CHEMICAL EQUILIBRIUM (K_c, K_p, and K_{sp})

Chemical equilibrium is a state in which the rate of forward reaction equals the rate of backward reaction. In other words, there is no net change in concentrations of reactants and products. This kind of equilibrium is also called dynamic equilibrium.

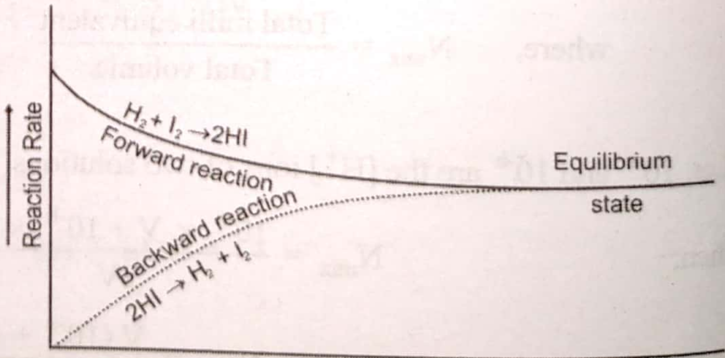
$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

k_f and k_b are the reaction constants for the forward and backward reaction, respectively

$$H_2 + I_2 \rightleftharpoons 2HI$$

Characteristics of chemical equilibrium

1. Equilibrium may only be obtained in a 'closed system'.
2. The rate of forward reaction is equal to the rate of backward reaction.
3. Catalysts have no effect on the equilibrium point.



However, changes in the concentrations of either the products or reactants, temperature, volume or pressure can offset the equilibrium point (Le Chatelier's Principle).

LE CHATELIER'S PRINCIPLE

It states that if a dynamic equilibrium is disturbed by changing the conditions the position of equilibrium shifts to counteract the change to reestablish equilibrium.

An action that changes the temperature, pressure or concentrations of reactants in a system at equilibrium stimulates a response that partially offsets the change while a new equilibrium is established. Hence, Le Chatelier's principle states that any changes to a system at equilibrium will adjust to compensate for that change.

It is important to understand that Le Chatelier's principle is only a useful guide to identify what happens when the conditions are changed in a reaction in dynamic equilibrium.

1. **Concentration Change**

According to the principle, the position of equilibrium will move in such a way as to counteract the change; In this case.

$$A + B \leftrightharpoons C + D$$

If we decrease the concentration of A then the reaction will move reverse and in backward direction. While if we increase the concentration then to attain equilibrium state the reaction will move forward.

2. **Pressure Change**

When the pressure increases then the difference of number of moles of product and reactant side (Δn) will be greater than 0, the reaction will move in backward direction. While when the pressure increases then Δn will be less than 0, the reaction will move in forward direction.

3. **Temperature Change**

By increasing or decreasing the temperature, there will be direct effect on the equilibrium constants of the reaction, i.e., when temperature increase then the reaction will move forward and the value of equilibrium constants will also increase while on decreasing temperature the reaction will move backward and the value of equilibrium will decrease. Reactions can be of two types; (a) endothermic reaction, and (b) exothermic reaction.

a) **In endothermic reaction ($\Delta H > 0$)**

$$\text{Reactant} + \text{Heat} \rightleftharpoons \text{Product}$$

$$\therefore \quad \text{Heat} + 6CO_2\,(g) + 6\,H_2O\,(l) \rightleftharpoons C_6H_{12}O_6\,(aq) + 6O_2\,(g)$$

b) **In exothermic reaction ($\Delta H < 0$)**

$$\text{Reactant} \rightleftharpoons \text{Product} + \text{Heat}$$

$$\therefore \quad CaO\,(s) + H_2O\,(l) \rightleftharpoons Ca\,(OH)_2\,(s) + \text{Heat}$$

Gas Equilibrium Constants

K_c and K_p are the equilibrium constants of gaseous mixtures. However the difference between the two constants is that K_c is defined by molar concentration, whereas K_p is defined by the partial pressures of the gases inside a closed system.

The equilibrium constants do not include the concentrations of single components such as liquids and solids, and they do not have any units. These gas equilibrium constants relates to the equilibrium (K) because they both are derived from 'ideal gas law' ($PV = nRT$).

Suppose the reaction is;

$$A + B \rightleftharpoons C + D$$

Rate of forward reaction (R_f) = Rate of Backward reaction (R_b)

$$\text{Equilibrium constant, } K_c = \frac{[C][D]}{[A][B]}$$

If the reaction is;

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

Then,

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

Example 18: If one mole of H_2 and 2 mole of I_2 reacts to form 14 mole of 2HI at equilibrium then calculate Kc

Solution

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$\frac{[HI]^2}{[H_2][I_2]} = \frac{[14]^2}{[1]^1[2]^1}$$

$$= 98$$

Kp

$$K_p = \frac{P_C \times P_D}{P_A \times P_B}$$

Where

(I) P_A= mole fraction × total pressure

(II) If Gas [A] and Gas [B] of Volume [V_1] and Volume [V_2], Pressure [P_1] and Pressure [P_2].

Then,

$$P_A = \frac{P_1V_1}{V} \qquad P_B = \frac{P_2V_2}{V}$$

Example 19: If

$$A + B \rightleftharpoons C + D$$

Given,

Mole of A = 0.5

Mole of B = 0.5

Mole of C = 1

Mole of D = 1

Total pressure = 6

Then

$$P_A = \frac{0.5}{3} \times 6 = 1 \quad P_B = \frac{0.5}{3} \times 6 = 1 \quad P_C = \frac{1.0}{3} \times 6 = 2 \quad P_D = \frac{1}{3} \times 6 = 2$$

$$K_p = \frac{P_C \times P_D}{P_A \times P_B} = \frac{2 \times 2}{1 \times 1} = 4$$

Relationship between Kp and Kc

$$K_p = K_c\,[RT]^{\Delta n}$$

Where

K_p = Partial pressure of gas

K_c = Molar concentration of gas

Δn = (Number of moles of gas on product side – number of moles gas on reactant side)

R = Gas constant (0.0821 lit. atm/mol K)

T = Temperature

Note

$\Delta n = 0;\ K_c = K_p$

$\Delta n < 0;\ K_c > K_p$

$\Delta n > 0;\ K_c < K_p$

Example 20: Find the relationship between Kp and Kc for the following reaction?

$$C\,(s) + O_2\,(g) \rightleftharpoons CO_2\,(g)$$

Solution

$$K_p = K_c\,[RT]^{\Delta n}$$

$$\Delta n = 1 - 1 = 0$$

$$K_p = K_c\,[RT]^0$$

$$K_p = K_c \times 1$$

$$K_p = K_c$$

SOLUBILITY AND SOLUBILITY PRODUCT

Solubility (S)

It is the ability of a substance to dissolve. The two participants in the dissolution process are the solute and the solvent. The solute is the substance that is being dissolved and the solvent is the substance that is doing the dissolving.

In other words, solubility is defined as the maximum amount of solute that can be dissolved in a solvent at equilibrium.

Solubility Product (K_{sp})

The solubility product constant describes the equilibrium between a solid and its constituent ions in a solution. The value of the constant identifies the degree to which the compound can dissociate in water.

$$M_xN_y \rightleftharpoons xM^{+y} + yN^{-x}$$

$$K_{sp} = X^x . Y^y . S^{(x+y)}$$