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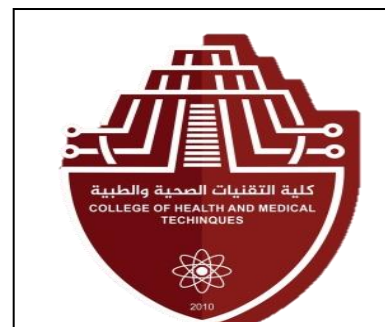
**College of Health and Medical Techniques**

**Medical Laboratories Techniques Department**

**Stage : First year students**

**Subject : Lecture 6A**

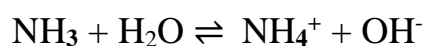
**Lecturer: Assistant professor Dr. SADIQ . J. BAQIR**



## **Chemical and ionic equilibrium:**

There are two types of reactions:

1) Reversible reaction,  $A + B \rightleftharpoons C + D$



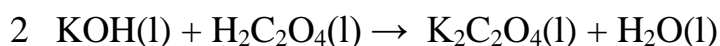
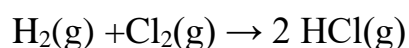
2) Irreversible reaction ,  $A + B \rightarrow C + D$



Generally , most of the chemical reactions are considered as reversible reactions.

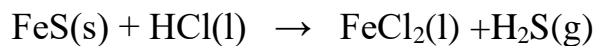
There are two kinds of systems :

a) **Homogenous reactions** : chemical reactions in which the reactants and products are in the same phase ( solid , liquid or gas )



b) **Heterogeneous reactions** :

Chemical reactions in which the reactants and products have more than one phase.



### **Equilibrium constant (K) :**

A numerical quantity that relate the concentration of reactants and products in a chemical reaction to one another.

For the chemical reaction :  $aA + bB \rightleftharpoons cC + dD$

According to **mass action law** Then:

$$V_f \propto [A]^a, [B]^b \quad (\text{f= forward})$$

$$V_f = K_f [A]^a [B]^b$$

$$V_b \propto [C]^c, [D]^d \quad (\text{b= backward})$$

$$V_b = K_b [C]^c [D]^d$$

**At equilibrium state :** ( $V_f = V_b$ )

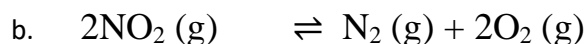
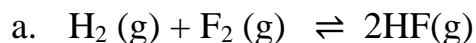
$$K_f [A]^a [B]^b = K_b [C]^c [D]^d$$

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

K = equilibrium constant

### **Example:**

Write the equilibrium constant expression for each of the reversible reactions:



solution:

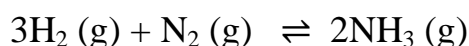
$$a. K_{eq} = \frac{[HF]^2}{[H_2][F_2]}$$

$$b. K_{eq} = \frac{[N_2][O_2]^2}{[NO_2]^2}$$

**Example:**

A container holds the following mixture at equilibrium:

$$[NH_3] = 0.25 \text{ M} \quad [H_2] = 1.91 \text{ M} \quad [N_2] = 0.11 \text{ M}$$



Calculate the equilibrium constant of the reaction.

Solution:

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{[0.25]^2}{[1.91]^3[0.11]} = 0.082$$

**Exercise:**

Given the equilibrium reaction:  $2HI \rightleftharpoons H_2 + I_2$

Calculate the molar concentration of  $I_2$  in the equilibrium mixture

Where  $[H_2] = 1.0 \times 10^{-2} \text{ M}$  and  $[HI] = 4.0 \times 10^{-2} \text{ M}$  and  $K_{eq} = 10$ .

**Le chatelier principle :**

The position of chemical equilibrium will always shift in a direction that tends to remove the effect of the applied stress .

**Factors effecting the reactions at equilibrium :**

- 1) Nature of reactants
- 2) Temperature
- 3) Concentration
- 4) Pressure ( in gas reactions)

**Some familiar equilibrium constant expressions :**

$K_w$  = ion product (or ionization) constant for water .

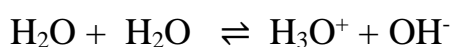
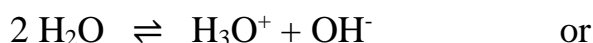
$K_{sp}$  = solubility product constant.

$K_a$  = ionization (or dissociation) constant of a weak acid.

$K_b$  = ionization (or dissociation) constant of a weak base.

### **Ion product constant for water ( $K_w$ ) :**

Aqueous solutions contains small amount of hydronium ions [ $H_3O^+$ ] and hydroxide [ $OH^-$ ] ions as a consequence of the dissociation reaction :



Some of  $H_2O$  molecule gives  $H^+$  to other  $H_2O$  molecule to produce  $H_3O^+$  ions and  $OH^-$  ions.

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K [H_2O]^2 = [H_3O^+][OH^-] = K_w$$

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{ mol}^2 / \text{L}^2 \text{ at } 25^\circ\text{C}$$

$K_w$  is **temperature dependant** it increases with temperature rise , and decreases with its decrease.

### **Variation of $K_w$ with temperature :**

Temperature $^\circ\text{C}$	$K_w$
0.0	$1.14 \times 10^{-15}$
25	$1.01 \times 10^{-14}$
40	$2.92 \times 10^{-14}$
50	$5.47 \times 10^{-14}$
70	$2.30 \times 10^{-13}$
100	$4.90 \times 10^{-13}$

$K_w$  is used only for water.

**Example :**

Calculate the hydronium  $[H_3O^+]$  and hydroxide ion  $[OH^-]$  concentrations of pure water at  $25^\circ C$  and  $100^\circ C$  ( $K_w = 4.9 \times 10^{-13}$ ) ?

solution:

Because  $OH^-$  and  $H_3O^+$  are formed from the dissociation of water only, then their concentrations are equal,



then :  $[H_3O^+] = [OH^-]$

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

Substitution in the above equation gives :

$$K_w = [H_3O^+]^2 \quad \text{also} \quad K_w = [OH^-]^2$$

$$[H_3O^+] = \sqrt{K_w} \quad \text{and} \quad [OH^-] = \sqrt{K_w}$$

$$\text{At } 25^\circ C \quad [H_3O^+] = \sqrt{K_w} = \sqrt{1.01 \times 10^{-14}} = 1.01 \times 10^{-7}$$

$$pH = -\log(1.01 \times 10^{-7}) = 7.00$$

$$[OH^-] = \sqrt{K_w} = \sqrt{1.01 \times 10^{-14}} = 1.01 \times 10^{-7}$$

At  $100^\circ C$

$$[H_3O^+] = \sqrt{K_w} = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}$$

$$pH = -\log(7 \times 10^{-7}) = 6.15$$

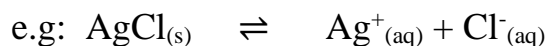
$$[OH^-] = \sqrt{K_w} = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}$$

**Exercise:**

Calculate the change in pH of pure water on heating from  $25^\circ C$  to  $50^\circ C$  ( $K_w = 5.47 \times 10^{-14}$ ) .

**Equilibrium involving sparingly soluble ionic solids :**

Most sparingly soluble salts are dissociated in saturated aqueous solution.



$$\mathbf{K} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}_{(s)}]}$$

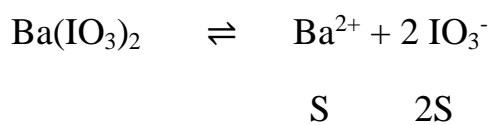
$$K [ \text{AgCl}_{(s)} ] = K_{sp} = [\text{Ag}^+_{aq}] [\text{Cl}^-_{aq}]$$

Where **K<sub>sp</sub> = solubility product constant** ( applied only for saturated solution) .

Example :

How many grams of Ba(IO<sub>3</sub>)<sub>2</sub> ( 487 g / mol) can be dissolved in 500 mL of water at 25°C ? K<sub>sp</sub> for Ba(IO<sub>3</sub>)<sub>2</sub> = 1.57x10<sup>-9</sup> .

Solution:



$$K_{sp} = [ \text{Ba}^{2+} ] [ \text{IO}_3^- ]^2$$

$$K_{sp} = (S)(2S)^2 = 1.57 \times 10^{-9} = 4S^3$$

$$S = \sqrt[3]{\frac{1.57 \times 10^{-9}}{4}} = 7.32 \times 10^{-4} \text{ mole/ L or (M) = Solubility}$$

$$\mathbf{\text{No. of moles}} = \frac{\text{Weight (g)}}{\text{Molar mass (g / mol)}}$$

$$\text{Weight} = \text{No. of moles} \times \text{Molar mass (g / mol)}$$

$$\text{As Molarity (M)} = \frac{\text{No. of moles}}{\text{Volume(liters)}}$$

$$\text{Then } \mathbf{\text{No. of moles}} = \text{Molarity} \times \text{Volume (liters)}$$

Substituting for the No. of moles gives:

$$\frac{\text{Weight (g)}}{\text{Molar mass (g / mol)}} = \text{Molarity} \times \text{Volume (liters)}$$

$$\mathbf{\text{Weight (g)} = \text{Molarity} \times \text{Volume (liters)} \times \text{Molar mass (g / mol)}}$$

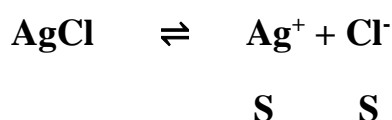
Weight in grams of  $\text{Ba}(\text{IO}_3)_2 = 7.32 \times 10^{-4} \text{ mol/liter} \times \frac{500}{1000} \text{ Liter} \times 487 \text{ g/mol} = 0.178 \text{ g}$

Then weight in grams of  $\text{Ba}(\text{IO}_3)_2$  that is dissolved in 500 mL water = 0.178 g

Example :

Calculate the weight in grams of  $\text{AgCl}$  (143.3 g / mol) that can be dissolved in 600 mL of water ?  $K_{sp}$  for  $\text{AgCl} = 1.8 \times 10^{-10}$ .

**Solution:**



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$K_{sp} = (S)(S) = 1.8 \times 10^{-10} = S^2$$

$$S = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} \text{ mole/L or (M) = solubility}$$

**Weight(g) = Molarity x Volume (liters) x Molar mass (g / mol)**

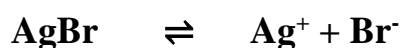
**Weight in grams of  $\text{AgCl} = 1.34 \times 10^{-5} \text{ mol/liter} \times \frac{600}{1000} \text{ Liter} \times 143.32 \text{ g/mol} = 1.15 \times 10^{-3} \text{ g} = 1.15 \text{ mg}$**

## Calculating Solubility Product Constant ( $K_{sp}$ ) From Solubility

**Example:**

**The weight of the sparingly soluble substance  $\text{AgBr}$  (187.8 g/mol) that dissolves in 500 mL of water to form a saturated solution is  $6.65 \times 10^{-5} \text{ g}$ . Calculate the  $K_{sp}$  of  $\text{AgBr}$ .**

**solution:**



S S

**S = molar solubility = Molarity**

$$\text{Molarity of AgBr (M)} = \frac{\text{wt (g)} \times 1000}{\text{M.wt} \times \text{Vml}}$$

$$\text{Molarity of AgBr (M)} = \frac{6.65 \times 10^{-5} \times 1000}{187.8 \times 500} = 7.08 \times 10^{-7} = \text{S}$$

$$\text{K}_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$$

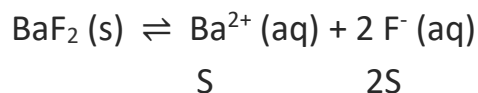
$$\text{K}_{\text{sp}} = (\text{S})(\text{S}) = \text{S}^2$$

$$\text{K}_{\text{sp}} = (7.08 \times 10^{-7})^2 = 5.01 \times 10^{-13}$$

### **Example:**

The solubility of barium fluoride,  $\text{BaF}_2$ , is  $7.94 \times 10^{-3} \text{ M}$  at  $25^\circ \text{C}$ . Calculate its solubility product constant,  $\text{K}_{\text{sp}}$ .

### **Solution:**



$$\text{Solubility} = [\text{Ba}^{2+}] = (\text{S}) = 7.94 \times 10^{-3} \text{ M}$$

$$\text{K}_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2$$

$$\text{K}_{\text{sp}} = (\text{S})(2\text{S})^2 = 4\text{S}^3$$

$$\text{K}_{\text{sp}} = 4(7.94 \times 10^{-3} \text{ M})^3$$

$$\text{K}_{\text{sp}} = 2 \times 10^{-6}$$

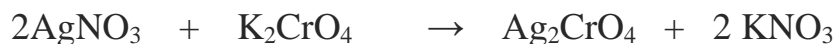
### **Estimation of precipitate formation**

1. If ionic product (I.P) <  $\text{K}_{\text{sp}}$  (dissolution Occurs)
2. If ionic product (I.P) =  $\text{K}_{\text{sp}}$  (equilibrium state) **saturation**
3. If ionic product (I.P) >  $\text{K}_{\text{sp}}$  (precipitation Occurs)



### Example:

Will a precipitate form when 20 mL of 0.01 M AgNO<sub>3</sub> solution is mixed with 2 Liter of 0.002 M K<sub>2</sub>CrO<sub>4</sub>. the K<sub>sp</sub> for Ag<sub>2</sub>CrO<sub>4</sub> is 1.1 x 10<sup>-12</sup>



$$\mathbf{K_{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12}$$

Having AgNO<sub>3</sub> gives Ag<sup>+</sup> and K<sub>2</sub>CrO<sub>4</sub> gives CrO<sub>4</sub><sup>2-</sup>



To calculate the ionic product (I.P) of [Ag<sup>+</sup>]<sup>2</sup> [CrO<sub>4</sub><sup>2-</sup>] after mixing

$$M_1V_1 \text{ (before mixing)} = M_2V_2 \text{ (after mixing)}$$

$$[\text{Ag}^+] = \frac{M_1V_1}{V_2} = \frac{(0.01\text{M})(20\text{mL})}{(2000+20)\text{mL}} = 9.9 \times 10^{-5} \text{ M}$$

$$[\text{CrO}_4^{2-}] = \frac{M_1V_1}{V_2} = \frac{(0.002\text{M})(2000\text{mL})}{(2000+20)\text{mL}} = 0.002 \text{ M}$$

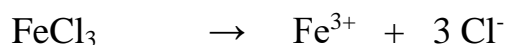
$$\text{I.P} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (9.9 \times 10^{-5})^2 (0.002) = 2.0 \times 10^{-11}$$

As I.P > K<sub>sp</sub> **then precipitate will form**

### Example:

What pH is required to just precipitate Fe(OH)<sub>3</sub> (K<sub>sp</sub> = 4x 10<sup>-38</sup>) from 0.1 M FeCl<sub>3</sub> solution?

solution:



0.1 M          0.1 M

$$k_{sp} = [Fe^{3+}][OH^{-}]^3 = 4 \times 10^{-38}$$

$$[0.1][OH^{-}]^3 = 4 \times 10^{-38}$$

$$[OH^{-}] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}$$

$$pOH = -\log(7 \times 10^{-13}) = 12.2$$

$$pH = 14 - 12.2 = 1.8$$