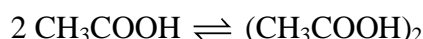


*Example Web4.1.* In the vapour phase, acetic acid (ethanoic acid) partially associates into dimers. At a total pressure of 0.200 bar, acetic acid is 92.0 mol% associated at 25 °C and 82.0 mol% associated at 45 °C. Calculate the enthalpy and entropy changes for the dimerization reaction. What will be the effect on the dissociation of changing the total pressure?

The reaction can be represented as



From Equation 4.3, the equilibrium constant is given by

$$K = \frac{a_{(\text{CH}_3\text{COOH})_2}}{a_{\text{CH}_3\text{COOH}}^2} = \frac{P_{(\text{CH}_3\text{COOH})_2} / P^\circ}{(P_{\text{CH}_3\text{COOH}} / P^\circ)^2}$$

Assuming that the vapours behave as ideal gases, the activity is given by the ratio of the pressure to the standard pressure of  $P^\circ = 1$  bar. The pressure of each component can be found from its mole fraction and the total pressure by  $p_i = x_i \times p_{\text{total}}$ .

Assume (for convenience) that we begin with 100 mol of  $\text{CH}_3\text{COOH}$ , If 92.0 % dimerizes; then 8.0 mol will remain at equilibrium. The 92.0 mol that react give rise to 46.0 mol of dimer. The total number of moles present is therefore 54.0. Hence, at 25 °C,

$$a_{\text{CH}_3\text{COOH}} = \frac{8.0}{54.0} \times \frac{0.20 \text{ bar}}{1.00 \text{ bar}} = 0.030; a_{(\text{CH}_3\text{COOH})_2} = \frac{46.0}{54.0} \times \frac{0.200 \text{ bar}}{1.00 \text{ bar}} = 0.170$$

so that the equilibrium constant,  $K$  is given by

$$K = \frac{0.170}{0.030^2} = 189$$

The corresponding values at 45 °C are dimer 41.0%, monomer 18.0%, total = 59.0 so that  $a_{\text{CH}_3\text{COOH}} = 0.061$ ,  $a_{(\text{CH}_3\text{COOH})_2} = 0.140$  and  $K = 37.6$ . We therefore have two values of  $K$  at two different temperatures so that the enthalpy change can be found using Equation 4.8,

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{37.6}{189}\right) = \frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{318.15 \text{ K}}\right)$$

Hence,

$$\Delta_r H^\circ = -63.67 \text{ kJ mol}^{-1}.$$

Combining Equations 3.15 and 4.5 for the results at 25 °C gives

$$-RT \ln K = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$-8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times \ln 189 = -63670 \text{ J mol}^{-1} - 298.15 \text{ K} \times \Delta_r S^\circ$$

leading to

$$\Delta_r S^\circ = -170.0 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Applying Le Chatelier's principle, an increase in pressure should favour the side of the reaction with the lower number of gas moles, *i.e.* favour the dimerization.

Note that, as expected, the extent of dimerization decreases as the temperature rises since it is an exothermic reaction. The dimerization leads to an increase in order, hence the negative value of the entropy change.

An alternative method for the calculation in Example 4.6 is to use the equilibrium constants to find the Gibbs energy changes (Equation 4.5:  $\Delta_r G^\circ = -13.1 \text{ kJ mol}^{-1}$  at 25 °C and  $\Delta_r G^\circ = -9.58 \text{ kJ mol}^{-1}$  at 45 °C) and to write the two equations using Equation 3.15.

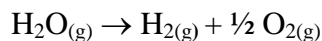
$$-13.1 \text{ kJ mol}^{-1} = \Delta_r H^\circ - 298.15 \text{ K} \times \Delta_r S^\circ$$

$$-9.58 \text{ kJ mol}^{-1} = \Delta_r H^\circ - 318.15 \text{ K} \times \Delta_r S^\circ$$

and solve the equations simultaneously assuming that  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  do not vary with temperature.

*Example Web4.2.* The standard enthalpy change of formation of water is  $-241.8 \text{ kJ mol}^{-1}$ . Use the mean heat capacities and standard entropies listed in Appendix 1 to estimate the percentage dissociation of water vapour at 2000 °C and 0.1 bar pressure.

The reaction of interest is the *dissociation* of water



This is the reverse of the formation of water so at 25 °C,

$$\begin{aligned}\Delta_{\text{r}}H_{298}^{\circ} &= -\Delta_{\text{f}}H_{298}^{\circ} \\ &= +241.8 \text{ kJ mol}^{-1}\end{aligned}$$

From Equation 3.8

$$\begin{aligned}\Delta_{\text{r}}S_{298}^{\circ} &= (130.7 + \frac{1}{2} \times 205.1) \text{ J mol}^{-1}\text{K}^{-1} - 188.3 \text{ J mol}^{-1}\text{K}^{-1} \\ &= 45.0 \text{ J mol}^{-1}\text{K}^{-1}.\end{aligned}$$

To convert  $\Delta_{\text{r}}H_{298}^{\circ}$  and  $\Delta_{\text{r}}S_{298}^{\circ}$  to the higher temperature, we need  $\Delta C_{\text{p}}$ . From Equation 2.19

$$\begin{aligned}\Delta C_{\text{p}} &= (28.8 + \frac{1}{2} \times 29.4) \text{ J mol}^{-1}\text{K}^{-1} - 33.6 \text{ J mol}^{-1}\text{K}^{-1} \\ &= 9.9 \text{ J mol}^{-1} \text{ K}^{-1}.\end{aligned}$$

At 2000 °C, 2273 K, the Kirchhoff Equation 2.17 estimates the enthalpy change at the higher temperature

$$\begin{aligned}\Delta_{\text{r}}H_{2273}^{\circ} &= \Delta_{\text{r}}H_{298}^{\circ} + \Delta C_{\text{p}} (2273 - 298) \\ &= 241.8 \text{ kJ mol}^{-1} + 9.9 \times 10^{-3} \text{ kJ mol}^{-1} \times 1975 \text{ K} \\ &= 261.4 \text{ kJ mol}^{-1}.\end{aligned}$$

From Equation 3.11

$$\begin{aligned}\Delta_{\text{r}}S_{2273}^{\circ} &= \Delta_{\text{r}}S_{298}^{\circ} + \Delta C_{\text{p}} \ln\left(\frac{2273}{298}\right) \\ &= 45.0 + 9.9 \times \ln 7.63 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 65.1 \text{ J mol}^{-1} \text{ K}^{-1}.\end{aligned}$$

From Equation 3.14

$$\begin{aligned}\Delta_{\text{r}}G_{2273}^{\circ} &= \Delta_{\text{r}}H_{2273}^{\circ} - T\Delta_{\text{r}}S_{2273}^{\circ} \\ &= 261.4 \text{ kJ mol}^{-1} - 2273 \text{ K} \times 65.1 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \\ &= +113.4 \text{ kJ mol}^{-1}.\end{aligned}$$

$$K = \exp\left(\frac{-\Delta_{\text{r}}G_{2273}^{\circ}}{RT}\right)$$

From Equation 4.5

$$\begin{aligned}&= \exp\left(\frac{-113.4 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 2273 \text{ K}}\right) \\ &= 2.5 \times 10^{-3}\end{aligned}$$

Now we need to express the equilibrium constant,  $K$ , in terms of the amounts of reactant and products.

$$K = \frac{(a_{\text{H}_2})_{\text{eqm}} (a_{\text{O}_2})_{\text{eqm}}^{1/2}}{(a_{\text{H}_2\text{O}})_{\text{eqm}}} = \frac{(p_{\text{H}_2} / p^\circ)_{\text{eqm}} (p_{\text{O}_2} / p^\circ)_{\text{eqm}}^{1/2}}{(p_{\text{H}_2\text{O}} / p^\circ)_{\text{eqm}}}$$

$$= \frac{(p_{\text{H}_2})_{\text{eqm}} (p_{\text{O}_2})_{\text{eqm}}^{1/2}}{(p_{\text{H}_2\text{O}})_{\text{eqm}} \times (1 \text{ bar})^{1/2}}$$

where  $p^\circ = 1 \text{ bar}$  and  $x$  is the mole fraction of the component. The partial pressure is given by mole fraction  $\times$  total pressure.

$$K = \frac{(x_{\text{H}_2} p_{\text{total}})_{\text{eqm}} (x_{\text{O}_2} p_{\text{total}})_{\text{eqm}}^{1/2}}{(x_{\text{H}_2\text{O}} p_{\text{total}})_{\text{eqm}}}$$

Say we start with 1 mol of water. If the fraction that dissociates is  $\alpha$ , then at equilibrium there will be  $(1 - \alpha)$  mol of  $\text{H}_2\text{O}$ ,  $\alpha$  mol of  $\text{H}_2$  and  $0.5\alpha$  mol of  $\text{O}_2$ . The total number of moles of gas is  $(1 - \alpha) + \alpha + 0.5\alpha = (1 + 0.5\alpha)$  mol. Substituting in

$$K = \frac{\left(\frac{\alpha}{1+0.5\alpha} \times p_{\text{total}}\right) \left(\frac{0.5\alpha}{1+0.5\alpha} \times p_{\text{total}}\right)^{1/2}}{\left(\frac{1-\alpha}{1+0.5\alpha} \times p_{\text{total}}\right)} = \frac{0.5^{1/2} \alpha^{3/2} \times p_{\text{total}}^{1/2}}{(1-\alpha)(1+0.5\alpha)^{1/2}}$$

This equation looks difficult to solve – and it is without the use of a computer! In situations like this, progress can often be made by introducing a simplifying assumption. For example, we can assume that water will not dissociate to any great extent even at such a high temperature so we can assume that  $\alpha$  is small.

If  $\alpha \ll 1$ , then  $(1 - \alpha) \approx 1$  and  $(1 + 0.5\alpha) \approx 1$  so that

$$K \approx \frac{0.5^{1/2} \alpha^{3/2} \times p_{\text{total}}^{1/2}}{(1)(1)^{1/2} \times (1 \text{ bar})^{1/2}}$$

$$2.5 \times 10^{-3} \approx \frac{0.5^{1/2} \alpha^{3/2} \times (0.1 \text{ bar})^{1/2}}{(1)(1)^{1/2} \times (1 \text{ bar})^{1/2}}$$

$$\alpha^{3/2} \approx \frac{2.47 \times 10^{-3} \times (1 \text{ bar})^{1/2}}{0.5^{1/2} \times (0.1 \text{ bar})^{1/2}} \approx 0.011$$

Hence  $\alpha \approx 0.05$  or 5 %.

Note that, as well as the mathematical approximation in the final steps, the result is an approximation in that the mean heat capacities used are unlikely to give an accurate result over such a large temperature range. However, for most uses such an approach can be useful.