

7.10: The van 't Hoff Equation

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

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

At equilibrium, we can equate ΔG° to $-RT \ln K$ so we get:

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

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 ΔH° 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:

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

If more precision is required we could correct for the temperature changes of ΔH° 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

$$K = e^{-\Delta_r G^\circ / RT} \quad (7.10.1)$$

However, since under constant pressure and temperature

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

Equation 7.10.1 becomes

$$K = e^{-\Delta H^\circ / RT} e^{\Delta S^\circ / R} \quad (7.10.2)$$

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

$$\ln K = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (7.10.3)$$

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 $-\Delta_r H^\circ / R$ and intercept $\Delta_r S^\circ / R$.

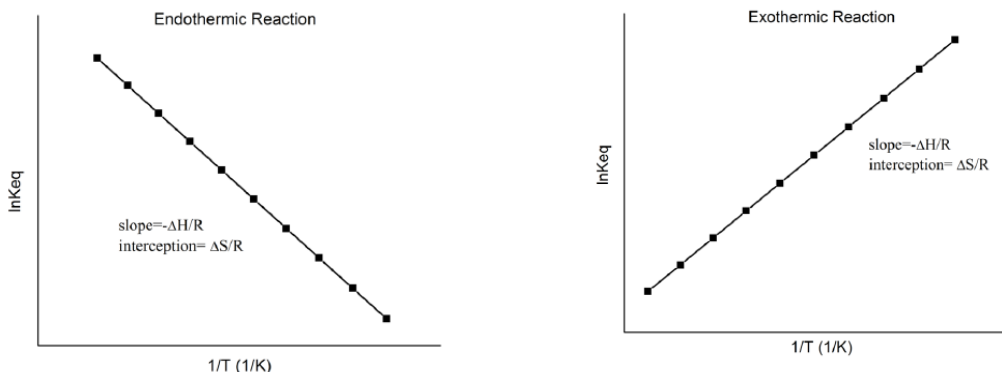


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

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 $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are only very weakly dependent on T , which is usually valid.

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