10.2: Temperature Dependence of Keq

To study the temperature dependence of K_{eq} we can use Equation 10.1.14 for the general equilibrium constant and write:

$$\ln K_{\text{eq}} = -\frac{\Delta G^{\ominus}}{RT}, \tag{10.2.1}$$

which we can then differentiate with respect to temperature at constant $P, \{n_i\}$ on both sides:

$$\left(\frac{\partial \ln K_{\text{eq}}}{\partial T}\right)_{P,\{n_i\}} = -\frac{1}{R}\left[\frac{\partial\left(\frac{\Delta G^{\ominus}}{T}\right)}{\partial T}\right]_{P,\{n_i\}}, \tag{10.2.2}$$

and, using Gibbs-Helmholtz equation (Equation ???) to simplify the left hand side, becomes:

$$\left(\frac{\partial \ln K_{\text{eq}}}{\partial T}\right)_{P,\{n_i\}} = -\frac{1}{R}\left(-\frac{\Delta H^{\ominus}}{T^2}\right) = \frac{\Delta H^{\ominus}}{RT^2}, \tag{10.2.3}$$

which gives the dependence of $\ln K_{\text{eq}}$ on T that we were looking for. Equation 10.2.3 is also called **van 't Hoff equation,**[1] and it is the mathematical expression of Le Chatelier's principle. The simplest interpretation is as follows:

- For an exothermic reaction ($\Delta H^{\ominus} < 0$): K_{eq} will decrease as the temperature increases.
- For an endothermic reaction ($\Delta H^{\ominus} > 0$): K_{eq} will increase as the temperature increases.

If we integrate the van 't Hoff equation between two arbitrary points at constant P, and assuming constant $\Delta H^{\ominus}$, we obtain the following:

$$\int_1^2 d\ln K_{\text{eq}} = \frac{\Delta H^{\ominus}}{R}\int_1^2 \frac{dT}{T^2}, \tag{10.2.4}$$

which leads to the linear equation:

$$\ln K_{\text{eq}}(2) = \ln K_{\text{eq}}(1) - \frac{\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{10.2.5}$$

which is the equation that produces the so-called **van 't Hoff plots**, from which $\Delta H^{\ominus}$ can be experimentally determined:

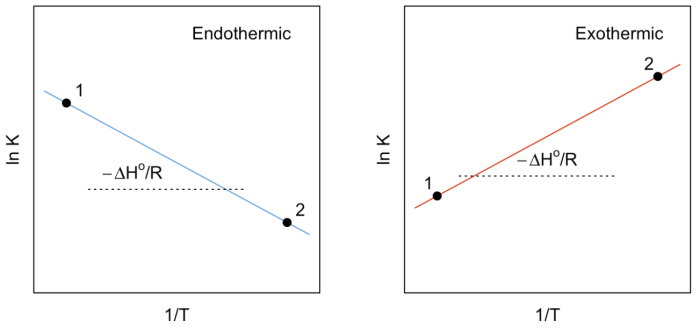

Figure 10.2.1: Van 't Hoff Plots for an Endothermic (Left, Blue) and an Exothermic (Right, Red) Reactions at Constant P.

1. named after Jacobus Henricus "Henry" van 't Hoff Jr. (1852–1911).