Equilibrium

• The given equation is known as law of chemical equilibrium. Law of chemical equilibrium is for a reversible reaction at equilibrium, the ratio of the product of the concentrations of the products and the product of the concentrations of the reactants is constant at constant temperature when each concentration term is raised to the power equal to the corresponding stoichiometric coefficient in the balanced chemical equation. The ratio is known as equilibrium constant.

Equilibrium Constant

• For a reaction,

$$aA + bB \rightleftharpoons cC + dD$$

Equilibrium constant, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

• For a homogeneous gas phase reaction, the molar concentration of a substance is directly proportional to its partial pressure p at constant temperature. Then equilibrium is denoted by K_p .

$$K_p = \frac{(p_C)^c \times (p_D)^d}{(p_A)^a \times (p_B)^b}$$

• Relation between K_p and K_c

$$P = \frac{n}{V}RT = CRT$$

• Characteristics of equilibrium constant

 $K_{p} = \frac{\left([C]RT\right)^{c} \left([D]RT\right)^{d}}{\left([A]RT\right)^{a} \left([B]RT\right)^{b}} = \frac{\left[C\right]^{c} \left[D\right]^{d}}{\left[A\right]^{a} \left[B\right]^{b}} \times \left(RT\right)^{(c+d)-(a+b)}$ if $(c + d) - (a + b) = \Delta n$ $K_{p} = K_{c}RT^{\Delta n}$ $\Delta n = (number of moles of gaseous product) - (number of moles of gaseous reactants)$

• Units of equilibrium constant $(K_c) = (\text{mol/L})^{\Delta n}$ $(K_n) = (\text{atm})^{\Delta n}$

Illustration 1

 $\begin{array}{l} \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+; \ K_1 = 1.8 \times 10^{-5} \\ 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-; \ K_2 = 1 \times 10^{-14} \\ \text{Calculate equilibrium constant for} \end{array}$

 $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

Soln.: It is given that

$$CH_{3}COOH + H_{2}O \rightleftharpoons CH_{3}COO^{-} + H_{3}O^{+}$$
$$K_{1} = 1.8 \times 10^{-5} \quad \dots (i)$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-, K_2 = 1 \times 10^{-14}$$
 ... (ii)

.: For reaction,

$$CH_3COOH+OH^- \rightleftharpoons CH_3COO^-+H_2O \qquad \dots (iii)$$

$$K = \frac{K_1}{K_2} = \frac{1.8 \times 10^{-5}}{1 \times 10^{-14}} = 1.8 \times 10^9$$

If for a reation, $A + B \rightleftharpoons C + D$, equilibrium constant, $K = \frac{[C][D]}{[A][B]}$

Characteristics	Reaction	Equilibrium constant
If reaction is reversed.	$A + B \rightleftharpoons C + D$	K' = 1/K
If reaction is divided by factor n .	$\frac{1}{n}A + \frac{1}{n}B \rightleftharpoons \frac{1}{n}C + \frac{1}{n}D$	$K' = \sqrt[n]{K}$
If reaction is multiplied by factor <i>n</i> .	$nA + nB \rightleftharpoons nC + nD$	$K' = K^n$
If reaction is written in n number of steps.	$A + B \stackrel{K_{1\sim}}{\longleftrightarrow} X + Y ; X + Y \stackrel{K_{2\sim}}{\longleftrightarrow} P + Q \dots \stackrel{K_{p\sim}}{\longleftrightarrow} C + D$	$K' = K_1 \times K_2 \times \dots K_n$

Illustration 2

A vessel at 1000 K contains carbon dioxide at a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K, if the total pressure at equilibrium is 0.8 atm. Soln.: $CO_2 + C_{(graphite)} \rightleftharpoons 2CO$

Let the decrease in pressure of CO_2 after reaction = p atm

Then, increase in pressure due to CO after reaction = 2p atm

Final total pressure = (0.5 - p) + 2p = 0.8 atm $\Rightarrow p = 0.3$ atm

Thus after reaction, $p_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$

$$p_{\rm CO} = 2p = 2 \times 0.3 = 0.6$$
 atm

$$\Rightarrow K = \frac{p_{CO}^2}{p_{CO_2}} = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$$

- Factors affecting equilibrium constant : Equilibrium constant is only affected by temperature.
 - > In exothermic reversible reactions, as temperature increases, K increases.
 - > In endothermic reversible reactions, as temperature increases, K decreases.

van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$