Chapter ⇒ 7

Equilibrium

- ### Chemical Equilibrium

In a chemical reaction chemical equilibrium is defined as the state at which there is no further change in concentration of reaction and products.

for example,

Consider a hypothetical reaction, $A + B \rightleftharpoons C + D$

At equilibrium the rate of forward reaction is equal to the rate of backward reaction.

(i) The reaction in which most of the reactant remains unchanged only small amounts of Products are formed.

(ii) The reaction in which most of the reactants remains un changed, i.e., only small amount of products are formed.

(iii) The reaction in which the concentrations of both the reactants and product are comparable when the system is in equilibrim.

Equilibrium in physical processes

(i) Solid - Liquid Equilibrium : The equilibrium is represented as

$$\boxed{H_2O(s) \rightleftharpoons H_2O(l)}$$

Rate of melting of ice = Rate of freezing of water.

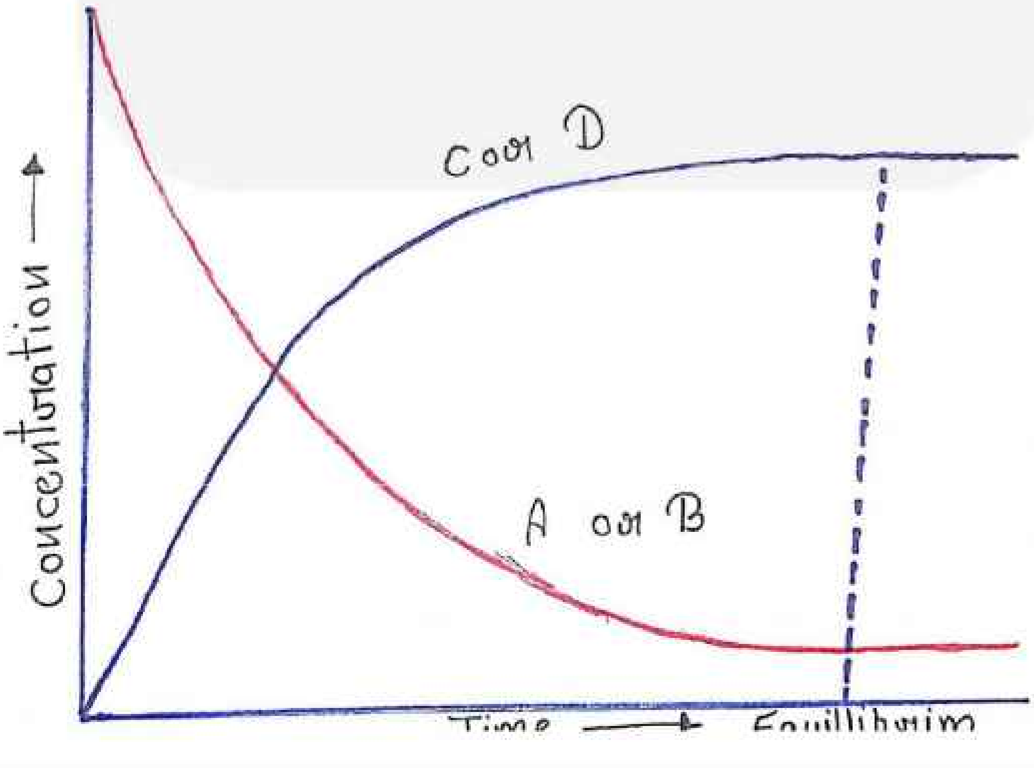
The system here is in dynamic equilibriums and following can be inferred.

(a) Both the opposing processes occur simultaneously.

(b) Both the processes occur at the same rate so that the amount of ice and water - remains constant

(ii) Liquid - Vapour Equilibrium

The equilibrium can be represented as .



Rate of evaporation = Rate of Condensation when there is an equilibrium between liquid and vapours, it is called liquid - vapour equilibrium.

(iii) Solid - Vapour Equilibrium

This Type of Equilibrium is attained where solid sublime to vapour phase. for example, when solid iodine is placed in a closed vessel violet vapours state appearing in the vessel whose intensity increass with time and ultimately. it becomes constant.

The equilibrium may be represented as

$$\boxed{I_2(s) \rightleftharpoons I_2\ (\text{vapour})}$$

Rate of sublimation of solid I_2 form vapour = Rate of condensation of I_2 vapour to give solide I_2

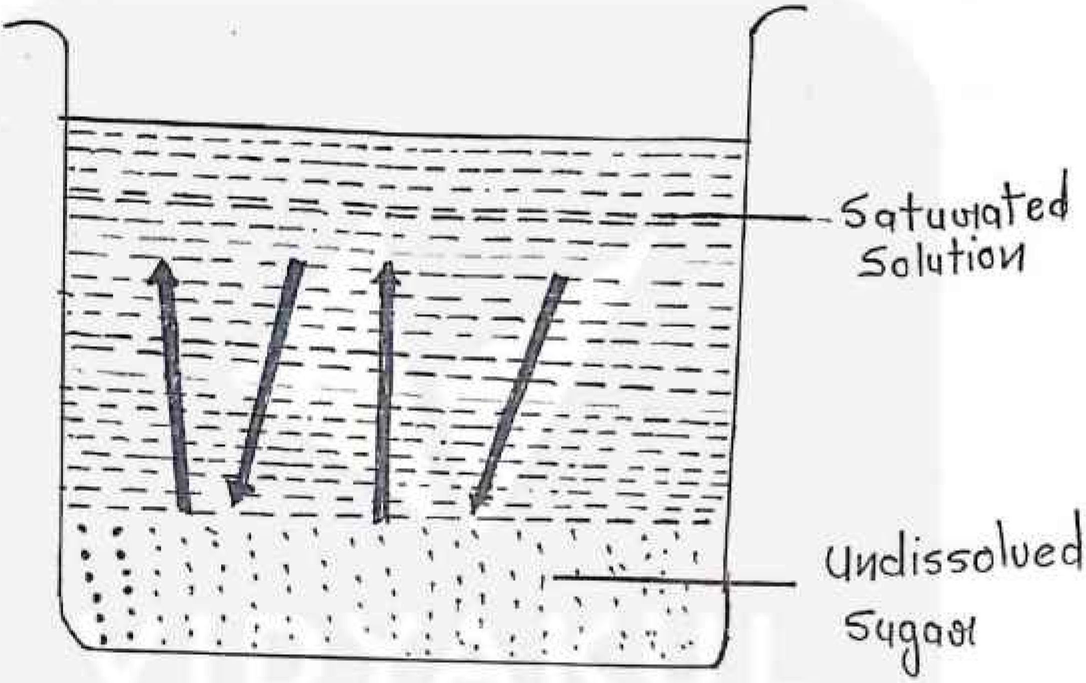
- Equilibrium involving Dissolution of Solid in Liquid.

· Solution : when a limited amount of salt or sugar or any solute dissolves in a given amount of water solution is formed.

At a give temperature state is reached when no more solute can be dissolved that the solution is called saturated solution

Rate of dissolution = Rate of precipitation

Sugar(s) $\rightleftharpoons$ Sugar (in solution)



Here dissolution and precipital take place with the same speed.

• Equilibrium between a Gas and the solution in Liquid :

This type of equilibrium can be seen by the follow example:

Let us consider a sealed soda water bottle in which CO_2 gas is dissolved under high pressure.

$CO_2(g) \rightleftharpoons CO_2$ (present in solution)

Henrys low:

The solubility of a gas in a liquid at a certain temperature is governed by Henrys low. It states that the mass of a gas that dissolves in a given mass of a solvent of any temperature is proportional to the Pressure of the gas above the surface of the solvent.

Mathematically, $m \propto P$

$m = K_H p$ (where K_H = Henry's constant)

• Characteristics of Equilibria involving:

: Physical processes

(i) The equilibrium can be attained only in closed systems at a given temperature.

(ii) At the equilibrium the measurable Properties of the system remain contstant.

iii) At equilibrium, the concetration of substances become constant at constant temperature.

(iv) The value of equilibrium constant represents the extent to which the process proceeds before equilibrium is achieved.

- ## Equilibrium in Chemical Processes

Like equilibria in physical systems it can also be achieved in chemical process involving reversible chemical reaction carried in closec container.

$$\boxed{A + B \rightleftharpoons C + D}$$

The dynamic nature of chemical equilibrium can be demonsturated in the synthesis of ammonia by Haber's process. Haber started his experiment with the Known amount of N_2 and H_2 at high temperature and pressure.

At regular intevals of time he determined the amount of ammonia present.

In general, for a reversible of equilibrium. can be show by

Accourdings to the equilibrium law. $\frac{[C][D]}{[A][B]} = Kc$)

where Kc is called the equilibrium constant four a general reaction, $aA + bB \rightleftharpoons cC + dD$.

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

four the reaction $H_2 + I_2 \rightleftharpoons 2HI$: $Kc = \frac{[HI]^2}{[H_2][I_2]}$

four the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $Kc \frac{[NH_3]^2}{[N_2][H_2]^3}$

• Equilibrium in Homogeneous system

when in a system involving reversible reaction reactants and products are in the same phase, then the system is called as homogeneous system.

$$\boxed{N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)}$$

After some time it can be observed that an equilibrium is form. The equilibrium can be seen by constant in the colour of the reaction mixture.

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Initial moles / litre $\frac{1}{10}$ $\frac{1}{10}$ 0 0

Mole / litre at the equilibrium point

$$\frac{1-0.4}{10} = \frac{0.6}{10} \quad \frac{1-0.4}{10} = \frac{0.6}{10} \quad \frac{0.4}{10} \quad \frac{0.4}{10}$$

Abblying low of Chemical equillbrium point

Equilibrium constant $(K)_c = \frac{[H_2(g)][CO_2(g)]}{[H_2O(g)][CO(g)]} = \frac{\left(\frac{0.4}{10}\ mol\ L^{-1}\right)}{\left(\frac{0.6}{10}\ mol\ L^{-1}\right)}$

$$\Rightarrow \frac{\left(\frac{0.4}{10}\ mol\ L^{-1}\right)^2}{\left(\frac{0.6}{10}\ mol\ L^{-1}\right)} = \frac{0.16}{0.36} = 0.44$$

- **Low of chemical Equilibrium :**

At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to the corresponding stoichiometric coefficients as represented by the balanced chemical equation.

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

- Relationship between Equilibrium constant K, reaction Quotient Q and Gibbs energy G. A mathematical expression of thermodynamic view of equilibrium can be described by tine equation.

- factours Affecting Equilibria.

Le chatelier's principle: If a system under equilibrium is subjected to a change in temperature, pressure or concentration them the equilibrium shift in such a manner as to reduce or to counteract the effect of change.

- Effect of change of concentration:

Concentration of any of the reactants or products in a reaction at equilibrium is changed. the composition of the equilibrium changes so as to minimise of the effect.

- Effect of Pressure change:

If the number of moles of gaseous reactants and products in a reaction at equilibrium is changed, the composition of the equilibrium changes so as to minimise the effect.

- It total number of moles of reactants are more than tatal number of moles of products, high pressure is favaurable to forward reaction.

• Effect of Inert Gas Addition.

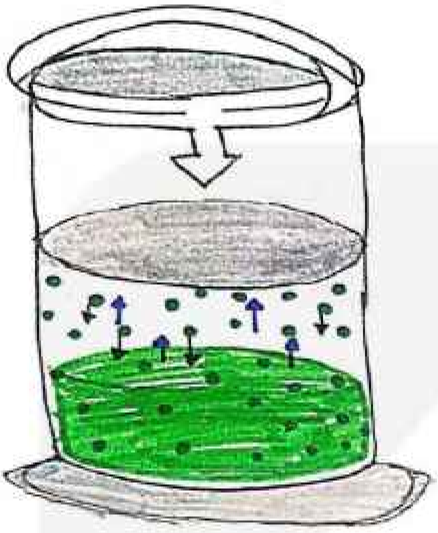
If the valume is kept constant there is no effect on equilibrium after the addition of an inert gas.

• Reason:

This is because the addintion of an inert gas at constant volume does not change the partial pressure or the molar concentration.

• Effect of temperature change.

when the temperature of the system is changed (increased or decreased). the equilibrium shifts opposite direction in order to neutralize the effect of change.



- Concentration Change
- Pressure Changes
- Temperature Change
- Addition of a catalyst

but practically very low temperature slows down the and thus a catalyst is used.

• Effect of a catalyst :

Catalyst has no effet on the equilibrium composition of a reaction mixture.

Reason: since catalyst increases the speed of both the forward and backward reaction to the same extent in a reversible reaction.

• Ionic Equilibrium in Solution.

- ## Electrolytes :

Substance which conduct electricity in their aqueous solution.

- ## Strong Electrolytes :

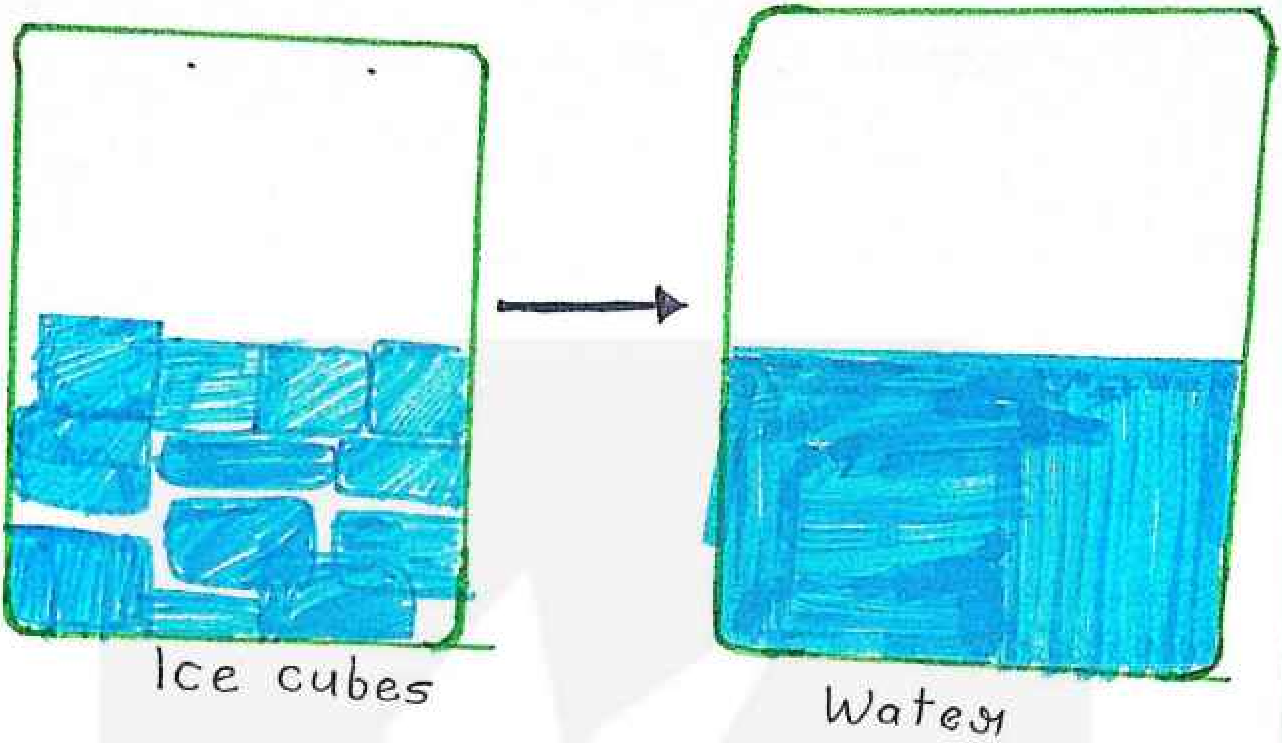
Those electrolytes which on dissolution in which water are ionized almost completety are called strong electrolytes.

- ## weak electrolytes :

Those electrolytes which on dissolution in water partially dissociated are called weak electrolyte.

- ## Ionic Equilibrium :

The equilibrium formed between ions and unionised substance is called ionic equilibrium:



Acids :

Acids are the substance which turn blue litmus paper to red and liberate dihydrogen on reacting with some metals.

Bases :

Bases are the substances which turn red litmus paper blue. It is bitter in taste. common

ex = $NaOH$, Na_2CO_3.

Arrhenius concept of Acids and Bases Acid :

Acids :

According to Arrhenius theory, acids are substance that dissociates in water to give hydrogen ions $H^+(aq)$.

Bases :

Bases are substances that produce $OH^-(aq)$ after dissociation in water.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO + H_3O^+$$

Limitations of the Arrhenius concept :-

(i) According to the Arrhenius concept, an acid gives H^+ ion in water but H^+ ions does not exist independently because of its very small size ($\sim H^{-18}$ m radius) and intense electric field.

(ii) It does not account for the basicity of substances like, ammonia which does not possess a hydroxyl group.

The Bronsted-Lowry Acids and Bases :-

According to Bronsted-Lowry, an acid is a substance which is capable of donating a hydrogen ion H^+ and Bases are substance capable of accepting a hydrogen ion H^+. In other words, acids are proton donors and bases are proton acceptors. This can be explained by the following example.

e.g HCl is an acid since it products H_3O^+ in aqueous Solution. $HCl_{(l)} + H_2O(l) \rightleftharpoons H_3O+(aq) + Cl-(aq)$
e.g. for base is NaOH $NaOH(s) + H_2O(l) \rightleftharpoons Na+(aq) + OH(-aq)$

Note: H+ ions exist in water as hydronium ions (H_3O^+) $H^+ + H_2O \rightleftharpoons H_3O^+$

⇒ Acid and Base as Conjugate Pairs :-

The acid-base pair that differs only by one proton is called a conjugate acid-base pairs. Let us consider the example of ionization of HCl in water.
For example,
in the reaction $NH_{3(l)} + H_2O_{(l)} \rightleftharpoons NH_4^+(aq) + OH^-aq$
Here water acts as a base because it accepts the proton.

⇒ Lewis Acids and Bases :-

According to Lewis, acid is a substance which accepts electron pair and base is a substance which donates an electron pair.

Electron deficient species like $AlCl_3$, BH_3 H^+

Electron deficient species like $AlCl_3$, BH_3, H^+ etc.

⇒ Ionization of Acids and Bases :-

Strength of acid or base is determined with the help of extent of Ionization in aqueous solution.

⇒ PH Scale :

Hydrogen-ion concetration are measured as the number of gram ions of gram ion of hydrogen ions present per litre of Solution. PH being the logarithm of the are reciprocal of the hydrogen ion concentration.

e.g. $\underset{\text{base}}{NH_3(l)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conj.acid}}{NH_4^+(aq)} + \underset{\text{conj.base}}{OH^-(aq)}$

In general $\boxed{\begin{array}{l} \text{Acid} - H^+ \rightarrow \text{Conjugate base} \\ \text{Base} + H^+ \rightarrow \text{Conjugate acid} \end{array}}$

$\underset{\text{Acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conj.acid}}{H_3O^+} + \underset{\text{conj.Base}}{Cl^-}$

⇒ Di and Polybasic Acids :-

Acids which contain more than one ionizable proton per molecule are called Dibasic acids.

only polybasic acids or polyprotic acid. a common examples are oxalic acid, sulphuric acid, Phosphoric acid etc.

$$PH = -\log[H_3O^+]$$

$$PH = \log \frac{1}{[H_3O^+]}$$

The PH range at 25°C is taken as 0 to 14.

$PH = 7$ Neutral
$PH > 7$ Basic
$PH < 7$ Acidic

The ionization reaction for a dibasic acid can be represented as:

$$H_2x\ (aq) \rightleftharpoons H^+(aq) + Hx^-(aq)$$

Their equilibrium constants can be written as:

$$K_{a_1} = \frac{[H]^+[HX^{-1}]}{[H_2X]};\ K_{a_2} = \frac{[H^+][X^{2-1}]}{[HX^{-1}]}$$

K_{a_1} and K_{a_2} are called first and second ionization constants respectively.

for dibasic acid

$$K_{a_1} > K_{a_2}$$

factors Affecting Acid Strength :

When the strength of H-A bond decreases

$$\xrightarrow{\text{Size increases}}$$

$$HF << HCl << HBr << HI$$

$$\xrightarrow[\text{Acid strength increases}]{}$$

⇒ Common ion Effect :-

If in aaqueous solution of a weak electrolyte a strong electrolyte is added having an ion common with electrolyte, than : the dissociation of the weak electrolyte is suppresed. The effect by which the are dissociation of weak electrolyte is suppresed is known as common ion effect.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

• Hydrolysis of Salts and the PH of their Solutions.

As Per the Salt hydrolysis formula, for the Salts of weak acid and weak base like CH_3COONa

$$K_h = \frac{K_w}{K_a \times K_b}$$

$$h = \frac{K}{\sqrt{K_a \times K_b}}$$

$$PH = \frac{1}{2}[PK_w + PK_a - PK_b]$$

$$PH = \frac{1}{2}[14 + 4.80 + 4.78]$$

$$PH = 7.01.$$

$CH_3COO^- + Na^+ H_2O \rightleftharpoons CH_2COOH + Na^+ +$
OH^-
or
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH-$

After hydrolysis, solution will be basis $PH > 7$ in this type of hydrolysis, only anions of salt take part in the hydrolysis, it is known as anionic hydrolysis.

Hydrolysis of weak Acid weak Base :

Salts belong to this type are : CH_3COONH, $(NH_4)CO_3$ etc. $CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

PH of Solution depends upon the relative strength of acid.

• Buffer Solutions :

The Solution so small amounts of acid or alkali, are called Buffer Solution.

e.g., $CH_3COOH + CH_3COONa$,
$H_2CO_3 + HCl$

⇛ Solubility products :-

It is applicable to sparingly soluble salts. There is equilibrium between ion and a unionised solid substance.

$$AgCl \rightleftharpoons Ag^{+} + Cl$$

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

K_{sp} is called solubility product

In pure water;

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

$$K_{sp} = S^{2} \; \{\because S = [Ag^{+}] = [Cl^{-}]\}$$

$$S = \sqrt{K_{sp}}$$

⇛ Equilibrium :-

It can be established for both physical and chemical process. At the state of equilibrium rate of forward and backward reaction are equal.

⇛ Equilibrium constant :-

K_c is expressed as the concentration of products divided by reactants each term raised to the stoichiometric cofficients. for example,

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

$$K_c = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}\ [B]^b_{eq}}$$

$K_c \gg 1$: Mixture contains mostly products

$K_c \ll 1$: Mixture contains mostly reactants

⇒ Le Chateller's principle :-

it states that the change in any factor such as temperature, pressure, concentration etc.., will cause the equilibrium to shift in such a direction so as to reduce the effect of the change.

⇒ Electrolytes :-

Substance that conduct electricity in aqueous solutions are called electrolytes.

⇒ Arrhenius Concept :-

According to Arrhenius, acid give hydrogen -neous while bases produce hydroxyl ions in their aqueous solution.

⇒ Bronsted-Lowry concept :

Bronsted-Lowry defined acid as proton donor and a base as a proton acceptor.

⇒ Conjugate base and Conjugate acid :

Conjugate pair of acid and base differs only by one proton.

⇒ Lewis acids :

define acid as an electron pair acceptor and a base as an electron pair donor.

⇒ PH Scale :-

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the PH scale. The PH of pure water is 7.

⇒ Buffer Solution :-

It is the Solution whose PH does not change by addition of small amount fo strong acid or base.

⇒ Solubility Product (Ksp) :-

for a sparingly Soluble Salt, it is defined as the product of molar concentration of the ions raised to the power equal to the number of times each ion occurs in the equation for solubilities.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

This equillibrium system may be described by the mass-action expression.