Reactions and Equilibrium

\[ A + B \rightarrow C \]

Define an equilibrium Constant

\[ \text{Keq} = \pi y_i v_i \text{. dimensionless} \]

This appears independent of pressure which it is if \( \Sigma v_i = 0 \).

Indeed, Keq is specifically a function of Temperature (and the thermodynamics of the process).

If \( \Sigma v_i \neq 0 \) then intuition tells us that total pressure will influence the extent of reaction.

\[ \text{Keq}_p = \pi p_i v_i \text{. units of } p^{\Sigma v_i} \]

*The Equilibrium constants change with temperature due to another thermodynamic quantity (the free energy). The relationship is:*

\[ \text{Keq} = a e^{-\Delta F/RT} = a e^{-b/T}. \]

Thus, a plot of ln K versus 1/T will yield a straight line:

\[ \ln \text{Keq} = \ln a - b/T \]

The higher the value of b (\( \Delta F \)) the more sensitive to temperature.
For Vaporization: the heat of vaporization ($\Delta H_v$) dictates the amount of energy required to leave the liquid to the vapor phase. The heat of vaporization also dictates the dependence of the vapor pressure on the temperature. The relevant equation is the Clausius-Clapeyron Equation:

$$\frac{d (\ln P_s)}{d (1/T)} = - \frac{\Delta H_v}{R}$$

$$\ln \frac{P_i}{P_0} = - \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T_0} \right)$$

Note units are absolute pressures and temperatures. The heat of vaporization is measurable (calorimeter) or it is estimated from this relationship. How?

There are several ways that this relationship is used! How do you think?

Another similar relationship is useful if the three constants are known, Antoine Equation:

$$\log_{10} P_s = A - \left( \frac{B}{T + C} \right)$$

Note the units here must be specified. Sometimes in °C. Log based 10!

What is the relationship between these two???