9.3: Activities and Fugacities

To this point, we have mostly ignored deviations from ideal behavior. But it should be noted that thermodynamic equilibrium constants are not expressed in terms of concentrations or pressures, but rather in terms of activities and fugacities (both being discussed in Chapter 7). Based on these quantities,

$$K_p = \prod_i f_i^{\nu_i} \tag{9.3.1}$$

and

$$K_c = \prod_i a_i^{\nu_i}$$

And since activities and fugacities are unitless, thermodynamic equilibrium constants are unitless as well. Further, it can be noted that the activities of solids and pure liquids are unity (assuming ideal behavior) since they are in their standard states at the given temperature. As such, these species never change the magnitude of the equilibrium constant and are generally omitted from the equilibrium constant expression.

> *Thermodynamic equilibrium constants are unitless.*

K_p and K_c

Oftentimes it is desirable to express the equilibrium constant in terms of concentrations (or activities for systems that deviate from ideal behavior.) To make this conversion, the relationship between pressure and concentration from the ideal gas law can be used.

$$p = RT\left(\frac{n}{V}\right)$$

And noting that the concentration is given by (n/V), the expression for the equilibrium constant (Equation 9.3.1) becomes

$$K_p = \prod_i (RT[X_i])^{\nu_i} \tag{9.3.2}$$

And since for a given temperature, RT is a constant and can be factored out of the expression, leaving

$$K_p = \left(\prod_i (RT)^{\nu_i}\right)\left(\prod_i [X_i]^{\nu_i}\right) \tag{9.3.3}$$

$$= (RT)^{\sum \nu_i} \prod [X_i]^{\nu_i} \tag{9.3.4}$$

$$= (RT)^{\sum \nu_i} K_c \tag{9.3.5}$$

This conversion works for reactions in which all reactants and products are in the gas phase. Care must be used when applying this relationship to heterogeneous equilibria.