

**ALMUSTAQBAL UNIVERSITY COLLEGE**

*Medical Laboratories Techniques Department*

**Stage : First year students**

**Subject : General chemistry -A - Lecture 6**

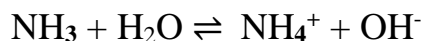
**Lecturer: Assistant professor Dr. SADIQ . J. BAQIR**



## **Chemical and ionic equilibrium:**

There are two types of reactions:

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



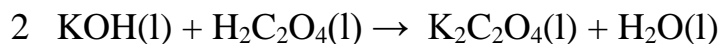
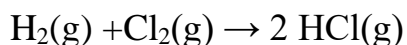
2) Irreversible reaction ,  $A + B \rightarrow C + D$



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

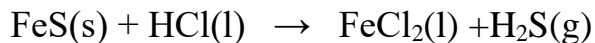
There are two kinds of systems :

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** which states that (The rate of chemical reaction is directly proportional with formula concentration of reaction substances each raise to the power indicated by the number of ion or molecule appearing in the balanced equation of the reaction). Then:

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

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

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

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

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

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

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

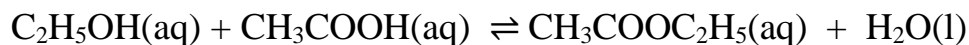
K = equilibrium constant

## Le chatelier principle :

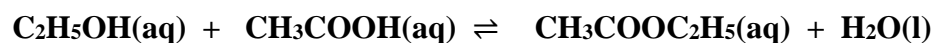
The position of chemical equilibrium will always shift in a direction that tends to remove the effect of the applied stress .

Example:

Consider the reaction between ethanol and ethanoic(acetic) acid:



In an experiment, 0.1 mole of ethanol and 0.2 mole of acetic acid were mixed together forming 1 liter solution and the mixture was allowed to reach equilibrium. The number of moles of acetic acid present at equilibrium were 0.115 mole . Calculate the equilibrium constant value (Kc).



**At Start**                    **0.1 mole**                    **0.2 mole**                    **0.0 mole**                    **0.0mole**

**At Equilibrium**

moles  $[\text{CH}_3\text{COOH}]_{\text{reacted}} = \text{Original} - \text{remain} = 0.2 - 0.115 = 0.085 \text{ mole}$

moles  $[\text{CH}_3\text{COOH}]_{\text{reacted}} = [\text{CH}_3\text{COOC}_2\text{H}_5]_{\text{produced}} = [\text{H}_2\text{O}]_{\text{produced}} = 0.085 \text{ mole}$

moles  $[\text{C}_2\text{H}_5\text{OH}]_{\text{remain}} = \text{Original} - \text{reacted} = 0.1 - 0.085 = 0.015 \text{ mole}$

$$\text{Molarity} = \frac{\text{No. of moles}}{V(\text{L})}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5]_{\text{eq}} = 0.085 \text{ M}$$

$$[\text{H}_2\text{O}]_{\text{eq}} = 0.085 \text{ M}$$

$$[\text{CH}_3\text{COOH}]_{\text{eq}} = 0.115 \text{ M}$$

$$[\text{C}_2\text{H}_5\text{OH}]_{\text{eq}} = 0.015 \text{ M}$$

$$\mathbf{Kc} = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq})][\text{H}_2\text{O}(\text{l})]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}(\text{aq})]}$$

$$\mathbf{Kc} = \frac{[0.085][0.085]}{[0.015][0.115]} = \mathbf{4.19}$$

### **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 .

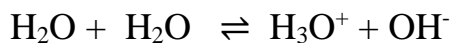
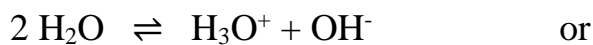
$K_{sp}$  = solubility product constant.

$K_a$  = 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 :



(base) (acid)

$H_2O$  acid molecule gives  $H^+$  to  $H_2O$  base molecule to produce  $H_3O^+$  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 °C	$K_w$
0.0	$1.14 \times 10^{-15}$
25	$1.01 \times 10^{-14}$
37	$2.6 \times 10^{-14}$
40	$2.92 \times 10^{-14}$
50	$5.47 \times 10^{-14}$
70	$2.30 \times 10^{-13}$
100	$4.9 \times 10^{-13}$

$K_w$  is used only for water.

**Example :**

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

Answer:

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 :

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

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

$$\text{At } 25^\circ\text{C} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.01 \times 10^{-14}} = 1.01 \times 10^{-7}$$

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

At  $100^\circ\text{C}$

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{4.9 \times 10^{-13}} = 7.0 \times 10^{-7}$$

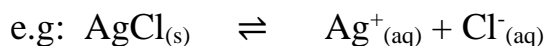
$$\text{pH} = -\log(7 \times 10^{-7}) = 6.15$$

### Exercise:

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

### Equilibrium involving sparingly soluble ionic solids :

Most sparingly soluble salts are dissociated in saturated aqueous solution .



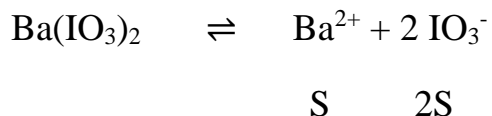
$$\mathbf{K} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(s)]}$$

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

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

Example :

How many grams of  $\text{Ba}(\text{IO}_3)_2$  (M.wt = 487 g / mol) can be dissolved in 500 mL of water at  $25^\circ\text{C}$  ?  $K_{sp}$  for  $\text{Ba}(\text{IO}_3)_2 = 1.57 \times 10^{-9}$  .



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

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

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

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

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

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

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

Substituting for the No. of moles gives:

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

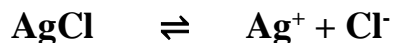
$$\text{Weight (g)} = \text{Molarity} \times \text{Volume (liters)} \times \text{Molar mass (g/mol)}$$

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

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

Example :

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



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

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

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

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

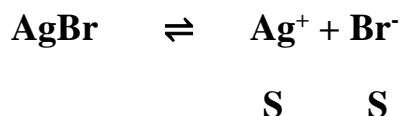
$$\text{Weight in grams of AgCl} = 1.34 \times 10^{-5} \text{ mol/liter} \times \frac{600}{1000} \text{ Liter} \times 143.32 \text{ g/mol} = 1.15 \times 10^{-3} \text{ g} = 1.15 \text{ mg}$$

## Calculating Solubility Product Constant (Ksp) From Solubility

### Example :

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

Answer:



S = molar solubility = Molarity

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

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

$$\text{Ksp} = [\text{Ag}^+] [\text{Br}^-]$$

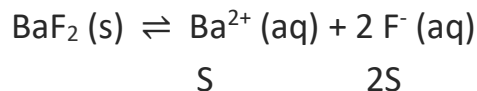
$$\text{Ksp} = (S)(S) = S^2$$

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

### EXAMPLE:

The solubility of barium fluoride, BaF<sub>2</sub>, is  $7.94 \times 10^{-3}$  M at 25 °C. Calculate its solubility product constant, K<sub>sp</sub> ,.

### SOLUTION



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

$$[\text{F}^-] = (2S)$$



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

$$K_{sp} = (S) (2 S)^2 = 4S^3$$

$$K_{sp} = 4(7.94 \times 10^{-3} \text{ M})^3 = 4(5 \times 10^{-7})$$

$$K_{sp} = 2 \times 10^{-6}$$

## Estimation of precipitate formation

### Example

Show if a precipitate of AgCl will form on mixing equal quantities of a solution of  $1 \times 10^{-5} \text{ M}$  of silver nitrate  $\text{AgNO}_3$  and a solution of  $1 \times 10^{-3} \text{ M}$  potassium chloride  $\text{KCl}$ . The  $K_{sp}$  of  $\text{AgCl} = 1.8 \times 10^{-10}$ .

### Answer



On mixing equal quantities of the two solutions, each concentration is halved.

$$M_1 V_1 (\text{before mixing}) = M_2 V_2 (\text{after mixing})$$

$$[\text{Ag}^+ (\text{aq})] = \frac{M_1 V_1}{V_2} = \frac{(1 \times 10^{-5} \text{ M})(1 \text{ mL})}{(2) \text{ mL}} = 5 \times 10^{-6} \text{ M}$$

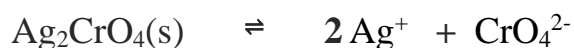
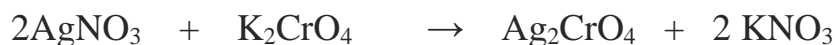
$$[\text{Cl}^- (\text{aq})] = \frac{M_1 V_1}{V_2} = \frac{(1 \times 10^{-3} \text{ M})(1 \text{ mL})}{(2) \text{ mL}} = 5 \times 10^{-4} \text{ M}$$

$$\text{I.P} = [\text{Ag}^+ (\text{aq})][\text{Cl}^- (\text{aq})] = (5.0 \times 10^{-6}) \times (5.0 \times 10^{-4}) = 2.5 \times 10^{-9}$$

As ionic product (I.P)  $>$   $K_{sp}$  then a precipitate ( $\text{AgCl}$ ) will form.

### Example:

Will a precipitate form when 20.0 mL of 0.01 M AgNO<sub>3</sub> solution is mixed with 2.00 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 1.1x10<sup>-12</sup>



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

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

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

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

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

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

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

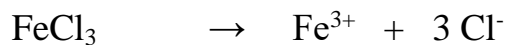
### Notes:

1. If ionic product (I.P) < K<sub>sp</sub> (dissolution Occurs)
2. If ionic product (I.P) = K<sub>sp</sub> (equilibrium state)
3. If ionic product (I.P) > K<sub>sp</sub> (precipitation Occurs)

Example:

What pH is required to just precipitate  $\text{Fe}(\text{OH})_3$  ( $K_{sp} = 4 \times 10^{-38}$ ) from 0.10 M  $\text{FeCl}_3$  solution?

Answer:



0.10 mole                      0.10 mole

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

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

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

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

$$\text{pH} = 14 - 12.2 = 1.8$$