Chapter 14. CHEMICAL EQUILIBRIUM

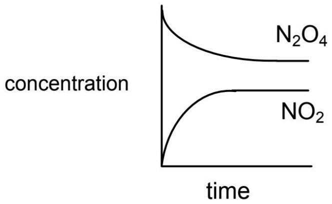
14.1 THE CONCEPT OF EQUILIBRIUM AND THE EQUILIBRIUM CONSTANT

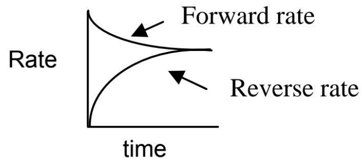
Many chemical reactions do not go to completion but instead attain a state of chemical equilibrium.

Chemical equilibrium: A state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.

⇒ Equilibrium is a dynamic process – the conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules.

For the reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$





The Equilibrium Constant

For a reaction: **aA + bB $\rightleftharpoons$ cC + dD**

equilibrium constant: $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

The **equilibrium constant, K_c,** is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

Example. Write the equilibrium constant, K_c, for $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Law of mass action - The value of the equilibrium constant expression, K_c, is constant for a given reaction at equilibrium and at a constant temperature.

⇒ The equilibrium concentrations of reactants and products may vary, but the value for K_c remains the same.

Other Characteristics of K_c

1) Equilibrium can be approached from either direction.
2) K_c does not depend on the initial concentrations of reactants and products.
3) K_c does depend on temperature.

Magnitude of K_c

⇒ If the K_c value is large (K_c >> 1), the equilibrium lies to the right and the reaction mixture contains mostly products.

⇒ If the K_c value is small (K_c <<1), the equilibrium lies to the left and the reaction mixture contains mostly reactants.

⇒ If the K_c value is close to 1 ($0.10 < K_c < 10$), the mixture contains appreciable amounts of both reactants and products.

14.2 WRITING EQUILIBRIUM CONSTANT EXPRESSIONS

Calculating Equilibrium Constants, K_c

K_c values are listed without units ⇒ don't include units when calculating K_c.

If equilibrium concentrations are known, simply substitute the concentrations into the equilibrium constant expression:

Example. For the reaction, $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$, calculate K_c from the following equilibrium concentrations: $[CO] = 0.0613$ M; $[H_2] = 0.1839$ M; $[CH_4] = 0.0387$ M; $[H_2O] = 0.0387$ M.

Homogeneous equilibria: reactants and products exist in a single phase.

For the gas phase reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity, K_c, is:

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

Gas Phase Expressions can also be expressed by K_p

⇒ The K_p expression is written using equilibrium partial pressures of reactants & products.

For the reaction given above, the K_p expression is:

$$\mathbf{K_p} = \frac{{P_{NO_2}}^2}{P_{N_2O_4}}$$

K_p is related to K_c

Since pressure and molarity are related by the Ideal Gas Law, the following equation relates K_p and K_c:

$$\mathbf{K_p = K_c(RT)^{\Delta n}}$$

where $R = 0.0821 \ \frac{L \cdot atm}{K \cdot mol}$; T = temperature in Kelvin

Δn = moles of gaseous products – moles of gaseous reactants

⇒ Note that $K_c = K_p$ when the number of gas molecules are the same on both sides.

Example. Does $K_c = K_p$ for (a) $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$? (b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$?

Example. For the reaction, $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ (a) write the equilibrium constant expression, K_p. (b) What is the value for K_p if $K_c = 2.8 \times 10^2$ at 1000 K?

Heterogeneous Equilibria and Solvents in Homogeneous Equilibria

Heterogeneous equilibria: reactants and products are present in more than one phase.

pure solids and liquids: concentrations of pure solids and liquids are fixed by their density and molar mass (both constants) and do not vary with the amount.

$$[\ ] = M = \frac{Density}{Molar\ Mass} \qquad\qquad M = \frac{mol}{L} = \frac{g}{ml} \times \frac{10^3\ ml}{1L} \times \frac{mol}{g}$$

⇒ Thus, the concentrations of solids and liquids are incorporated in the K_c value; they are not part of the variable K_c expression:

Example. Write the K_c expression for $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

- **Omit concentration terms for solids and liquids from K_c and K_p expressions; only include terms for gases (g) and aqueous substances (aq).**

Example. Write the K_c expression for the following reaction:

$$3Cu_{(s)} + 2NO_3^-{}_{(aq)} + 8H^+{}_{(aq)} \rightleftharpoons 3Cu^{2+}{}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

Modifying Equilibrium Constant Expressions:

A. Changing stoichiometric coefficients:

1) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ $K_1 =$

2) $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$ $K_2 =$

⇒ If we multiply an equation by a factor, we must raise its K to that power to get the new K.

B. Reversing the reaction:

3) $2SO_3 \rightleftharpoons 2SO_2 + O_2$ $K_3 =$

⇒ K is the reciprocal of the K value for the reverse reaction.

C. Adding Equations for Multiple Equilibrium Reactions:

1. $A + 2B \rightleftharpoons C$ $K_1 =$

2. $A + D \rightleftharpoons B$ $K_2 =$

3. $2A + B + D \rightleftharpoons C$ $K_3 =$

⇒ When we add equations to get a new equation, the new K is the product of the other K's.

Example. $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ $K_c = 1.7x10^{27}$

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $K_c = 1.5x10^2$

Calculate the value of K_c for $4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$