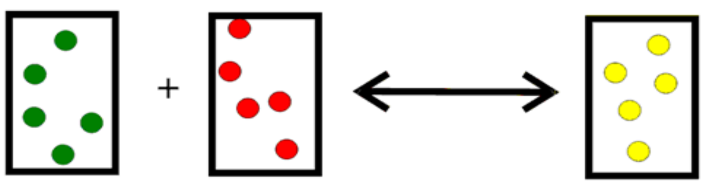
م.د. مسار علي عواد

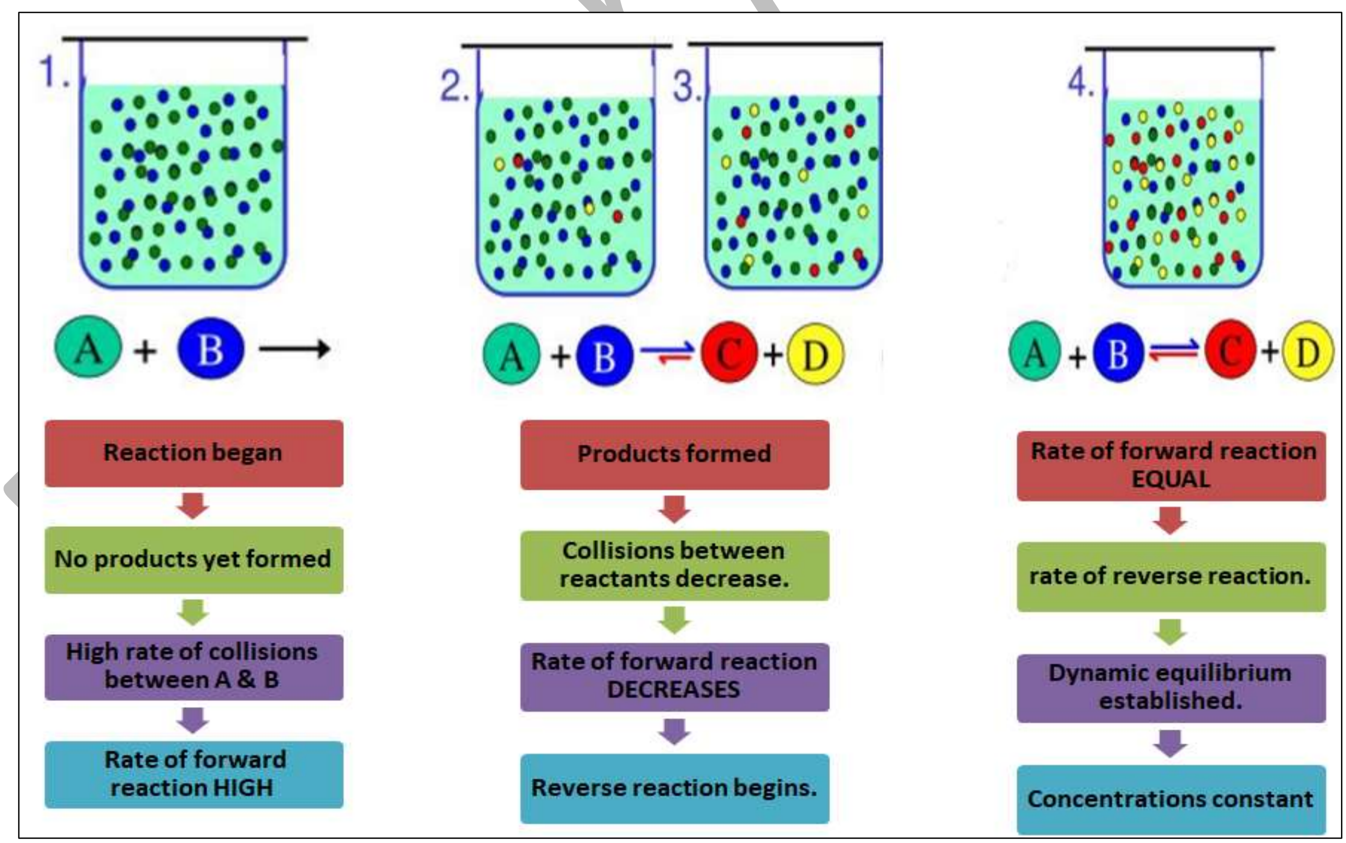
المحاضرة رقم 2

Chemical equilibrium

- Most reactions DO NOT go to completion.
- Reactions that do not go to completion are REVERSIBLE.
- Reversible reactions exist in a state of EQUILIBRIUM.
- **Equilibrium** is reached when the rate of the forward reaction equals the rate of the reverse reaction.
- All reactant and product concentrations are **constant** at equilibrium.
- The equilibrium reaction **does not** mean the amounts of products and reactants are equal.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$





Equilibrium- constant expressions

- **Consider the following equilibrium system:**

$$aA + bB \underset{Kr}{\overset{Kf}{\rightleftharpoons}} cC + dD$$

$$Rate2 = K_r \quad [C]^c \ [D]^d$$

$$Rate1 = K_f \quad [A]^a \ [B]^b$$

$$K_r [C]^c \ [D]^d = K_f \quad [A]^a \ [B]^b$$

Rate 1 = Rate 2

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

$$\frac{K_f}{k_r} = k_{eq} \longrightarrow \frac{Kf}{Kr} = _{Keq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- **The numerical value of K_{eq} is calculated using the concentrations of reactants and products that exist at equilibrium** (equilibrium constant)

What does the magnitude of K_{eq} tell us about the reaction at equilibrium?

1-When the equilibrium constant is very small. k_{eq} = ~0.001 or less, we will have mostly reactant species present at equilibrium.

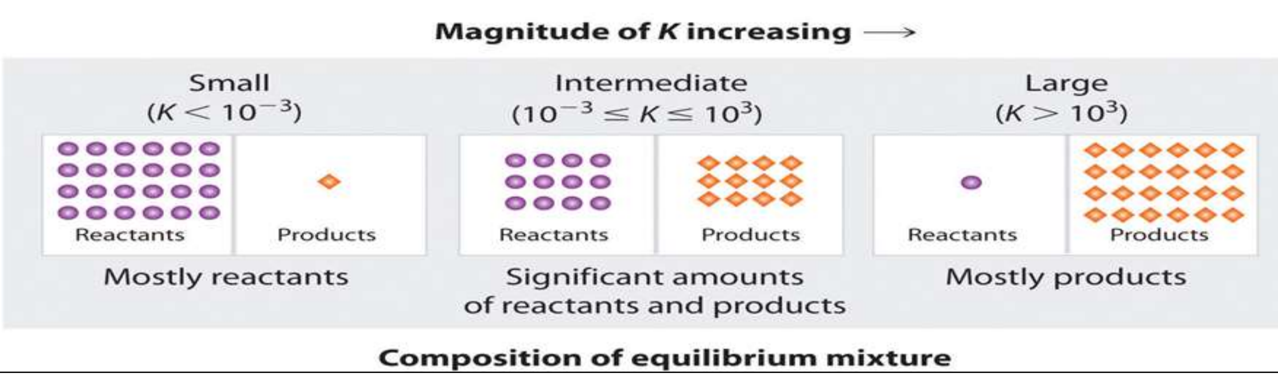
$$K_{eq} = small\ value$$

2- When the equilibrium constant is very high., k_{eq} =1000 or more, we will have mostly product species present at equilibrium.

$$K_{eq} = high\ value$$

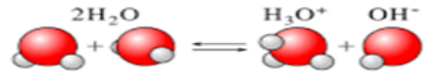
3- When the equilibrium constant is moderate. If k_{eq} is in between 0.001 and 1000, we will have a significant concentration of both reactant and product species present at equilibrium.

$$[C]^c \ [D\ ]^d \cong [A]^a \ [B\ ]^b$$



م.د. مسار علي عواد

Applying the Ion-Product Constant for Water



- The **self-ionization of water**
  (the process in which water ionizes to hydronium ions and hydroxide ions)
- When two molecules of water collide, there can be a transfer of a hydrogen ion from one molecule to the other.
- The products are a positively charged hydronium ion and a negatively charged hydroxide ion.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$H2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$k = \frac{[OH^-][H3O^+]}{[H_2O][H_2O]}$$

$$K_w = K\cdot[H_2O]\cdot[H_2O] = [OH^-]\cdot[H_3O^+]$$

$$K_w = [OH^-]\,[H_3\,O^+]$$

K_w characterizes the degree of dissociation of water. Generally, its negative logarithm is used:

$$pK_w = -\log\,(K_w) = 14$$

The value of Kw at 25°C is 1 x 10^{-14}. Since pure water is neutral in nature. H+ ion concentration must be equal to OH- ion concentration.

$$[H_3O^+] = [OH^-] = x$$

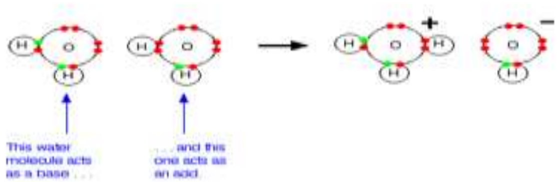
$$K_w = X^2 \longrightarrow X^2 = 1\,x\,10^{-14}$$

$$X = 1\,x\,10^{-7} \longrightarrow [OH^{-1}] = [H_3O^+] = 1x\,10^{-7}$$

Applying the Ion-Product Constant for Water

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$



- In pure water,

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

$$[H^+] = \frac{K_w}{[OH^-]} \qquad [OH^-] = \frac{K_w}{[H^+]}$$

	Acidic, basic or neutral	pH at 298 K
[H⁺] = [OH⁻]	neutral	7
[H⁺] > [OH⁻]	acidic	<7
[OH⁻] > [H⁺]	basic	>7

Because

$$[H_3O^+]\,[OH^-] = K_w = 1.0 \times 10^{-14},$$

we know that

$$-\log\,[H_3O^+] + -\log\,[OH^-] = -\log\,K_w = 14.00$$

or, in other words,

$$pH + pOH = pK_w = 14.00$$

$[H^+] = 10^{-pH}$ $[OH^-] = 10^{-pOH}$
$pH = -\log\,[H^+]$ $pOH = -\log\,[OH^-]$
$pH + pOH = 14$

م.د. مسار علي عواد

Dissociation Constants

The greater the value of **Ka**, the **stronger** the acid.

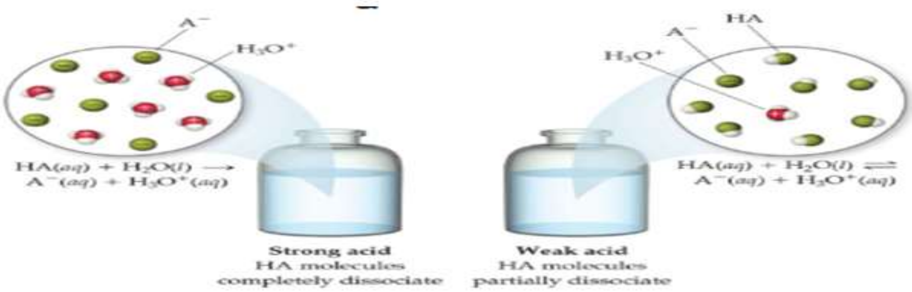
- For a generalized acid dissociation,

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

the equilibrium expression would be

$$K_c = \frac{[H_3O^+][A^-]}{[HA]}$$

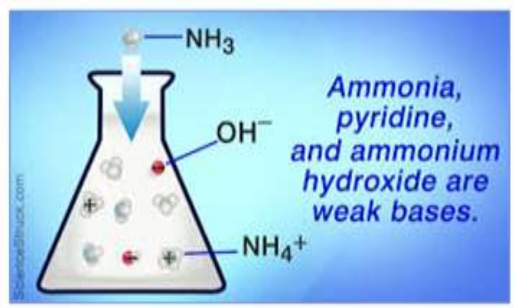
- This equilibrium constant is called the acid-dissociation constant, K_a.



Weak Bases

Weak Bases react with water to produce hydroxide ion.

$$\underset{\text{Base}}{NH_3(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

The equilibrium constant expression for this reaction is:

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

where K_b is the base-dissociation constant.