction 3)}$$

Strategy

Use Equation 13.6 to determine the enthalpy change and Equation 14.12 to determine the entropy change for Reaction 3 using the enthalpies of formation and entropies in the table. Use the values and Equation 14.16 to determine the standard Gibbs energy change.

Solution

Using Equation 13.6

$$\begin{aligned}\Delta_r H^{\ominus}_{298} &= \sum \nu_i\, \Delta_f H^{\ominus}_{298}\,(\text{products}) - \sum \nu_i\, \Delta_f H^{\ominus}_{298}\,(\text{reactants})\\ &= \{\Delta_f H^{\ominus}_{298}(\text{Si(s)}) + \Delta_f H^{\ominus}_{298}(\text{CO}_2(\text{g}))\} - \{\Delta_f H^{\ominus}_{298}(\text{SiO}_2(\text{s})) + \Delta_f H^{\ominus}_{298}(\text{C(s)})\}\\ &= \{0 + (-393.5\ \text{kJ mol}^{-1})\} - \{(-910.9\ \text{kJ mol}^{-1}) + 0\}\\ &= +517.4\ \text{kJ mol}^{-1}\end{aligned}$$

and Equation 14.11

$$\Delta_r S^{\ominus}_{298} = \sum \nu_i\, S^{\ominus}_{298}\,(\text{products}) - \sum \nu_i\, S^{\ominus}_{298}\,(\text{reactants})$$

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= \{S^{\ominus}_{298}(\text{Si(s)}) + S^{\ominus}_{298}(\text{CO}_2(\text{g}))\} - \{S^{\ominus}_{298}(\text{SiO}_2(\text{s})) + S^{\ominus}_{298}(\text{C(s)})\}\\ &= \{18.8\ \text{J K}^{-1}\text{mol}^{-1} + 213.7\ \text{J K}^{-1}\text{mol}^{-1}\}\\ &\qquad - \{41.8\ \text{J K}^{-1}\text{mol}^{-1} + 5.7\ \ \text{J K}^{-1}\text{mol}^{-1}\}\\ &= +185\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Using Equation 14.16

$$\begin{aligned}\Delta_\mathrm{r}G^{\ominus}_{298} &= \Delta_\mathrm{r}H^{\ominus}_{298} - T\Delta_\mathrm{r}S^{\ominus}_{298}\\ &= +517.4\times10^{3}\,\mathrm{J\ mol^{-1}} - 298\ \mathrm{K}\times +185\ \mathrm{J\ K^{-1}mol^{-1}}\\ &= +462.3\times10^{3}\,\mathrm{J\ mol^{-1}} = \ +462.3\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

From Equation 14.16

$$\Delta_\mathrm{r}G^{\ominus}_{298} = \Delta_\mathrm{r}H^{\ominus}_{298} - T\Delta_\mathrm{r}S^{\ominus}_{298} = 0$$

then, rearranging,

$$T = \Delta_\mathrm{r}H^{\ominus}_{298}/\Delta_\mathrm{r}S^{\ominus}_{298} = +517.4\times10^{3}\,\mathrm{J\ mol^{-1}}/{+185}\ \mathrm{J\ K^{-1}mol^{-1}} = 2797\ \mathrm{K}$$

(h) How does the change in entropy influence which reaction is actually used?

Strategy

Consider the magnitude of $\Delta_\mathrm{r}S^{\ominus}{}_{298}$ for Reactions 2 and 3.

Solution

A large positive entropy change lowers the temperature at which $\Delta_\mathrm{r}G^{\ominus}{}_{298} = 0$. Reaction 2, with its larger entropy change, occurs at a lower temperature than Reaction 3 and so at 2500 K, Reaction 2 will be the spontaneous process.

Box 14.8 Energetics of biochemical reactions (on p. 683 in *Chemistry*^{3})

(a) The enthalpy change for the hydrolysis of ATP under biochemical standard conditions at 37°C (310 K) is $\Delta_\mathrm{r}H^{\ominus} = -20\ \mathrm{kJ\ mol^{-1}}$ (Reaction 2). Calculate the entropy change under these conditions and comment on the value.

Strategy

Use Equation 14.16, and substitute the know values for the Gibbs energy and enthalpy changes of reaction.

Solution

Using Equation 14.16

$$\Delta_\mathrm{r}G^{\ominus\prime} = \Delta_\mathrm{r}H^{\ominus\prime} - T\Delta_\mathrm{r}S^{\ominus\prime}$$

and rearranging

$$\begin{aligned}\Delta_r S^{\ominus\prime} &= \frac{\Delta_r H^{\ominus\prime} - \Delta_r G^{\ominus\prime}}{T}\\ &= \frac{-20\times 10^3\ \mathrm{J\ mol^{-1}} - (-30.5\times 10^3\ \mathrm{J\ mol^{-1}})}{(273+37)\ \mathrm{K}}\\ &= +33.9\ \mathrm{J\ K^{-1} mol^{-1}}\end{aligned}$$

The reaction has a positive entropy change. Since the enthalpy change is also negative, the reaction is spontaneous under all conditions.

(b) Calculate the overall Gibbs energy change for the following reaction at 37°C

glucose (aq) + ATP (aq) → glucose-6-phosphate (aq) + ADP (aq) + H⁺ (aq)

Strategy

Express the reaction as a combination of Reactions 1 and 2. Hence determine the Gibbs energy change as the equivalent combination of the Gibbs energy changes for Reactions 1 and 2

Solution

The reaction

$$C_6H_{12}O_6\ (aq) + ATP\ (aq) \rightarrow C_6H_{11}O_6P_i^{2-}\ (aq) + ADP\ (aq) + H^+\ (aq)$$

is the sum of Reactions 1 and 2

$$C_6H_{12}O_6\ (aq) + P_i^{2-}\ (aq) \rightarrow C_6H_{11}O_6P_i^{2-}\ (aq) + H_2O\ (l) \qquad \Delta_r G_1^{\ominus\prime} = +13.4\ \mathrm{kJ\ mol^{-1}}$$

$$ATP\ (aq) + H_2O\ (l) \rightarrow ADP\ (aq) + H^+\ (aq) + P_i^{2-}\ (aq) \qquad \Delta_r G_2^{\ominus\prime} = -30.5\ \mathrm{kJ\ mol^{-1}}$$

The Gibbs energy change is thus

$$\Delta_r G^{\ominus\prime} = \Delta_r G_1^{\ominus\prime} + \Delta_r G_2^{\ominus\prime} = +13.4\ \mathrm{kJ\ mol^{-1}} - 30.5\ \mathrm{kJ\ mol^{-1}} = -17.1\mathrm{kJ\ mol^{-1}}$$

Box 14.9 How much work can you get from glucose? (on p. 686 in *Chemistry*³)

The Shard in London has an observation platform at a height of 244 m. Rather than taking the lift, a person weighing 65 kg climbs the stairs to the platform. How much glucose would the person need to consume to replace the energy used in climbing the stairs?

Strategy

Determine the work done, which is equivalent to the increase in potential energy, in climbing the stairs from Equation 1.16. Calculate the mass of glucose required as a multiple of the energy release by 1 g.

Solution

The potential energy of an object at a height *h* above the surface of the Earth is, from Equation 1.16,

$$E_{\mathrm{PE}} = mgh$$

The work done in climbing the stairs is thus

$$w = 65\ \mathrm{kg} \times 9.81\ \mathrm{m\ s^{-2}} \times 244\ \mathrm{m} = 156 \times 10^3\ \mathrm{J} = 156\ \mathrm{kJ}$$

A mass of 1 g glucose provides 16 kJ so

$$156\ \mathrm{kJ}/16\ \mathrm{kJ\ g^{-1}} = 9.8\ \mathrm{g}$$

glucose would be needed. In practice, more than this would be needed because of inefficiencies in the transfer of energy; the body does not use sugars with 100% efficiency.

Box 14.10 Extraction of metals from ores (on p. 689 in *Chemistry*^{3})

(a) Predict the sign of the entropy changes for Reactions 1–3.

Strategy

Consider in turn, whether each reaction results in an increase, or a decrease in the amount of gas. An increase in the amount of gas would correspond to an increase in disorder, and hence a positive value for the change in entropy. Conversely, a decrease would correspond to a decrease in disorder and hence a negative value for the change in entropy.

Solution

Reaction 1:

$$\mathrm{M(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \mathrm{MO\,(s)}$$

Gas is converted into solid so $\Delta n_{\text{gas}} = -½$. There is thus an increase in order, so that the value of ΔS is negative.

Reaction 2:

$$\text{C(s)} + ½\ \text{O}_2\ \text{(g)} \rightarrow \text{CO (g)}$$

The reaction results in an increase in the amount of gas, $\Delta n_{\text{gas}} = +½$, so there is an increase in the disorder and the value of ΔS is positive.

Reaction 3:

$$\text{C(s)} + \text{O}_2\ \text{(g)} \rightarrow \text{CO}_2\ \text{(g)}$$

There is no change in the amount of gas, $\Delta n_{\text{gas}} = 0$, so any change in the entropy will be small.

(b) Explain why the line for CO slopes upwards, that for CO_2 is almost horizontal while those for the metal oxides slope downward.

Strategy

Differentiate Equation 14.16 and so obtain an expression that shows how the gradients of the lines on the Ellingham diagram depend on the standard entropy change of reaction.

Solution

Differentiating Equation 14.16,

$$\Delta_{\text{r}}G^{\ominus} = \Delta_{\text{r}}H^{\ominus} - T\Delta_{\text{r}}S^{\ominus}$$

with respect to temperature results in an expression for the rate of change of the Gibbs energy with temperature, which is just the gradient of the lines on the Ellingham diagram. Thus

$$\left(\frac{\partial \Delta_{\text{r}}G^{\ominus}}{\partial T}\right)_p = \left(\frac{\partial \Delta_{\text{r}}H^{\ominus}}{\partial T}\right)_p - \left(\frac{\partial (T\Delta_{\text{r}}S^{\ominus})}{\partial T}\right)_p \approx -\Delta_{\text{r}}S^{\ominus}$$

because the enthalpy and entropy of reaction vary little with temperature, so that

$$\left(\frac{\partial \Delta_{\text{r}}H^{\ominus}}{\partial T}\right)_p \approx 0$$

and

$$\left(\frac{\partial \Delta_\mathrm{r} S^\ominus}{\partial T}\right)_p \approx 0$$

Ellingham diagrams are conventionally drawn so that the Gibbs energy is plotted as running from negative to positive, so that the gradient of the plot is

$$m = -\left(\frac{\partial \Delta_\mathrm{r} G^\ominus}{\partial T}\right)_p = +\Delta_\mathrm{r} S^\ominus$$

The gradient of the line for a reaction for which the entropy change is negative, $\Delta_\mathrm{r} S^\ominus < 0$, thus has a negative slope. For a reactions such as Reaction 1, for which $\Delta_\mathrm{r} S^\ominus > 0$, then we should expect the line on the diagram to slope upwards, which it does. Conversely, for Reaction 2, because $\Delta_\mathrm{r} S^\ominus < 0$, the line slopes downwards. Because for Reaction 3, $\Delta_\mathrm{r} S^\ominus \approx 0$, then the line is almost horizontal.

(c) Use the Ellingham diagram to estimate the lowest temperature at which zinc oxide can be reduced to the metal by carbon.

Strategy

Find the temperature at which the two lines cross. This will be the point at which the Gibbs energy of the two reactions are equal.

Solution

The ZnO and CO lines cross over at around 1300 K, so this is the lowest temperature at which reduction will occur spontaneously.

(d) Suggest why aluminium is produced using an electrochemical method rather than by reduction of the oxide.

Strategy

Using the Ellingham diagram, decide which metals could be used to reduce aluminium oxide and under what conditions.

Solution

It appears from the Ellingham diagram that aluminium oxide may only be reduced by carbon and magnesium, and even then only at high temperatures. The line for aluminium oxide crosses that for carbon at a temperature of approximately 2300 K. Achieving this temperature would make the process too expensive to be economically feasible.

Answers to end of chapter questions

1. (a) Explain the meaning of the term ‘spontaneous’ as applied to a chemical or physical change.

(b) Explain why some reactions which appear to be spontaneous from thermodynamic data do not in fact take place. Illustrate your answer by referring to the following changes:

(i) $H_2O(s) \rightarrow H_2O(l)$

(iii) Oxidation of aluminium in air.

Strategy

Whether a reaction is *thermodynamically* favourable depends on the conditions, particularly temperature and pressure according to the Second Law. Even if a reaction is thermodynamically favourable it may be *kinetically* unfavourable and so proceed so slowly as to be unobservable.

Solution

(a) Spontaneous changes are those that, once started, will continue without any outside intervention.

(b) A reaction needs to be both thermodynamically and kinetically favourable in order to take place under a given set of conditions. In example (i), $H_2O(s)$ only melts when the temperature is above 273 K, because this is the temperature at which the entropy changes in the system and surroundings are equal. Above this temperature the total entropy change for melting is positive and the $H_2O(s)$ melts spontaneously. Kinetic factors can play a part in the reverse process – freezing of water to form ice. If very pure water is cooled slowly it can exist as a ‘supercooled’ liquid at temperatures lower than 0°C. In example (ii), the reaction is thermodynamically favourable at room temperature, but it is kinetically unfavourable because the aluminium becomes covered in a thin layer of aluminium oxide which prevents oxygen reaching the metal surface. Further reaction occurs extremely slowly, and the aluminium effectively remains unoxidized.

2. Predict the sign of the change in entropy *in the system* in the following processes.

Strategy

Use the general rule that gases, and solids in aqueous solution, have a higher entropy than liquids, which have a higher entropy than solids.

Solution

a Steam condensing on a cold window. Negative because entropy decreases as a less ordered gas forms a liquid.

b A cloud forming in the atmosphere. As for (a).

c Inflating a bicycle tyre with air Negative because the entropy of a gas decreases with pressure.

d Dissolving sugar in hot coffee. Positive (a solid changes to an aqueous solution with an increase in disorder.)

e $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ Negative because the number of molecules of gas decreases, increasing the order in the system.

f $H_2O(g) + CaSO_4(s) \rightarrow CaSO_4{\bullet}H_2O(s)$ Negative because the number of molecules of gas decreases and so does the disorder.

g $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ As the equation is written this will be negative (one molecule each of a gas and a liquid are converted to a molecule in aqueous solution). However, if the solution is dilute the H_2SO_4 will dissociate into $2H^+(aq)$ and $SO_4^{2-}(aq)$, so the entropy change is likely to be positive.

h 2 $KCl(s) + H_2SO_4(l) \rightarrow K_2SO_4(s) + 2\ HCl(g)$ Positive because two molecules of gas are formed increasing the disorder.

i $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$. Negative because two molecules of gas are converted to a molecule of liquid with a decrease in disorder.

3. An apparatus consists of two bulbs of the same volume connected by a tap. Initially, the tap is closed with one bulb containing nitrogen gas and the other oxygen gas. Both bulbs are at the same temperature and pressure.

(a) What happens when the tap is opened? What will be the equilibrium state of the system?

(b) What are the signs of ΔH, ΔS and ΔG for the process in (a)?

(c) Is this consistent with the Second Law of Thermodynamics?

Strategy

(a) Decide what will happen to the gases when the tap is opened and whether this is likely to be a spontaneous process. (b) Consider how the enthalpy changes for a system containing ideal gases in which the temperature and pressure remain constant. Determine the sign of the entropy change by deciding whether the process results in an increase or decrease in disorder. Apply Equation 14.16 to determine the change in the Gibbs energy. (c) Consider the conditions on the total entropy or Gibbs energy of the system for a process to be spontaneous.

Solution

(a) The two gases gradually diffuse into each other and mix until the concentrations of each gas are the same in both bulbs.

(b) There is no temperature change and the mixing occurs at constant pressure, so the enthalpy change for ideal gases where no interactions occur is

$$\Delta_r H^{\ominus} = 0$$

The mixed gases have greater disorder (randomness) than when in separate bulbs so the entropy change will be positive

$$\Delta_r S^\ominus > 0$$

From Equation 14.16,

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -T\Delta_r S^\ominus$$

so

$$\Delta_r G^\ominus < 0$$

(c) The diffusion and mixing of gases is a spontaneous process. The Second Law states that for a change to be spontaneous

$$\Delta S_{\text{total}} > 0$$

which is equivalent to the condition

$$(\mathrm{d}G)_{p,T} < 0$$

Thus, this is all consistent with the Second Law.

4. Estimate the change in entropy when 1.00 mol of argon is heated from 300 K to 1200 K. What assumptions have you made and how could you make your estimate more accurate? (The heat capacity, C_p of argon gas is 20.8 J K^{-1} mol^{-1}.)

Strategy

Use Equation 14.7 to calculate how the molar entropy changes on heating.

Solution

From Equation 14.7

$$S_{T_\mathrm{f}} = S_{T_\mathrm{i}} + C_p \ln(T_\mathrm{f}/T_\mathrm{i})$$

then the molar entropy change

$$\Delta S_\mathrm{m} = S_{T_\mathrm{f}} - S_{T_\mathrm{i}} = C_{p,\mathrm{m}} \ln(T_\mathrm{f}/T_\mathrm{i})$$

Thus, the entropy change for 1 mol is

$$\Delta S = n\Delta S_\mathrm{m} = nC_{p,\mathrm{m}} \ln(T_\mathrm{f}/T_\mathrm{i})$$
$$= 1.0\ \mathrm{mol} \times 20.8\ \mathrm{J\ K^{-1} mol^{-1}} \times \ln(1200\ \mathrm{K}/300\ \mathrm{K})$$

$$= +28.8\ \mathrm{J\ K^{-1}mol^{-1}}$$

The calculation assumes that the heat capacity remains constant across the whole temperature range. The estimate could be improved by accounting for the variation using a series function to describe how C_p varies with temperature.

5. For each of the following reactions, suggest whether the entropy change in the system would be (i) near zero; (ii) positive or (iii) negative. Explain your answers.

(a) $N_2\ (g) + 3H_2\ (g) \rightarrow 2\ NH_3\ (g)$

(b) $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

(c) $3\ Mg\ (s) + 2\ Fe^{3+}\ (aq) \rightarrow 3\ Mg^{2+}(aq) + 2\ Fe\ (s)$

(d) $CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$

(e) $C\ (diamond) \rightarrow C\ (graphite)$

Strategy

Consider whether there is an increase or decrease in the disorder of the system. An increase in disorder, such as that expected when there is an increase in the amount of gas or ions in solution, will lead to a positive value for the entropy change. Conversely, a decrease in disorder will lead to a negative entropy change.

Solution

(a) The amount of gas decreases as a result of the reaction,

$$\Delta n_{\mathrm{gas}} = 2 - 4 = -2$$

so the entropy is reduced. Thus, ΔS is negative.

(b) There is little change in disorder and so only a small change in entropy. $\Delta S \approx 0$

(c) The reaction increases the number of ions in solution and so results in greater disorder. ΔS is positive.

(d) There is no change in the amount of gas

$$\Delta n_{\mathrm{gas}} = 3 - 3 = -0$$

so only a small change in entropy, $\Delta S \approx 0$

(e) Diamond has a more organised structure than graphite so the entropy increases. ΔS is positive.

6. Dissolving solid potassium iodide in water results in a lowering of the temperature. Explain why this endothermic process can be spontaneous.

Strategy

Consider the entropy changes in the system and the surroundings for this process.

Solution

The entropy change in the system is positive because a solid is being converted to aqueous ions which have much higher entropy. This is more than enough to compensate for the negative entropy change in the surroundings caused by absorption of heat as the solid dissolves.

7. Calculate the entropy change when 1 mol of water is heated from 250 K to 300 K.

The enthalpy change of fusion for water is at 0 °C is +6.01 kJ mol^{-1} and the heat capacities are C_p = 75.3 J K^{-1} mol^{-1} and 37.2 J K^{-1} mol^{-1} for water and ice respectively.

Strategy

There are three stages, each with its own entropy change.

Stage 1: heating $H_2O(s)$ from 250 K to its melting point at 273 K (equation 14.7).

Stage 2: melting $H_2O(s)$ to $H_2O(l)$ (equation 14.6)

Stage 3: heating $H_2O(l)$ from 273 K to 300 K (equation 14.7)

The total entropy change is given by adding together the entropy change for each of these three stages.

Solution

$$\Delta S^{\ominus}_{total} = \int_{250}^{273} \frac{C_\text{p}(\text{solid})}{T}\text{d}T + \frac{\Delta_\text{fus}H^{\ominus}}{T_\text{m}} + \int_{273}^{300} \frac{C_\text{p}(\text{liquid})}{T}\text{d}T$$

$$\Delta S^{\ominus}_{total} = C_\text{p}(\text{solid}) \times \ln\frac{273}{250} + \frac{\Delta_\text{fus}H^{\ominus}}{T_\text{m}} + C_\text{p}(\text{liquid}) \times \ln\frac{300}{273}$$

$$\Delta S^{\ominus}_{total} = 37.2\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln\frac{273\text{K}}{250\text{K}} + \frac{\Delta_\text{fus}H^{\ominus}}{T_\text{m}} + 75.3\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln\frac{300\text{K}}{273\text{K}}$$

$\Delta S_{total}{}^{\ominus}$ = 3.27 J K^{-1} mol^{-1} + 22.01 J K^{-1} mol^{-1} + 7.10 J K^{-1} mol^{-1}

$\Delta S_{total}{}^{\ominus}$ = 32.38 J K^{-1} mol^{-1}

8. 100.0 g of water at 30 °C were placed in a refrigerator at 4 °C. When the water cools down, what is the entropy change of (a) the water and (b) the refrigerator? What is the overall entropy change? Comment on the results.

Strategy

(a) Use equation 14.7 to find the entropy change when water is cooled from 30 °C to 4 °C.

(b) Use equation 13.2 to calculate the quantity of heat, *q*, released by the water when it is cooled from 30 °C to 4 °C. Then use equation 14. 4 to find the entropy change in the refrigerator (the surroundings).

Add the two entropy changes in (a) and (b) and see whether the overall entropy change is positive as the Second Law of Thermodynamics would predict.

Solution

(a). The amount of water in 100.0 g $n = \dfrac{100\ \text{g}}{18.02\ \text{g mol}^{-1}} = 5.55\ \text{mol}$

$$\Delta S = nC_\text{p}\ \ln\left(\frac{T_\text{f}}{T_\text{i}}\right) = 5.55\ \text{mol} \times 75.3\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln\frac{277\ \text{K}}{303\ \text{K}}$$

ΔS (water) = - 37.5 J K^{-1}

(b) The heat released by the water as it cools, and absorbed by the refrigerator,

$q = n\,C_p\,\Delta T$

q = 5.55 mol × 75.3 J K^{-1} mol^{-1} × (303 K – 277 K) = + 10870 J

The refrigerator is maintained at 277 K so $\Delta S = \dfrac{q}{T} = \dfrac{10870\ \text{J}}{277\ \text{K}}$

ΔS (refrigerator) = + 39.2 J K^{-1}

The *overall* entropy change is therefore (- 37.5 J K^{-1} + 39.2 J K^{-1}) = + 1.7 J K^{-1}. There is an overall increase in entropy as expected from the Second Law of Thermodynamics.

9. Given that the normal melting and boiling points of CO are 74 K and 82 K respectively, sketch a plot to show how the entropy of CO varies with temperature between 0 K and 273 K.

Strategy

Think about ΔS for each of the following stages:

Stage 1: heating CO(s) from 0 to 74 K

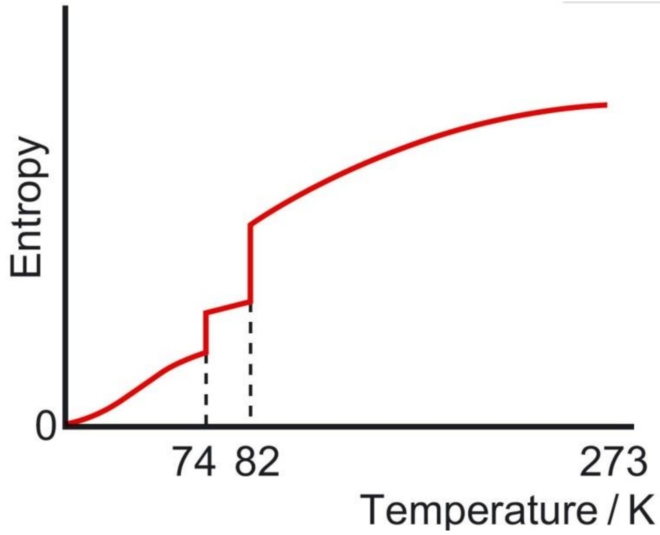
Stage 2: melting CO(s) to CO(l) at 74 K

Stage 3: heating CO(l) from 74 K to 82 K

Stage 4: vaporising CO(l) to CO(g) at 82 K (this will be larger than ΔS for Stage 2)

Stage 5: heating CO(g) from 82 K to 273 K

Solution



10. What are the signs of ΔH, ΔS and ΔG for the process of a vapour condensing to form a liquid?

Strategy

Consider whether heat is released by or transferred to the vapour on condensation and hence determine the sign of the enthalpy change. Also consider how the degree of disorder changes and thus the effect on the sign of the entropy change. Finally, use Equation 14.16 to predict the sign of the Gibbs energy change based on your previous answers.

Solution

Heat is released during condensation so $\Delta_{\text{vap}}H$ is negative. In condensing, a disordered vapour becomes a more ordered liquid, so that $\Delta_{\text{vap}}S$ is negative. Since, from Equation 14.16

$$\Delta_{\text{vap}}G = \Delta_{\text{vap}}H - T\Delta_{\text{vap}}S$$

then if

$$\Delta_{\text{vap}}H < 0$$

and if

$$\Delta_{\text{vap}}S > 0$$

then

$$-T\Delta_{\text{vap}}S > 0$$

The enthalpic and entropic terms are thus in competition. The balance between the two, and thus the sign of the change in the Gibbs energy will depend upon the temperature. Condensation will become spontaneous at a temperature when

$$\Delta_{\text{vap}}G = \Delta_{\text{vap}}H - T\Delta_{\text{vap}}S = 0$$

and which is given by

$$T = \frac{\Delta_{\text{vap}}H}{\Delta_{\text{vap}}S}$$

11. An ice cube of mass 18 g is added to a large glass of water just above 0 °C. Calculate the change of entropy for the ice and for the water, (without the ice). The enthalpy change of fusion for water is +6.01 kJ mol^{-1}.

Strategy

Determine the amount of ice that corresponds to a mass of 18 g from the molar mass of water. Hence determine the enthalpy change and the heat transferred on melting. Use Equation 14.4 to determine the entropy change.

Solution

The molar mass of water is

$$M = \{16.00 + (2 \times 1.01)\}\ \text{g mol}^{-1} = 18.02\ \text{g mol}^{-1}$$

Thus, 18 g is equivalent to 1 mol. The heat transferred from the water to the ice as it melts reversibly is

$$q_{\text{rev}} = q = \Delta H = \Delta_{\text{fus}}H = +6.01 \times 10^3\ \text{J mol}^{-1}$$

Treating the ice as the system and the water as the surroundings, then from Equation 14.4, the entropy change is

$$\Delta S_{\text{ice}} = \frac{q_{\text{rev}}}{T} = \frac{+6.01 \times 10^3\ \text{J mol}^{-1}}{273\ \text{K}} = +22.0\ \text{J K}^{-1}\text{mol}^{-1}$$

assuming that the temperature remains constant.

Now considering the water, the heat transferred from the ice to the water is thus

$$q_{\text{rev}} = -6.01 \times 10^3\ \text{J mol}^{-1}$$

and so

$$\Delta S_{\text{water}} = \frac{q_{\text{rev}}}{T} = \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}} = -22.0 \text{ J K}^{-1}\text{mol}^{-1}$$

12. Calculate the change in entropy when 100 g of water at 90 °C is added to an insulated flask containing 100 g of water at 10 °C.

Strategy

Deduce the final temperature of the water. Calculate the molar mass of water and hence determine the amount of water that corresponds to 100 g. Then use Equation 14.7, using the value for the heat capacity of water, to determine the entropy change for this amount.

Solution

Since 100 g of hot water is added to 100 g of cold water, the final temperature will be the mean of the two starting temperatures, i.e. 50 °C. The molar mass of water is

$$M = \{16.00 + (2 \times 1.01)\} \text{ g mol}^{-1} = 18.02 \text{ g mol}^{-1}$$

so that 100 g is equivalent to

$$n = m/M = 100 \text{ g} / 18.02 \text{ g mol}^{-1} = 5.55 \text{ mol}$$

The heat transferred from the water to the ice

From Equation 14.7

$$S_{T_\text{f}} = S_{T_\text{i}} + C_p \ln(T_\text{f}/T_\text{i})$$

then the molar entropy change

$$\Delta S_\text{m} = S_{T_\text{f}} - S_{T_\text{i}} = C_{p,\text{m}} \ln(T_\text{f}/T_\text{i})$$

Remembering that the temperatures must be in units of kelvin, so that for the cold water,

$$T_\text{i} = (273 + 10) \text{ K} = 283 \text{ K}$$
$$T_\text{f} = (273 + 50) \text{ K} = 323 \text{ K}$$

then the entropy change for an amount n is

$$\begin{aligned}\Delta S &= n\Delta S_\mathrm{m} = nC_{p,\mathrm{m}}\ln(T_\mathrm{f}/T_\mathrm{i})\\ &= 5.55\ \mathrm{mol} \times 75.2\ \mathrm{J\ K^{-1}mol^{-1}} \times \ln(323\ \mathrm{K}/283\ \mathrm{K})\\ &= +55.2\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

For the hot water,

$$T_\mathrm{i} = (273 + 90)\ \mathrm{K} = 363\ \mathrm{K}$$

$$T_\mathrm{f} = (273 + 50)\ \mathrm{K} = 323\ \mathrm{K}$$

then the entropy change for an amount *n* is

$$\begin{aligned}\Delta S &= n\Delta S_\mathrm{m} = nC_{p,\mathrm{m}}\ln(T_\mathrm{f}/T_\mathrm{i})\\ &= 5.55\ \mathrm{mol} \times 75.2\ \mathrm{J\ K^{-1}mol^{-1}} \times \ln(323\ \mathrm{K}/363\ \mathrm{K})\\ &= -48.7\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

The total entropy change is thus

$$\Delta S_\mathrm{total} = +55.2\ \mathrm{J\ K^{-1}mol^{-1}} - 48.7\ \mathrm{J\ K^{-1}mol^{-1}} = +6.5\ \mathrm{J\ K^{-1}mol^{-1}}$$

13. Calculate the standard entropy change at 298 K for the reactions:

(a) $N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$

(b) $Hg\ (l) + Cl_2\ (g) \rightarrow HgCl_2\ (s)$

(c) $C_6H_{12}O_6\ (s) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (g)$

Strategy

Use Equation 14.11, and the data for the standard entropies of the various reactants and products in Appendix 7.

Solution

(a) Using Equation 14.11

$$\Delta_\mathrm{r}S^\ominus_{298} = \sum \nu_i\ S^\ominus_{298}\,(\text{products}) - \sum \nu_i\ S^\ominus_{298}\,(\text{reactants})$$

where the terms in ν_i represent the stoichiometric coefficients of the products and reactants. Using data from Appendix 7, then

$$\begin{aligned}\Delta_\mathrm{r}S^\ominus_{298} &= 2 \times S^\ominus_{298}(\mathrm{NH_3(g)}) - \{S^\ominus_{298}(\mathrm{N_2(s)}) + 3 \times S^\ominus_{298}(\mathrm{H_2(g)})\}\\ &= 2 \times 192.5\ \mathrm{J\ K^{-1}mol^{-1}} - \{191.6\ \mathrm{J\ K^{-1}mol^{-1}} + 3 \times 130.7\ \mathrm{J\ K^{-1}mol^{-1}}\}\end{aligned}$$

$$= -198.7\ \mathrm{J\ K^{-1}mol^{-1}}$$

(b) In the same way,

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= S^{\ominus}_{298}(\mathrm{HgCl_2(s)}) - \{S^{\ominus}_{298}(\mathrm{Hg(l)}) + S^{\ominus}_{298}(\mathrm{Cl_2(g)})\} \\ &= 146.0\ \mathrm{J\ K^{-1}mol^{-1}} - \{76.0\ \mathrm{J\ K^{-1}mol^{-1}} + 223.1\ \mathrm{J\ K^{-1}mol^{-1}}\} \\ &= -153.1\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

(c)

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= \{6 \times S^{\ominus}_{298}(\mathrm{CO_2(g)}) + 6 \times S^{\ominus}_{298}(\mathrm{H_2O(g)})\} \\ &\quad -\{S^{\ominus}_{298}(\mathrm{C_6H_{12}O_6(s)}) + 6 \times S^{\ominus}_{298}(\mathrm{O_2(g)})\} \\ &= \{6 \times 213.7\ \mathrm{J\ K^{-1}mol^{-1}} + 6 \times 188.8\ \mathrm{J\ K^{-1}mol^{-1}}\} \\ &\qquad -\{212.0\ \mathrm{J\ K^{-1}mol^{-1}} + 6 \times 205.1\ \mathrm{J\ K^{-1}mol^{-1}}\} \\ &= +972.4\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

14. Calculate the entropy changes for the system and surroundings when 1.00 mol of NaCl melts at 1100 K. Calculate $\Delta_{\mathrm{fus}}G$ and estimate the melting point of NaCl. (For the melting of sodium chloride (NaCl) $\Delta_{\mathrm{fus}}H = +30.2\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{\mathrm{fus}}S = +28.1\ \mathrm{J\ K^{-1}\ mol^{-1}}$.)

Strategy

Use the value for the standard entropy of fusion to determine the entropy change for the system and the surroundings.. Use Equation 14.16 to calculate the change in Gibbs energy. Rearrange Equation 14.16 and use it to determine the melting temperature at which the solid and liquid are in equilibrium and the Gibbs energy change is 0.

Solution

Standard molar entropy changes refer to the system rather than the surroundings. Thus,

$$\Delta S_{\mathrm{system}} = \Delta_{\mathrm{fus}}S = +28.1\ \mathrm{J\ K^{-1}mol^{-1}}$$

For the surroundings, it is necessary to determine the entropy change from the Second Law of Thermodynamics,

$$\Delta S_{\mathrm{surroundings}} = \frac{-q_{\mathrm{rev}}}{T} = \frac{-\Delta H_{\mathrm{system}}}{T} = \frac{-30.2 \times 10^3\ \mathrm{J\ mol^{-1}}}{1100\ \mathrm{K}} = -27.5\ \mathrm{J\ K^{-1}mol^{-1}}$$

where q_{rev} refers to the heat transferred from the surroundings *to* the system. The total entropy change at this temperature is therefore

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= +28.1\ \mathrm{J\ K^{-1} mol^{-1}} - 27.5\ \mathrm{J\ K^{-1} mol^{-1}} \\ &= +0.6\ \mathrm{J\ K^{-1} mol^{-1}}\end{aligned}$$

The total entropy change of system and surroundings is therefore positive, and so melting must be spontaneous at 1100 K.

Using Equation 14.16,

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= +30.2 \times 10^3\ \mathrm{J\ mol^{-1}} - 1100\ \mathrm{K} \times +28.1\ \mathrm{J\ K^{-1} mol^{-1}} \\ &= -710\ \mathrm{J\ mol^{-1}}\end{aligned}$$

The Gibbs energy change is therefore negative, which is consistent with the observation that melting must be spontaneous at this temperature.

At the melting point,

$$\Delta G = 0$$

and so, using Equation 14.16

$$\Delta_{\text{fus}} G^{\ominus} = \Delta_{\text{fus}} H^{\ominus} - T_{\text{m}} \Delta_{\text{fus}} S^{\ominus} = 0$$

then

$$T_{\text{m}} = \frac{\Delta_{\text{fus}} H^{\ominus}}{\Delta_{\text{fus}} S} = \frac{+30.2 \times 10^3\ \mathrm{J\ mol^{-1}}}{+28.1\ \mathrm{J\ K^{-1} mol^{-1}}} = 1075\ \mathrm{K}$$

15. Calcium carbonate ($CaCO_3$) decomposes to form CaO and CO_2 with $\Delta_{\mathrm{r}}H_{298}$ = +178 kJ mol^{-1} and $\Delta_{\mathrm{r}}S_{298}$ = +161 J K^{-1} mol^{-1}. Estimate the temperature at which the decomposition becomes spontaneous.

Strategy

Rearrange Equation 14.16 and use it to determine the temperature at which the Gibbs energy of reaction is 0.

Solution

Assuming that $\Delta_r H$ and $\Delta_r S$ remain constant, the reaction becomes spontaneous at the temperature when the value of $\Delta_r G$ changes from positive to negative i.e. when $\Delta_r G = 0$. Thus, using Equation 14.16

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} = 0$$

then

$$T = \frac{\Delta_r H^{\ominus}}{\Delta_r S} = \frac{+178 \times 10^3 \,\mathrm{J\ mol^{-1}}}{+161 \,\mathrm{J\ K^{-1} mol^{-1}}} = 1106 \,\mathrm{K}$$

16. You expend about 100 kJ a day keeping your heart beating. What is the minimum mass of glucose you must oxidise per day in order to produce this much energy?

$C_6H_{12}O_6$ (s) + $6O_2$ (g) → $6CO_2$ (g) + 6 H_2O (l) $\Delta G^{\ominus} = -2872$ kJ mol^{-1}

Strategy

Determine the amount of glucose that is required to produce 100 kJ of energy as a proportion of the molar change in Gibbs energy. Calculate the molar mass of glucose and hence determine the mass to which this amount corresponds.

Solution

If the molar change in Gibbs energy of reaction is –2872 kJ mol^{-1}, then –100 kJ must be provided by

$$\frac{-100 \,\mathrm{kJ}}{-2872 \,\mathrm{kJ\ mol^{-1}}} = 0.035 \,\mathrm{mol}$$

The molar mass of glucose is

$$M = \{(6 \times 12.01) + (12 \times 1.01) + (6 \times 16.00)\} \,\mathrm{g\ mol^{-1}} = 180.18 \,\mathrm{g\ mol^{-1}}$$

Thus,

$$m = n \times M = 0.035 \,\mathrm{mol} \times 180.18 \,\mathrm{g\ mol^{-1}} = 6.27 \,\mathrm{g}$$

17. For the reaction:

CH_4 (g) + $2O_2$ (g) $\rightarrow$ CO_2 (g) + $2H_2O$ (l) $\Delta_c H^\ominus_{298} = -890$ kJ mol^{-1}.

(a) Calculate $\Delta_c G^\ominus_{298}$ for the combustion of methane.

(b) How much of the heat produced by burning 1.00 mol of methane cannot be used to do work?

(c) A heat engine uses methane as a fuel. What height could a 1.00 kg mass be raised to by burning 1.00 dm^3 of methane?

Strategy

(a) Use Equation 14.16 to determine the Gibbs energy change from the enthalpy and entropy of combustion. The value for the enthalpy of combustion is given, but it is necessary to use Equation 14.11 and the data in Appendix 7 to determine the entropy change.

(b) Calculate the energy that is not available for work as the difference between the Gibbs energy and enthalpy changes.

(c) The Gibbs energy change is equivalent to the amount of energy that is available for non-expansion work. Determine the amount of methane that corresponds to a volume of 1 dm^3 from the ideal gas equation, and hence calculate the Gibbs energy change for this volume. Use Equation 1.11 to determine the height through which a mass may be lifted by doing this amount of work.

Solution

(a) Using Equation 14.16,

$$\Delta_c G^\ominus = \Delta_c H^\ominus - T\Delta_c S^\ominus$$

The value for the standard enthalpy change is given, but in order to determine the entropy change, then it is necessary to use Equation 14.11

$$\Delta_r S^\ominus_{298} = \sum \nu_i\, S^\ominus_{298}\,(\text{products}) - \sum \nu_i\, S^\ominus_{298}\,(\text{reactants})$$

where the terms in ν_i represent the stoichiometric coefficients of the products and reactants. Using data from Appendix 7, then

$$\Delta_r S^\ominus_{298} = \{S^\ominus_{298}(\text{CO}_2(\text{s})) + 2 \times S^\ominus_{298}(\text{H}_2\text{O}(\text{l}))\} - \{S^\ominus_{298}(\text{CH}_4(\text{g})) + 2 \times S^\ominus_{298}(\text{O}_2(\text{g}))\}$$

$$= \{213.7\ \mathrm{J\ K^{-1} mol^{-1}} + 2 \times 69.9\ \mathrm{J\ K^{-1} mol^{-1}}\}$$
$$-\{186.3\mathrm{J\ K^{-1} mol^{-1}} + 2 \times 205.1\ \mathrm{J\ K^{-1} mol^{-1}}\}$$
$$= -243.0\ \mathrm{J\ K^{-1} mol^{-1}}$$

Thus,

$$\Delta_c G^{\ominus} = \Delta_c H^{\ominus} - T\Delta_c S^{\ominus}$$
$$= -890 \times 10^3 \mathrm{J\ mol^{-1}} - 298\ \mathrm{K} \times -243.0\ \mathrm{J\ K^{-1} mol^{-1}}$$
$$= -818\ \times 10^3 \mathrm{J\ mol^{-1}} = -818\ \mathrm{kJ\ mol^{-1}}$$

(b) The Gibbs energy change represents the maximum amount of non-expansion work that can be done. The amount of energy that cannot be used to do work is therefore the difference between the enthalpy and Gibbs energy changes.

$$= -890 \mathrm{kJ\ mol^{-1}} - (-818\ \mathrm{kJ\ mol^{-1}}) = -72\ \mathrm{kJ\ mol^{-1}}$$

(c) Rearranging the ideal gas equation, Equation 8.5, then a volume of 1 $\mathrm{dm^3} \equiv 10^{-3}\ \mathrm{m^3}$ is equivalent to an amount

$$n = \frac{pV}{RT} = \frac{101325\ \mathrm{Pa} \times 1.00 \times 10^{-3} \mathrm{m^3}}{8.3145\ \mathrm{J\ K^{-1} mol^{-1}} \times 298\ \mathrm{K}} = 0.041\ \mathrm{mol}$$

Burning this amount of methane would result in a Gibbs energy change,

$$\Delta G = n \times \Delta_c G^{\ominus} = 0.041\ \mathrm{mol} \times -818\ \mathrm{kJ\ mol^{-1}} = 33.5\ \mathrm{kJ} = 33.5 \times 10^3 \mathrm{J}$$

This energy is available as work to lift the mass.

$$w = \Delta G$$

The potential energy of an object and thus the work that must be done to raise the object to that position, is given by Equation 1.16,

$$w = \Delta G = E_{\mathrm{PE}} = mgh$$

Rearranging,

$$h = \Delta G/mg = 33.5 \times 10^3 \mathrm{J}/1.00\ \mathrm{kg} \times 9.81\ \mathrm{m\ s^{-2}} = 3.42 \times 10^3\ \mathrm{m} = 3.42\ \mathrm{km}$$

18. Ethanoic acid can be produced by a number of methods, including

(a) the reaction of methanol with carbon monoxide,

$$\mathrm{CH_3OH\ (l) + CO\ (g) \rightarrow CH_3COOH\ (l)}$$

(b) the oxidation of ethanol with oxygen gas,

$$CH_3CH_2OH\ (l) + O_2\ (g) \rightarrow CH_3COOH\ (l) + H_2O\ (l)$$

(c) the reaction of carbon dioxide with methane,

$$CO_2\ (g) + CH_4\ (g) \rightarrow CH_3COOH\ (l)$$

Calculate the standard Gibbs energy change for each of these reactions at 298 K and 773 K.

Strategy

Use Equation 13.6 and 14.11 to determine the standard enthalpy and entropy changes for the reactions at 298 K using the data given in Appendix 7. Also calculate the change in the heat capacity for the reactions using Equation 13.11 using the data in the Appendix and use Equations 13.10 and 14.12 to determine the standard enthalpy and entropy changes for the reactions at 773 K. Determine the Gibbs energy change at both temperatures using Equation 14.16.

Solution

(a) Using Equation 13.6

$$\Delta_r H^{\ominus}_{298} = \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants})$$

$$= \Delta_f H^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) - \{\Delta_f H^{\ominus}_{298}(\mathrm{CH_3OH(g)}) + \Delta_f H^{\ominus}_{298}(\mathrm{CO(g)})\}$$

$$= -484.5\ \mathrm{kJ} - \{-238.4\ \mathrm{kJ\ mol^{-1}} + (-110.5\ \mathrm{kJ\ mol^{-1}})\}$$

$$= -135.6\ \mathrm{kJ\ mol^{-1}}$$

and using Equation 14.11

$$\Delta_r S^{\ominus}_{298} = \sum \nu_i\ S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ S^{\ominus}_{298}\ (\text{reactants})$$

$$\Delta_r S^{\ominus}_{298} = S^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) - \{S^{\ominus}_{298}(\mathrm{CH_3OH(g)}) + S^{\ominus}_{298}(\mathrm{CO(g)})\}$$

$$= 158\ \mathrm{J\ K^{-1}mol^{-1}} - \{126.8\ \mathrm{J\ K^{-1}mol^{-1}} - 197.7\ \mathrm{J\ K^{-1}mol^{-1}}\}$$

$$= -166.5\ \mathrm{J\ K^{-1}mol^{-1}}$$

Combining the two values using Equation 14.16 to calculate $\Delta_r G^{\ominus}_{298}$,

$$\Delta_r G^{\ominus}_{298} = \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298}$$

$$= -135.6 \times 10^3\ \mathrm{J\ mol^{-1}} - 298\ \mathrm{K} \times -166.5\ \mathrm{J\ K^{-1}mol^{-1}}$$

$$= -86.0\ \times 10^3\ \mathrm{J\ mol^{-1}} = -86.0\ \mathrm{kJ\ mol^{-1}}$$

Calculating ΔC_p from Equation 13.11 to convert $\Delta H^\ominus{}_{298}$ and $\Delta S^\ominus{}_{298}$ to the higher temperature,

$$\Delta_r C_p = \sum \nu_i\, C_p\,(\text{products}) - \sum \nu_i\, C_p\,(\text{reactants})$$

$$\begin{aligned}\Delta_r C_p &= C_p(\mathrm{CH_3COOH(l)}) - \{C_p(\mathrm{CH_3OH(g)}) + C_p(\mathrm{CO(g)})\} \\ &= 123.1\ \mathrm{J\ K^{-1}mol^{-1}} - \{81.6\ \mathrm{J\ K^{-1}mol^{-1}} + 29.1\ \mathrm{J\ K^{-1}mol^{-1}}\} \\ &= +12.4\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

Using Equation 13.10 to convert $\Delta_r H^\ominus{}_{298}$ to the higher temperature

$$\Delta_r H^\ominus_{T_2} = \Delta_r H^\ominus_{T_1} + \Delta C^\ominus_p (T_2 - T_1)$$

so that

$$\begin{aligned}\Delta_r H^\ominus_{773} &= \Delta_r H^\ominus_{298} + \Delta C^\ominus_p (773\ \mathrm{K} - 298\ \mathrm{K}) \\ &= -135.6\ \times 10^3\ \mathrm{J\ mol^{-1}} + 12.4\ \mathrm{J\ K^{-1}mol^{-1}} \times 475\ \mathrm{K} \\ &= -130 \times 10^3\mathrm{J\ mol^{-1}} = -130\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Using Equation 14.12

$$\Delta S^\ominus_{T_2} = \Delta S^\ominus_{T_1} + \Delta C^\ominus_p \ln(T_2/T_1)$$

then

$$\begin{aligned}\Delta S^\ominus_{650} &= \Delta S^\ominus_{298} + \Delta C^\ominus_p \ln(773\ \mathrm{K}/298\ \mathrm{K}) \\ &= -166.5\ \mathrm{J\ K^{-1}\ mol^{-1}}\ + 12.4\ \mathrm{J\ K^{-1}mol^{-1}} \ln(773\ \mathrm{K}/298\ \mathrm{K}) \\ &= -154.7\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

so that

$$\begin{aligned}\Delta_r G^\ominus_{773} &= \Delta_r H^\ominus_{773} - T\Delta_r S^\ominus_{773} \\ &= -129.7 \times 10^3\ \mathrm{J\ mol^{-1}} - 773\ \mathrm{K} \times -154.7\ \mathrm{J\ K^{-1}mol^{-1}} \\ &= -10.1\ \times 10^3\ \mathrm{J\ mol^{-1}} = -10.1\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

(b) In the same way for the reaction

$$\mathrm{CH_3CH_2OH\ (l) + O_2\ (g) \rightarrow CH_3COOH\ (l) + H_2O\ (l)}$$

using Equation 13.6

$$\Delta_r H^\ominus_{298} = \sum \nu_i\, \Delta_f H^\ominus_{298}\,(\text{products}) - \sum \nu_i\, \Delta_f H^\ominus_{298}\,(\text{reactants})$$

$$\begin{aligned}
&= \{\Delta_f H^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) + \Delta_f H^{\ominus}_{298}(\mathrm{H_2O(l)})\} \\
&\qquad - \{\Delta_f H^{\ominus}_{298}(\mathrm{CH_3CH_2OH(g)}) + \Delta_f H^{\ominus}_{298}(\mathrm{O_2(g)})\} \\
&= \{-484.5\ \mathrm{kJ\ mol^{-1}} - 285.8\ \mathrm{kJ\ mol^{-1}}\} \\
&\qquad - \{-277.64\ \mathrm{kJ\ mol^{-1}} - 0\} \\
&= -492.7\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

and using Equation 14.11

$$\begin{aligned}
\Delta_r S^{\ominus}_{298} &= \sum \nu_i\ S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ S^{\ominus}_{298}\ (\text{reactants}) \\
&= \{S^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) + S^{\ominus}_{298}(\mathrm{H_2O(l)})\} \\
&\quad -\{S^{\ominus}_{298}(\mathrm{CH_3CH_2OH(g)}) + S^{\ominus}_{298}(\mathrm{O_2(g)})\} \\
&= \{158\ \mathrm{J\ K^{-1} mol^{-1}} + 69.9\mathrm{J\ K^{-1} mol^{-1}}\} \\
&\quad -\{159.9\ \mathrm{J\ K^{-1} mol^{-1}} + 205.1\ \mathrm{J\ K^{-1} mol^{-1}}\} \\
&= -137.1\ \mathrm{J\ K^{-1} mol^{-1}}
\end{aligned}$$

Combining the two values using Equation 14.16 to calculate $\Delta_r G^{\ominus}{}_{298}$,

$$\begin{aligned}
\Delta_r G^{\ominus}_{298} &= \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298} \\
&= -492.7 \times 10^3\ \mathrm{J\ mol^{-1}} - 298\ \mathrm{K} \times -137.1\ \mathrm{J\ K^{-1} mol^{-1}} \\
&= -452\ \times 10^3\ \mathrm{J\ mol^{-1}} = -452.0\ \mathrm{kJ\ mol^{-1}}
\end{aligned}$$

Calculating ΔC_p from Equation 13.11 to convert $\Delta H^{\ominus}{}_{298}$ and $\Delta S^{\ominus}{}_{298}$ to the higher temperature,

$$\begin{aligned}
\Delta_r C_p &= \sum \nu_i\ C_p\ (\text{products}) - \sum \nu_i\ C_p\ (\text{reactants}) \\
&= \{C_p(\mathrm{CH_3COOH(l)}) + C_p(\mathrm{H_2O(l)})\} \\
&\quad -\{C_p(\mathrm{CH_3CH_2OH(g)}) + C_p(\mathrm{O_2(g)})\} \\
&= \{123.1\ \mathrm{J\ K^{-1} mol^{-1}} + 75.3\ \mathrm{J\ K^{-1} mol^{-1}}\} \\
&\quad -\{111.5\ \mathrm{J\ K^{-1} mol^{-1}} + 29.4\ \mathrm{J\ K^{-1} mol^{-1}}\} \\
&= +57.5\ \mathrm{J\ K^{-1} mol^{-1}}
\end{aligned}$$

Using Equation 13.10 to convert $\Delta_r H^{\ominus}{}_{298}$ to the higher temperature

$$\Delta_r H^{\ominus}_{T_2} = \Delta_r H^{\ominus}_{T_1} + \Delta C^{\ominus}_p (T_2 - T_1)$$

so that

$$\begin{aligned}\Delta_r H^{\ominus}_{773} &= \Delta_r H^{\ominus}_{298} + \Delta C^{\ominus}_p(773\ \mathrm{K} - 298\ \mathrm{K})\\ &= -492.7\ \times 10^3\ \mathrm{J\ mol^{-1}} + 57.1\ \mathrm{J\ K^{-1} mol^{-1}} \times 475\ \mathrm{K}\\ &= -465 \times 10^3 \mathrm{J\ mol^{-1}} = -465\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Using Equation 14.12

$$\Delta S^{\ominus}_{T_2} = \Delta S^{\ominus}_{T_1} + \Delta C^{\ominus}_p \ln(T_2/T_1)$$

then

$$\begin{aligned}\Delta S^{\ominus}_{650} &= \Delta S^{\ominus}_{298} + \Delta C^{\ominus}_p \ln(773\ \mathrm{K}/298\ \mathrm{K})\\ &= -137.1\ \mathrm{J\ K^{-1}\ mol^{-1}}\ + 57.1\ \mathrm{J\ K^{-1} mol^{-1}} \ln(773\ \mathrm{K}/298\ \mathrm{K})\\ &= -82.7\ \mathrm{J\ K^{-1} mol^{-1}}\end{aligned}$$

so that

$$\begin{aligned}\Delta_r G^{\ominus}_{773} &= \Delta_r H^{\ominus}_{773} - T\Delta_r S^{\ominus}_{773}\\ &= -465 \times 10^3\ \mathrm{J\ mol^{-1}} - 773\ \mathrm{K} \times -82.7\ \mathrm{J\ K^{-1} mol^{-1}}\\ &= -401\ \times 10^3\ \mathrm{J\ mol^{-1}} = -401\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

(c) And for the reaction

$$\mathrm{CO_2\ (g) + CH_4\ (g) \rightarrow CH_3COOH\ (l)}$$

using Equation 13.6

$$\begin{aligned}\Delta_r H^{\ominus}_{298} &= \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}\ (\text{reactants})\\ &= \Delta_f H^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) - \{\Delta_f H^{\ominus}_{298}(\mathrm{CO_2(g)}) + \Delta_f H^{\ominus}_{298}(\mathrm{CH_4(g)})\}\\ &= -484.5\ \mathrm{kJ\ mol^{-1}} -\ \{-74.8\ \mathrm{kJ\ mol^{-1}} - 393.5\ \mathrm{kJ\ mol^{-1}}\}\\ &= -16.2\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

and using Equation 14.11

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= \sum \nu_i\ S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ S^{\ominus}_{298}\ (\text{reactants})\\ &= S^{\ominus}_{298}(\mathrm{CH_3COOH(l)}) - \{S^{\ominus}_{298}(\mathrm{CO_2(g)}) + S^{\ominus}_{298}(\mathrm{CH_4(g)})\}\\ &= 158.0\ \mathrm{J\ K^{-1} mol^{-1}} - \{186.3\ \mathrm{J\ K^{-1} mol^{-1}} + 213.7\ \mathrm{J\ K^{-1} mol^{-1}}\}\\ &= -242.0\ \mathrm{J\ K^{-1} mol^{-1}}\end{aligned}$$

Combining the two values using Equation 14.16 to calculate $\Delta_r G^{\ominus}{}_{298}$,

$$\begin{aligned}\Delta_r G^\ominus_{298} &= \Delta_r H^\ominus_{298} - T\Delta_r S^\ominus_{298}\\ &= -16.2\times 10^3\ \mathrm{J\ mol^{-1}} - 298\ \mathrm{K}\times -242.0\ \mathrm{J\ K^{-1}mol^{-1}}\\ &= +55.9\ \times 10^3\ \mathrm{J\ mol^{-1}} = +55.9\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Calculating ΔC_p from Equation 13.11 to convert $\Delta H^\ominus{}_{298}$ and $\Delta S^\ominus{}_{298}$ to the higher temperature,

$$\begin{aligned}\Delta_r C_p &= \sum \nu_i\ C_p\ (\text{products}) - \sum \nu_i\ C_p\ (\text{reactants})\\ &= S^\ominus_{298}(\mathrm{CH_3COOH(l)}) - \{S^\ominus_{298}(\mathrm{CO_2(g)}) + S^\ominus_{298}(\mathrm{CH_4(g)})\}\\ &= 123.1\ \mathrm{J\ K^{-1}mol^{-1}} - \{35.7\ \mathrm{J\ K^{-1}mol^{-1}} + 37.1\ \mathrm{J\ K^{-1}mol^{-1}}\}\\ &= +50.3\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

Using Equation 13.10 to convert $\Delta_r H^\ominus{}_{298}$ to the higher temperature

$$\Delta_r H^\ominus_{T_2} = \Delta_r H^\ominus_{T_1} + \Delta C^\ominus_p(T_2 - T_1)$$

so that

$$\begin{aligned}\Delta_r H^\ominus_{773} &= \Delta_r H^\ominus_{298} + \Delta C^\ominus_p(773\ \mathrm{K} - 298\ \mathrm{K})\\ &= -16.2\ \times 10^3\ \mathrm{J\ mol^{-1}} + 50.3\ \mathrm{J\ K^{-1}mol^{-1}} \times 475\ \mathrm{K}\\ &= +7.7\times 10^3\ \mathrm{J\ mol^{-1}} = +7.7\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Using Equation 14.12

$$\Delta S^\ominus_{T_2} = \Delta S^\ominus_{T_1} + \Delta C^\ominus_p \ln(T_2/T_1)$$

then

$$\begin{aligned}\Delta S^\ominus_{650} &= \Delta S^\ominus_{298} + \Delta C^\ominus_p \ln(773\ \mathrm{K}/298\ \mathrm{K})\\ &= -242.0\ \mathrm{J\ K^{-1}\ mol^{-1}}\ + 50.3\ \mathrm{J\ K^{-1}mol^{-1}} \ln(773\ \mathrm{K}/298\ \mathrm{K})\\ &= -194.1\ \mathrm{J\ K^{-1}mol^{-1}}\end{aligned}$$

so that

$$\begin{aligned}\Delta_r G^\ominus_{773} &= \Delta_r H^\ominus_{773} - T\Delta_r S^\ominus_{773}\\ &= 7.7\times 10^3\ \mathrm{J\ mol^{-1}} - 773\ \mathrm{K}\times -194.1\ \mathrm{J\ K^{-1}mol^{-1}}\\ &= +158\times 10^3\ \mathrm{J\ mol^{-1}} = +158\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

19. The reaction of methanol, (CH_3OH (l)), with oxygen can be used in a fuel cell. Using data from Appendix 7 (p.1350), calculate the enthalpy change for the combustion reaction at 298 K and the maximum work that can be produced by the oxidation of 1.00 mol of methanol.

Strategy

Write a balanced chemical equation for the combustion of methanol. Use it, along with Equations 13.6, 14.11 and 14.16 to determine the standard enthalpy, entropy and hence Gibbs energy change for combustion. The maximum non-expansion work that may be performed is equivalent to the Gibbs energy change.

Solution

The chemical equation for the combustion of methanol is

$$CH_3OH\ (l) + 1\tfrac{1}{2}\ O_2\ (g) \rightarrow CO_2\ (g) + H_2O\ (l)$$

Using Equation 13.6 to calculate $\Delta_r H^{\circ}{}_{298}$

$$\begin{aligned}\Delta_r H^{\circ}_{298} &= \sum \nu_i\, \Delta_f H^{\circ}_{298}\,(\text{products}) - \sum \nu_i\, \Delta_f H^{\circ}_{298}\,(\text{reactants})\\ &= \{\Delta_f H^{\circ}_{298}(CO_2(g)) + \Delta_f H^{\circ}_{298}(H_2O(g))\}\\ &\quad - \{\Delta_f H^{\circ}_{298}(CH_3OH(g)) + 1.5 \times \Delta_f H^{\circ}_{298}(O_2(g))\}\\ &= \{-393.5\ \text{kJ mol}^{-1} + (-285.8\ \text{kJ mol}^{-1})\} - \{-238.4\ \text{kJ mol}^{-1} - 0\}\\ &= -440.9\ \text{kJ mol}^{-1}\end{aligned}$$

and using Equation 14.11

$$\Delta_r S^{\circ}_{298} = \sum \nu_i\, S^{\circ}_{298}\,(\text{products}) - \sum \nu_i\, S^{\circ}_{298}\,(\text{reactants})$$

$$\begin{aligned}\Delta_r S^{\circ}_{298} &= \{S^{\circ}_{298}(CO_2(g)) + S^{\circ}_{298}(H_2O(g))\}\\ &\quad - \{S^{\circ}_{298}(CH_3OH(g)) + 1.5 \times S^{\circ}_{298}(O_2(g))\}\\ &= \{213.7\ \text{J K}^{-1}\text{mol}^{-1} + 69.9\ \text{J K}^{-1}\text{mol}^{-1}\}\\ &\quad - \{126.8\ \text{J K}^{-1}\text{mol}^{-1} + (1.5 \times 205.1\ \text{J K}^{-1}\text{mol}^{-1})\}\\ &= -150.9\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Combining the two values using Equation 14.16 to calculate $\Delta_r G^{\circ}{}_{298}$,

$$\begin{aligned}\Delta_r G^{\circ}_{298} &= \Delta_r H^{\circ}_{298} - T\Delta_r S^{\circ}_{298}\\ &= -440.9 \times 10^3\ \text{J mol}^{-1} - 298\ \text{K} \times -150.9\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

$$= -396 \times 10^3 \text{ J mol}^{-1} = -396 \text{ kJ mol}^{-1}$$

The maximum work that can be done by consuming 1 mol of methanol is thus

$$w = \Delta G = -396 \text{ kJ mol}^{-1}$$

20. Calculate the normal boiling point of ethanol given that $\Delta_{\text{vap}}H$ = +42.6 kJ mol^{-1} and $\Delta_{\text{vap}}S$ = +122.0 J K^{-1} mol^{-1}.

Strategy

Use the fact that, at the normal boiling point, the liquid and vapour are in equilibrium so that $\Delta_{\text{vap}}G = 0$.

Solution

$\Delta G = \Delta H - T\Delta S$

$\Delta_{\text{vap}}G = \Delta_{\text{vap}}H - T_b\, \Delta_{\text{vap}}S$

$\Delta_{\text{vap}}G = 0 = \Delta_{\text{vap}}H - T_b\, \Delta_{\text{vap}}S$

$$T_{\text{b}} = \frac{\Delta_{vap}H}{\Delta_{vap}S} = \frac{42.6\times10^3 \text{ J mol}^{-1}}{122 \text{ J K}^{-1} \text{ mol}^{-1}} = 349.2 \text{ K}$$

21. 'Synthesis gas' is a mixture of hydrogen and carbon monoxide, prepared by reacting water or steam with a source of carbon such as coal. The reaction can be represented as:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

Estimate the temperature at which the reaction become thermodynamically spontaneous.

Strategy

The reaction just becomes spontaneous when $\Delta_r G = 0$.

To find $\Delta_r G$, we need $\Delta_r H$ and $\Delta_r S$. These can be calculated from tabulated values for standard enthalpy change of formation, $\Delta_f H^{\circ}_{298}$, and standard entropy, S°_{298}.

Solution

$$\Delta_r H^{\circ}_{298} = \sum \nu_i \; \Delta_f H^{\circ}_{298}(\text{products}) - \sum \nu_i \; \Delta_f H^{\circ}_{298}(\text{reactants})$$

$\Delta_r H^{\circ}_{298} = [0 + (-110.5 \text{ kJ mol}^{-1})]-[(-241.8 \text{ kJ mol}^{-1}) + (0)]$

$= +131.3 \text{ kJ mol}^{-1}$

$$\Delta_r S^{\circ}_{298} = \sum \nu_i \; S^{\circ}_{298}(\text{products}) - \sum \nu_i \; S^{\circ}_{298}(\text{reactants})$$

$\Delta_r S^{\circ}_{298} = [197.7 \text{ J K}^{-1} \text{ mol}^{-1} + 130.7 \text{ J K}^{-1} \text{ mol}^{-1}] - [5.7 \text{ J K}^{-1} \text{ mol}^{-1} + 188.8 \text{ J K}^{-1} \text{ mol}^{-1}]$

$= +133.9 \text{ J K}^{-1} \text{ mol}^{-1}$.

$\Delta_r G^{\circ} \approx \Delta_r H^{\circ}_{298} - T\,\Delta_r S^{\circ}_{298}$

$0 = +131.3 \text{ kJ mol}^{-1} - T \times (+133.9 \text{ J K}^{-1} \text{ mol}^{-1})$

$$T = \frac{131.3 \times 10^3 \text{ J mol}^{-1}}{133.9 \text{ J K}^{-1}\text{mol}^{-1}} = 980.6 \text{ K}$$

This assumes that $\Delta_r H$ and $\Delta_r S$ do not change with temperature and so is only an estimate.

22. Use the mean heat capacities and standard entropies listed in Appendix 7 to estimate the Gibbs energy change for the decomposition of water vapour into hydrogen and oxygen at 2000°C and 1 bar pressure. (The standard enthalpy of formation of water vapour is –241.8 kJ mol^{-1}.)

Strategy

Deduce the enthalpy change for the decomposition reaction at 298 K from the standard enthalpy of formation. Calculate the entropy change at this temperature using Equation 14.12. Use Equation 13.11 to calculate the change in the heat capacity and use this value, along with Equation 13.10 and Equation 14.11 to determine the enthalpy and entropy changes at 2000°C. Combine the two values using Equation 14.16 to determine the Gibbs energy change at this temperature.

Solution

The decomposition of water into hydrogen and oxygen

$$H_2O\ (g) \rightarrow H_2\ (g) + ½\ O_2\ (g)$$

is just the reverse of the formation reaction, so that

$$\Delta_r H^{\ominus}_{298} = -\Delta_f H^{\ominus}_{298} = +241.8\ \text{kJ mol}^{-1}$$

Using Equation 14.11 to calculate $\Delta_r S^{\ominus}{}_{298}$,

$$\begin{aligned}\Delta_r S^{\ominus}_{298} &= \sum \nu_i\ S^{\ominus}_{298}\ (\text{products}) - \sum \nu_i\ S^{\ominus}_{298}\ (\text{reactants})\\ &= \{½ \times S^{\ominus}_{298}(O_2(g)) + S^{\ominus}_{298}(H_2(g))\} - S^{\ominus}_{298}(H_2O(g))\\ &= \{½ \times 205.1\ \text{J K}^{-1}\text{mol}^{-1} + 130.7\ \text{J K}^{-1}\text{mol}^{-1}\} - 188.8\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +44.5\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Calculating ΔC_p using Equation 13.11 to convert $\Delta H^{\ominus}{}_{298}$ and $\Delta S^{\ominus}{}_{298}$ to the higher temperature,

$$\begin{aligned}\Delta_r C_p &= \sum \nu_i\ C_p\ (\text{products}) - \sum \nu_i\ C_p\ (\text{reactants})\\ &= \{½ \times C_p(O_2(g)) + C_p(H_2(g))\} - C_p(H_2O(g))\\ &= \{½ \times 29.4\ \text{J K}^{-1}\text{mol}^{-1} + 28.8\ \text{J K}^{-1}\text{mol}^{-1}\} - 33.6\ \text{J K}^{-1}\text{mol}^{-1}\\ &= +9.9\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Using Equation 13.10 to calculate the enthalpy change at 2000°C ≡ 2273 K

$$\Delta_r H^{\ominus}_{T_2} = \Delta_r H^{\ominus}_{T_1} + \Delta C^{\ominus}_p(T_2 - T_1)$$

so that

$$\begin{aligned}\Delta_r H^{\ominus}_{2273} &= \Delta_r H^{\ominus}_{298} + \Delta C^{\ominus}_p(2273\ \text{K} - 298\ \text{K})\\ &= +241.8\ \times 10^3\ \text{J mol}^{-1} + 9.9\ \text{J K}^{-1}\text{mol}^{-1} \times 1975\ \text{K}\\ &= +261 \times 10^3\ \text{J mol}^{-1} = +261\ \text{kJ mol}^{-1}\end{aligned}$$

Using Equation 14.12

$$\Delta S^{\ominus}_{T_2} = \Delta S^{\ominus}_{T_1} + \Delta C^{\ominus}_p \ln(T_2/T_1)$$

then

$$\begin{aligned}\Delta S^{\ominus}_{2273} &= \Delta S^{\ominus}_{298} + \Delta C^{\ominus}_p \ln(2273\ \mathrm{K}/298\ \mathrm{K})\\ &= +44.5\ \mathrm{J\ K^{-1}\ mol^{-1}}\ + 9.9\ \mathrm{J\ K^{-1} mol^{-1}} \ln(2273\ \mathrm{K}/298\ \mathrm{K})\\ &= +64.6\ \mathrm{J\ K^{-1} mol^{-1}}\end{aligned}$$

so that

$$\begin{aligned}\Delta_\mathrm{r} G^{\ominus}_{2773} &= \Delta_\mathrm{r} H^{\ominus}_{2773} - T\Delta_\mathrm{r} S^{\ominus}_{2773}\\ &= 261 \times 10^3\ \mathrm{J\ mol^{-1}} - 2273\ \mathrm{K} \times +64.6\ \mathrm{J\ K^{-1} mol^{-1}}\\ &= +114 \times 10^3\ \mathrm{J\ mol^{-1}} = +114\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

23. The standard Gibbs energy for a reaction is -332.9 kJ mol^{-1} at 298 K and -339.5 kJ mol^{-1} at 500 K. Estimate the standard entropy change for the reaction.

Strategy

From Equation 14.26, $\left(\dfrac{\mathrm{d}\,\Delta_r G}{dT}\right)_p = -\Delta_r S$

To find the standard entropy change for the reaction, use the integrated form of this equation, assuming $\Delta_\mathrm{r}H$ and $\Delta_\mathrm{r}S$ do not change over the temperature range concerned.

$$\Delta_r S = -\left(\frac{\Delta_r G(T_2) - \Delta_r G(T_1)}{T_2 - \Delta T_1}\right)_p$$

Solution

$$\Delta_r S = -\left(\frac{\Delta_r G(T_2) - \Delta_r G(T_1)}{T_2 - \Delta T_1}\right)_p = -\left(\frac{339.5\ \mathrm{kJ\ mol^{-1}} - 332.9\ \mathrm{kJ\ mol^{-1}}}{500\ \mathrm{K} - 298\ \mathrm{K}}\right)$$

$$\Delta_r S = -\left(\frac{6.6\ \mathrm{kJ\ mol^{-1}}}{202\ \mathrm{K}}\right)$$

$$\Delta_r S = -\,32.7\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

24. Find the changes in enthalpy, entropy and Gibbs energy for the freezing of water at -10 °C at 1 bar pressure. (The enthalpy change of fusion for water at 0 °C is +6.01 kJ mol^{-1} and the heat capacities are C_p = 75.3 J K^{-1} mol^{-1} and 37.2 J K^{-1} mol^{-1} for water and ice respectively.)

Strategy

The process of interest is: $H_2O\ (l) \rightarrow H_2O\ (s)$

(a) You know $\Delta_r H^\ominus_{273}$ and you can use the Kirchhoff Equation (Equation 13.10) to find $\Delta_r H^\ominus_{263}$.

(b) Use Equation 14.6 to find $\Delta_{fus} S^\ominus_{273}$ from $\Delta_r H^\ominus_{273}$. Then use Equation 14.7 to find $\Delta_{fus} S^\ominus_{263}$ from $\Delta_{fus} S^\ominus_{273}$.

(c) Then use these values of $\Delta_r H^\ominus_{263}$ and .$\Delta_{fus} S^\ominus_{263}$ to calculate $\Delta_r G^\ominus_{263}$.

Solution

(a) $\Delta_r H^\ominus_{273} = -(\Delta_{fus} H^\ominus_{273}) = -6010$ J mol^{-1}.

From the Kirchhoff Equation (Equation 13.10),

$\Delta_r H^\ominus_{263} = \Delta_r H^\ominus_{273} + \Delta C_p\,(263 - 273)$ K

$\Delta C_p = C_p\,(H_2O\ (s)) - C_p\,(H_2O\ (l))$

$= 37.2$ J K^{-1} mol^{-1} – 75.3 J K^{-1} mol^{-1}

$= -37.9$ J K^{-1} mol^{-1}.

$\Delta_r H^\ominus_{263} = -6010$ J mol^{-1} + (-37.9) J K^{-1} mol^{-1}) × (-10 K)

$= -5631$ J mol^{-1}.

(b) At the normal melting point, $\Delta_{fus} S^\ominus_{273} = \Delta_r H^\ominus_{273} / T_m$ (Equation 14.6)

$\Delta_{fus} S^\ominus_{273} = 6010$ J mol^{-1} / 273 K

$= +22.0$ J K^{-1} mol^{-1}.

For the process of interest, $\Delta_r S^\ominus_{273} = -(\Delta_{fus} S^\ominus_{273}) = -22.0$ J K^{-1} mol^{-1}

From Equation 14.7,

$$\Delta_r S^{\ominus}{}_{263} = \Delta_r S^{\ominus}{}_{273} + \Delta C_p \ln\left(\frac{263\text{ K}}{273\text{ K}}\right)$$

$$= -22.0\text{ J K}^{-1}\text{ mol}^{-1} + (-37.9\text{ J K}^{-1}\text{ mol}^{-1}) \times (-0.04)$$

$$= -20.5\text{ J K}^{-1}\text{ mol}^{-1}.$$

(c) $\Delta_r G^{\ominus}{}_{263} = \Delta_r H^{\ominus}{}_{263} - T\Delta_r S^{\ominus}{}_{263}$

$$= -5631\text{ J mol}^{-1} - (263\text{ K})(-20.5\text{ J K}^{-1}\text{ mol}^{-1})$$

$$= -239.5\text{ J mol}^{-1}$$

25. Use data from Appendix 7 to consider the following reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) Calculate the changes in enthalpy, entropy and Gibbs energy at 298 K.

(b) Is the reaction spontaneous at 25°C and 1bar? Explain the signs of $\Delta_r H$ and $\Delta_r S$.

Strategy

You can find the enthalpy change for the reaction at 298 K from the standard enthalpies of formation and Hess’ Law (Equation 13.6). The entropy change at this temperature can be calculated from Equation 14.11 and the Gibbs energy change from Equation 14.16. Consideration of the sign of the latter will tell you whether it is spontaneous.

Solution

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) $$\Delta_r H^{\ominus}_{298} = \sum \nu_i\ \Delta_f H^{\ominus}_{298}(\text{products}) - \sum \nu_i\ \Delta_f H^{\ominus}_{298}(\text{reactants})$$

$$\Delta_r H^{\ominus}_{298} = \{(2 \times 33.2) - (2 \times 90.3 + 0)\}\ \text{kJ mol}^{-1}$$

$$= -114.2\ \text{kJ mol}^{-1}.$$

$$\Delta_r S^{\ominus}_{298} = \Sigma\, \nu_i\, S^{\ominus}_{298\ (\text{products})} - \Sigma\, \nu_i\, S^{\ominus}_{298\ (\text{reactants})}$$

$$\Delta_r S^{\ominus}_{298} = \{(2 \times 240.1) - (2 \times 210.8 + 205.1)\}\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= -146.5\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Now calculate $\Delta_r G^{\ominus}_{298}$

$$\Delta_r G^{\ominus}_{298} = \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298}$$

$$= -114.2 - 298 \times (-146.5 \times 10^{-3})\ \text{kJ mol}^{-1}.$$

$$= -70.5\ \text{kJ mol}^{-1}$$

(b)

Yes, it is spontaneous since $\Delta_r G^{\ominus}_{298} < 0$. $\Delta_r H^{\ominus}_{298}$ is negative since strong N=O bonds are formed while $\Delta_r S^{\ominus}_{298} < 0$ due to the increase in order as the number of moles of gas falls during the reaction.

26. Impure nickel metal is purified using the Mond process where it is first reacted at 80 °C with carbon monoxide to form $Ni(CO)_4(g)$

$$Ni(s) + 4\ CO\ (g) \rightarrow Ni(CO)_4(g)$$

followed by heating to 200 °C when the reverse reaction occurs. Use the following data to show that this approach is thermodynamically feasible.

	Ni (s)	$Ni(CO)_4$ (g)	CO (g)
$\Delta_f H^{\ominus}_{298}$ / kJ mol^{-1} :	0	-601.6	-110.5

$S^{\ominus}_{298}$ / J K^{-1} mol^{-1} : 29.9 415.5 197.6

Strategy

You can find the enthalpy and entropy changes for the reaction at 298 K from the data using Equation 13.6 and Equation 14.11. As an approximation, these can be assumed to be constant with temperature so that the Gibbs energy changes at the two temperatures can be found from Equation 14.16 and the signs of the changes used to assess the thermodynamic feasibility of the reactions.

Solution

As a first approximation, assume that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ do not vary with temperature.

$$\Delta_r H^{\ominus}_{298} = -601.6 - \{4 \times (-110.5) + (0)\}\ \text{kJ mol}^{-1} = -159.6\ \text{kJ mol}^{-1}.$$

$$\Delta_r S^{\ominus}_{298} = \Sigma\, \nu_i\, S^{\ominus}_{298\ \text{(products)}} - \Sigma\, \nu_i\, S^{\ominus}_{298\ \text{(reactants)}}$$

$$\Delta_r S^{\ominus}_{298} = +415.5 - \{4 \times (197.6) + 29.9\}\ \text{J K}^{-1}\,\text{mol}^{-1} = -404.8\ \text{J K}^{-1}\,\text{mol}^{-1}$$

Now calculate $\Delta_r G^{\ominus}$. At 80 °C (353 K)

$$\begin{aligned}\Delta_r G^{\ominus}_{353} &= \Delta_r H^{\ominus}_{353} - T\Delta_r S^{\ominus}_{353}\\ &= -159.6\ \text{kJ mol}^{-1} - \{353 \times (-404.8 \times 10^{-3})\}\ \text{kJ mol}^{-1}\\ &= -16.7\ \text{kJ mol}^{-1}\end{aligned}$$

At 200 °C (473 K)

$$\Delta_r G^{\ominus}{}_{473} = \Delta_r H^{\ominus}{}_{473} - T\Delta_r S^{\ominus}{}_{473}$$

$$= -159.6 \;-\{\,(473) \times (-404.8 \times 10^{-3})\}\;\; \text{kJ mol}^{-1}.$$

$$= +31.9 \;\; \text{kJ mol}^{-1}$$

The reaction changes from being spontaneous ($\Delta_r G^{\ominus}{}_{353} < 0$) at 80 °C to non-spontaneous (i.e. the reverse reactions becomes spontaneous) at higher temperatures ($\Delta_r G^{\ominus}{}_{473} > 0$). Thus at 80 °C, the forward reaction is spontaneous so Ni forms $Ni(CO)_4$ vapour, leaving the impurities behind. At 200 °C, the reverse reaction is spontanous so metallic Ni is recovered (free from impurities) and the CO gas can be recycled for further use.

27. Determine the standard Gibbs energy change for the acid-base neutralisation reaction

$$\text{NaOH (aq)} + \text{HCl (aq)} \rightarrow \text{NaCl (aq)} + \text{H}_2\text{O (l)}$$

Strategy

You need to decide what reaction is taking place. Essentially, the sodium and chloride ions take no part in the reaction. You can then find the Gibbs energy change from the Gibbs energy of formation data and Equation 14.18.

Solution

The reaction is: $\text{OH}^- \text{(aq)} + \text{H}^+ \text{(aq)} \rightarrow \text{H}_2\text{O (l)}$

$\Delta_f G^{\ominus}_{298}$ / kJ mol^{-1}: OH^- (aq) -157.3; H^+ (aq) 0; H_2O (l) -237.1

$$\Delta_r G^{\circ}_{298} = \sum v_i \Delta_f G^{\circ}_{298}(\text{products}) - \sum v_i \Delta_f G^{\circ}_{298}(\text{reactants})$$

$$\begin{aligned}\Delta_r G^{\circ}_{298} &= [\Delta_f G^{\circ}_{298}(H_2O(l))\ ] - [\Delta_f G^{\circ}_{298}(H^+(aq)) + \Delta_f G^{\circ}_{298}(OH^-(aq))] \\ &= [(-273.1\,\text{kJmol}^{-1})] - [(0) + (-157.3\,\text{kJmol}^{-1})] \\ &= -79.8\,\text{kJmol}^{-1}\end{aligned}$$

The neutralisation is spontaneous.

28. Two chemists were discussing the possibility of using the waste methane from an oil field to produce useful chemicals. The first suggested it could be reacted with atmospheric $CO_2(g)$ to produce ethanoic acid.

$$CH_4(g) + CO_2(g) \rightarrow CH_3COOH\ (l)$$

The other chemist suggested that the methane should be converted to ethanol by reacting with water.

$$2\ CH_4(g) + H_2O(l) \rightarrow C_2H_5OH\ (l) + 2\ H_2\ (g)$$

Use Gibbs energy of formation data in Appendix 7 to examine the thermodynamic feasibility of these reactions around room temperature.

Strategy

For each reaction, you can find the Gibbs energy change from the Gibbs energy of formation data and Equation 14.18. The sign of $\Delta_f G^{\circ}_{298}$ can be used to assess the feasibility or otherwise of the reaction.

Solution

$$\Delta_r G^{\circ}_{298} = \sum v_i \Delta_f G^{\circ}_{298}(\text{products}) - \sum v_i \Delta_f G^{\circ}_{298}(\text{reactants})$$

$$\begin{aligned}\Delta_r G^{\circ}_{298} &= [\Delta_f G^{\circ}_{298}(\mathrm{CH_3COOH(l)})] - [\Delta_f G^{\circ}_{298}(\mathrm{CH_4(g)}) + \Delta_f G^{\circ}_{298}(\mathrm{CO_2(g)})] \\ &= [(-389.9\,\mathrm{kJmol^{-1}})] - [(-394.4\,\mathrm{kJmol^{-1}}) + (-50.8\,\mathrm{kJmol^{-1}})] \\ &= +55.3\,\mathrm{kJmol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r G^{\circ}_{298} &= [\Delta_f G^{\circ}_{298}(\mathrm{C_2H_5OH(l)}) + 2\times\Delta_f G^{\circ}_{298}(\mathrm{H_2(g)})] - [2\times\Delta_f G^{\circ}_{298}(\mathrm{CH_4(g)}) + \Delta_f G^{\circ}_{298}(\mathrm{H_2O(l)})] \\ &= [(-174.8\,\mathrm{kJmol^{-1}}) + 2\times 0] - [(-237.1\,\mathrm{kJmol^{-1}}) + 2\times(-50.8\,\mathrm{kJmol^{-1}})] \\ &= +163.9\,\mathrm{kJmol^{-1}}\end{aligned}$$

Neither reaction is spontaneous at 298 K (and given the values, unlikely to become so at any reasonable temperature) so the chemists should go back to the drawing board!

29. Nitrogen and oxygen have very similar electronegativites. Estimate the entropy of NO at 0 K (the "zero-point entropy").

Strategy

The entropy can be estimated from the Boltzmann equation (Equation 14.2). Since the electronegativites are similar then there will be little preference for one orientation so that we can assume the orientations will be random so you need to count the number of possible arrangements.

Solution

From the Boltzmann equation, $S = k_B \ln W$ (Equation 14.2)

$k_B = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$.

If we assume equal probabilities of the molecules O-N or N-O then $W = 2$.

$S = k_B \ln W$

$= (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times \ln(2)$

$= 9.6 \times 10^{-23}\ \mathrm{J\ K^{-1}}$

$= 5.8\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

The latter result comes from multiplying the entropy by the Avogardro constant to find the entropy per mole.