Different Ways of Expressing Equilibrium Constants

To calculate equilibrium constants, we need the concentrations of reactants and products that are not always in the same phase. Therefore, it becomes necessary express equilibrium constants in more than one way.

Homogeneous Equilibrium

The **homogeneous equilibrium** applies to reactions in which all the species are in the *same phase*. An example of homogeneous gas-phase equilibrium is the dissociation of N_2O_4, the equilibrium reaction of which is

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

The equilibrium constant is given by

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Here the subscript in K_c denotes the concentrations of reacting species expressed in molar concentrations, i.e., moles per liter (mol/l ≡ M).

The concentrations of **gaseous** reacting species can also be expressed in terms of partial pressures. Hence

$$K_p = \frac{p^2{}_{NO_2}}{p_{N_2O_4}}$$

where $p^2{}_{NO_2}$ and $p_{N_2O_4}$ are the equilibrium partial pressures (in atm) of NO_2 and N_2O_4. The subscript in K_p indicates that the concentrations are expressed in terms of partial pressures.

In reality, the K_p is not equal to K_c because the partial pressures of reactants and products are not equal to the concentrations expressed in mol/l. In general, the relation between K_p and K_c is given by the following equation.

$$K_p = K_c\,(RT)^{\Delta n} = K_c\,(0.0821x\ T)^{\Delta n}$$

Here R is the gas constant, the value of which is 0.0821 L.atm/K, T is the absolute temperature, and Δn is the difference in number of moles of products and reactants ($\Delta n = \sum n_{products} - \sum n_{reactnats}$). The Δn could be zero if $\sum n_{products} = \sum n_{reactnats}$ or could be positive if $\sum n_{products} > \sum n_{reactnats}$ or could be negative if $\sum n_{products} < \sum n_{reactnats}$.

Important: If the reaction is in gaseous phase, either K_p or K_c can be written depending upon available experimental data.

Another example of homogeneous equilibrium is the ionization of acetic acid in water:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The equilibrium constant is given by

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

There is one problem in writing the equilibrium constant in this way. The concentration of pure water ([H_2O]) is very large (55.5 M) and does not change very much during the course of the reaction and hence may be assumed as constant. Therefore, the above expression is rewritten without water concentration as

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

In general, if the reaction is involved a pure liquid, the concentration of that liquid is excluded in equilibrium constant expression.

Heterogeneous Equilibrium

The **heterogeneous equilibrium** applies to a reaction where the reacting species are in *different phases* like solid and gas. For example, the calcium carbonate (solid) is heated in a closed container to establish an equilibrium with calcium oxide(solid) and carbon dioxide gas:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant expression is written as

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

However, the concentration of solid, like its density does not change and hence it is excluded from the equilibrium constant expression. Thus we have

$$K_c = [CO_2]$$

Since CO_2 is a gas, we can also write the equilibrium constant expression in terms of partial pressure. Thus

$$K_p = p_{CO_2}$$

Example

Write expressions for K_c or K_p where appropriate for the following equilibrium reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+ + F^-(aq)$

(c) $Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g)$

Answer

(a) This is a gaseous reaction and hence both K_c and K_p may be written.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{and} \quad K_p = \frac{p^2_{NH_3}}{p_{N_2} p^3_{H_2}}$$

(b) Here water is in pure liquid form and its concentration is eliminated from the expression.

$$K_c = \frac{[H_3O^+][F^-]}{[HF]}$$

(c) There are two solids in this reaction. The concentrations of both are not included in the expression. Since oxygen is a gas, both K_c and K_p can be written.

$$K_c = [O_2]^{\frac{1}{2}} \quad \text{and} \quad K_p = p^{\frac{1}{2}}_{O_2}$$

Equilibrium Equation and Equilibrium Constant

Consider the following equilibrium reaction at 25^0C. The equilibrium constant at this temperature is 4.63 x 10^{-3}.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Thus, we have

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \text{ x } 10^{-3}$$

(a) If we reverse the above equilibrium reaction, what will be the expression for K_c and what is the value of K_c?

The reverse equation is written as

$$2NO_2(g) \rightleftarrows N_2O_4(g)$$

The equilibrium constant expression for this is

$$K'_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K_c} = \frac{1}{4.63x10^{-3}} = 216$$

We can see that $K'_c = 1/K_c$. Therefore, when the equation is reversed, the new equilibrium constant expression is just upside-down of the original expression. The equilibrium constant value is just 1 divided by the original value.

(b) The value of the K depends on how the equilibrium equation is balanced. Consider the following balanced equation:

$$\frac{1}{2}N_2O_4(g) \rightleftarrows NO_2(g)$$

The equilibrium constant expression for this is

$$K''_c = \frac{[NO_2]}{[N_2O_4]^{1/2}}$$

Now you can see that $K''_c = \sqrt{K_c} = \sqrt{4.63 \text{ x } 10^{-3}} = 6.8\text{x}10^{-2}$

In general, if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original value; if you triple the equation, the corresponding equilibrium constant will be cube of the original value, and so on.
