# 26.7: The van 't Hoff Equation

We can use Gibbs-Helmholtz to get the temperature dependence of $K$

$$\left(\frac{\partial[\Delta G^o/T]}{\partial T}\right)_P = \frac{-\Delta H^o}{T^2}$$

At equilibrium, we can equate $\Delta G^o$ to $-RT\ln K$ so we get:

$$\left(\frac{\partial[\ln K]}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}$$

We see that whether $K$ increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that $\Delta H^o$ can be considered constant, we can translate a $K$ value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

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

If more precision is required we could correct for the temperature changes of $\Delta H^o$ by using heat capacity data.

> *How $K$ increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.*

The expression for $K$ is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients One way to see the sensitive temperature dependence of equilibrium constants is to recall that

$$K = e^{-\Delta_r G^o/RT} \tag{26.7.1}$$

However, since under constant pressure and temperature

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

Equation 26.7.1 becomes

$$K = e^{-\Delta H^o/RT}e^{\Delta S^o/R} \tag{26.7.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$ and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{26.7.3}$$

which is known as the van 't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.
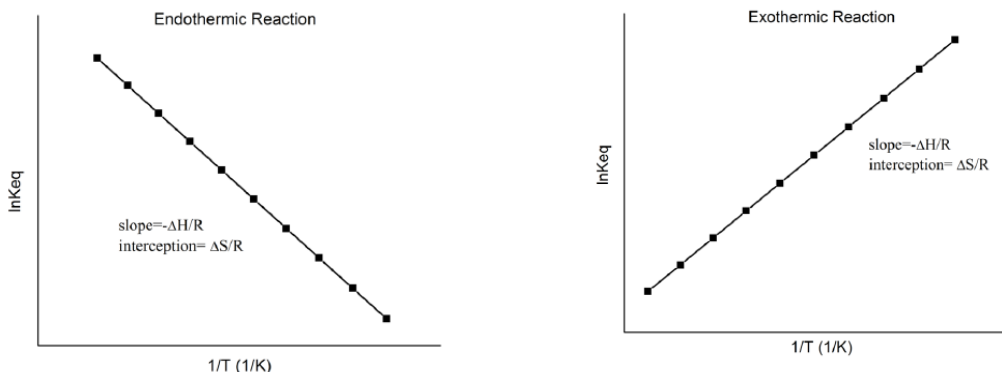


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

Hence, these quantities can be determined from the $\ln K$ vs. $1/T$ data without doing calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on $T$, which is usually valid.