Equilibrium

Equilibrium in Physical Processes

Solid–Liquid Equilibria

- A perfectly insulated thermos flask is taken in which ice and water are kept at 273 K and atmospheric pressure.

- Observation – There is no change of mass of ice and water. (Despite being at the boundary between ice and water, molecules from the liquid water collide against ice and adhere to it. Similarly, some molecules of ice also escape into the liquid phase.)

- Reason: At 273 K and atmospheric pressure, the rate of transfer of molecules from ice to water is equal to that of transfer of molecules from water to ice.

- This state is known as equilibrium state.

$H_2O_{(s)} \longleftrightarrow H_2O_{(l)}$

- It may be noted that ice and water are in equilibrium only at particular temperature and pressure.

- Normal melting point or normal freezing point – Temperature at which the solid and liquid phases of the substance are at equilibrium at atmospheric pressure

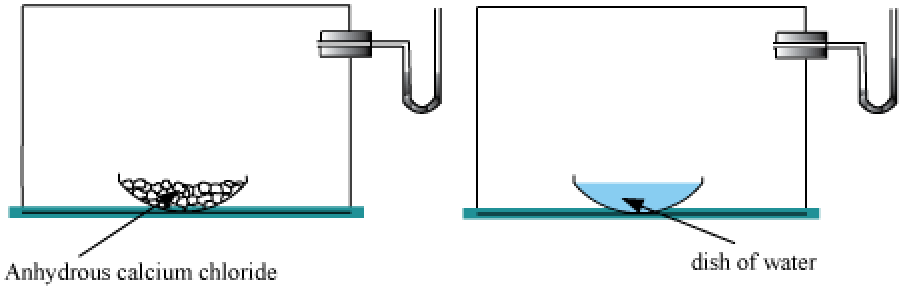
- Conclusion:

- Both the opposing processes occur simultaneously.

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

Liquid-Vapour Equilibrium

- Experimental set up



- Anhydrous $CaCl_2$ is taken for few hours.

- Anhydrous $CaCl_2$ is removed and a dish of water is quickly placed.

- Observation

- Mercury level in the right limb of the manometer slowly increases and attains a constant value. That is, pressure inside the box increases and reaches a constant value.

- Volume of water in the watch glass decreases.

- Reason:

  In the beginning, there was no water vapour inside the box. After addition of water, evaporation starts and water molecules escape into the gaseous phase. As a result, pressure goes on increasing. However, the rate of increase in pressure decreases with time due to condensation of vapour into water and after sometime, rate of evaporation becomes equal to the rate of condensation.

  $H_2O_{(l)} \longleftrightarrow H_2O_{(g)}$

  Therefore, the pressure becomes constant. This state is called equilibrium state.

- Vapour Pressure

- Equilibrium vapour pressure: Constant pressure exerted by water molecules at equilibrium at a given temperature

- Increases with increase in temperature

- Equilibrium vapour pressure is different for different liquids at the same temperature.

- Higher the vapour pressure, more volatile is the liquid and lower is the boiling point.

- Time taken for evaporation depends upon the
- nature of the liquid
- amount of the liquid
- temperature
- It is not possible to reach equilibrium in open system.
- Reason: The rate of condensation is much less than the rate of evaporation in open system.
- Boiling Point
- Normal boiling point: Temperature at which the liquid and the vapours are at equilibrium at atmospheric pressure (1.013 bar)
- It depends upon the atmospheric pressure, which depends upon the altitude of the place. Higher the altitude, lower is the boiling point.
- Exists when solids sublime to vapour
- Example:
- When some solid iodine is warmed in a closed vessel, iodine sublimes to iodine vapours (violet). The intensity of colour increases with time but after sometime, the intensity becomes constant. This state represents equilibrium state.

  $I_{2(solid)} \longleftrightarrow I_{2(vapour)}$

- Some other examples:
- $Camphor_{(solid)} \longleftrightarrow Camphor_{(vapour)}$
- $NH_4Cl_{(solid)} \longleftrightarrow NH_4Cl_{(vapour)}$

Equilibrium Involving Dissolution of Solids or Gases in Liquids

- Solids in liquids

- In saturated solution, a dynamic equilibrium exists between the solute molecules in the solid state and in the solution.

- Example:

  $\text{Sugar}_{(\text{solution})} \longleftrightarrow \text{Sugar}_{(\text{solid})}$

  At equilibrium,

  Rate of dissolution of sugar = Rate of crystallisation of sugar

- Confirmation of equilibrium with the help of radioactive sugar: If some radioactive sugar is dropped into a saturated solution of non-radioactive sugar, then after sometime, radioactivity is observed both in the solid sugar and in the solution. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

- Gases in Liquids

- Equilibrium exists between the molecules in the gaseous state and the molecules dissolved in the liquid.

- Example: The following equilibrium exists when carbon dioxide is dissolved in soda water.

  $CO_{2(\text{gas})} \longleftrightarrow CO_{2(\text{in solution})}$

- This equilibrium is governed by Henry's Law.

- According to Henry's law, the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

- When soda water bottle is opened, the carbon dioxide dissolved in it escapes out rapidly with fizz. Carbon dioxide escapes to reach a new equilibrium condition required for the lower pressure (partial pressure in the atmosphere).

Generalisation of Physical Equilibria

- For solid $\longleftrightarrow$ liquid equilibrium, the two phases can coexist only at one temperature (melting point or freezing point) at 1 atm (1.013 bar) pressure.

- For liquid $\longleftrightarrow$ vapour equilibrium, the vapour pressure is constant at a given temperature.

- For dissolution of solids in liquids, the solubility is constant at a given temperature.

- For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid.

General Characteristics of Equilibria Involving Physical Processes

- Equilibrium can be established only in a closed system at a given temperature.

- Both opposing processes occur at the same rate and there is a dynamic equilibrium.

- All the measurable properties of the system are constant at equilibrium.

- When equilibrium is attained, it is characterized by constant value of one of its parameters at a given temperature.

- The magnitude of such parameters at any stage gives indication of the extent to which the physical process has proceeded before attaining the equilibrium.

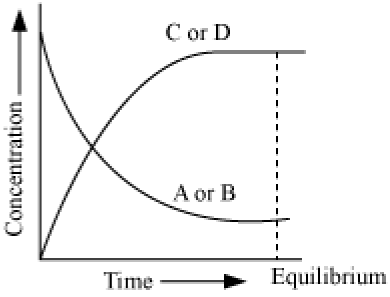
Equilibrium in Chemical Processes: Dynamic Equilibrium

- Consists of forward and reverse reactions

- The state of chemical reaction in which the rate of the forward reaction becomes equal to that of the reverse reaction, and there is no net change in composition

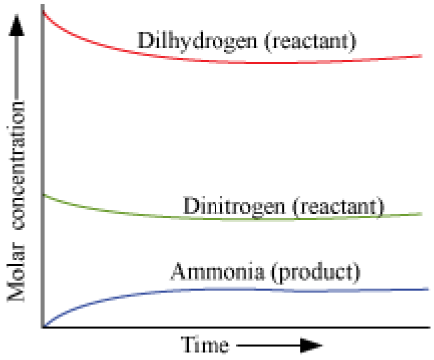
- Plot of concentration vs. time for a reversible reaction:

$$A + B \longleftrightarrow C + D$$

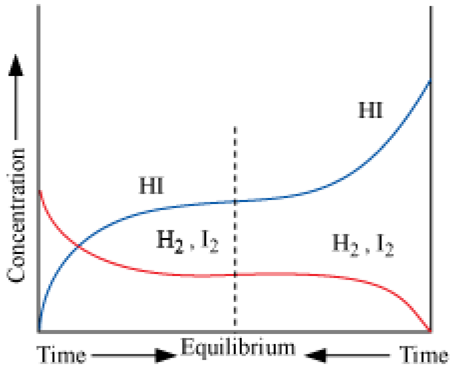


- Depiction of equilibrium for the reaction,

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



- Depiction of equilibrium in the reaction, $H_{2(g)} + I_{2(g)} \longleftrightarrow 2HI_{(g)}$ from either direction:



Law of Chemical Equilibrium and Equilibrium Constant

Law of chemical equilibrium or equilibrium law

At a given temperature, the product of the concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation, divided by the product of the concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the law of chemical equilibrium or equilibrium law.

- For a general reaction,

$aA + bB \longleftrightarrow cC + dD$

Equilibrium equation is,

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

Where, K_C = Equilibrium constant

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

- Example:

  $$H_{2(g)} + I_{2(g)} \longleftrightarrow 2HI_{(g)}$$

  $$K_C = \frac{\left[HI_{(g)}\right]_{eq}^2}{\left[H_{2(g)}\right]_{eq}\left[I_{2(g)}\right]_{eq}}$$

- The subscript '*C*' indicates concentrations in terms of mol L^{-1}

- $K'_C = \frac{1}{K_C}$

  Where, K_C = Equilibrium constant for the forward reaction

  K'_C = Equilibrium constant for the reverse reaction

- If K_C is the equilibrium constant for the reaction,

  $aA + bB \longleftrightarrow cC + dD$

  Then, the equilibrium constant for the reaction,

  $naA + nbB \longleftrightarrow ncC + ndD$ is equal to K_C^n

Types of Chemical Equilibria

Two types of chemical equilibria – Homogeneous equilibria

Heterogeneous equilibria

Homogeneous Equilibria

- All the reactants and products are in the same phase.
- Example:
- In gaseous phase,

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

- In solution phase,

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \longleftrightarrow Fe(SCN)^{2+}{}_{(aq)}$$
$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \longleftrightarrow CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

- Equilibrium constant for homogeneous reaction in gaseous systems:

Ideal gas equation is given by,

$pV = n\mathrm{R}T$

$$\Rightarrow p = \frac{n}{V}\mathrm{R}T$$

If concentration C is in mol L^{-1} or mol dm^{-3} and p is in bar, then we can write

$p = c\,\mathrm{R}T$

Or, $p = [\text{gas}]\,\mathrm{R}T$ …..(i)

Where, $\mathrm{R} = 0.0831$ bar L mol^{-1} K^{-1}

For a general reaction,

$$aA + bB \longleftrightarrow cC + dD$$

$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)}$$

$$= \frac{([C]RT)^c([D]RT)^d}{([A]RT)^a([B]RT)^b} \qquad \left[\text{From equation (i)}\right]$$

$$= \frac{[C]^c[D]^d(RT)^{(c+d)}}{[A]^a[B]^b(RT)^{a+b}}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n}$$

$$= K_c(RT)^{\Delta n} \qquad \left[\text{Since, } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}\right]$$

Where, Δn = (number of moles of gaseous products)

− (number of moles of gaseous reactants) in the balanced chemical equation

- While calculating K_p, pressure should be expressed in bar.
- 1 bar = 10^5 Pa = 10^5 Nm^{-2}

Heterogeneous Equilibria

- Have more than one phase
- Example:

$$H_2O_{(l)} \longleftrightarrow H_2O_{(g)}$$

$$Ca(OH)_{2(s)} + (aq) \longleftrightarrow Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$$

- Equilibrium constant
- $CaCO_{3(s)} \xleftrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$

$$K_C = \frac{\left[\mathrm{CaO}_{(s)}\right]\left[\mathrm{CO}_{2(g)}\right]}{\left[\mathrm{CaCO}_{3(s)}\right]}$$

As CaO and $CaCO_3$ are pure solids, [CaO] and [$CaCO_3$] are constants.

Now, $K'_C = \left[\mathrm{CO}_{2(g)}\right]$

Or $K_p = p_{\mathrm{CO}_2}$

- $\mathrm{Ni}_{(s)} + 4\mathrm{CO}_{(g)} \longleftrightarrow \mathrm{Ni(CO)}_{4(g)}$

$$K_C = \frac{\left[\mathrm{Ni(CO)}_{4(g)}\right]}{\left[\mathrm{CO}_{(g)}\right]^4} \qquad \left(\text{Because } \left[\mathrm{Ni}_{(s)} = \text{Constant}\right]\right)$$

- $\mathrm{Ag_2O}_{(s)} + 2\mathrm{HNO}_{3(aq)} \longleftrightarrow 2\mathrm{AgNO}_{3(aq)} + \mathrm{H_2O}_{(l)}$

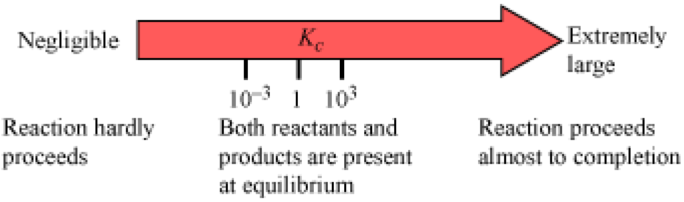
$$K_C = \frac{\left[\mathrm{AgNO}_{3(aq)}\right]^2}{\left[\mathrm{HNO}_{3(aq)}\right]^2} \quad \left(\begin{array}{l}\text{Because } \left[\mathrm{Ag_2O}_{(s)}\right] = \text{Constant} \\ \text{and } \left[\mathrm{H_2O}_{(l)}\right] = \text{Constant}\end{array}\right)$$

Applications of Equilibrium Constant

- Important features of equilibrium constant:
- Applicable only in equilibrium state
- Independent of initial concentration of reactants and products
- Depends on temperature; has a unique value for a particular reaction at a given temperature
- Equilibrium constant for the forward direction $= \frac{1}{\text{Equilibrium constant for the reverse direction}}$
- The equilibrium constant for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Applications of Equilibrium Constant

- Predicting the extent of a reaction:
- If $K_C > 10^3$, then the products predominate over the reactants.
- If $K_C < 10^{-3}$, then the reactants predominate over the products.
- If $10^{-3} < K_C < 10^3$, then appreciable concentrations of both reactants and products are present.



- Predicting the direction of a reaction:

Reaction quotient, Q (Q_C with molar concentration and Q_p with partial pressure)

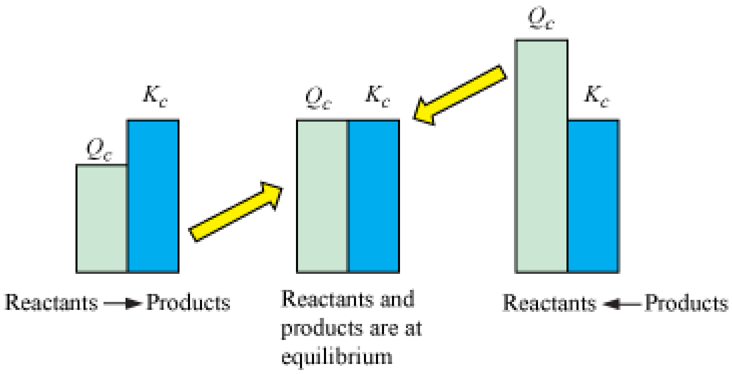
For a general reaction,

$$aA + bB \longleftrightarrow cC + dD$$

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

The concentrations are not necessarily equilibrium values.

- If $Q_C > K_C$, then the reaction will proceed in the reverse direction.
- If $Q_C < K_C$, then the reaction will proceed in the forward direction.
- If $Q_C = K_C$, then the reaction is at equilibrium.



- Calculating equilibrium concentrations:

Example

Chlorides of phosphorus, PCl_5 and PCl_3, and Cl_2 exist in an equilibrium mixture. A 1.00 L vessel contains an unknown amount of PCl_5 at equilibrium. It contains 0.020 moles each of PCl_3 and Cl_2 at equilibrium. What is the number of moles of PCl_5 in the vessel?

(For the equilibrium reaction, K_C is 0.0415 at 250°C)

Solution:

The given equilibrium reaction can be written as

$$PCl_{5(g)} \longleftrightarrow PCl_{3(g)} + Cl_{2(g)}$$

In 1.00 L, there are 0.020 mol each of PCl_3 and Cl_2

Molarity of PCl_3 = 0.020 M

Molarity of Cl_2 = 0.020 M

Equilibrium constant for the given equation is,

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$\Rightarrow [PCl_5] = \frac{[PCl_3][Cl_2]}{K_C}$$

$$= \frac{(0.020)(0.020)}{(0.0415)}$$

$$= 0.0096 \text{ mol}$$

Hence, 0.0096 mol of PCl_5 is present in the vessel.

Relationship between Equilibrium Constant (*K*), Reaction Quotient (*Q*) and Gibbs Energy (*G*)

- If $\Delta G = -$ ve, then the reaction is spontaneous and proceeds in the forward direction.
- If $\Delta G = +$ ve, then the reaction is non-spontaneous and proceeds in the backward direction.
- If $\Delta G = 0$, then the reaction is at equilibrium.

Relationship between *K*, *Q* and *G*

$\Delta G = \Delta G^{\ominus} + RT \ln Q$, where $\Delta G^{\ominus}$ = Standard Gibbs energy

At equilibrium, $\Delta G = 0$, $Q = K_C$

Now,

$$\Delta G = \Delta G^{\ominus} + RT \ln Q$$

$$\Rightarrow 0 = \Delta G^{\ominus} + RT \ln K$$

$$\Rightarrow \Delta G^{\ominus} = -RT \ln K$$

$$\Rightarrow \ln K = -\frac{\Delta G^{\ominus}}{RT}$$

$\Rightarrow K = e^{-\frac{\Delta G^{\ominus}}{RT}}$ (Taking antilog of both sides)

Interpretation of Spontaneity, Using the Equation $K = \mathrm{e}^{-\frac{\Delta G^\ominus}{\mathrm{R}T}}$ in Terms Of $\Delta G^\ominus$

- If $\Delta G^\ominus < 0$

$$\Rightarrow -\frac{\Delta G^\ominus}{\mathrm{R}T} > 0$$
$$\Rightarrow \mathrm{e}^{-\frac{\Delta G^\ominus}{\mathrm{R}T}} > 1$$
$$\Rightarrow K > 1$$

Hence, the reaction is spontaneous.

- If $\Delta G^\ominus > 0$

$$\Rightarrow -\frac{\Delta G^\ominus}{\mathrm{R}T} < 0$$
$$\Rightarrow \mathrm{e}^{-\frac{\Delta G^\ominus}{\mathrm{R}T}} < 1$$
$$\Rightarrow K < 1$$

Hence, the reaction is non-spontaneous.

Factors Affecting Equilibria

- **Le Chatelier's principle**

- Statement –

According to this principle, if a system is in equilibrium and it is subjected to any change in any of the factors that determine the equilibrium conditions of the system, then it will shift the equilibrium in such a way so as to reduce or to counteract the effect of the change.

Effect of Concentration Change

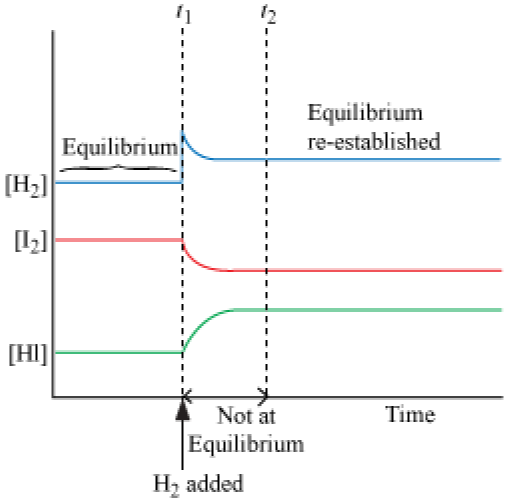
- The concentration stress of an **added reactant/ product** is relieved by the net reaction in the direction that **consumes the added substance**.

- The concentration stress of a **removed reactant/product** is relieved by the net reaction in the direction that **replenishes the removed substance.**

- Example:

$$H_{2(g)} + I_{2(g)} \longleftrightarrow 2HI_{(g)}$$

- Effect of addition of H_2: Equilibrium shifts in the forward direction



In terms of reaction quotient Q_C,

$$Q_C = \frac{[HI]^2}{[H_2][I_2]}$$

When H_2 is added at equilibrium, Q_C becomes less than K_C. Therefore, equilibrium shifts in the forward direction until $Q_C = K_C$

Effect of Pressure Change

- In case of solids and liquids, the effect of pressure change is neglected.
- Reason: The volume of solid or liquid is independent of pressure.
- If pressure is increased, then the equilibrium shifts in the direction in which the number of moles of gas or pressure decreases.
- Example:

$$C_{(s)} + CO_{2(g)} \longleftrightarrow 2CO_{(g)}$$

When pressure in increased, the reaction goes in the reverse direction.

Effect of Addition of Inert Gas

- If an inert gas is added at constant volume, then the equilibrium remains undisturbed.
- Reason: Partial pressures or molar concentrations of the substance do not change with addition of inert gas at constant volume.

Effect of Change in Temperature

- When concentration, pressure, or volume is changed, equilibrium is disturbed.
- Reason – Q_C changes and no longer equals to K_C
- When temperature is changed, equilibrium is disturbed.
- Reason – K_C changes
- Change in equilibrium constant with temperature depends upon the sign of ΔH for the reaction.
- For exothermic reaction (negative ΔH), the equilibrium constant decreases with the increase in temperature.
- For endothermic reaction (positive ΔH), the equilibrium constant increases with the increase in temperature.
- Example:

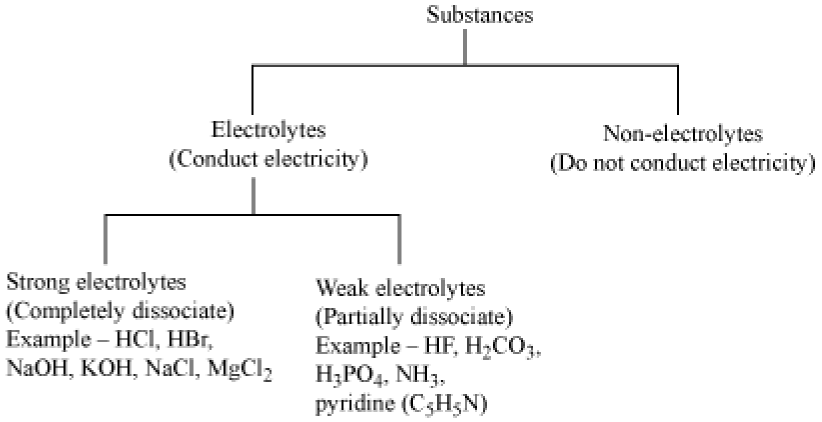
$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)}; \Delta H = -92.38\,\text{kJ mol}^{-1}$$

With increase in temperature, the equilibrium shifts in the backward direction.

Effect of a Catalyst

- Catalyst increases the rate of reaction by lowering the activation energy for the forward and reverse reactions by exactly the same amount.
- Catalyst does not affect the equilibrium.

Ionic Equilibrium in Solution



- Ionic equilibrium: Equilibrium that involves ions in aqueous solution

Acids, Bases and Salts

- Arrhenius concept of acids and bases:

- **Acids –** substances that dissociate in water to give hydrogen ions $H^+_{(aq)}$ or H_3O^+

$$HX_{(aq)} \longrightarrow H^+_{(aq)} + X^-_{(aq)}$$

Or

$$HX_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + X^-_{(aq)}$$

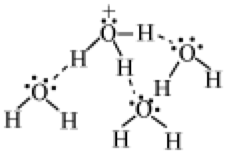
- H^+ exists as hydronium ion H_3O^+ {$[H(H_2O)]^+$}

  Reason – H^+ is very reactive and cannot exist freely, so it binds to the oxygen atom in H_2O.

Hydronium ion

Found in many compounds (Example – $H_3O^+Cl^-$) in solid state

Further hydrated in aqueous solution to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$



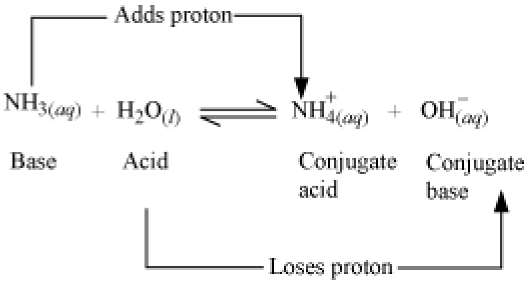
- **Bases –** substances that produce hydroxyl ions $OH^-_{(aq)}$

$$MOH_{(aq)} \longrightarrow M^+_{(aq)} + OH^-_{(aq)}$$

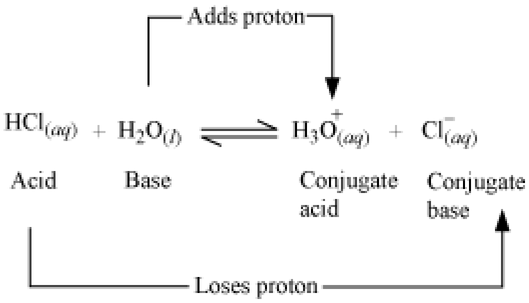
Hydroxyl ion:

Exists in hydrated forms in aqueous solution such as $H_3O_2^-, H_5O_3^-, H_7O_4^-$, etc.

- The Bronsted-Lowry acids and bases:
- Acids – substances that can donate a hydrogen ion H^+
- Bases – substances that can accept a hydrogen ion H^+
- Representation of dissolution of NH_3 in H_2O is shown in the figure.



- Representation of dissolution of HCl in H_2O is shown in the figure.



- Conjugate acid-base pair: Acid-base pair that differs only by one proton
- Some species that can act both as Bronsted acids and bases are listed in the following table with their respective conjugate acids and bases.

Species	**Conjugate acid**	**Conjugate base**
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

- Lewis acids and bases:
- Acids – species that accept an electron pair
- Bases – species that donate an electron pair
- Though BF_3 does not have a proton, it acts as an acid. This is because it accepts a lone pair of electrons.

$BF_3 + :NH_3 \longrightarrow BF_3:NH_3$

- Examples of Lewis acids – $AlCl_3$, BF_3, BCl_3 CO^{3+}, Mg^{2+}, H^+
- Examples of Lewis bases – H_2O, NH_3, OH^-, F^-

Ionisation of Acids and Bases

Arrhenius Concept

- Strong acids are those which completely dissociate in aqueous solutions to give H^+ ions which form H_3O^+ ions.
- Examples: Perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), sulphuric acid (H_2SO_4), nitric acid (HNO_3)
- Strong bases are those which completely dissociate in aqueous solutions to give OH^- ions.
- Examples: Lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), barium hydroxide ($Ba(OH)_2$)

Bronsted-Lowry Concept

- The conjugate base of a strong acid is a weak base.

$HCl_{(aq)} + H_2O_{(l)} \longleftrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

Strong acid   Weak base

- The conjugate base of a weak acid is a strong base.

$CH_3COOH_{(aq)} + H_2O_{(l)} \longleftrightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

Weak acid   Strong base

- The conjugate acid of a strong base is a weak acid.

$CH_3COOH_{(aq)} + OH^-_{(aq)} \longleftrightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$

Strong base   Weak acid

- The conjugate acid of a weak base is a strong acid.

$HCl_{(aq)} + H_2O_{(l)} \longleftrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

Weak base Strong acid

- Weaker the conjugate base, stronger is the acid. Similarly, weaker the conjugate acid, stronger is the base.

- Phenolphthalein and bromothymol blue

- Weak acids

- Exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.

$HIn_{(aq)} + H_2O_{(l)} \longleftrightarrow H_3O^+_{(aq)} + In^-_{(aq)}$

Acid	base	Conjugate acid	Conjugate base
colour (A)			colour (B)

- Used as indicators in acid-base titration

Strong and Weak Electrolyte

1. Strong electrolyte: Electrolytes which ionise in water completely are termed as strong electrolytes such as NaCl, $MgCl_2$ etc. Strong acids, strong bases, and soluble salts are strong electrolytes.

2. Weak electrolyte: Electrolytes which do not ionise completely in water are termed as weak electrolytes such as acetic acid. Weak acids, weak bases, and sparingly soluble salts are weak electrolytes.

Degree of Dissociation

When an electrolyte is dissolved in water or any solvent it may either completely dissociate or partially dissociate. Their solubility in a solvent such as water is expressed by the degree of dissociation.

It is defined as the extent to which an electrolyte dissociates into ions in a solvent. It is represented by the symbol α. It is calculated as follows

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Initial number of moles}}$$

The value of α is 1 for strong electrolytes as they are completely dissociated and less than 1 for weak electrolytes since they are not completely dissociated.

The value of α for an electrolyte depends on
(i) Nature of solvent: Solvent having a high dielectric constant will favour the dissociation.
(ii) Nature of electrolytes: Strong electrolytes dissociate completely while weak electrolyte dissociates partially.
(iii) Dilution: Increasing dilution will increase the degree of dissociation of weak electrolytes.
(iv) Temperature: Increase in temperature generally favours the dissociation.

Ionic Product of Water and Titration

Ionisation constant of water and its ionic product

- Water acts as acid as well as base.

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

  Acid Base Conjugate Conjugate

  base acid

  Dissociation constant, $K = \frac{[H_3O^+][OH^-]}{[H_2O]}$

  $[H_2O]$ is omitted as H_2O is a pure liquid and $[H_2O]$ is constant.

  Now, $K_w = [H^+]\,[OH^-]$

  Where, K_w = Ionic product of water

- At 298 K, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M

  So, $K_w = [H^+]\,[OH^-]$

  $= (1.0 \times 10^{-7}\ M)^2$

  $= 1.0 \times 10^{-14}\ M^2$

- The value of K_w depends upon temperature.

- Density of pure water = 1000 g L^{-1}

  Molar mass of water = 18 g mol^{-1}

  Therefore, molarity of pure water, $[H_2O] = \frac{\text{density}}{\text{molar mass}}$

  $= \frac{1000 \text{ g L}^{-1}}{18 \text{ g mol}^{-1}}$

  = 55.55 M

  Therefore, the ratio of dissociated water to un-dissociated water

  $= \frac{1\times10^{-7}}{55.55}$

  $= 1.8 \times 10^{-9}$

  $\approx 2 \times 10^{-9}$

  Thus, equilibrium lies mainly towards un-dissociated water.

- Comparison between $[H_3O^+]$ and $[OH^-]$

- For acidic solution, $[H_3O^+] > [OH^-]$

- For neutral solution, $[H_3O^+] = [OH^-]$

- For basic solution, $[H_3O^+] < [OH^-]$

Titration
The word titration comes from the Latin word "titulus", which means title. The French word title means rank. Therefore, titration means the determination of concentration of a solution with respect to water with a pH of 7. The process of adding standard solution until the reaction is just complete is termed as titration.

Theory of Indicators

- Indicators are usually weak organic bases or acids.
- They have different colours in their ionised and unionised forms.

- They are used to determine the end point in titrations, as they change colours within certain pH ranges.

$$\underset{\text{Colour A}}{\mathrm{HIn}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \underset{\text{Colour B}}{\mathrm{In^-}}$$

- The indicator constant is given as:

$$K_{in} = \frac{[H_3O^+][In^-]}{[HIn]}$$

It is dependent only on temperature.

- $$\left[H_3O^+\right] = K_{in}\frac{[HIn]}{[In^-]}$$

$$\Rightarrow pH = pK_{in} + \log\frac{[In^-]}{[HIn]}$$

pH=pKin+log[In-][HIn]

- The transition of colour at equivalence point takes place in the pH range (pK_{in} - 1)–(pK_{in} + 1).
- If the solution has pH≤pK_{in} - 1, then the solution has the characteristic colour of HIn.
- If the solution has pH≥pK_{in} +1, then the solution has the characteristic colour of In^-.

Equivalence Point:

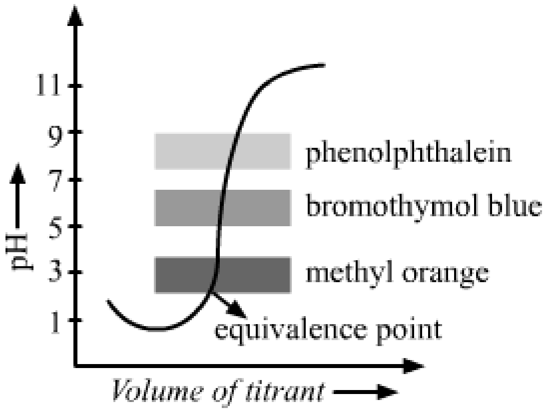
- The pH value of the solution undergoing titration changes drastically at the equivalence point.
- The pH range for this drastic change depends on the nature of the acid–base pair being titrated.
- At the equivalence point:

$$\left[In^-\right] = \left[HIn\right]$$
$$pH = pK_{in}$$

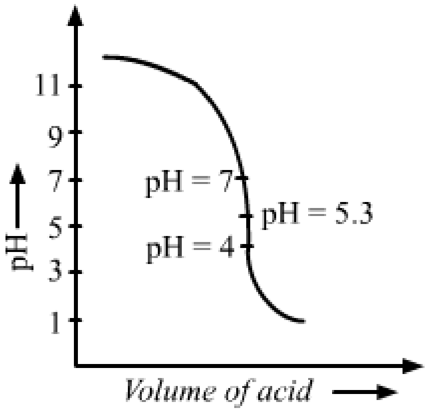
Titration Curves

- The choice of an indicator for a particular titration depends on its pH transition range, which must coincide with the steep portion of the titration curve.

Titration of Strong Acid (HCl) with Strong Base (NaOH):

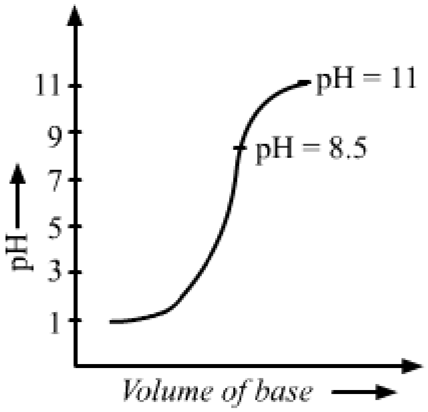


Titration of Weak Base (NH_4OH) with Strong Acid (HCl):



- Phenolphthalein cannot be used as an indicator in such titrations.
- Methyl orange or methyl red can be used as indicators.

Titration of Weak Acid (CH_3COOH) and Strong Base (NaOH):



- Here, phenolphthalein is a suitable indicator.

The pH Scale

- Logarithmic scale in which the concentration of hydronium ion (in molarity) is expressed.

- pH = $-\log a_{\mathrm{H^+}}$

  $= -\log \{[\mathrm{H^+}] / \mathrm{mol\ L^{-1}}\}$($a_{\mathrm{H^+}} = [\mathrm{H^+}]/\mathrm{mol\ L^{-1}}$ = activity of $\mathrm{H^+}$ ion)

- For pure water:
  pH = $-\log (10^{-7})$
  $= 7$

- Value of pH:

- For acidic solution − pH < 7

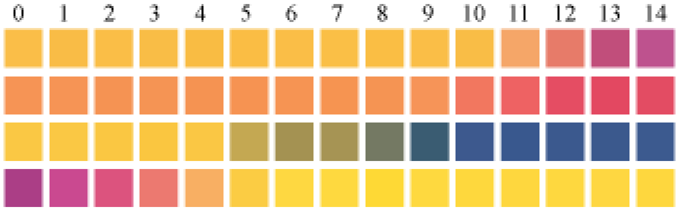
- For basic solution − pH > 7

- For neutral solution − pH = 7

- $K_w = [\mathrm{H_3O^+}]\ [\mathrm{OH^-}] = 10^{-14}$
  $\Rightarrow -\log K_w = -\log \{[\mathrm{H_3O^+}]\ [\mathrm{OH^-}]\} = -\log 10^{-14}$
  $\Rightarrow \mathrm{p}K_w = -\log [\mathrm{H_3O^+}] - \log [\mathrm{OH^-}] = 14$
  $\Rightarrow \mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH} = 14$

- Determination of pH:

- Can be roughly determined with a pH paper. The given figure is that of a pH paper with four strips that have different colours at the same pH.



- Can be accurately determined by a pH meter.

Examples

1. Calculate the pH of the solution having the hydrogen ion concentration 1.9×10^{-5} mol L^{-1}.

Solution:

Given, $[H^+] = 1.9 \times 10^{-5}$ mol L^{-1}

We know that $pH = -\log [H^+]$

$= -\log (1.9 \times 10^{-5})$

$= 4.72$

Hence, the pH of the solution is 4.72.

2. What is the concentration of OH^- ion in a solution having pH value of 8.6?

Solution:

Given, pH = 8.6

We know that,

$pH + pOH = 14$

$\Rightarrow pOH = 14 - pH$

$\Rightarrow pOH = 14 - 8.6$

$\Rightarrow pOH = 5.4$

$\Rightarrow -\log [OH^-] = 5.4$

$\Rightarrow \log [OH^-] = -5.4$

$\Rightarrow [OH^-] = 10^{-5.4}$

$= 3.98 \times 10^{-6}$ M

Hence, the concentration of OH^- ions in the solution is 3.98×10^{-6} M.

Ionization Constants of Weak Acids

- Ionization of weak acids HX:

$$HX_{(aq)} + H_2O_{(l)} \longleftrightarrow H_3O^+_{(aq)} + X^-_{(aq)}$$

Initial Conc. (M) c 0 0

Let α be the extent of ionization.

Change $-c\alpha$ $+c\alpha$ $+c\alpha$

Conc. at eq. $c - c\alpha$ $c\alpha$ $c\alpha$

Where, c = Initial concentration of the undissociated acid HX

- Equilibrium constant of above acid-base equilibrium,

$$K_a = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

- K_a is called the dissociation or ionization constant of acid HX.

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

- Significance of K_a

- Measure of strength of acid
- Stronger the acid, larger is the value of K_a.
- Dimensionless quantity

- $pK_a = -\log(K_a)$

Example

The acid dissociation constant of 0.1 M acetic acid is 1.74×10^{-5}. Calculate the degree of ionization and pH of the solution.

Solution:

The following proton transfer reactions are possible.

(i) $CH_3COOH + H_2O \longleftrightarrow CH_3COO^- + H_3O^+$; $K_a = 1.74 \times 10^{-5}$

(ii) $H_2O + H_2O \longleftrightarrow H_3O^+ + OH^-$; $K_a = 1.0 \times 10^{-14}$

As $K_a >> K_w$, reaction (i) is the principle reaction.

The concentration of various species in reaction (i) can be shown as:

	$CH_3COOH + H_2O \longleftrightarrow$	CH_3COO^- +	H_3O^+
Initial Conc. (M)	0.1	0	0
Change	-0.1α	$+0.1\alpha$	$+0.1\alpha$
At eq.	$(0.1 - 0.1\alpha)$	(0.1α)	(0.1α)

On substituting the equilibrium concentrations in the equilibrium reaction, we obtain

$$K_a = \frac{(0.1\alpha)^2}{(0.1-0.1\alpha)} = 1.74 \times 10^{-5}$$

$\Rightarrow 0.01\alpha^2 = 1.74 \times 10^{-6} - (1.74 \times 10^{-6})\alpha$

$\Rightarrow \alpha^2 + (1.74 \times 10^{-4})\,\alpha - 1.74 \times 10^{-4} = 0$

Solving for α as

$$\alpha = -\frac{(1.74\times10^{-4})\pm\sqrt{(1.74\times10^{-4})^2-4.1(-1.74\times10^{-4})}}{2.1}$$

$\Rightarrow \alpha = -1.31 \times 10^{-2}$ or $+ 1.31 \times 10^{-2}$

Since negative roots are not acceptable,

$\alpha = 1.31 \times 10^{-2}$

Therefore, degree of ionization = 1.31×10^{-2}

At equilibrium, $[H_3O^+] = (0.1)\alpha$

$= 0.1 \times 1.31 \times 10^{-2}$

$= 1.31 \times 10^{-3}$ M

Now, $pH = -\log [H_3O^+]$

$= -\log (1.31 \times 10^{-3})$

$= -(-2.88)$

$= 2.88$

Hence, the pH of the given solution is 2.88.

Ionization Constants of Weak Bases

- Ionization of weak base MOH:

  $MOH_{(aq)} \longleftrightarrow M^+_{(aq)} + OH^-_{(aq)}$

- Equilibrium constant is given by,

$K_b = \frac{[M^+][OH^-]}{[MOH]}$

- K_b is called base ionization constant.
- If c = Initial concentration of base

  α= Degree of ionization of base

  Then, $K_b = \frac{c^2\alpha^2}{c(1-\alpha)}$

  $= \frac{c\alpha^2}{1-\alpha}$

- $pK_b = -\log(K_b)$

Example

A solution is formed by mixing 0.1 M NH_4Cl and 0.2 M NH_3. What is the pH of the resulting solution? (Given: pK_b of NH_3 is 4.75)

Solution:

NH_4Cl being a strong electrolyte undergoes complete ionization in solution. Therefore, concentration of NH_4^+ ions from NH_4Cl is 0.3 M.

$NH_4Cl \longleftrightarrow NH_4^+ + Cl^-$

NH_3 being a weak base ionizes partially.

$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$

Let *x* be the number of moles of ammonia ionized.

Total [NH_4^+] = 0.3 + *x* ≈ 0.3 (Since *x* is small)

Total concentration of NH_3 left unionized = 0.2 − *x* ≈ 0.2 (since *x* is small)

At equilibrium, $NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$

Eq conc. 0.2 0.3 *x*

Now, $pK_b = -\log K_b = 4.75$

$\Rightarrow \log K_b = -4.75$

$\Rightarrow K_b = \text{antilog}\ (-4.75)$

$= 1.78 \times 10^{-5}$

Now, $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

$\Rightarrow 1.78 \times 10^{-5} = \frac{(0.3)x}{0.2}$

$\Rightarrow x = 1.19 \times 10^{-5}$

That is, $[OH^-] = 1.19 \times 10^{-5}$

We know that,

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

$\Rightarrow [H_3O^+] = \frac{K_w}{[OH^-]}$

$$= \frac{1\times10^{-14}}{1.19\times10^{-5}}$$

$= 8.4 \times 10^{-10}$

Therefore, pH $= -\log [H_3O^+]$

$= -\log (8.4 \times 10^{-10})$

$= 9.08$

Hence, pH of the solution is 9.08.

Relation between K_a and K_b

For weak acid HA,

$$HA_{(aq)} + H_2O \longleftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_a(HA) = \frac{[H_3O^+][A^-]}{[HA]}$$

The conjugate base A^- behaves as a weak base in water.

$$A^- + H_2O \longleftrightarrow HA + OH^-$$

$$K_b(A^-) = \frac{[HA][OH^-]}{[A^-]}$$

$$\text{Now, } K_a(HA) \times K_b(A^-) = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

$= [H_3O^+]\,[OH^-]$

$= K_w$

That is, K_a(acid) × K_b(conjugate base) = K_w

In general, at 298 K,

$K_a \times K_b = K_w = 10^{-14} \text{mol}^2\text{L}^{-2}$

$pK_a + pK_b = pK_w = 14$

Example

K_a of HF is 0.00068. Calculate the dissociation constant of the conjugate base of HF.

Solution

HF undergoes dissociation as

$HF \longleftrightarrow H^+ + F^-$

Acid Conjugate base

Now, K_a (acid) × K_b (conjugate base) = K_w

Therefore, $K_a(HA) \times K_b(F^-) = K_w$

$\Rightarrow 0.00068 \times K_b(F^-) = 10^{-14}$

$\Rightarrow K_b(F^-) = \frac{10^{-14}}{0.00068}$

$= 1.47 \times 10^{-11}$

Hence, the dissociation constant of the conjugate base of HF is 1.47×10^{-11}.

Di- and Polybasic Acids, and Di- and Polyacidic Bases, Factors Affecting Acid Strength, Common Ion Effect

- **Polybasic or polyprotic acids**

- Donate more than one proton per molecule
- Examples: Oxalic acid ($H_2C_2O_4$), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4)
- Ionisation reaction for a dibasic acid, H_2X

$$H_2X_{(aq)} \longleftrightarrow H^+_{(aq)} + HX^-_{(aq)}; K_{a_1} = \frac{[H^+][HX^-]}{[H_2X]}$$

$$HX^-_{(aq)} \longleftrightarrow H^+_{(aq)} + X^{2-}_{(aq)}; K_{a_2} = \frac{[H^+][X^{2-}]}{[HX^-]}$$

K_{a_1} = First ionisation constant of H_2X

K_{a_2} = Second ionisation constant of H_2X

- Higher order ionisation constants $\left(K_{a_2}, K_{a_3}\right)$ are smaller than the lower order ionisation constant (K_{a_1})

  Reason: Difficult to remove a positively charged proton from a negatively charged ion due to increased electrostatic force

- **Polyacidic base**
- Accept more than one proton
- Examples: carbonate $\left(CO_3^{2-}\right)$ ion, oxalate $\left(C_2O_4^{2-}\right)$ ion.
- K_{b_1}, K_{b_2}, K_{b_3} are first, second and third constants respectively for a tri-acidic base

Factors Affecting Acid Strength

- For an acid, HA
- Stronger the H − A bond, weaker is the acid
- More the electronegativity difference between H and A, stronger is the acid

Reason: Easier to break the H − A bond due to charge separation

- Acidic strength of HA increases down the group

$$\xrightarrow[\text{Size increases}]{\text{HF} \ll \text{HCl} \ll \text{HBr} \ll \text{HI}}$$

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

- Reason: Down the group, the size of A increases, so, the strength of the H − A bond decreases

- Acid strength of HA increases from left to right across a period

$$\xrightarrow[\text{Electronegativity of A increases}]{CH_4 < NH_3 < H_2O < HF}$$

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

- Reason: Across a period, electronegativity increases

Common Ion Effect in the Ionisation of Acids and Bases

- Shift in the equilibrium by the addition of a substance which dissociates to give more of an ionic species already present in the dissociation equilibrium

- Based on Le Chatelier's principle

- Ionisation suppresses, i.e., the equilibrium shifts towards the un-dissociated substance when any one of the product is added to the solution

- Dissociation of acetic acid:

$$CH_3COOH_{(aq)} \longleftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$$

If any one of H^+ ions or CH_3COO^- is added from an external source, then the equilibrium will shift in the direction of the un-dissociated acetic acid (i.e., in the backward direction).

- Let us illustrate this effect by considering the effect on the pH of the solution by adding 0.05 M acetate ion to 0.05 M acetic acid solution.

- Dissociation equilibrium of acetic acid:

$$\begin{array}{lccccc} & \mathrm{CH_3COOH_{(aq)}} & \longleftrightarrow & \mathrm{H^+_{(aq)}} & + & \mathrm{CH_3COO^-_{(aq)}} \\ \text{Initial concentration (M)} & 0.05 & & 0 & & 0.05 \end{array}$$

Let x be the extent of the dissociation of acetic acid.

Then, concentration at equilibrium:

$[CH_3COOH] = 0.05 - x$

$[H^+] = x$

$[CH_3COO^-] = 0.05 + x$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$
$$= \frac{(0.05 + x)x}{(0.05 - x)}$$

Since K_a is very small for a weak acid, $x << 0.05$

Therefore, $0.05 + x \approx 0.05 \approx 0.05 - x$

Thus, $K_a = \frac{0.05x}{0.05} = x$

But for acetic acid, $K_a = 1.8 \times 10^{-5}$

Therefore, $x = 1.8 \times 10^{-5}$

$\Rightarrow [H^+] = 1.8 \times 10^{-5}$

Hence, $pH = -\log [H^+]$

$= -\log (1.8 \times 10^{-5})$

$= 4.74$

Hydrolysis of Salts and pH of Their Solutions

- Hydrolysis: Interaction of the anion or the cation (or both) of a salt with water to produce an acidic or a basic solution.

- Salts of strong acids and strong bases are neutral (pH = 7)

- Reason: The cations of strong bases and the anions of strong bases do not undergo hydrolysis; they only get hydrated.

Hydrolysis of salts of strong acids and strong base
For example, NaCl

- Completely dissociates into ions

$NaCl_{(aq)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

Sodium chloride undergoes hydrolysis in water

$Na^{+}_{(aq)} + Cl^{-}_{(aq)} + H_2O \rightleftharpoons HCl_{(aq)} + NaOH_{(aq)}$
$Na^{+}_{(aq)} + Cl^{-}_{(aq)} + H_2O \rightleftharpoons H^{+}_{(aq)} + Cl^{-}_{(aq)} + Na^{+}_{(aq)} + OH^{-}_{(aq)}$

- pH is 7 (neutral)

Reason:

- Identical ions presence in both side reactant and product (Na^+ and Cl^-).
- In salt neither cation nor anion reacts with water.
- No hydrolysis occurs because of ($[H^+] = [OH^-]$)
- Neutral solution and no effect on litmus.

Hydrolysis of the salts of a weak acid and a strong base:

For example, CH_3COONa

- Completely ionised

$CH_3COONa_{(aq)} \longrightarrow CH_3COO^{-}_{(aq)} + Na^{+}_{(aq)}$

Acetate ion undergoes hydrolysis in water

$CH_3COO^{-}_{(aq)} + H_2O_{(l)} \longleftrightarrow CH_3COOH_{(aq)} + OH^{-}_{(aq)}$

- pH is more than 7

Reason:

Acetic acid is a weak acid
↓
Remains mainly un-ionised in solution
↓
Increase in concentration of OH^- ion in solution
↓
Solution becomes alkaline (pH > 7)

Hydrolysis of the salts of a strong acid and a weak base:

For example, NH_4Cl

- Completely ionised

$$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

- Ammonium ion undergoes hydrolysis in water

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \longleftrightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}$$

- pH is less than 7
- Reason:

Ammonium hydroxide is a weak base
↓
Remains mainly un-ionised in solution
↓

Increase in concentration of H^+ ion in solution
↓
Solution becomes acidic ($pH < 7$)

Hydrolysis of the salts of a weak acid and a weak base

For example, CH_3COONH_4

- Is not completely ionised
- The ions undergo hydrolysis in water

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

- CH_3COOH and NH_4OH remain partially ionised in solution

$$CH_3COOH \longleftrightarrow CH_3COO^- + H^+$$
$$NH_4OH \longleftrightarrow NH_4^+ + OH^-$$
$$H_2O \longleftrightarrow H^+ + OH^-$$

- $pH = 7 + \frac{1}{2}(pK_a - pK_b)$

$$pH > 7 \text{ when } pK_a - pK_b = \text{positive}$$
$$pH < 7 \text{ when } pK_a - pK_b = \text{negative}$$

Buffer Solution

- Solution which resists change in hydrogen ion concentration (and, thereby pH) on dilution, or with the addition of a small amount of an acid or a base
- Two types:
- **Acidic buffer –** equimolar mixture of a weak acid and its salt with a strong base. E.g., mixture of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa); pH = 4.75

- Mechanism of acidic buffer : In this buffer solution CH_3COOH reserve for acidity while CH_3COO^- reserve for basicity.

  Dissociation of acid and salt
  $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$ (Partial dissociation)
  $CH_3COONa_{(aq)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ (Complete dissociation)

- If small quantity of acid is added in such buffer solution then acid (H^+) reacts with basic component CH_3COO^-which is present in excess and forms CH_3COOH. It gives nonionized CH_3COOH molecule and decrease in pH is not appreciable.
- If small quantity of base (OH^-) is added to the buffer solution then it reacts with CH_3COOH and give CH_3COO^- and water. In this case also no appreciable changes in pH.
- **Basic buffer –** equimolar mixture of a weak base and its salt with a strong acid. E.g., mixture of ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl); pH = 9.25
- Mechanism of basic buffer : In this buffer solution NH_4^+reserve for acidity while NH_4OH reserve for basicity.

  Dissociation of base and salt
  $NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$ (Partial hydrolysis)
  $NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$ (Complete hydrolysis)

- If small amount of acid (H^+) is added then its consumed by NH_4OH and there is no appreciable change in pH.
- If small amount of base (OH^-) is added then its consumed by NH_4^+ and there is no appreciable change in pH.

Properties of buffer solutions:

- It resists to change the pH of solution even small amount of addition of either acids or bases .
- pH of buffer solution does not depend on the volume of solution.
- pH of the solution does not change even kept for long time.

Henderson Equation

Buffers are required to maintain the pH level of the solution. So they must be chosen wisely according to the pH range. The pH range of buffer solution is determined by the Henderson's equation.
Dissociation of an acid is given as

$$HA \rightleftharpoons H^+ + A^-$$

Equilibrium constant for the above reaction is represented as

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\left[H^+\right] = K_a \cdot \frac{[HA]}{[A^-]}$$

Taking negative logarithm on both sides

$$-\log\left[H^+\right] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

The above equation represents the Henderson equation for acids.

Application of buffer solution :

- It is used in qualitative analysis for the precipitation of group IIIA radicals.
- For preservation of jams and jellies sodium benzoate is used.
- It is used for the preparations of penicillin by addition of sodium citrate.
- Magnesium citrate is formed when citric acid is added in the milk. Its buffer action stabilise the milk of magnesia

Solubility Equilibria of Sparingly Soluble Salts

- Factors on which solubility depends:

- Lattice enthalpy of the salt
- Solvation enthalpy of the ions in a solution
- For a salt to be dissolved, lattice enthalpy should be less than solvation enthalpy.

Category I	Soluble salt	Solubility > 0.1 M
Category II	Slightly soluble salt	0.01 M < Solubility < 0.1 M
Category III	Sparingly soluble salt	Solubility < 0.01 M

- Solubility product constant:

- Equilibrium between the un-dissolved solid and the ions in a saturated solution

$$BaSO_{4(s)} \xrightleftharpoons[\text{in water}]{\text{Saturated solution}} Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Equilibrium constant, $K = \dfrac{\left[Ba^{2+}\right]\left[SO_4^{2-}\right]}{\left[BaSO_4\right]}$

$BaSO_4$ is a pure solid, so $\left[BaSO_4\right]$ = Constant

We can write,

$$K_{sp} = K\left[BaSO_4\right]$$
$$\Rightarrow K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right]$$

Where, K_{sp} = Solubility product constant or Solubility product

It is found experimentally that at 298 K,

$K_{sp} = 1.1 \times 10^{-10}$

If molar solubility of $BaSO_4$ is S, then

$$(S)(S) = 1.1\times10^{-10}$$
$$\Rightarrow S^2 = 1.1\times10^{-10}$$
$$\Rightarrow S = 1.05\times10^{-5}$$

- General formula:

  $$M_xX_{y(s)} \longleftrightarrow xM^{p+}{}_{(aq)} + yX^{q-}{}_{(aq)}$$

  Where, $xp^{+} = yq^{-}$

  Solubility product:

$$K_{sp} = \left[M^{p+}\right]\left[X^{q-}\right]$$
$$\Rightarrow K_{sp} = (xS)^x (yS)^y$$
$$\Rightarrow S^{x+y} = \frac{K_{sp}}{x^x y^y}$$
$$\Rightarrow S = \left(\frac{K_{sp}}{x^x y^y}\right)^{\frac{1}{x+y}}$$

Example:

If the solubility product of nickel hydroxide is 1.6 × 10^{-14}, then what is its solubility?

Solution:

At equilibrium, $Ni(OH)_2$ exists as

$$Ni(OH)_{2(s)} \longleftrightarrow Ni^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Let, the solubility of $Ni(OH)_2$ beS mol L^{-1}

So, $[Ni^{2+}] = S$

And $[OH^-] = 2S$

$$K_{sp} = \left[Ni^{2+}\right]\left[OH^-\right]^2$$
$$K_{sp} = [S][2S]^2$$
$$\Rightarrow K_{sp} = 4S^3$$
$$\Rightarrow 1.6\times10^{-14} = 4S^3$$
$$\Rightarrow 4S^3 = 1.6\times10^{-14}$$
$$\Rightarrow S^3 = 4\times10^{-15}$$
$$\Rightarrow S = 1.58\times10^{-5} \text{ mol L}^{-1}$$

Hence, the solubility of nickel hydroxide is 1.58 × 10^{-5} mol L^{-1}.

- Common ion effect on the solubility of ionic salts:

- According to Le Chatelier’s principle, if the concentration of any one of the ions is increased, then it would combine with the ion of its opposite charge, and some of the salt will be precipitated, till once again $K_{\text{sp}} = Q_{\text{sp}}$.
- Similarly, if the concentration of one of the ions is decreased, then more salt will need to be dissolved to increase the concentration of both the ions, till once again $K_{\text{sp}} = Q_{\text{sp}}$.
- Effect of pH on solubility:
- The solubility of the salts of weak acids increases with a decrease in pH.
- Reason: With the decrease in pH, the concentration of the anion decreases due to its protonation. This increases the solubility of the salt, till $K_{\text{sp}} = Q_{\text{sp}}$.

If considered quantitatively, two equilibria have to be satisfied simultaneously.

$$K_{\text{sp}} = \left[\text{M}^{+}\right]\left[\text{X}^{-}\right]$$

$$\text{HX}_{(aq)} \longleftrightarrow \text{H}^{+}{}_{(aq)} + \text{X}^{-}_{(aq)}$$

$$K_a = \frac{\left[\text{H}^{+}{}_{(aq)}\right]\left[\text{H}^{-}_{(aq)}\right]}{\left[\text{XH}_{(aq)}\right]}$$

$$\Rightarrow \frac{\left[\text{X}^{-}_{(aq)}\right]}{[\text{HX}]} = \frac{K_a}{\left[\text{H}^{+}_{(aq)}\right]}$$

On taking the reciprocal of both sides and then adding 1, we get

$$\frac{\left[\text{HX}_{(aq)}\right]}{\left[\text{X}^{-}_{(aq)}\right]} + 1 = \frac{\left[\text{H}^{+}_{(aq)}\right]}{K_a} + 1$$

$$\Rightarrow \frac{\left[\text{HX}_{aq}\right] + \left[\text{X}^{-}_{(aq)}\right]}{\left[\text{X}^{-}_{(aq)}\right]} = \frac{\left[\text{H}^{+}_{(aq)}\right] + K_a}{K_a}$$

On taking the reciprocal again, we get

$$\frac{\left[\text{X}^{-}_{(aq)}\right]}{\left[\text{HX}_{(aq)}\right]\left[\text{X}^{-}_{(aq)}\right]} = \frac{K_a}{K_a + \left[\text{H}^{+}_{(aq)}\right]} = f$$

It can be observed that *f* decreases with increase in [H^{+}] that is, with the decrease in pH.

Let S be the solubility of the salt at the given pH

Now,

$$K_{sp} = [S][fS]$$

$$\Rightarrow K_{sp} = S^2 \frac{K_a}{\left(K_a + \left[H^+\right]\right)}$$

$$\Rightarrow S = \left(\frac{K_{sp}\left(K_a + \left[H^+\right]\right)}{K_a}\right)^{\frac{1}{2}}$$

Now, it can be concluded that S increases with an increase in $\left[H^+\right]$, i.e., with a decrease in pH.