9.6: Temperature Dependence of Equilibrium Constants - the van 't Hoff Equation

The value of K_p is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of ΔG^o_{rxm} is dependent on temperature, the value of K_p is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

$$\frac{\Delta G^o_{T_2}}{T_2} - \frac{\Delta G^o_{T_1}}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting

$$\Delta G^o = -RT \ln K$$

For the two values of ΔG^o and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

And simplifying the expression so that only terms involving K are on the left and all other terms are on the right results in the **van 't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{9.6.1}$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if ΔH^o is independent of temperature over the range being considered. This expression also suggests that a plot of $\ln(K)$ as a function of $1/T$ should produce a straight line with a slope equal to $-\Delta H^o/R$. Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

> ✔ **Example 9.6.1**
>
> A certain reaction has a value of $K_p = 0.0260$ at 25 °C and $\Delta H^o_{rxm} = 32.4 \, kJ/mol$. Calculate the value of K_p at 37 °C.
>
> **Solution**
>
> This is a job for the van 't Hoff equation!
>
> - T_1 = 298 K
> - T_2 = 310 K
> - $\Delta H^o_{rxm} = 32.4 \, kJ/mol$
> - K_1 = 0.0260
> - K_2 = ?
>
> So Equation 9.6.1 becomes
>
> $$\ln \left(\frac{K_2}{0.0260} \right) = -\frac{32400 \, J/mol}{8.314 \, K/(mol \, K)} \left(\frac{1}{310 \, K} - \frac{1}{298 \, K} \right)$$
>
> $$K_2 = 0.0431$$
>
> Note: the value of K_2 **increased** with **increasing** temperature, which is what is expected for an **endothermic** reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

> ✔ **Example 9.6.2**
>
> Given the following average bond enthalpies for $P-Cl$ and $Cl-Cl$ bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction
>
> $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

X-Y	D(X-Y) (kJ/mol)
P-Cl	326
Cl-Cl	240

Solution

The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.

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