

ALMUSTAQBAL UNIVERSITY COLLEGE

Biomedical Engineering Department

Stage : Second year students

Subject : Chemistry 1 - Lecture 8

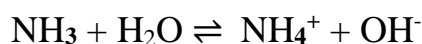
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Chemical and ionic equilibrium:

There are two types of reactions:

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



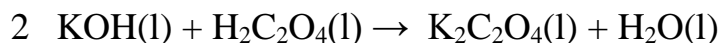
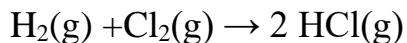
2) Irreversible reaction, $A + B \rightarrow C + D$



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

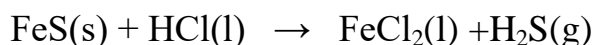
There are two kinds of systems :

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:

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

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

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

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

At equilibrium state : ($V_f = V_b$)

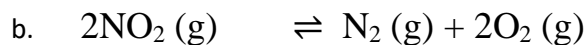
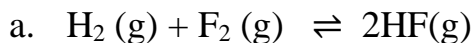
$$K_f [A]^a [B]^b = K_b [C]^c [D]^d$$

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

K = equilibrium constant

Example:

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



solution:

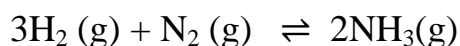
$$a. K_{eq} = \frac{[HF]^2}{[H_2][F_2]}$$

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

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 .

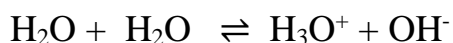
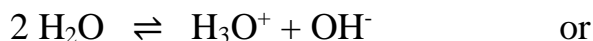
K_{sp} = solubility product constant.

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 :



(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 | 1.14×10^{-15} |
| 25 | 1.01×10^{-14} |
| 40 | 2.92×10^{-14} |
| 50 | 5.47×10^{-14} |
| 70 | 2.30×10^{-13} |
| 100 | 4.90×10^{-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 ?

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 :

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

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

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

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

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

At 100° C

$$[\text{H}_3\text{O}^+] = \sqrt{K_w} = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}$$

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

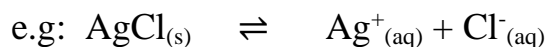
$$[\text{OH}^-] = \sqrt{K_w} = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}$$

Exercise:

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

Equilibrium involving sparingly soluble ionic solids :

Most sparingly soluble salts are dissociated in saturated aqueous solution .



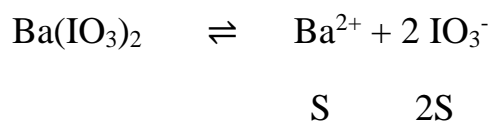
$$\mathbf{K} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(s)]}$$

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

Where **K_{sp} = solubility product constant** (applied only for saturated solution) .

Example :

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



$$K_{sp} = [Ba^{2+}] [IO_3^-]^2$$

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

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

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

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

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

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

Substituting for the No. of moles gives:

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

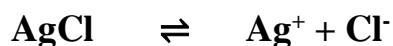
$$\text{Weight (g)} = \text{Molarity} \times \text{Volume (liters)} \times \text{Molar mass (g/mol)}$$

$$\text{Weight in grams of } Ba(IO_3)_2 = 7.32 \times 10^{-4} \text{ mol/liter} \times \frac{500}{1000} \text{ Liter} \times 487 \text{ g/mol} = 0.178 \text{ g}$$

Then weight in grams of $Ba(IO_3)_2$ that is dissolved in 500 mL water = 0.178 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 $AgCl = 1.8 \times 10^{-10}$.



$$S \quad S$$

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

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

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

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

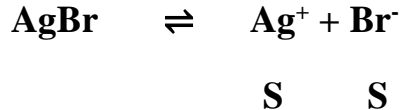
$$\text{Weight in grams of AgCl} = 1.34 \times 10^{-5} \text{ mol/liter} \times \frac{600}{1000} \text{ Liter} \times 143.32 \text{ g /mol} = 1.15 \times 10^{-3} \text{ g} = 1.15 \text{ mg}$$

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 6.65×10^{-5} g . Calculate the Ksp of AgBr.

Answer:



S = molar solubility = Molarity

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

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

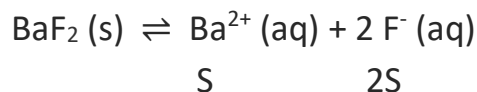
$$\text{Ksp} = [\text{Ag}^+] [\text{Br}^-]$$

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

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

EXAMPLE:

The solubility of barium fluoride, BaF_2 , is 7.94×10^{-3} M at 25°C . Calculate its solubility product constant, K_{sp} .

SOLUTION

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

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

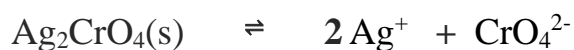
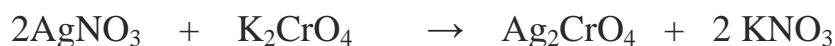
$$K_{\text{sp}} = (\text{S})(2\text{S})^2 = 4\text{S}^3$$

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

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

Estimation of precipitate formation**Example:**

Will a precipitate form when 20 mL of 0.01 M AgNO_3 solution is mixed with 2 Liter of 0.002 M K_2CrO_4 . the K_{sp} for Ag_2CrO_4 is 1.1×10^{-12}



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

Having AgNO_3 gives Ag^{+} and K_2CrO_4 gives CrO_4^{2-}

To calculate the ionic product (I.P) of $[\text{Ag}^{+}]^2 [\text{CrO}_4^{2-}]$ 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 $\text{I.P} > K_{sp}$ then precipitate will form

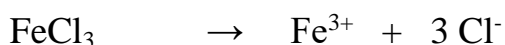
Notes:

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

Example:

What pH is required to just precipitate $\text{Fe}(\text{OH})_3$ ($K_{sp} = 4 \times 10^{-38}$) from 0.1 M FeCl_3 solution?

Answer:



0.1 mole 0.1 mole

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

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

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

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

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