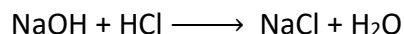# 6. EQUILIBRIUM

Reversible and irreversible reactions
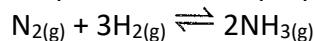
A reaction that takes place in only one direction is called an ***irreversible reaction***.

e.g. Reaction between NaOH and HCl

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Reversible reactions are those which take place in both directions. i.e. here reactants combined to form products and the products recombine to form reactants.

E.g. Haber process for the preparation of ammonia.

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

The process by which reactants are converted to products is called *forward reaction* and the process by which products recombine to form reactants is called *backward reaction*. After sometimes, the rate of forward reaction becomes equal to the rate of backward reaction and the reaction attains equilibrium. Thus *equilibrium is a state in which the rates of forward and backward reactions are equal.*

Equilibrium is dynamic in nature. i.e. at equilibrium the reaction does not stop. The reactant molecules collide to form products and the product molecules collide to form the reactants and the rates of these reactions are equal.

Physical equilibrium

Equilibrium involving physical process is called physical equilibrium. E.g. melting of ice, evaporation of water, sublimation, dissolution of solids or gases in liquids etc.

1. **Solid-Liquid Equilibrium**

When ice and water are kept in a perfectly insulated thermos flask at 273K and 1 atm pressure, there exist an equilibrium between ice and water. i.e. ice is converted to water (melting or fusion) and water is converted to ice (freezing) at the same rate. At this stage, there is no change in the mass of ice and water.

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$
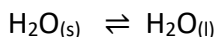
Ice and water are in equilibrium only at particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called ***the normal melting point or normal freezing point*** of the substance.

2. **Liquid-Vapour Equilibrium**

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. At this stage, the conversion of water to water-vapour [evaporation] and the reverse process [condensation] takes place in equal rates.

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
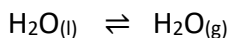
For any pure liquid, the temperature at which the liquid and vapours are at equilibrium at one atmospheric pressure (1.013 bar), is called ***normal boiling point of the liquid***. The normal boiling point of water is 100°C.

Boiling point of the liquid depends on the atmospheric pressure. It also depends on the altitude of the place. At high altitude the boiling point decreases.

3. **Solid – Vapour Equilibrium**

If we place solid iodine in a closed vessel, after sometimes the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage, equilibrium is attained. $I_{2(solid)} \rightleftharpoons I_{2\ (vapour)}$

4. **Dissolution of Solid in Liquids**

Consider the dissolution of sugar in a fixed amount of water. When we add sugar into water, at first, we can dissolve more amount of sugar, since the solution is unsaturated. But after sometime, the

rate of dissolution of sugar decreases and rate of its crystallisation increases. i.e. the sugar molecules in the solution separate out as solid sugar. At equilibrium state, the rate of dissolution becomes equal to the rate of crystallisation. At this stage, the solution is called saturated solution. It is a solution in which no more solute can be dissolved at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature.

$$\text{Sugar (solution)} \rightleftharpoons \text{Sugar (solid)}$$
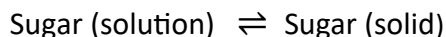
5. **Dissolution of Gases in Liquids**

The solubility of a gas in a liquid depends on nature of the gas, pressure of the gas and temperature. When pressure of the gas increases, its solubility also increases. A quantitative relation between pressure and solubility was proposed by Henry and is known as **Henry's law**. The law states that the mass of a gas dissolved in a given mass of a solvent is proportional to the pressure of the gas above the solvent, at a constant temperature.

In soda water, CO_2 gas is dissolved in water at high pressure. There is an equilibrium between the $CO_2(g)$ in the solution and that in the free state above the solution.

i.e., CO_2 (gas) $\rightleftharpoons$ CO_2 (in solution)
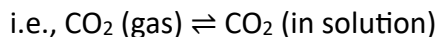
When the bottle is opened, some of the dissolved carbon dioxide gas, escapes out with a fizzing sound and a new equilibrium at low pressure is attained.

The solubility of a gas in a liquid decreases with increase in temperature.

General Characteristics of Physical Equilibrium

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) Both the opposing processes (forward and backward processes) occur at the same rate and there is a dynamic but stable condition.

(iii) All measurable properties of the system remain constant at equilibrium.

(iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.

(v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

Chemical Equilibrium

Equilibrium associated with chemical reactions is called chemical equilibrium. At equilibrium, the concentrations of reactants and products are constant.

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

As the reaction proceeds, the concentration of the reactants decreases and that of the products increases. After sometimes, the two reactions occur at the same rates and an equilibrium state is reached. This can be illustrated by the following graph.
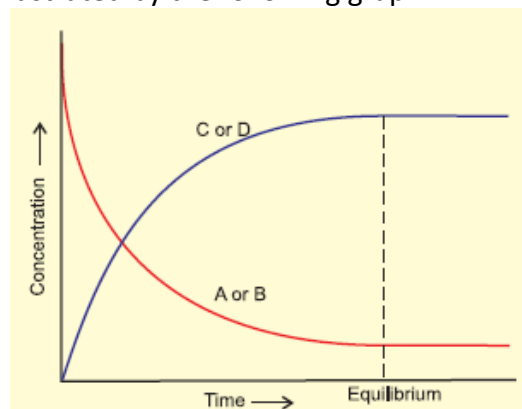

After the equilibrium is attained, the concentration of the reactants and products become constant. At equilibrium, the rate of forward reaction (r_f) = the rate of backward reaction (r_b).

Law of Chemical Equilibrium and Equilibrium Constant

This law was proposed by Guldberg and Waage. It states that *at constant temperature, the ratio of the product of concentration of the products to that of the reactants, in which each concentration terms is raised to a power which is equal to the stoichiometric coefficients in the balanced chemical equation, has a constant value*.

For a general reversible reaction:

$$A + B \rightleftharpoons C + D$$
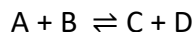
According to the equilibrium law, $\dfrac{[C][D]}{[A][B]} = K_c$

Where K_c is called the equilibrium constant.

For a general reaction, $aA + bB \rightleftharpoons cC + dD$,

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

For the reaction $H_2 + I_2 \rightleftharpoons 2HI$; $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

Equilibrium constant for the reverse reaction is the inverse of that for the forward reaction.

i.e. if the equilibrium constant for the reaction: $H_2 + I_2 \rightleftharpoons 2HI$ is K_c,

then that for the reverse reaction: $2HI \rightleftharpoons H_2 + I_2$ is $\dfrac{1}{K_c}$.

Equilibrium constant for gaseous reactions

For a reaction involving gases, the concentration terms are replaced by partial pressures.

For example, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$; $K_p = \dfrac{p_{HI}^2}{p_{H_2}p_{I_2}}$

Where K_p is called equilibrium constant in terms of partial pressure, p_{HI}, p_{H2} and p_{I2} are the partial pressures of HI, H_2 and I_2 respectively.

Relation between K_c and K_p

Consider a general reaction, $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant in terms of concentration for this reaction is $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ .... (1)

And the equilibrium constant in terms of partial pressures is $K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$ ....(2)

From ideal gas equation, $pV = nRT$, $p = \dfrac{nRT}{V} = CRT$ (since $n/V = C$, the concentration)

Therefore, $p_A = C_A RT$, $p_B = C_B RT$, $p_C = C_C RT$ and $p_D = C_D RT$

Substitute these values in equation (2), we get

$K_p = \dfrac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a \ (C_B RT)^b}$

Or, $K_p = \dfrac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} \dfrac{(RT)^{c+d}}{(RT)^{a+b}}$

Or, $K_p = \dfrac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} (RT)^{(c+d)-(a+b)}$

Or, $K_p = K_c \cdot (RT)^{\Delta n}$, where $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

And Δn is the change in no. of moles of gaseous species.
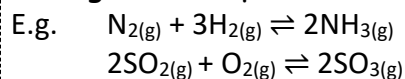
i.e. Δn = no. of moles of gaseous products – no. of moles of gaseous reactants.

Special cases:

    i)   If $\Delta n = 0$, then $K_p = K_c$

    ii)   If $\Delta n > 0$, then $K_p > K_c$ and

    iii)   If $\Delta n < 0$, then $K_p < K_c$

Homogeneous and heterogeneous equilibria

Equilibrium reaction in which all the reactants and products are in the same phase is called homogeneous equilibrium.

E.g. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

         $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Equilibrium reaction in which the reactants and products are in different phases is called heterogeneous equilibrium.

E.g. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

    $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$
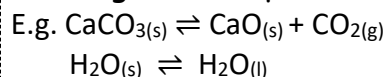
Characteristics of Equilibrium constant

The important characteristics of equilibrium constant are:

1. Equilibrium constant is applicable only when the concentrations of the reactants and products have attained their equilibrium state.
2. The value of equilibrium constant is independent of the initial concentrations of reactants and products.
3. The value of equilibrium constant depends on temperature.
4. The equilibrium constant for the reverse reaction is the reciprocal of that of the forward reaction.
5. If for the reaction A $\rightleftharpoons$ B, the value of equilibrium constant is K_c, then for the reaction nA $\rightleftharpoons$ nB, its value is K_c^n.

Applications of Equilibrium constant

The important applications of equilibrium constant are:

1. *Prediction of the extent of a reaction*

    Greater the value of equilibrium constant, greater will be the concentration of products. In general,

  a) If $K_c > 10^3$ (i.e. K_c is very large), the reaction proceeds nearly to completion.

  b) If $K_c < 10^{-3}$ (i.e. if K_c is very small), the reaction proceeds rarely.

  c) If the value of K_c is in between 10^3 and 10^{-3} appreciable concentrations of both reactants and products are present at equilibrium.

2. *Prediction of the direction of a reaction*

    By knowing the values of K_c and Q_c, we can predict the direction of a reaction. The reaction quotient(Q_c) is defined in the same way as the equilibrium constant (K_c) except that the concentrations in Q_c are not necessarily the equilibrium values.

For a general reaction, aA + bB $\rightleftharpoons$ cC + dD, the reaction quotient, $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse direction).

If $Q_c < K_c$, the reaction will proceed in the direction of products (forward direction).

If $Q_c = K_c$, the reaction mixture is at equilibrium.

3. *Calculation of equilibrium concentrations*

    By knowing the value of equilibrium constant, we can calculate the equilibrium concentrations of reactants and products.

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT (K_c), REACTION QUOTIENT (Q_c) AND GIBBS ENERGY CHANGE (ΔG)

The Gibb's energy change of a reaction is related to the reaction quotient (Q_c) by the equation:

$$\Delta G = \Delta G^\ominus + RT \ln Q_c$$

where, $\Delta G^\ominus$ is standard Gibbs energy change.

At equilibrium, $\Delta G = 0$ and $Q_c = K_c$, so the equation becomes,

$$0 = \Delta G^\ominus + RT \ln K_c$$

Or, $\quad \Delta G^\ominus = - RT \ln K_c$

On changing the base, we get $\Delta G^\ominus = - 2.303 RT \log K_c$

We know that for a spontaneous process ΔG should be negative. So the value of K_c should be positive.

Factors affecting equilibrium

The important factors affecting equilibrium are temperature, pressure, concentration and catalyst. The effect of these factors on equilibrium state can be explained by using **Le Chartier's Principle**. It states that whenever there is a change in concentration, pressure or temperature of a system at equilibrium, the system will try to readjust in such a way so as to cancel the effect of that change.

1. Effect of concentration change

If we change the concentration of reactants or products in an equilibrium process, then according to Le Chatelier's principle, the system will try to reduce the effect of that change. For this the rate of either forward or backward reaction changes.

In general, an increase in concentration of reactants increases the rate of forward reaction (i.e. the equilibrium is shifted to the products side) and an increase in concentration of products increase the rate of backward reaction (i.e. the equilibrium is shifted to the reactants side).

For example in the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, if we increase the concentration of SO_2 or O_2, the system will try to reduce the concentration by shifting the equilibrium to the forward direction. If we remove SO_3 from the reaction mixture, its concentration decreases. To increase the concentration, the equilibrium is shifted to the forward direction.

In Haber process for the preparation of ammonia, the amount of ammonia formed can be increased by increasing the concentration of N_2 or H_2 or by removing NH_3 from the reaction mixture.

2. Effect of temperature change

According to Le Chatelier's principle, increase in temperature favours endothermic process and decrease in temperature favours exothermic process. In a reversible reaction, if the forward reaction is endothermic, the backward reaction will be exothermic.

E.g.: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2 NH_{3(g)}$; $\Delta H = -92.38 kJ/mol$

Here since ΔH is negative, the forward reaction is exothermic. So to increase the production of NH_3, temperature should decrease. At higher temperature, the rate of backward reaction increases. i.e. the ammonia formed is decomposed to N_2 and H_2.

3. Effect of pressure change

Pressure has its effect only in gaseous reactions. In general, an increase in pressure favours the reaction in which number of moles decreases and vice versa.

Thus in the reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2 NH_{3(g)}$, when the pressure increases, the system will try to reduce the pressure. This can be achieved by shifting the reaction into the direction in which no. of moles decreases (since pressure is directly proportional to the number of moles). So in this reaction, the equilibrium will shift to the forward direction.

If the volume of the reaction mixture is halved, the concentration and the partial pressure become doubled. So the reaction is shifted to the direction in which the number of moles or volume decreases.

4. Effect of catalyst

A catalyst is a substance that increases the rate or speed of a chemical reaction.

In an equilibrium reaction, a catalyst increases the rate of both forward and backward reactions simultaneously and helps to attain the equilibrium faster. It lowers the activation energy for the forward and backward reactions by exactly the same amount. It does not affect the equilibrium composition of the reaction mixture.

Thus in Haber process for the manufacture of ammonia, spongy iron (Fe) acts as the catalyst. In contact process for the manufacture of sulphuric acid, V_2O_5 (Vanadium pentoxide) is used as the catalyst.

5. Effect of inert gas addition

If an inert gas (which does not take part in the reaction) is added to an equilibrium mixture at constant volume (or, at constant pressure), there is no change to the equilibrium. It is because the addition of inert gas at constant volume (or, at constant pressure) does not change the partial pressure or the concentration of the reactants and the products.

Ionic equilibrium in solution

Equilibrium involving ions is called ionic equilibrium. E.g. dissociation of acetic acid in water.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
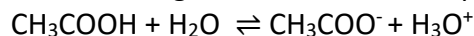
Electrolytes and non-electrolytes

Based on the ability to conduct electricity, Michael Faraday divided substances into two – electrolytes and non-electrolytes.

Electrolytes are substances which conduct electricity in molten state or in solution state.

E.g. All acids, bases and almost all salts

Non- electrolytes are substances which do not conduct electricity in molten state or in solution state.

E.g. sugar, urea etc.

Electrolytes are further classified into two - strong electrolytes and weak electrolytes.

Strong electrolytes are electrolytes which dissociate almost completely in aqueous solution.

E.g. strong acids like HCl, HNO_3, H_2SO_4 etc., strong bases like NaOH, KOH etc. and salts like NaCl, KCl, Na_2SO_4, K_2SO_4, KNO_3, $NaNO_3$ etc.

Electrolytes which dissociate only partially in aqueous solution are called *weak electrolytes*. E.g. weak acids like acetic acid [CH_3COOH], formic acid [HCOOH] etc., weak bases like $Mg(OH)_2$, $Ca(OH)_2$, NH_4OH etc. and some salts like $CaSO_4$, $BaSO_4$ etc.

A weak electrolyte dissociates only partially in aqueous solution and so an equilibrium is formed between the ions and the unionised molecules. This type of equilibrium, which involve ions in aqueous solution is called ionic equilibrium.
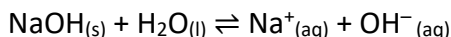
Acids, Bases and Salts

Acid – base concepts:

1. **Arrhenius concept**: According to this concept, acids are substances which give hydrogen ion (H^+) or hydronium ion (H_3O^+) in aqueous solution and bases are substances which give hydroxyl ion (OH^-) in aqueous solution.
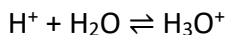
    E.g. HCl is an acid since it produces H_3O^+ in aqueous solution.

    $$HCl_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$
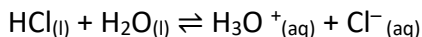
    E.g. for base is NaOH

    $$NaOH_{(s)} + H_2O_{(l)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

Note: H^+ ions exist in water as hydronium ions (H_3O^+)

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

Limitations: This concept is applicable only to aqueous solutions.

2. The Bronsted – Lowry concept:

*According to this concept acids are proton (H^+) donors and bases are (H^+) acceptors.*
For example in the reaction $NH_{3(l)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

Here NH_3 is a base since it accepts an H^+ ion to form NH_4^+ and H_2O is an acid since it donates an H^+ ion to form OH^-. In the reverse reaction, NH_4^+ is an acid and OH^- is a base.

The acid-base pair that differs by only one proton is called a conjugate acid–base pair.
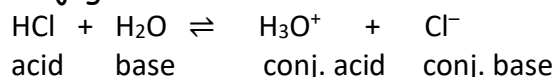An acid formed from a base is called conjugate acid and a base formed from an acid is called conjugate base.
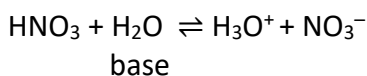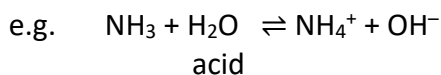
For example
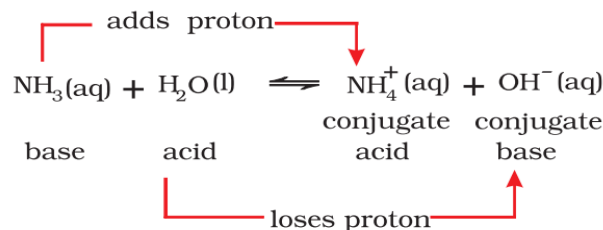
In general, Conjugate base = Acid – H^+

Conjugate acid = Base + H^+

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
acid   base   conj. acid   conj. base

If the acid is strong, its conjugate base is weak and vice versa. So in the above example Cl^- is a weak conjugate base of the strong acid HCl.

Water can act both as acid and base. So it is an amphoteric substance.

e.g. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
             acid

 $HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$
          base

3. Lewis concept:

According to this concept acids are electron pair acceptors and bases are electron pair donors. Substances which donate electron pair are called Lewis bases and substances which accept electron pair are called Lewis acids.

Example for Lewis acids are BF_3, $AlCl_3$, H^+, Co^{3+}, Mg^{2+} etc.
Example for Lewis bases are NH_3, H_2O, OH^-, Cl^-, Br^- etc.

For a substance to act as Lewis acid, it should contain vacant orbitals and for a substance to act as Lewis base, it should contain lone pairs of electrons.
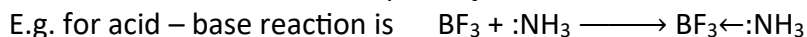
E.g. for acid – base reaction is $BF_3 + :NH_3 \longrightarrow BF_3 \leftarrow :NH_3$
All cations are Lewis acids and all anions are Lewis bases.

The ionization constant of water (The ionic product of water)

Water is a weak electrolyte and hence it ionizes only partially as:
    $H_2O \rightleftharpoons H^+ + OH^-$ Or, $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

The dissociation constant, $K = \dfrac{[H^+][OH^-]}{[H_2O]}$ or, $K = \dfrac{[H_3O^+][OH^-]}{[H_2O]^2}$

Or, $K.[H_2O] = [H^+][OH^-]$ Or, $K.[H_2O]^2 = [H_3O^+][OH^-]$
Or, $K_w = [H^+][OH^-]$ Or, $K_w = [H_3O^+][OH^-]$

Where K_w is called the ionization constant of water or ionic product of water. It is defined as *the product of the molar concentration of hydrogen ion (hydronium ion) and hydroxyl ion in water or in any aqueous solution.*

For pure water at 298K, [H⁺] = [OH⁻] = 10⁻⁷M.

Therefore, $K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}\, M^2$

The value of K_w is temperature dependent.

By knowing the concentrations of H_3O^+ and OH^- ions, we can predict the nature of an aqueous solution.

If $[H_3O^+] > [OH^-]$, the solution is acidic

If $[H_3O^+] < [OH^-]$, the solution is basic

If $[H_3O^+] = [OH^-]$, the solution is neutral

The p^H scale

p^H is defined as the negative logarithm of the hydrogen ion or hydronium ion concentration in moles per litre (i.e. molarity).

i.e. $p^H = - \log[H^+]$ or $p^H = - \log[H_3O^+]$

Negative logarithm of hydroxyl ion concentration in mol/L is called p^{OH}.

i.e. $p^{OH} = - \log[OH^-]$

For pure water, at 298K (25^0c), $[H^+] = 10^{-7}$. Therefore p^H of pure water is 7.

The p^H scale was introduced by Sorensen. It contains numbers from 0 to 14. If the p^H is less than 7, the solution is acidic, if it is greater than 7, it is basic and if it is 7, the solution is neutral.

If the p^H is 0, 1, 2 etc., the solution is a strongly acidic and if it is 12, 13, 14 etc, it is strongly basic. The p^H of our blood is 7.4 and that of our saliva is 6.4. So blood is slightly basic and saliva is slightly acidic.

Relation between p^H and p^{OH}

We know that $K_w = [H^+][OH^-] = 10^{-14}$ at 298K

Taking negative logarithm on both sides:

$-\log K_w = -\log[H^+] + -\log[OH^-] = -\log 10^{-14}$

Or, $p^{Kw} = p^H + p^{OH} = 14$

Thus by knowing the p^H, we can calculate p^{OH} as $p^{OH} = 14 - p^H$

Ionisation constant of weak acids (K_a)

Consider a weak acid HX, which ionizes only partially as: $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

Let 'c' be the initial concentration of HX and 'α' is the degree (extent) of dissociation. (It is the ratio of the number of moles of the electrolyte dissociated to the total number of moles).

Then, $\qquad HX_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + X^-_{(aq)}$

Initial concn. $\qquad$ c $\qquad\qquad\qquad$ 0 $\qquad$ 0

Eqm. concn. $\qquad$ c(1-α) $\qquad\qquad$ cα $\qquad$ cα

The dissociation constant, $K_a = \dfrac{[H_3O^+][X^-]}{[HX]}$

Where K_a is the dissociation constant of the weak acid.

Or, $K_a = \dfrac{c\alpha.c\alpha}{c(1-\alpha)} = \dfrac{c\alpha^2}{1-\alpha}$

Larger the value of K_a, stronger is the acid. The negative logarithm of K_a is called p^{Ka}.

i.e. $p^{Ka} = - \log K_a$.

Greater the value of K_a, smaller will be the value of pK_a and stronger will be the acid.

Ionisation constant of weak bases (K_b)

Consider a weak base MOH, which ionizes partially as: $MOH \rightleftharpoons M^+ + OH^-$

Let 'c' be the initial concentration of MOH and 'α' is the degree of dissociation.

Then, $\qquad MOH_{(aq)} + H_2O_{(l)} \rightleftharpoons M^+_{(aq)} + OH^-_{(aq)}$

Initial concn. $\qquad$ c $\qquad\qquad\qquad$ 0 $\qquad$ 0

Eqm. concn. $\qquad$ c(1-α) $\qquad\qquad$ cα $\qquad$ cα

The dissociation constant of weak base, $K_b = \frac{[M^+][OH^-]}{[MOH]}$

Or, $K_b = \frac{c\alpha.c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$
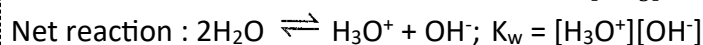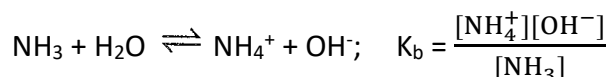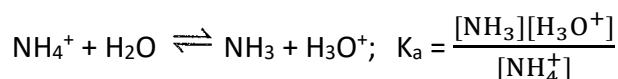
The negative logarithm of K_b is called p^{Kb}.

   i.e. $p^{Kb} = -logK_b$.

As the value of K_b increases, p^{Kb} decreases and the basic strength increases.

Relation between K_a, K_b and K_w

For conjugate acid – base pair K_a and K_b are related as: K_a x $K_b = K_w$

This can be deduced as follows:

   $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$; $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$

   $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$; $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

Net reaction : $2H_2O \rightleftharpoons H_3O^+ + OH^-$; $K_w = [H_3O^+][OH^-]$

   K_a x $K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ x $\frac{[NH_4^+][OH^-]}{[NH_3]}$ = $[H_3O^+][OH^-] = K_w$

   i.e. K_a x $K_b = K_w = 10^{-14}$

   or, **$p^{Ka} + p^{Kb} = p^{Kw} = 14$**

Factors Affecting Acid Strength

The extent of dissociation of an acid and its acidic strength depend on the strength and polarity of the H-A bond. Weaker the H-A bond, more easily it dissociates to give H^+ ion and hence stronger is the acid. Also, greater the polarity of the H – A bond (when the electronegativity difference between the atoms H and A increases) the more easily it dissociates and hence greater is the acidity.

In a group, acidity is mainly determined by bond strength. From top to bottom in a group, as the size of A increases, H-A bond strength decreases and so the acid strength increases. Thus acidic strength of hydrohalic acids increases in the order: HF < HCl < HBr < HI.

In a period, acidity is mainly determined by polarity of the bond. As the electronegativity of A increases from left to right in a period, the strength of the acid also increases. So the acidity of hydrides of second period elements increases in the order: $CH_4 < NH_3 < H_2O < HF$.

Hydrolysis of Salts and the p^H of their Solutions

The interaction of anion or cation or both of a salt with water is known as salt hydrolysis. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., Cl^-, Br^-, NO_3^-, ClO_4^- etc.) of strong acids do not get hydrolyse. So the solutions of salts formed from strong acids and bases (e.g. NaCl, KCl, NaNO₃, KNO₃, Na₂SO₄, K₂SO₄ etc.) are neutral. i.e., their p^H is 7.

1. **Hydrolysis of salt of strong base and weak acid:** Sodium acetate (CH₃COONa), sodium carbonate (Na₂CO₃), potassium cyanide (KCN) etc. are examples for such type of salts. Here only the anion of the weak acid undergoes hydrolysis (since cation of the strong base does not hydrolyse). So the solution of such salts will be basic. i.e. $p^H > 7$.
   p^H of such salt solution is given by **$p^H = 7 + ½ (pK_a + log C)$** where C is the concentration of salt.
2. **Hydrolysis of salt of weak base and strong acid:** NH₄Cl, NH₄NO₃, CuSO₄ etc. are examples for such type of solutions. Here only cation of weak base undergoes hydrolysis. So the solution is acidic.
 p^H of such a solution is given by **$p^H = 7 – ½ (pK_b + log C)$**.

3. **Hydrolysis of salt of weak base and weak acid:** Ammonium acetate (CH_3COONH_4), ammonium carbonate [$(NH_4)_2CO_3$] etc. are examples for such type of salts. Here both cation and anion undergo hydrolysis and hence weak acid and weak base are produced in solution. So the solution may be neutral, acidic or basic depending upon the relative strength of acid and base formed. p^H of such a solution is given by $p^H = 7 + \frac{1}{2}(pK_a - pK_b)$.

Common Ion Effect

It is the suppression of the dissociation of a weak electrolyte by the addition of a strong electrolyte containing a common ion.
For e.g. consider the dissociation of acetic acid (a weak electrolyte).

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$
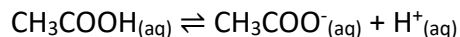
If we add some sodium acetate (CH_3COONa) to the above equilibrium reaction, the concentration of acetate ion increases. Then according to Le-Chatelier's principle, the equilibrium will be shifted towards left or, the rate of forward reaction decreases. i.e. the dissociation rate of acetic acid decreases. This is known as common ion effect.

Another example is the dissociation of the weak base ammonium hydroxide (NH_4OH)

$NH_4OH_{(aq)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$

If we add some NH_4Cl to the above equilibrium process, the concentration of NH_4^+ increases and hence the equilibrium is shifted to the left. i.e. the dissociation rate of NH_4OH decreases.

Buffer Solutions

Solution which resists the change in p^H on dilution or with the addition of small amount of acid or alkali is called Buffer solution. There are two types of buffer solutions – acidic buffer and basic buffer.

Acidic buffer is a mixture of a weak acid and its salt with a strong base. E.g. a mixture of acetic acid and sodium acetate acts as an acidic buffer around p^H 4.75.

Basic buffer is a mixture of a weak base and its salt with a strong acid. E.g. a mixture of NH_4OH and NH_4Cl acts as a basic buffer around p^H 9.25.

P^H of a Buffer solution – Henderson - Hasselbalch Equation

Consider an acidic buffer prepared by mixing a weak acid HA and its conjugate base A^-. The weak acid HA ionises in water as:

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$
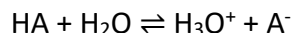
The dissociation constant of weak acid, $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

Taking –ve logarithm on both sides:

$-\log K_a = -\log[H_3O^+] + -\log[A^-] - -\log[HA]$

Or, $-\log[H_3O^+] = -\log K_a + \log[A^-] - \log[HA]$

Or, $p^H = p^{Ka} + \log\dfrac{[A^-]}{[HA]}$

This equation is known as ***Henderson-Hasselbalch equation***.

The equation can be written in general form as: $\mathbf{p^H = p^{K_a} + \log\dfrac{[Salt]}{[Acid]}}$

For a basic buffer, $p^{OH} = p^{K_b} + \log\dfrac{[Salt]}{[Base]}$

or, $\mathbf{p^H = 14 - \left[p^{K_b} + \log\dfrac{[Salt]}{[Base]}\right]}$

Solubility Equilibrium

The solubility of a salt in solvent mainly depends on the lattice enthalpy and solvation enthalpy. As a general rule, for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy.

Each salt has its characteristic solubility which depends on temperature. We can classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	Solubility in between 0.01M and 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

Solubility Product Constant

Consider the dissociation of a sparingly soluble salt in water. Since it dissolves only partially, there exists an equilibrium between the undissolved solid and the ions.

e.g. Solution of barium sulphate ($BaSO_4$)

$$BaSO_{4\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}_{\,(aq)}$$
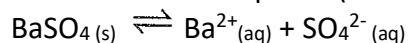
The equilibrium constant, $K = \dfrac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$

For a pure solid, the concentration remains constant.

Therefore, $K.[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$ Or, $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

Where K_{sp} is called the *solubility product constant* or simply the *solubility product. It is defined as the product of the molar concentration of ions of a sparingly soluble salt or in a saturated solution.*

If S is the molar solubility of $BaSO_4$, then $K_{sp} = S \times S = S^2$

For a general salt A_xB_y, its dissociation can be denoted as:

$A_xB_y(s) \rightleftharpoons xA^{y+} (aq) + yB^{x-} (aq);$ $K_{sp} = [A^{y+}]^x[B^{x-}]^y$
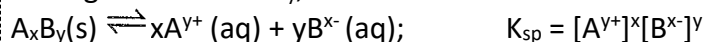
If the concentration in the above equation is not the equilibrium concentration, then K_{sp} is given by Q_{sp}. *At equilibrium, $K_{sp} = Q_{sp}$.*

If $K_{sp} > Q_{sp}$, the dissolution process occurs and if $K_{sp} < Q_{sp}$, the precipitation of the salt occurs.

Solubility product and common ion effect found application in the purification of NaCl. If we take a saturated solution of NaCl and pass HCl gas through it, then NaCl gets precipitated due to the increased concentration of Cl^- ions. NaCl thus obtained has very high purity.

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Q1) If the concentration of hydrogen ion in a soft drink is 3 x 10⁻³ M, calculate its pH.

Ans: Here $[H^+] = 3 \times 10^{-3}$

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

$= -log (3 \times 10^{-3}) = \underline{2.523}$

Q2) Calculate the solubility (S) of $CaSO_4$ at 298 K, if its solubility product constant (Ksp) at this temperature is 9 x 10⁻⁶.

Ans: $CaSO_{4\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}_{\,(aq)}$

$K_{SP} = S^2$. Here $K_{SP} = 9 \times 10^{-6}$

So, $S = \sqrt{K_{SP}} = \sqrt{(9 \times 10^{-6})} = \boldsymbol{3 \times 10^{-3}\,M}$

Q3) Find the value of K_c for the following equilibrium if the value of K_p is 1.8 x 10⁻² atm at 600 K. (R= 0.0821 L atm K⁻¹mol⁻¹): $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

Ans: Here $Kp = 1.8 \times 10^{-2}$, $R = 0.0821$ atm/K/mol

$\Delta n = n_{P(g)} - n_{R(g)} = 3 - 2 = 1$ and $T = 600K$

$$K_p = K_c (RT)^{\Delta n}$$
$$1.8 \times 10^{-2} = K_c (0.0821 \times 600)^1$$
$$K_c = \frac{1.8 \times 10^2}{0.0821 \times 600} = \textbf{3.65 x 10}^{\textbf{-4}}$$

Q4) Calculate the p^H of a 0.01 M acetic acid solution with the degree of ionization 0.045.

Ans: *Degree of ionisation, $\alpha = 0.045$*

$[H_3O^+] = c\alpha = 0.01 \times 0.045 = 4.5 \times 10^{-4}$

$p^H = -log[H_3O^+] = -log(4.5 \times 10^{-4}) = \textbf{3.3468}$

Q5) Calculate the p^H of an acidic buffer containing 0.1 M CH_3COOH and 0.5 M CH_3COONa. [K_a for CH_3COOH is 1.8 x 10⁻⁶].

Ans: *For an acidic buffer Henderson – Hasselbalch equation, $p^H = p^{Ka} + log\frac{[salt]}{[acid]}$*

Here [acid] = 0.1M, [salt] = 0.5M and $K_a = 1.8 \times 10^{-6}$

$pK_a = -log\,K_a = -log(1.8 \times 10^{-6}) = 5.7447$

$p^H = p^{Ka} + log\frac{[salt]}{[acid]}$

$= 5.7447 + log\frac{[0.5]}{[0.1]} = \textbf{6.444}$

Q6) The solubility of $Mg(OH)_2$ at 298K is 1.5 x 10⁻⁴. Calculate the solubility product.

Ans: *Let the solubility of $Mg(OH)_2$ is S. The dissociation of $Mg(OH)_2$ can be represented as:*

$Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\,OH^-_{(aq)}$

Eqm. Concn: S   S   2S

$K_{SP} = [Mg^{2+}][OH^-]^2 = S \times (2S)^2$

i.e. $K_{SP} = 4S^3$

Here $S = 1.5 \times 10^{-4}$

So, $K_{SP} = 4 \times (1.5 \times 10^{-4})^3 = \textbf{1.35 x 10}^{\textbf{-11}}$

Q7) The ionization constant of nitrous acid is 4.5 x 10⁻⁴. Calculate the pH of 0.04 M solution of nitrous acid in water. (Hint: $HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$; $K_a = C\alpha^2$)

Ans: *$K_a = 4.5 \times 10^{-4}$, C = 0.04M*

$K_a = C\alpha^2$

$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.5 \times 10^{-4}}{0.04}} = 0.106$

$[H_3O^+] = c\alpha = 0.04 \times 0.106 = 0.00424$

$p^H = -log[H_3O^+] = -log(0.00424) = \textbf{2.373}$

Q8) Calculate the p^H of a 0.1 M solution of NaOH.

Ans: *$NaOH \rightarrow Na^+ + OH^-$*

*   0.1 M   0.1 M*

$[OH^-] = 0.1$ M

$p^{OH} = -log[OH^-] = -log(0.1) = 1$

$p^H = 14 - p^{OH} = 14 - 1 = \textbf{13}$

!!