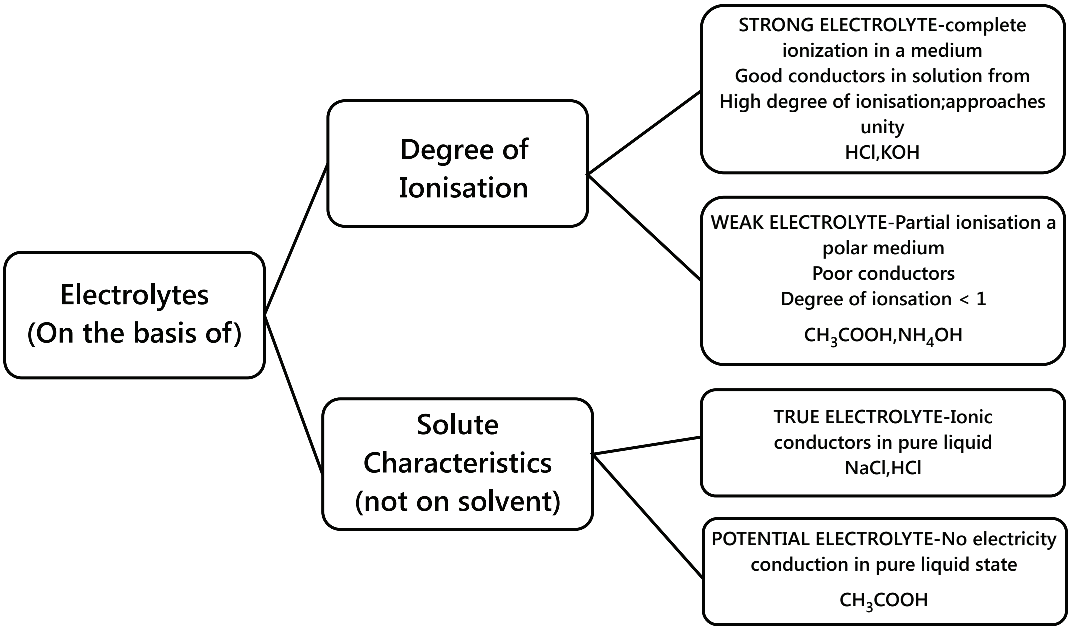
6.

IONIC EQUILIBRIUM

1. INTRODUCTION

1.1 What is an Electrolyte?

Compounds which supply ions, either in the molten state or in a solution are called electrolytes. In the solid state, they are bad conductors of electricity, which, become good conductors either in the molten state or in a solution.



Flowchart 6.1: Classification of electrolyte

* Substances which on dissolution in water form non- conducting liquids are called non-electrolytes, urea, glucose, etc.

1.2 Dissociation and Ionization

Dissociation

(a) A reversible decomposition is called dissociation, e.g., $CaCO_3 \rightleftharpoons CaO + CO_2$

(b) Formation of ions by a weak electrolyte is also called dissociation. e.g. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Ionization: Separation of ions either on fusion or dissolution is called ionization

$NaCl + aq. \rightarrow Na^+(aq.) + Cl^-(aq.)$

MASTERJEE CONCEPTS

- **Misconception:** The two terms ionisation and dissociation often appears confusing.

  When an ionic compound is dissolved in water, the ions which are already present in the solid compound separate out this process is known as dissociation. Whereas, when a neutral molecule like HCl (i. e. a polar covalent compound) which does not contain ions is dissolved in water, splits to produce ions in the solution, the process is called ionization. However, generally the two terms are used without any difference.

  Also, note that the general term used for weak electrolyte is dissociation and strong electrolyte is ionization.

- **How does dissociation occur?**

  An ionic compound is a cluster of positively and negatively charged ions held together by electrostatic forces of attraction. When such an ionic compound is put into water, the high dielectric constant of water (i. e., 80) reduces the electrostatic forces of attraction (to 1/80th). Thus, ions become free to move in the solution. For NaCl solid, the situation may be represented as shown in the Figure.

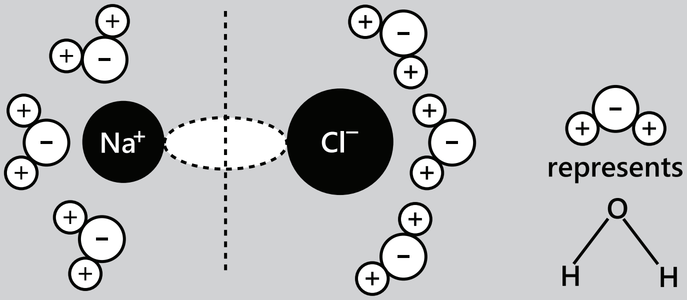


Figure 6.1 :Dissociation of NaCl in water

- **Key Note:** In the case of weak electrolytes, the extent of ionization depends on the strength of the bond and the extent of solvation of ions produced.

Vaibhav Krishnan (JEE 2009, AIR 22)

1.3 Factors Influencing Degree of Dissociation

The extent of dissociation of a substance is expressed in terms of degree of dissociation. The degree of dissociation of an electrolyte in a solution is given by:

$$\alpha = \frac{\text{Moles dissociated at any time}}{\text{Total moles present or dissolved initially}}$$

The variation of 'α' of an electrolyte is governed by:

(a) **Nature of solute:** All ionic compounds, i.e. strong electrolytes have $\alpha \approx 1$ at normal dilution. Most of the polar covalent compounds, i.e. weak electrolytes have $\alpha << 1$.

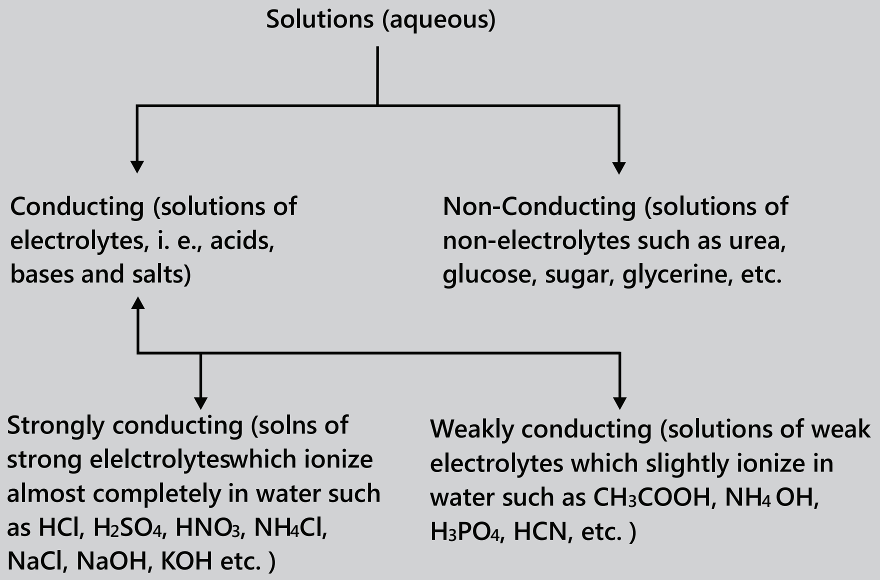
(b) **Nature of solvent:** Solvents having a high dielectric constant are themselves feebly ionized, but an electrolyte in a solvent with a high dielectric constant, for instance water shows a higher degree of dissociation than in a solvent of low dielectric constant (say methanol).

(c) **Dilution:** The extent of dissociation of a weak electrolyte increases with the dilution of solution.

(d) **Temperature:** The extent of dissociation of a weak electrolyte also increases with an increase in temperature.

(e) **Addition of other species:** The addition of another solute having an ion common to that of a weak electrolyte shows a decrease in the degree of dissociation of a weak electrolyte (see common ion effect).

MASTERJEE CONCEPTS



Flowchart 6.2: Types of solution

The degree of dissociation of an electrolyte is assumed to be unity at infinite dilution, i. e., $\alpha = 1$ at infinite dilution

Vaibhav Krishnan (JEE 2009, AIR 22)

2. OSTWALD'S DILUTION LAW

This is an application of the law of mass action for a weak electrolyte dissociation equilibria. Consider ionization of a weak electrolyte say a monoprotic acid, HA

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$ or

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

Moles before dissociation 1 0 0

Moles after dissociation $1 - \alpha$ α a

Where, α is degree of dissociation of a weak acid HA. Let 'c' mol litre^{-1} be the concentration of the acid, HA, then, $[HA] = c(1 - \alpha)$; $[H^+] = c\alpha$; $[A^-] = c\alpha$

According to equilibrium constant expression,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha.c\alpha)}{c(1-\alpha)}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \qquad \text{.... (i)}$$

Where, K_a is the dissociation constant of a weak acid, Since, α is small for weak electrolytes, thus, $1 - a \approx 1$

$$\therefore K_a = ca^2 \text{ or } \alpha = \sqrt{\left(\frac{K_a}{c}\right)} = \sqrt{K_a V} \qquad \text{.... (ii)}$$

Where, V is the volume in litre, containing 1 mole of electrolyte. Thus, it may be concluded that the degree of dissociation of a weak electrolyte is inversely proportional to the square root of its concentration.

Similar expression can also be made for a weak base B or BOH as

$$B(aq) + H_2O \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$\text{Or } BOH \rightleftharpoons B^+ + OH^-; K_b = \frac{c\alpha^2}{(1-\alpha)}$$

If $1 - \alpha \approx 1$ and $K_b = c\alpha^2$ .... (iii)

$$\text{or } \alpha = \sqrt{\left(\frac{K_b}{c}\right)} \qquad \text{.... (iv)}$$

Where, K_b is the dissociation constant of a weak base.

Eqs. (i) and (iii) also reveals that when $c \to 0$, $(1 - \alpha) \longrightarrow 0$, i. e. α approaches unity, i. e. at infinite dilution, the whole of the weak electrolyte gets dissociated. This is the Ostwald's dilution law.

MASTERJEE CONCEPTS

Smaller the value of K_a or K_b, weaker will be the electrolyte. This can be used to solve objective questions easily & directly. The approximation $1 - \alpha \cong 1$ can be applied only if $\alpha < 5\%$. If on solving a problem by applying Ac approximate formula, α comes out to be $\geq 5\%$, the problem may be solved again by applying exact formula and α may be calculated by applying solution of a quadratic equation, i. e. A =

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ (Equation (ii) implies } Ca^2 + K\alpha - K = 0)$$

Misconception: Generally, it is assumed that Ostwald's Dilution law can be used for any electrolyte. But electrolytes having, $\alpha \cong 1$, i. e., $K_a \to \infty$(from equation (ii)) can be studied.

Rohit Kumar (JEE 2012, AIR 79)

2.1 Limitations of Ostwald's Dilution Law

The law is applicable only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula $\wedge / \wedge_\infty$

(i)The law is based on the notion that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilution and $\wedge / \wedge_\infty$ does not give an accurate value of 'α'

(ii)When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, the law of mass action in its simple form cannot be strictly applied in the case of strong electrolytes.

Illustration 1: Calculate the conc. of fluoroacetic acid when $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid = 2.6×10^{-3} **(JEE MAIN)**

Sol: This problem can be solved using Ostwald's Dilution law. From the given value of hydrogen ion concentration and equilibrium constant calculate degree of dissociation. By using the value of α determine the concentration of fluoroacetic acid.

$$\begin{array}{lll} CH_2FCOOH \rightleftharpoons & CH_2FCOO^- + & H^+ \\ 1 & 0 & 0 \\ 1-\alpha & a & a \end{array}$$

Given, $[H^+] = c\alpha = 1.5 \times 10^{-3}$; $Ka = 2.6 \times 10^{-3}$

Also, $\because$ $Ka = \dfrac{c\alpha^2}{(1-\alpha)}$

$\therefore$ $2.6 \times 10^{-3} = \dfrac{1.5\times10^{-3}.\alpha}{(1-\alpha)}$ [See α is not small]

$\therefore$ $\alpha = 0.634$

$\therefore$ $c\alpha = 1.5 \times 10^{-3}$

$\therefore$ $c = \dfrac{1.5\times10^{-3}}{0.634} = 2.37 \times 10^{-3}$ M

Illustration 2: At 30°C, the degree of dissociation of 0.006 M HA is 0.0145. What would be the degree of dissociation of 0.02 M solution of the acid at the same temperature? **(JEE MAIN)**

Sol: Solve the problem using Ostwald dilution law. Use the expression relating degree of dissociation and concentration.

Let the ionization constant of the acid be K_a. Degree of dissociation of 0.066 M concentration = 0.0145.

Applying $\alpha = \sqrt{\dfrac{K_a}{C}}$

$$0.0145 = \sqrt{\frac{K_a}{0.066}} \qquad \text{.... (i)}$$

Let the degree of dissociation of the acid at 0.02 M concentration be α.

$$a_1 = \sqrt{\frac{K_a}{0.02}} \qquad \text{.... (ii)}$$

$\therefore \left(0.0145\right)^2 \times 0.066 = \alpha_1^2 \times 0.02$

$\therefore \alpha_1 = 0.0145 \times \sqrt{\dfrac{0.066}{0.02}}$

$\alpha_1 = 0.0263$

Illustration 3: Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC . Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2 litre of solution. **(IIT 1993)**

Sol: Initial concentration of the nicotinic acid = $\dfrac{0.01}{2} = 0.05$ mol L^{-1}

$$\begin{array}{llll} & HNiC \rightleftharpoons & H^+ + & NiC^- \\ \text{Equilibrium conc.} & (0.05 - x) & x & x \end{array}$$

As x is very small, (0.05 – x) can be taken as 0.05

$$K_a = \frac{[H^+][NiC^-]}{[HNiC]} = \frac{x \times x}{0.05}$$

or $x^2 = (0.05) \times (1.4 \times 10^{-5})$ or $x = 0.83 \times 10^{-3}$ mol L^{-1}

$$\% \text{ dissociation} = \frac{0.83 \times 10^{-3}}{0.05} \times 100 = 1.66\%$$

Alternative method: Let α be the degree of dissociation

	$HNiC \rightleftharpoons$	H^+ +	NiC^-
At equilibrium	$0.05(1-\alpha)$	0.05α	0.05 a

$$K_a = \frac{0.05\alpha \times 0.05\alpha}{0.05(1-\alpha)}$$

As α is very small, $(1-\alpha) \rightarrow 1$

So, $1.4 \times 10^{-5} = 0.05\underline{a}^2$

$$\text{Or } \alpha = \sqrt{\frac{1.4 \times 10^5}{0.05}} = 1.67 \times 10^{-2}$$

Percent dissociation = $100 \times \alpha = 100 \times 1.67 \times 10^{-2} = 1.67\%$

2.2 Phenomenon of Autoprotolysis

Water shows autoprotolysis as:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

The phenomenon of self-ionisation is called autoprotolysis.

Many liquids are likely to undergo autoprotolysis like H_2O, e.g.,

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$CH_3OH + CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$$

The autoprotolysis is confirmed by the conducting nature of solvents in a pure state, although its molecular formula does not indicate the presence of ions in its molecule. Pure water is a weak electrolyte and dissociates as

Or $H_2O \rightleftharpoons H^+ + OH^-$

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_w = [H^+][OH^-] \qquad \text{.... (7)}$$

For pure water $[H^+] = [OH^-]$

$\therefore$ By eq. (7), $[H^+]^2 = K_w = 10^{-14}$ ($[H^+]=[OH^-]=10^{-7}$ M at 25°C)

$\therefore$ $[H^+] = 10^{-7}$ or $c\alpha = 10^{-7}$

Since, concentration or molarity of H_2O = 55.6

$$\therefore \alpha = \frac{10^{-7}}{55.6} = \frac{1}{(556 \times 10^6)} = 1.8 \times 10^{-9}$$

$$\text{Thus, } K_{eq} = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.6} = 1.79 \times 10^{-16}$$

3. COMMON ION EFFECT

The phenomenon in which the degree of dissociation of a weak electrolyte is suppressed by the addition of a strong electrolyte having an ion common to weak electrolyte is known as common ion effect. Consider dissociation of a weak electrolyte, say, acetic acid.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ The equilibrium constant, K_a is given by:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Now, suppose sodium acetate is added to this solution.

$CH_3COONa \rightarrow CH_3COO + Na^+$

The concentration of CH_3COO^- in the solution increases and thus, in order to have K_a constant, $[H^+]$ must decrease or the concentration of undissociated acetic acid must increase. In other words, the dissociation of acetic acid is suppressed on addition of CH_3COONa to its solution. Similar results are obtained on addition of HCl to acetic acid solution, this time H^+ provided by HCl acts as common ion.

Illustration 4: Liquid ammonia ionises to a slight extent. At -50°C, its ionisation constant, $K_b = K_{NH_3} = [NH_4^+].[NH_2^-] = 10^{-30}$. How many amide ions, are present per cm^3 of pure liquid ammonia? Assume $N = 6.0 \times 10^{23}$.

(JEE MAIN)

Sol: $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (self-ionisation)

and $K_{NH_3} = [NH_4^+].[NH_2^-]$

$\therefore [NH_4^+] = [NH_2^-]$

$\therefore [NH_2^-] = \sqrt{K_{NH_3}} = \sqrt{10^{-30}} = 10^{-15}M$

Number of amide ions in $10^3 cm^3 = 10^{-15} \times 6 \times 10^{23}$

$\therefore$ Number of amide ions in 1 $cm^3 = \dfrac{10^{-15} \times 6 \times 10^{23}}{10^3} = 6 \times 10^5$ ions

Illustration 5: What is the H^+ ion concentration of a solution known to contain 0.1 g mole of CH_3COONH_4 in one litre of 0. 1 M CH_3COOH? Assume effective ionisation of ammonium acetate is 80%. K_a for acetic acid is 1.8×10^{-5}.

(JEE MAIN)

Sol: Write down the complete reaction for dissociation of acetic acid and expression for equilibrium constant. By using Ostwald's dilution law determine the hydrogen ion concentration.

$CH_3\ COOH \rightleftharpoons CH_3\ COO^- + H^+$

(0. 1 – x) x x

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

The solution also contains CH_3COONH_4 which is 80% dissociated i. e. $\alpha = 0.8$. Thus, the acetate concentration provided by 0. 1 M $CH_3COONH_4 = 0.1 \times 0.8 = 0.08$ M

Total$[CH_3COO^-] = (0.08 + x)$ M

So, $K_a = \dfrac{(0.08+x)x}{(0.1-x)}$

As x is very small, (0. 1 – x) → 0. 1 and neglecting x^2,

$K_a = \dfrac{0.08x}{0.1}$ or $1.8 \times 10^{-5} \times 0.1 = 0.08x$

or $x = [H^+] = \dfrac{1.8\times10^{-5}\times0.1}{0.08} = 2.25 \times 10^{-5}$ mol L^{-1}

Illustration 6: The ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOD^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1. 22 g/cm³. **(JEE ADVANCED)**

Sol: We are asked to find out the % dissociation of formic acid. The density of acetic acid is provided so from density determine the weight of acetic acid in 1 litre solution. By using weight and molecular weight relation find out the initial molarity of the solution.

According to definition, $\alpha = \dfrac{\text{Moles dissociated at any time}}{\text{Totalmoles present or dissolved initially}}$

Given density of formic acid = 1. 22 g/cm³

∴ Weight of formic acid in 1 litre solution = 1.22×10^3g

Thus, $[HCOOH] = \dfrac{1.22\times10^3}{46} = 26.5$ M

Since, in case of auto ionization,

$[HCOOH_2^+] = [HCOO^-]$

and $[HCOO^-][HCOOH_2^+] = 10^{-6}$

∴ $[HCOO^-] = 10^{-3}$

Now, % dissociation of HCOOH = $\dfrac{[HCOO^-]\times100}{[HCOOH]} = \dfrac{10^{-3}}{26.5} \times 100 = 0.004\%$

Illustration 7: A solution contains 0. 1 M H_2S and 0. 3 M HCl. Calculate the concentration of S^{2-} and HS^- ions in solution. Given, K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively. **(JEE ADVANCED)**

Sol: $H_2S \rightleftharpoons H^+ + HS^-$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \quad \text{.... (i)}$$

Further $HS^- = H^+ + S^{2-}$

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \quad \text{.... (ii)}$$

Multiplying both the equations

$$K_{a_1} \times K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Due to common ion, the ionization of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of 0. 3 M HCl.

$$[S^{2-}] = \frac{K_{a_1}\times K_{a_2}[H_2S]}{[H^+]^2} = \frac{1.0\times10^{-7}\times1.3\times10^{-13}\times(0.1)}{(0.3)^2} = 1.44 \times 10^{-20} \text{ M}$$

Putting the value of $[S^{2-}]$ in eq. (ii)

$$1.3 \times 10^{-13} = \frac{0.3 \times 1.44 \times 10^{-20}}{[HS^-]} \text{ or } [HS^-] = \frac{0.3 \times 1.44 \times 10^{-20}}{1.3 \times 10^{-13}} = 3.3 \times 10^{-8} \text{ M}$$

4. SOLUBILITY PRODUCT

When a solute is added gradually to an amount of solvent, at a particular temperature, there comes a point when no more solute can be dissolved. This point gives a saturated solution. A solution which remains in contact with undissolved solute is said to be saturated. At the saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

Consider in general, the electrolyte of the type $A_x B_y$ which is dissociated as:

$$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Applying law of mass action, $\frac{[A^{y+}]^x [B^{x-}]^y}{[A_x B_y]} = K$

When the solution is saturated,

$[A_x B_y] = K'$ (constant)

Or $[A^{y+}]^x [B^{x-}]^y = K[A_x B_y] = KK' = K_{sp}$ (constant)

Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times, the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

4.1 Relationship between Solubility and Solubility Product

Salts like AgI, $BaSO_4$, $PbSO_4$, PbI_2, etc.. are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolytes contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, i. e., it is completely dissociated.

The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:

$$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Thus, solubility product, $K_{sp} = [A^{y+}]^x [B^{x-}]^y$

Let 'S' mol litre^{-1} be the solubility of the salt; then

$$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$$

xS.yS

So, $K_{sp} = [xS]^x [yS]^y = x^x \cdot y^y (S)^{x+y}$

Special Cases:

(i) 1: 1 type salts: Examples: AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

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

(ii) 1: 2 or 2: 1 type salts: Examples: Ag_2CO_3, Ag_2CrO_4, $PbCl_2$, CaF_2, etc.

$$S = \sqrt[3]{K_{sp} / 4}$$

(iii) 1: 3 type salts: Examples: AlI_3, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$,etc.

$S = \sqrt[4]{K_{sp}\ /27}$

MASTERJEE CONCEPTS

The presence of a common ion affects the solubility of a salt. Let AB be a sparingly soluble salt in solution and A′B be added to it. Let S and S′ be the solubilities of the salt AB before and after addition of the electrolyte A ′B. Let c be the concentration of A′B.

Before addition of A′B, $K_{sp}=S^2$ .... (i)

After addition of A′B, the concentration of A^+ and B^- ions become S′ and (S′ + c)., respectively.

So, $K_{sp} = S'(S' + c)$ .... (ii)

Equating (i) and(ii),

$S^2 = S' (S' + c)$

T P Varun (JEE 2012, AIR 64)

4.2 Simultaneous Solubility

The solubility of two electrolytes having a common ion; when they are dissolved in the same solution, is called simultaneous solubility, e.g.

(i) Solubility of AgBr and AgSCN, when dissolved together.

(ii) Solubility of CaF_2 and SrF_2, when dissolved together.

(iii) Solubility of MgF_2 and CaF_2, when dissolved together.

Calculation of simultaneous solubility is divided into two cases:

Case I: When the two electrolytes are almost equally strong (having close solubility product), e.g.,
AgBr ($K_{sp} = 5 \times 10^{-13}$); AgSCN ($K_{sp} = 10^{-12}$)

Case II: When solubility products of two electrolytes are not close, i. e., they are not equally strong, e.g. CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$); SrF_2 ($K_{sp} = 2.9 \times 10^{-9}$)

Most of fluoride ions come from stronger electrolyte.

MASTERJEE CONCEPTS

- It must be noted that hydration of molecule doesn't influence K_{sp}
- K_{sp} of a hydrated molecule say $Na_2CO_3 . 10H_2O$ can be given by $K_{sp} = [Na^+]^2[CO_3^{2-}]$

Aishwarya Karnawat (JEE 2012, AIR 839)

Illustration 8: K_{sp} of AgCl is 2.8×10^{-10} at 25°C. Calculate solubility of AgCl in

(i) Pure water (ii) 0. 1 M $AgNO_3$. (iii) 0. 1 M NaCl.

Sol: Solubility and Solubility product are related by the expression, $S = \sqrt{K_{sp}}$

second and third example contains common ion, hence for theses example we can use the expression, $K_{sp} = S'(S' + c)$

(i) In pure water: Let solubility of AgCl be S mol litre^{-1}

$AgCl(s) + Aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$\therefore K_{sp} = [Ag^+][Cl^-] = S \times S$

Or S = $\sqrt{K_{sp}} = \sqrt{(2.8 \times 10^{-10})}$ = 1. 673 × 10^{-5} mol litre^{-1}

(ii) In 0. 1 M $AgNO_3$: $AgCl(s) + Aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$AgNO_3(aq) \rightarrow \underset{0.1}{Ag^+}(aq) + \underset{0.1}{NO_3^-}(aq)$

$\therefore K_{sp} = [Ag^+]\,[Cl^-] = (0.1 + S)\,(S)$

Here, $\left[Ag^+\right] = 0.1 + S$

$\because S <<< 0.1, \left[Ag^+\right] = 0.1\ M$

$\because$ S <<< 0. 1 since solubility decreases in presence of common ion

$\therefore S \times 0.1 = 2.8 \times 10^{-10}$

or S = 2. 8 × 10^{-9} mol litre^{-1}

(iii) In 0. 1 M NaCl: $AgCl(s) + \underset{S}{Aq} \rightleftharpoons \underset{S}{Ag^+} + Cl^-$

$NaCl(aq) \rightarrow \underset{0.1}{Na^+}(aq) + \underset{0.1}{Cl^-}(aq)$

$\therefore K_{sp} = [Ag^+][Cl^-] = (0.1 + S)(S)$

Here, $\left[Cl^-\right] = 0.1 + s$ but $s <<< 0.1$

$\therefore \left[Cl^-\right] = 0.1M$

$\therefore S <<< 0.1$

$\therefore S \times 0.1 = 2.8 \times 10^{-10}$

$\therefore$ S = 2. 8 × 10^{-9} mol litre^{-1}

Illustration 9: Equal volumes of 0. 02 M $CaCl_2$ and 0. 0004 M Na_2SO_4 are mixed. Will a precipitate be formed? K_{sp} for $CaSO_4$ = 2. 4 × 10^{-5} **(JEE MAIN)**

Sol: Assuming volume of 0.02 M $CaCl_2$ soln = volume of 0.0004 M Na_2SO_4 = VL.

$\therefore$ no. of moles of $Ca^{2+} = 0.02$ V and

No. of moles of $SO_4^{2-} = 0.0004\,V$

$\therefore [Ca^{2+}] = \dfrac{0.02\,V}{2V}$ = 0. 01 mol litre^{-1}

$[SO_4^{2-}] = \dfrac{0.0004\,V}{2V}$ = 0. 0002 mol litre^{-1}

$\therefore [Ca_4^{2+}][SO_4^{2-}] = [0.01][0.0002] = 2 \times 10^{-6}$

Thus, $[Ca^{2+}]\,[SO_4^{2-}]$ in solution < K_{sp} [Here Ionic product < K_{sp}]

($\because$ $2 \times 10^{-6} < 2.4 \times 10^{-5}$)

$\therefore CaSO_4$ will not precipitate.

Illustration 10: What $[H_3O^+]$ must be maintained in a saturated H_2S solution to precipitate Pb^{2+}, but not Zn^{2+} from a solution in which each ion is present at a concentration of 0. 1 M?

(K_{sp} for $H_2S = 1.\ 1 \times 10^{-22}$, K_{sp} for ZnS $= 1.\ 0 \times 10^{-21}$). **(JEE ADVANCED)**

Sol: For ZnS not to be precipitated from a solution of Zn^{2+} and Pb^{2+}

$[Zn^{2+}][S^{2-}] < K_{sp}$ of ZnS

$[10^{-2}][S^{2-}] < 1.\ 0 \times 10^{-21}$

Or the maximum $[S^{2-}] = 10^{-19}$ at which ZnS will begin to precipitate or upto this concentration, no precipitation will occur.

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$\therefore\ [H^+]^2[S^{2-}] = 1.\ 1 \times 10^{-22} \therefore\ [H^+]^2[10^{-19}] = 1.\ 1 \times 10^{-22}$

$\therefore [H^+]^2 = 11 \times 10^{-4} \therefore [H^+] = 3.\ 3 \times 10^{-2}$ M

Thus, if $[H^+] = 3.\ 3 \times 10^{-2}$ or slightly higher, the precipitation of ZnS will not take place and only PbS will precipitate.

Illustration 11: 25 mL of 0. 10 M $AgNO_3$ are mixed with 35 mL of 0. 05 M K_2CrO_4 solution. Calculate (a) The concentration of each ionic species at equilibrium (b) Is the precipitation of silver quantitative (> 99. 9%)? K_{sp} of $Ag_2CrO_4 = 1.\ 1 \times 10^{-12}$. **(JEE ADVANCED)**

Sol: First calculate the K_{sp} of Ag_2CrO_4 in solution in order to check whether precipitation will occur or not on mixing.

As concentration of solution and volume term is given concentration of each ionic species at equilibrium can be determined easily.

$2AgNO_3 + K_2CrO_4 \rightleftharpoons Ag_2CrO_4 + KNO_3$

Millimoles at equilibrium = 25×0.1 & 35×0.5 respectively.

= 2.5 & 1.75

Let us first see whether precipitation occurs or not on mixing.

$[Ag^+]^2\ [Cro_4^{2-}] = K_{sp} = 1.\ 1 \times 10^{-12}$

Also after mixing

$$[Ag^+]^2\ [Cro_4^{2-}] = \left[\frac{2.5}{60}\right]^2 \left[\frac{1.75}{60}\right] = 5.\ 06 \times 10^{-5} > K_{sp}$$

Thus, precipitation will take place

$2AgNO_3 + K_2CrO_4 \rightleftharpoons Ag_2CrO_4 + 2KNO_3$

Millimoles before mixing = 2.5 & 1.75 respectively

Millimoles after mixing = (1.75 – 1.25) 21.25=0.50 & 21.25 respectively.

$$\text{Now, } [K^+] = \frac{1.25}{60} = 0.0208$$

$$[NO_3^-] = \frac{2.5}{60} = 0.\ 0417 \text{ M}$$

$$[CrO_4^{2-}] = \frac{0.5}{60} = 0.\ 0083 \text{ M}$$

Let solubility of Ag_2CrO_4 be S mol litre^{-1}, then

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$1.\ 1 \times 10^{-12} = (2s)^2 \times (0.\ 0083)$

$\therefore s = 5.8 \times 10^{-6}$

Or $[Ag^+] = 2 \times 5.8 \times 10^{-6} = 1.16 \times 10^{-5}$ M

The % of Ag precipitated = $\dfrac{2.5-(60\times1.16\times10^{-5})}{2.5}$ × 100 = 99. 97%

i.e. precipitation is quantitative.

Illustration 12: K_{sp} of AgCl and AgBr are 1.0×10^{-10} and 5.0×10^{-13}. Calculate the simultaneous solubility of AgCl and AgBr in water. **(JEE ADVANCED)**

Sol: $AgCl \rightleftharpoons \underset{(S_1+S_2)}{Ag^+} + \underset{S_1}{Cl^-}$ Let solubility of AgCl and AgBr be S_1, S_2 mol litre^{-1}

$AgBr \rightleftharpoons \underset{(S_1+S_2)}{Ag^+} + \underset{S_2}{Br^-}$

$$\therefore \frac{K_{sp\,AgCl}}{K_{sp\,AgBr}} = \frac{S_1(S_1+S_2)}{S_2(S_1+S_2)}$$

$$\therefore \frac{S_1}{S_2} = \frac{1.0\times10^{-10}}{5.0\times10^{-13}} = 200$$

Now, $K_{sp}(AgCl) = S_1(S_1+S_2)$

$$\frac{S_1}{S_2} = 200 \quad S_2 = \frac{S_1}{200}$$

$$\frac{S_1}{S_2} = 200\ ,\ S_2 = \frac{S_1}{200}$$

Or $1 \times 10^{-10} = S_1\left(S_1 + \dfrac{S_1}{200}\right)$

$$\therefore \frac{201}{200}S_1^2 = 1\times 10^{-10}$$

$\therefore S_1 = 9.98 \times 10^{-6}$ M

And $S_2 = \dfrac{9.98\times10^{-6}}{200} = 4.99 \times 10^{-8}$M

4.3 Selective Precipitation

The phenomenon involving the precipitation of sparingly soluble species one by one on the addition of a precipitating reagent in a solution of two or more soluble compounds is known as selective precipitation. The principle of a selective precipitation is of much importance in the qualitative and quantitative aspects of chemistry.

For example, a solution contains $CaCl_2$ and $BaCl_2$. If we add Na_2SO_4 to this solution slowly and slowly, we can first precipitate the sulphate of Ba (on the basis of K_{sp} values of $CaSO_4$ and $BaSO_4$ which are 2×10^{-4} and 1.5×10^{-9} respectively.

This is due to the fact that as we go on adding Na_2SO_4, the concentration of SO_4^{2-} ion increases and since $[Ba^{2+}][SO_4^{2-}] = K_{sp}$,the lower value is attained first.

4.4 Solubility of Salts in the Presence of an Acid or Base

The solubility of salts is greatly influenced by the presence of acids or bases.

For example, BaF_2(aq)

$BaF_2\,(aq) \rightleftharpoons Ba^{2+} + 2F^-$

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

In an acidic medium, the higher $[H^+]$ shifts the equilibrium from left to right:

$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$

As $[F^-]$ decreases, $[Ba^{2+}]$ increases to maintain the equilibrium.

4.5 Stability Constant

Let us consider dissociation of the ion, $FeBr^+$, $FeBr^+ \rightleftharpoons Fe^{2+} + Br^-$

Dissociation constant for above the equilibria may be given as: $K_d = \dfrac{[Fe^{2+}][Br^-]}{[FeBr^+]}$

Reciprocal of dissociation constant is called stability constant. $K_s = \dfrac{[FeBr^+]}{[Fe^{2+}][Br^-]}$

Let us consider the formation of a complex $K_2Cd(CN)_4$. Complex ion is $Cd\,(CN)_4^{2-}$ where the oxidation state of a central metal $Cd^{2+}$is (+2). The complexing process proceeds in four steps as:

$Cd^{2+} + CN^- \rightleftharpoons CdCN^+;K_1 = \dfrac{[CdCN^+]}{[Cd^{2+}][CN^-]}$

$CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2;K_2 = \dfrac{[Cd(CN)_2]}{[CdCN^+][CN^-]}$

$Cd(CN)_2 + CN^- \rightleftharpoons Cd\ (CN)_3^-\,;K_3 = \dfrac{[Cd(CN)_3^-]}{[Cd(CN)_2][CN^-]}$

$Cd\,(CN)_3^- + CN^- \rightleftharpoons Cd((CN)_4^{-2}\,;K_4 = \dfrac{[Cd(CN)_4^{2-}]}{[Cd(CN)_3^-][CN^-]}$

Overall reaction may be given as: $Cd^{2+} + 4CN^- \rightleftharpoons [Cd\,(CN)_4^{2-}];K_5 = \dfrac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4}$

Here, $K_5 = K_1 K_2 K_3 K_4$

MASTERJEE CONCEPTS

(a) Greater the stability constant, more stable is the compound.

(b) **(i)** If on the addition of a common ion in a bait solution (sparingly soluble), formation of a complex ion takes place, then ionization increases, i. e.. Equilibrium shifts towards the right hand direction to maintain the value of K_{sp} constant. It means, addition of a common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the CONCEPTS of the common ion effect.

(ii) When we add an electrolyte to another electrolyte solution having no common ion, then the ionisation of the latter increases.

(iii) For a given electrolyte, solubility product is always constant at a particular temperature

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4.6 Application of Solubility Product

(a) In the purification of common salt: A saturated solution of NaCl leads to precipitation of NaCl on passing HCl gas through it. An increase in $[Cl^-]$, shifts the equilibrium, $NaCl(s) \rightleftharpoons Na^+ + Cl^-$ to backward direction because of higher Ionic product concentration, i. e.,$[Na^+][Cl^-] > K_{sp}$.

(b) In the preparation of $NaHCO_3$: The precipitation of $NaHCO_3$ from its saturated solution in Solvay's ammonia soda process from its saturated solution is made by the addition of NH_4HCO_3.

(c) Predicting precipitation in ionic reactions: During an ionic reaction, the product's precipitation can be predicted when the product of ionic concentration of solute exceeds its K_{sp}.

(d) Salting out action of soap: A saturated solution of soap (RCOONa), the sodium salt of higher fatty acids show precipitation of soap on the addition of sodium chloride. This is because of the fact that an increase in Na^+ ion concentration helps in crossing over $[Na^+][RCOO^-]$ to their K_{sp} value.

(e) In Qualitative Analysis: The Qualitative analysis of a mixture is based on the principle of solubility product.

Illustration 13: Calculate the solubility of AgCN in 1 M HNO_3 if $K_{sp\ AgCN} = 1.2 \times 10^{-16}$ and $K_a(HCN) = 6.2 \times 10^{-10}$ **(JEE MAIN)**

Sol: Let solubility of AgCN be 'a' mol/lit

$$AgCN \rightarrow \underset{a}{Ag^+} + \underset{a}{CN^-}$$

$CN^- + H^+ \rightarrow HCN;$

$$K^-_{aHCN} = \frac{[H^+][CN^-]}{[HCN]}$$

$$\therefore [CN^-] = \frac{K_{aHCN} \times [HCN]}{[H^+]}$$

$$\therefore K_{sp\ AgCn} = [Ag^+][CN^-] = \frac{a \times K_{aHCN} \times [HCN]}{[H^+]}$$

$$1.2 \times 10^{-16} = \frac{a \times 6.2 \times 10^{-10} \times a}{(1-a)} \quad (1 - a \approx 1)$$

$$\therefore a = \sqrt{\frac{1.2 \times 10^{-16}}{6.2 \times 10^{-10}}} = 4.39 \times 10^{-4}$$

Illustration 14: $Mg(OH)_2$ is soluble in NH_4Cl and not in NaCl. Why? **(JEE MAIN)**

Sol: Addition of NH_4Cl to $Mg(OH)_2$ brings in interaction:

$Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$

The NH_4OH being a weak base reduces the OH^- in solution and thus product of $[Mg^{2+}]$ and $[OH^-]^2$ remains lower than K_{sp} of $Mg(OH)_2$ to give no precipitation of $Mg(OH)_2$. On the other hand, interaction of NaCl with $Mg(OH)_2$ gives strong alkali NaOH and the product of $[Mg^{2+}]$ and $[OH^-]^2$ exceeds their K_{sp} to show precipitation.

Illustration 15: 0.01 mole of $AgNO_3$ is added to 1 litre of a solution which is 0.1 M in Na_2CrO_4 and 0.005 M in $NaIO_3$. Calculate the mole of precipitate formed at equilibrium and the concentrations of Ag^+, IO_3^- and CrO_4^{2-} (K_{sp} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively) **(JEE ADVANCED)**

Sol: From the given values of K_{sp} of $[Ag^+][IO_3^-]$ and $[Ag^+][CrO_4^{2-}]$ in solution first determine the $[Ag^+]_{needed}$ and $[CrO_4^{2-}]$ left in solution.

Remaining concentration $[Ag^+]_{left}$ $[IO_3^-]_{left}$ can be determined as, $[A^+]_{left} = \dfrac{K_{sp}[AB]}{[B^-]}$

The K_{sp} values of Ag_2CrO_4 and $AgIO_3$ reveals that CrO_4^{2-} and IO_3^- will be precipitated on addition of $AgNO_3$ as:

$[Ag^+][IO_3^-] = 10^{-13}$

$$[Ag^+]_{needed} = \frac{10^{-13}}{[0.005]} = 2 \times 10^{-11}$$

$[Ag^{+2}][CrO_4^{2-}] = 10^{-8}$

$$[Ag^+]_{needed} = \sqrt{\frac{10^{-8}}{0.1}} = 3.16 \times 10^{-4}$$

Thus, $AgIO_3$ will be precipitated first. Now, in order to precipitate $AgIO_3$, one can show:

$AgNO_3 + NaIO_3 \rightarrow AgIO_3 + NaNO_3$

$AgNO_3$	$NaIO_3$	$AgIO_3$	$NaNO_3$
0. 01	0. 005	0	0
0. 005	0	0. 005	0. 005

The left mole of $AgNO_3$ are now used to precipitate Ag_2CrO_4

$2AgNO_3 + Na_2CrO_4 \rightarrow Ag_2CrO_4 + 2NaNO_3$

$2AgNO_3$	Na_2CrO_4	Ag_2CrO_4	$2NaNO_3$
0. 005	0. 01	0	0
0	0. 0975	0. 0025	0. 005

Thus, $[CrO_4^{2-}]$ left in solution = 0. 0975

Now, solution has $AgIO_3(s) + Ag_2CrO_4(S) + CrO_4^{2-}$ ions

$AgIO_3(s)$	$Ag_2CrO_4(S)$	CrO_4^{2-}
0. 005	0. 0025	0. 0975

$$\therefore [Ag^+]_{left} = \frac{K_{sp\,Ag_2CrO_4}}{[CrO_4^{2-}]} = \sqrt{\frac{10^{-8}}{0.0975}} = 3.2 \times 10^{-4}\ M$$

$$\therefore [IO_3^-]_{left} = \frac{K_{sp\,AgIO_3}}{[Ag^+]} = \frac{10^{-13}}{3.2 \times 10^{-4}} = 3.1 \times 10^{-10}\ M$$

5. ACIDS AND BASES

5.1 Arrhenius Concept

(a) An Arrhenius acid is a substance which furnishes the hydrogen ion (H^+ ions) in an aqueous solution, e.g.

$HCl \rightarrow H^+ + Cl^-$ (strong acid)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (weak acid)

(b) An Arrhenius base is a substance which furnishes the hydroxyl (OH^-) ions in an aqueous solution, e.g.

$NaOH \rightarrow Na^+ + OH^-$ (Strong base)

$NH_4OH \rightarrow NH_4^+ + OH^-$ (Weak base)

(c) The strength of an acid or a base depends upon its tendency to furnish H+ or OH– ions in the solution respectively.

(d) Water is amphoteric because it furnishes both H^+ and OH^- ions in the solution $H_2O \rightleftharpoons H^+ + OH^-$

(e) The neutralization of an acid and base is basically a neutralization reaction between H^+ and OH^- ions.

$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$

Limitations of Arrhenius Concept:

(a) It fails to explain the behaviour of acids and bases in non-aqueous solvents.

(b) It fails to explain the neutralisation reactions giving rise to salt formation in the absence of a solvent

e.g. $CO_2 + CaO \rightarrow CaCO_3$; $NH_3(g) + HCl(g) \rightarrow NH_4Cl(g)$ or (s)

(c) It fails to explain the acidic character of certain salts, e.g., $AlCl_3$, BF_3, etc., and the basic character of NH_3, PH_3, Na_2CO_3, etc. Neither $AlCl_3$ nor BF_3 on dissolution in water directly produces a proton. Similarly, when Na_2CO_3 is dissolved in water, it neutralises an acid but Na_2CO_3 cannot dissociate itself directly to produce hydroxyl ions.

(d) It fails to explain the fact that the H^+ ion exists in water as H_3O^+, i. e., hydronium ion. Since H^+ is the simplest and smallest ion and thus, possesses strong tendency of hydration (hydration energy of H^+ is – 256 kcal mol^{-1}).

5.2 Bronsted Lowry Concept

(a) A Bronsted acid is proton donor whereas, a Bronsted base is proton acceptor.

(b) The strength of acids and bases depends upon their tendency to donate or accept protons respectively.

(c) Water is amphoteric because it donates as well as accepts proton.

$$\underset{Acid_1}{H_2O} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Base_1}{OH^-} + \underset{Acid_2}{H_3O^+}$$

(d) The proton donated by an acid is not capable of a separate existence and is always solvated.

$$\underset{Acid}{CH_3COOH} + \underset{Base}{H_2O} \rightleftharpoons CH_3COO^- + H_3O^+$$

(e) Each cation behaves as an acid and each anion behaves as base. However, some of them behave as amphoteric by nature.

$$\underset{Acid}{Na^+} + 2H_2O \rightleftharpoons NaOH + H_3O^+$$

$$\underset{Base}{Cl^-} + H_2O \rightleftharpoons HCl + OH^-$$

$$\text{Acid} \xrightarrow{-H^+} \text{Conjugate Base Base} \xrightarrow{+H^+} \text{Conjugate Acid}$$

$$HCl \xrightarrow{-H^\oplus} Cl^\ominus$$

$$NH_3 \xrightarrow{+H^\oplus} NH_4^+$$

$$C_2H_2 \xrightarrow{-H^+} C_2H^- C_2 \xrightarrow{+H^+} C_2H_6$$

$$C_6H_5NH_2 \xrightarrow{+H^+} C_6H_5NH_3^+$$

$$C_6H_5OH \xrightarrow{-H^+} C_6H_5O^- Al(OH)_3 \xrightarrow{+H^+} Al(aq)$$

According to Bronsted-Lowry, all acid-base reactions involve two conjugate acid-base pairs

$Acid_1 + Base_2 \rightarrow Base_1 + Acid_2$

$Acid_1$ has its conjugate $base_1$ in product and $base_2$ has its conjugate $acid_2$

$$\underset{B_1}{NH_3} + \underset{A_2}{NH_3} \rightarrow \underset{A_1}{NH_4^+} + \underset{B_2}{NH_2^-}$$

Limitations of Bronsted-Lowry Concept: This classification also fails to explain the behaviour of acids and bases in non-aqueous solvents, as well as acid-base neutralisation in the absence of solvents; e.g., BF_3, an electron deficient molecule reacts directly with NH_3 to show the formation of $[F_3B \neg NH_3]$ molecule.

Retain In Memory: All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases. This is because an Arrhenius acid is a substance which can give a H^+ ion whereas a Bronsted acid is a substance which can donate a proton which is also a H^+ ion. On the other hand, an Arrhenius base is a substance which gives the OH^-ion in the solution but Bronsted base is a substance which accepts a proton. It may not contain OH^- ion. For example, NaOH is an Arrhenius base because it gives OH^- ion in aqueous solutions but not a Bronsted base because it cannot accept a proton.

5.3 Levelling Effect

The levelling effect, or solvent levelling, is an effect that places an upper-limit on the strength of an acid (or base) in a given solvent when the solvent is Lewis acidic or Lewis basic. The strength of a strong acid is limited ("levelled") by the basicity of the solvent. Similarly, the strength of a strong base is levelled by the acidity of the solvent. When a strong acid is dissolved in water, it reacts with it to form the hydronium ion (H_3O^+) in the following reaction:

$A + H_2O \rightarrow A^- + H_3O^+$

Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+. Therefore, no acid stronger than H_3O^+ exists in H_2O. Similarly, when ammonia is the solvent, the strongest acid is ammonium (NH_4^+), thus HCl and a super acid (one with a low pKa) exert the same acidifying effect in water.

The same argument applies to bases. In water, OH- is the strongest base. Thus, even though sodium amide ($NaNH_2$) is an exceptional base (pKa of NH_3 ~ 33), in water it is only as good as sodium hydroxide. On the other hand, $NaNH_2$ is a far more basic reagent in ammonia than is NaOH.

Levelling Versus Differentiating Solvents: In a differentiating solvent, various acids dissociate to different degrees and thus, have different strengths. In a levelling solvent, several acids are completely dissociated and are thus of the same strength. A weakly basic solvent has fewer tendencies than a strongly basic one to accept a proton. Similarly, a weak acid has fewer tendencies to donate protons than a strong acid. As a result, a strong acid (such as perchloric acid) exhibits more strongly acidic properties than a weak acid (such as acetic acid) when dissolved in a weakly basic solvent. On the other hand, all acids tend to become indistinguishable in strength when dissolved in strongly basic solvents owing to the greater affinity of strong bases for protons. This is called the levelling effect. Strong bases are levelling solvents for acids; weak bases are differentiating solvents for acids. Because of the levelling effect of common solvents, studies on super acids are conducted in solvents that are very weakly basic such as sulphur dioxide (liquefied) and SO_2ClF (these solvents would be considered differentiating solvents).

MASTERJEE CONCEPTS

- If a strong acid is added to a solvent that it can protonate, such as water, then the acid will protonate the water to produce the hydronium ion, now the strongest acid in the solution. Because of this, acid stronger than the pKa of the conjugate acid of the solvent are all "levelled" to the same strength.
- A similar phenomenon is observed with bases, for example, in water, where any base stronger than hydroxide will simply deprotonate water to produce hydroxide, again providing an upper limit of pK_b beyond which all bases behave the same in that solvent.
- Discriminating solvents are those that do not have a significant levelling effect, because they are themselves not acidic or basic to an appreciable extent. The study of particularly strong acid and bases is often conducted in a levelling solvent.

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5.4 Lewis Concepts (1923)

Bronsted concept was extended to give a new theory by Lewis. According to Lewis:

(a) A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.

(b) An acid base reaction takes place when a base shares an electron pair with an acid. The process is called neutralization or simply, co-ordination. The product is a co-ordinated compound, co-ordinated complex or adduct, made up of an acid portion and a base portion, e.g.,

Acid + Base → Co-ordinate complex

$BF_3 + NH_3 \rightarrow (H_3N \rightarrow BF_3)$

$BF_3 + F^- \rightarrow [BF_4]^-$

$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$

(c) **Lewis acids**

(i) Simple cations: Fe^{2+}, Fe^{3+}, K^+, etc., are all Lewis acids.

Acid strength of simple cations increases with

- An increase in +ve charge on the ion, i. e., $Fe^{2+} < Fe^{3+}$
- A decrease in ionic radius, i. e., $K^+ < Na^+ < Li^+$
- An increase in the effective nuclear charge for atoms, i. e., $Li^+ < Be^{2+} < B^{3+}$

(ii) Compounds whose central atom has an incomplete octet: All compounds having a central atom with a lack of electrons are Lewis acids, e.g., BF_3, BCl_3, $AlCl_3$, RMgX, $MgCl_2$, etc.

Strength of these Lewis acids increases with

- An increase in the nuclear charge of the central atom.
- An increase in the no. and the relative electronegativity of atoms attached on central atoms $SO_2 < SO_3$.
- A decrease in the atomic radius of the central atom. However, these rules show some anomalies, e.g., acidic strength of boron trihalides is $BF_3 < BCl_3 < BBr_3 < BI_3$.

This anomaly to rule (b) has been explained in terms of back bonding.

(iii) Compounds whose central atom can show expansion of octet: SiF_4 and $SiCl_4$ act as Lewis acids because Si can expand its octet using vacant d-orbitals.

Note: The strength of cations as acids can be alternatively expressed in terms of effective nuclear charge. More the effective nuclear charge, greater is the tendency to attract a lone pair of electrons and thus, more is the acidic nature, i. e.,

Acidic nature order: $Li^+ > Na^+ > K^+$

(d) **Lewis Base:** Compounds having electron pair available for co-ordination show Lewis base nature

e.g., $:NH_3$, $:PH_3$, $:PCl_3$, $(CH_3)_2\ddot{O}:$, ligands, i. e., CN^-, CNS^-, OH^-, SH^- etc.

Note: The strength of anions as a base can alternatively be expressed in terms of the electronegativity of the atom. More the electronegativity of the atom carrying negative charge, greater will be its basic nature, i. e.,

Basic nature order: $F^- > Cl^- > Br^- > I^-$

$NH_2^- > OH^- > SH^-$

The Lewis base nature of nitrogen trihalides follows the order: $NF_3 < NCl_3 < NBr_3 < NI_3$.

This may be explained in terms of the electronegativity of halogens. Greater the electronegative difference in N —X bond, more is the partial +ve charge on N-atom and thus, tendency to donate electron pair by N-atom becomes lesser.

Limitations of Lewis Concepts

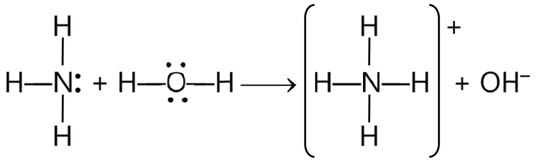
(a) It does not explain the behaviour of protonic acids such as HCl, H_2SO_4, HNO_3, etc., which do not accept electron pair, i. e., do not undergo co-ordination bonding with bases.

(b) It does not predict the magnitude of the relative strength of acids and bases.

(c) It is specially a general approach for the co-ordination compound formation and co-ordination reaction.

(d) Usually, co-ordination reactions are slow. It means that neutralization of acid-base should occur slowly, but these are extremely fast.

Retain In Memory: All Lewis bases are also Bronsted bases but all Bronsted acids may not be Lewis acids. This is because a substance that is capable of giving an electron pair has the tendency to accept a proton. For example, consider the reaction:



Here, NH_3 is Lewis base as well as Bronsted base. However, in the above case, H_2O is a Bronsted acid because it is giving a proton but is not a Lewis acid because it is electronically satisfied. Similarly, HCl, H_2SO_4 etc. are Bronsted acids but not Lewis acids as they cannot accept pairs of electrons.

Some Conceptual Questions

Q.1 Sulphuric acid is a very strong acid yet it can also act as a base in some reactions. Explain how?

Ans. Sulphuric acid (H_2SO_4) is a weaker acid with respect to perchloric acid ($HClO_4$). H_2SO_4 can take up a proton from $HClO_4$ to form $H_3SO_4^+$. Hence, it acts as a base in this reaction.

Q.2 Metal ions like Ag^+, Cu^{2+}, etc. can also act as acids. Explain how?

Ans. Metal ions (cations) can accept lone pairs of electrons. Hence, they act as Lewis acids.

5.5 Classification of Solvents

Table 6.1: Classification of solvents

Name		Characteristic	Example
(i)	Protophilic	Tendency to accept protons	H_2O, liq. NH_3, CH_3OH etc
(ii)	Protogenic	Tendency to give protons	H_2O,CH_3COOH, HCl etc.
(iii)	Amphiprotic	Act as both (i) & (ii)	H_2O, NH_3, CH_3OH etc.
(iv)	Aprotic	Neither donate nor accept protons	Benzene

Nature of Oxides

(a) Basic character of oxides decreases along the period and increases down the group, e.g.,

Basic character decreases along the period:

$Na_2O > MgO > Al_2O_3 > SiO_2 > P_2O_5 > SO_2 > Cl_2O_3$

Basic character increases down the group:

(i) $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$

(ii) $OF_2 < Cl_2O < Br_2O < I_2O$

(b) Oxides of metals are normally basic (few exceptions are amphoteric), oxides of non-metals are normally acidic. CO, N_2O and NO are neutral. _

Table 6.2: Classifications of oxides

Basic oxides	Acidic oxides	Amphoteric
K_2O, CaO, MgO CuO, Fe_2O_3, etc. All are metal ox-ides	CO_2 CO(Neutral) $\underbrace{N_2O, NO}_{\text{Neutral}}$, N_2O_3, N_2O_4, N_2O_5, F_2O, SiO_2, P_2O_3, P_2O_5, SO_2, etc. (All are non-metal oxides)	ZnO, Al_2O_3, BeO,SnO_2, (All are metal oxides) As_2O_3 (metalloid oxide)

Note: 1. CO acts as an acid, if allowed to react with NaOH at high P and T.

$$CO + NaOH \xrightarrow{P.T} HCOONa$$

(c) CO acts as Lewis base (ligand) in complex formation.

(i) Oxides of non-metals having same oxidation no. of non-metal in their respective oxo-acids are known as acid anhydrides. The acid anhydrides on dissolution in water give their respective oxo-acids.

Table 6.3: Oxo-acids of non-metals

Acid anhydride	Oxo-acids
Non-metal oxides	HPO_3, H_3PO_4
P_2O_5	HPO_2, H_3PO_3
P_2O_3	H_2SO_3
SO_2	H_2SO_4
SO_3	H_2CO_3
CO_2	HNO_3
N_2O_5	HNO_2
N_2O_3	
Metal Oxides	
CrO_3	H_2CrO_4
Mn_2O_7	$HMnO_4$

(ii) Greater the number of oxygen atoms and more is the electronegative nature of the atom of oxo-acid, stronger is the acid.

E.g., $HClO_4 > HClO_3$

Note: However, this rule is not obeyed in oxo-acids of phosphorus.

$H_3PO_2 > H_3PO_3 > H_3PO_4$

K_{a1} 6. 3 × 10^{-2} 1. 5 × 10^{-2} 7. 5 × 10^{-3}

This is due to overall inductive effect of the added O-atom on the central atom which decreases from H_3PO_2 to H_3PO_4 on account of increasing number of unprotonated O-atoms from H_3PO_2 to H_3PO_4.

(iii) On the other hand, basic anhydrides are the oxides of metals which form an alkali in water, e.g., Na_2O is basic anhydride of NaOH.

(iv) Some oxides of metals are amphoteric as they react with both acid and base,

e.g. ZnO, As_2O_3, PbO, Sb_2O_3, Al_2O_3, etc.

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

(v) Oxides of some metals in higher oxidation state, acidic in nature.

e.g., Mn_2O_7, CrO_3, MoO_3, WO_3, etc.

$Mn_2O_7 + H_2O \xrightarrow{H^+} 2HMnO_4$

$CrO_3 + H_2O \xrightarrow{H^+} H_2CrO_4$

5.6 Relative Strength of Acids and Bases

The ratio of strengths of acids is known as relative strength, i. e.

$$\text{Relative Strength} = \frac{\text{Strength of I acid}}{\text{Strength of II acid}}$$

For weak acids: Relative strength for weak acids can be derived as follows:

Say acid HA_1 and HA_2 are taken, then for, $HA_1 \rightleftharpoons H^+ + A_1^-$; $K_{a1} = c_1\alpha_1^2$

For, $HA_2 \rightleftharpoons H^+ + A_2^-$; $K_{a2} = c_2\alpha_2^2$

$$\text{Now, relative strength} = \frac{[H^+]\text{ furnished by acid } HA_1}{[H^+]\text{ furnished by acid } HA_2} = \frac{c_1\alpha_1}{c_2\alpha_2} = \frac{c_1\sqrt{\left(\frac{K_{a1}}{c_1}\right)}}{c_2\sqrt{\left(\frac{K_{a2}}{c_2}\right)}} = \sqrt{\frac{(K_{a1}\cdot c_1)}{(K_{a2}\cdot c_2)}} \quad \left[\because \alpha = \sqrt{\frac{K_a}{c}}\right]$$

If concentrations are same, then

$$\text{Relative strength} = \sqrt{\frac{K_{a1}}{K_{a2}}} \quad \text{...(5)}$$

For strong acids: Relative strength for strong acids can be derived by studying the rate constant (see chemical kinetics) of ester hydrolysis or inversion of cane sugar in the presence of different acids.

$$\text{Relative strength} = \frac{\text{Rate constant for the reaction catalysed by I acid}}{\text{Rate constant for the reaction catalysed by II acid}} \quad \text{...(6)}$$

Some definitions which will be important

Retain in memory: Just as we have pH = $-\log[H^+]$, similarly, we have

$pOH = -\log[OH^-]$, $pK_a = -\log K_a$, $pK_b = -k_b$, $pk_w = -\log k_w$ where K_a and K_b represent ionization constants of the acid and the base respectively and K_w is ionic product of water.

This can be effectively used as a problem solving trick.

5.7 Acid-Base Neutralization: Salt

(a) **Simple Salts:** The salts formed by the neutralization process, i. e., the interaction between acid and base, are termed as simple salts. These are of three types:

(i) **Normal salts:** The salts formed by the loss of all possible protons of an acid (replaceable hydrogen atoms as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen or a hydroxyl group, e.g., NaCl, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_3BO_3, Na_2HPO_3 (one H-atom is not replaceable as H_3PO_3 is a dibasic acid), NaH_2PO_2 (both H-atoms are not replaceable as H_3PO_2 is a monobasic acid), etc.

(ii) **Acid Salts:** Salts formed by the incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen atoms. These salts when neutralized by bases form normal salts. This is because $NaHCO_3$ + NaOH cannot exist together in a mixture, e.g., $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4, etc.

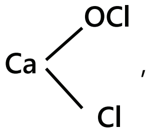
(iii) **Basic Salts:** Salts formed by the incomplete neutralisation of poly acidic bases are called basic salts. Such salts still contain one or more hydroxyl groups. These salts when neutralized by acids form normal salts, e.g., Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$, etc.

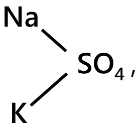
(b) **Double Salts:** The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only and lose their identity in the solution state.

(c) **Complex Salts:** Complex salts are formed by the combination of simple salts or molecular compounds. These are stable in the solid state as well as retain their identity in solutions.

$$\frac{FeSO_4 + 6KCN}{\text{Simple salts}} \rightarrow \frac{K_4[Fe(CN)_6]}{\text{Complex salts}} + K_2\,SO_4$$

(d) **Mixed Salts:** The salt which furnishes more than one cation (excluding H^+) or more than one anion (excluding OH^-) when dissolved in water is called in mixed salt.





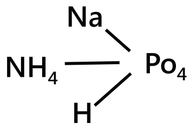


Illustration 16: What type of salts are Na_2HPO_3 and NaHS? **(JEE MAIN)**

Sol: Na_2HPO_3 is obtained through a reaction between NaOH and H_3PO_3 (a dibasic acid), i. e. Both displaceable hydrogens are replaced by Na. No acidic hydrogen is left. Hence, Na_2HPO_3 is a normal salt. NaHS is obtained by the replacement of one acidic hydrogen of H_2S by Na (on reaction with NaOH). Hence, NaHS is an acidic salt.

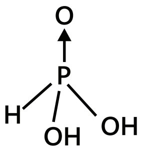


Illustration 17: Arrange the given compounds in the decreasing order of basicity on the basis of the Bronsted-Lowry concept: BaO, CO_2, SO_3, B_2O_3, Cl_2O_7 **(JEE MAIN)**

Sol: According to the Bronsted-Lowry theory, base is a substance which can accept a proton.

$BaO + H_2O \rightleftharpoons Ba(OH)_2$ (Basic) $CO_2 + H_2O \rightleftharpoons H_2CO_3$ (Weakly acidic)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (Strongly acidic) $B_2O_3 + 3H_2O \rightleftharpoons 2\,H_3BO_3$ (Very weakly acidic)

$Cl_2O_7 + H_2O \rightleftharpoons 2\,HClO_4$ (Very strongly acidic)

Hence, in the decreasing order of basicity, we have $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$.

Illustration 18: Why is the PO_4^{3-} ion is not amphiprotic? **(JEE MAIN)**

Sol: An amphiprotic ion is one which can donate protons as well as accept protons. PO_4^{3-} ion can accept proton(s) but cannot donate any proton. Hence, PO_4^{3-} is not amphiprotic.

Illustration19: Classify the following as an acid or base according to Bronsted-Lowry theory and name their corresponding conjugate base or acid **(JEE MAIN)**

(i) NH_3 (ii) CH_3COO^- (iii) H_3O^+ (iv) H^+ (v) HOO^- (vi) $S_2O_8^{2-}$.

Sol: According to the Bronsted-Lowry theory, an acid is a substance which can donate a proton while a base is a substance which can accept a proton.

(i) NH_3 is a Bronsted base because it can accept a proton. Its conjugate acid is NH_4^+ .

NH_3 is also a Bronsted acid because it can donate a proton.

Its conjugate base NH_2^-.

(ii) CH_3COO^- is a Bronsted base ($CH_3COO^- + H^+ \rightarrow CH_3COOH$).

Its conjugate acid is CH_3COOH.

(iii) H_3O^+ is a Bronsted acid ($H_3O^+ \rightarrow H_2O + H^+$). Its conjugate base is H_2O.

(iv) H^- is a Bronsted base ($H^- + H^+ \rightarrow H_2$ in the reaction $H^- + H_2O \rightleftharpoons H_2 + OH^-$). Its conjugate acid is H_2.

(v) HOO^- is a Bronsted acid ($HOO^- \rightarrow O_2^{2-} + H^+$ in the reaction $HOO^- + H_2O \rightarrow O_2^{2-} + H_3O^+$).

Its conjugate acid is O_2^{2-} (peroxide ion).

(vi) $S_2O_8^{2-}$ is a Bronsted base ($S_2O_8^{2-} + 2H^+ \rightarrow 2HSO_4^-$ in the reaction $S_2O_8^{2-} + 2H_2O\ _7\ 2HSO_4^- + 2OH^-$).

Its conjugate acid is HSO_4^- .

Illustration 20: Classify each of the following substances into an acid or base or both and mention the concept/ concepts on the basis of which you can do so. **(JEE ADVANCED)**

(i) HCl (aq) (ii) NH_3 (g) (iii) Na_2CO_3 (aq) (iv) CH_3COOH (aq) (v) CO_2 (g) (vi) BF_3 (vii) Ag^+

(viii) CN^- (ix) H_2O (x) H_2SO_4 (xi) HCO_3^- (xii) SiF_4

Sol: (i) HCl (aq) — Acid (Arrhenius concepts and Bronsted - Lowry concept)

(ii) NH_3 (g) — Base (Bronsted concepts and Lewis concept)

(iii) Na_2CO_3 (aq) — Base (Bronsted concept)

(iv) CH_3COOH (aq) — Acid (Arrhenius concepts and Bronsted concept)

(v) CO_2 (g) — Acid (Bronsted concepts and Lewis concept)

(vi) BF_3 — Acid (Lewis concept)

(vii) Ag^+ — Acid (Lewis concept)

(viii) CN^- — Base (Lewis concept)

(ix) H_2O — Both an acid and base, i. e., amphoteric (Bronsted concept)

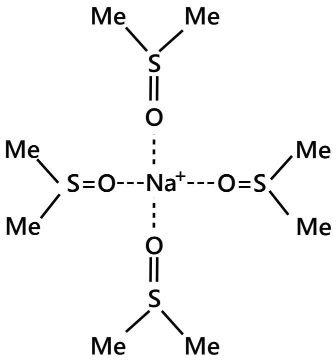
(x) H_2SO_4 — Both an acid and base, i. e., amphoteric (Bronsted concept)

(xi) HCO_3^- — Both an acid and base, Le. t amphoteric (Bronsted concept)

(xii) SiF_4 — Acid (Lewis concept), as silicon can expand its octet.

Illustration 21: How a polar aprotic solvent acts to dissolve an ionic solute? Also report one polar aprotic solvent which can dissolve NaCl. **(JEE ADVANCED)**

Sol: A polar aprotic solvent strongly solvates the cation by ion-dipole attraction using the negative end of its dipole which is exposed (aprotic solvent solvate anion and cations both by forming H-bonds and thus, stabilise them to exist freely in the solution state). Thus, the anion is left free because it is only very weakly solvated by the positive end of the dipole which is deeply buried within the molecules. A polar aprotic solvent is DMSO, i. e., dimethyl sulphoxide.



Cl^- (free; since bulky methyl groups prevent Cl^- to approach + ve end i. e., S-atom of solvent).

6. pH VALUE

As $[H^+]$ increases, the effective concentration of H^+ ions becomes progressively less than might be expected, because of the increased inter ionic attractions at higher concentrations. A more precise definition of pH is pH = $-\log a_{H^+}$ where, a_{H^+} is the hydrogen ion activity (or the effective H^+ concentration). The H^+ activity is obtained by multiplying $[H^+]$ by a suitable activity coefficient based on thermodynamic measurements. They approach 1. 0 for very dilute solutions but get smaller as concentration increases.

The pH Scale

It is clear from the dissociation of water at 25°C.

$H_2O\ H^+ + OH^-$

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

For pure water, $[H^+] = [OH]$

$\therefore [H^+]^2 = 10^{-14}$ and $[H^+] = 10^{-7}$

Thus, if $[H^+] > 10^{-7}$ solution is acidic,i. e.,pH < 7

$< 10^{-7}$ solution is alkaline,i. e.,pH > 7

$= 10^{-7}$solution is netural,i. e.,pH = 7

pH of a solution decreases as $[H^+]$ in the solution increases. For all practical purposes, the pH scale extends from 0 to 14 (at 25°C). A solution of pH = 0 is acidic and pH = 14 is alkaline.

The mid-point of the scale at pH = 7 represents neutrality, pH below 7 being increasingly acidic and those above 7 increasingly basic.

Theoretically, pH values greater than 14 are possible for concentrated strong bases and negative pH values are possible for concentrated strong acids, but it is for dilute solutions that the pH scale is most useful. The pH for concentrated solution should be derived by

pH = $-\log a_{H^+}$ where a_{H^+} represents active mass of H^+ ions.

For any aqueous solution at 25°C it must be true that

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

No matter how acidic or basic a solution might be. It must contain H^+ and OH^- ions and the product of effective molar concentration equal to 10^{-14} 'OR $K_{w.}$

Also. $\log[H^+] + \log[OH] = -14$

Or $-\log[H^+] + (-\log(OH)) = 14$

Or pH + pOH = 14

Note:

(1) The relationship between pH and acidic nature is an inverse one. Thus, as the pH goes up, the acidic nature goes down.

(2) The pH of a mixture of two weak acids can be obtained as:

$$pH = \sqrt{K_{al} \times c_1 + K_{a2} \times c_2}$$

However, if both acids are too weak (pK_a ranging in 10^{-10} to 10^{-14}) or the solutions are too dilute the alternate formula from charge-balance ____ method is given as

$$\left[H^+\right] = \sqrt{K_{a_1} c_1 + K_{a_2} c_2 + K_w}\ .$$

(3) The pH of a dipolar ion molecule say glycine ($H_2N — CH_2 — COOH$) at isoelectric point can be represented as $\overset{+}{N}H_3 — CH_2 — COO^{\ominus}$. The pH at isoelectric point can be calculated or evaluated by the formula: pH = $\dfrac{pK_{a_1} + pK_{a_2}}{2}$

(4) Same is the case with Amphiprotic Salts

A weak acid in water

(a) if $c_0 \geq 2500\ K_{a,}$ $[H^+] \approx \sqrt{K_a c_o + K_w}$

Mostly, K_w is insignificant and is neglected so $[H^+] \approx \sqrt{K_a c_0}$

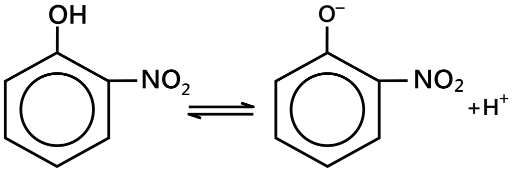
(5) This is sometimes called Ostwald's Dilution Law.

Total concentration of $[H^+]$ or $[H_3O^+]$ in a mixture of weak acid and a strong acid = $\dfrac{C_2 + \sqrt{C_2^2 + 4K_a C_1}}{2}$

Where, C_1 is the concentration of weak acid (in mol litre^{-1}) having a dissociation constant of K_a and C_2 is the concentration of a strong acid.

Illustration 22: A saturated solution of o-nitrophenol has a pH equal to 4.53. What is the solubility of o-nitrophenol in water? pK_a for o-nitrophenol is 7.23 **(JEE ADVANCED)**

Sol: According to Ostwald's dilution law $[H^+] = c\alpha$, where $\alpha = \sqrt{\dfrac{K_a}{c}}$ using the log term of this expression, concentration can be determine as pH = $\dfrac{1}{2}\ pK_a - \dfrac{1}{2}\ \log C$



$$\therefore [H^+] = c\alpha = c \times \sqrt{\frac{K_a}{c}} = \sqrt{K_a.c}$$

$$\text{Or } pH = -\log[H^+] = \frac{1}{2}\ pK_a - \frac{1}{2}\ \log C$$

$$\text{Or } 4.53 = \frac{1}{2} \times 7.23 - \frac{1}{2}\ \log C$$

C = 0.015 M

∴ Solubility in g/litre = 0.015 × mol. Wt. of compound

= 0.015 × 139 = 2.085 g/litre

7. BUFFER SOLUTIONS

A solution which has reserve acidic nature or alkaline nature or a solution with reserve pH is buffer solution. A solution whose pH does not change significantly on addition of a small amount of acid or alkali.

(a) General Characteristics of a Buffer Solution

- **(i)** It has a definite pH, i. e., it has reserve acidity or alkalinity.
- **(ii)** Its pH does not change on standing for long.
- **(iii)** Its pH does not change on dilution.
- **(iv)** Its pH is slightly changed by the addition of a small quantity of an acid or a base.

(b) Buffer solutions can be obtained by:

- **(i)** By mixing a weak acid with its salt with a strong base,
  - $CH_3COOH + CH_3COONa$
  - Boric acid + Borax
  - Phthalic acid + Potassium acid phthalate
- **(ii)** By mixing a weak base with its salt with a strong acid,
  - NH_4OH + NH4Cl
  - Glycine + Glycine hydrochloride
- **(iii)** By a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.
- **(iv)** By a mixture of an acid salt and a normal salt of a polybasic acid, e.g.,$Na_2HPO_4 + Na_3PO_4$ or a salt of a weak acid and a weak base, such as CH_3COONH_4.

(c) **Basic buffer:** Consider the case of the solution containing NH_4OH and its salt NH_4Cl. The solution will have NH_4OH molecule. NH_4^+ ions, Cl^- ions. OH^- ions and H^+ ions.

$NH_4OH\ NH_4^+ + OH^-$ (Feebly ionised)

$NH_4Cl\ NH_4^+ + Cl^-$ (Completely ionised)

$H_2O\ H^+ + OH^-$ (Very feebly ionised)

When a drop of NaOH is added, the added OH^- ions combine with NH_4^+ ions to form feebly ionised NH_4OH whose ionization is further suppressed due to the common ion effect. Thus, pH is not disturbed considerably.

$NH_4^+ + OH^- NH_4OH$

↑

(From strong base)

When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.

$NH_4OH + H^+\ NH_4^+ + H_2O$

↑

(From strong acid)

Thus, pH of the buffer is practically unaffected.

A similar thing will also happen in an Acidic Buffer. The overall picture is represented in the following diagram.

Acid Buffer ($CH_3COOH + CH_3COONa$)

Basic Buffer ($NH_4OH + NH_4\ Cl$)

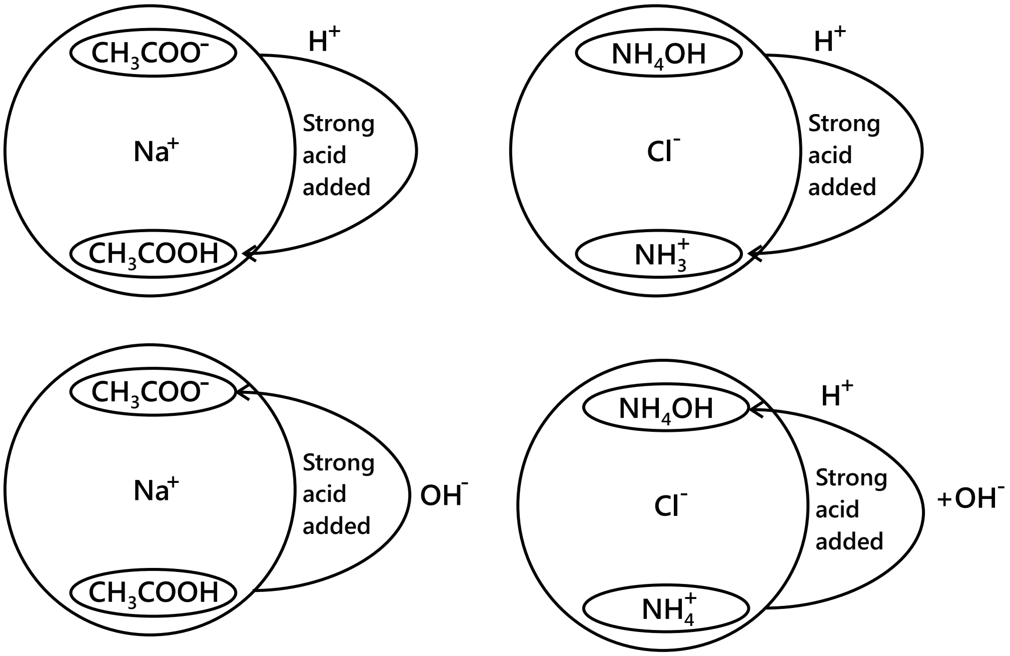


Figure 6.2: Mechanism of buffer solution

7.1 Henderson's Equation

pH of a Buffer-Mixtures

Consider a buffer mixture say an acidic buffer, e.g., HA + NaA

HA $H^+ + A^-$ and NaA $\rightarrow Na^+ + A^-$

Applying law of mass action to dissociation equilibrium of HA.

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

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

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

$$\text{Or pH} = -\log K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{Or pH} = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} \quad \text{.... (11)}$$

Where, $[A^-]$ = [conjugate base] or [conjugate base of HA] obtained from concentration of the salt which is 100% ionised. All the $[A^-]$ come from the salt since the dissociation of HA in the presence of NaA is appreciably suppressed.

[HA] = [Acid] = Initial concentration of acid since it is almost unionised in presence of NaA

Similarly for basic buffer mixture, one can write

$$\text{pOH} = pK_b + \log \frac{[\text{Conjugate base}]}{[\text{Base}]} \quad \text{.... (12)}$$

Key concept: When $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$, then pH = 1 + pK_a

And when $\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{10}$, then pH = $pK_a - 1$

So, weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid has a pKa of about 4. 8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3. 8 to 5. 8.

7.2 Buffer Capacity

Buffer capacity: The property of a buffer solution to resist an alteration in its pH value is known as its buffer capacity. It has been found that if the ratio $\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\frac{[\text{Salt}]}{[\text{Base}]}$ is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as number of moles of acid or base added in one litre of solution as to change the pH by unity, i. e.

$$\text{Buffer capacity } (\phi) = \frac{\text{No. of moles of acid or base added to 1 litre}}{\text{Change in pH}} \text{ or } (\phi) = \frac{\partial b}{\partial (\text{pH})}$$

where, $\partial b \rightarrow$ number of moles of acid or base added to 1 litre solution and

$\partial(\text{pH}) \rightarrow$ change in pH.

Buffer capacity is maximum:

(i) When [Salt] = [Acid], I. e.,pH $= pK_a$ for acid buffer

(ii) When [Salt] = [Base], i. e., pOH $= pK_b$ for base buffer

Under the above conditions, the buffer is called efficient.

Uses

(a) Buffer Solutions in Analytical Chemistry

- **(i)** To determine the pH with the help of indicators.
- **(ii)** For the removal of the phosphate ion in the qualitative inorganic analysis after the second group using $CH_3COOH + CH_3COONa$ buffer.
- **(iii)** For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer, $CH_3COOH + CH_3COONa$, is used.
- **(iv)** For precipitation of hydroxides of the third group of qualitative analysis, a buffer, $NH_4Cl + NH_4OH$, is used.
- **(v)** A buffer solution of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ is used for the precipitation of carbonates of fifth group in qualitative inorganic analysis.
- **(vi)** The pH of intracellular fluid, blood is naturally maintained. This maintenance of pH is essential to sustain life because, enzyme catalysis is pH sensitive process. The normal pH of blood plasma is 7. 4. Following two buffers in the blood help to maintain pH (7. 4):
  - Buffer of carbonic acid (H_2CO_3 and $NaHCO_3$)
  - Buffer of phosphoric acid ($H_2PO_4^-$, HPO_4^{2-})

(b) Buffers are used in industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc. Buffers are also employed in agriculture, dairy products and in the preservation of various types of foods and fruits.

Illustration 23: How many moles of HCl will be required to prepare one litre of buffer solution (containing NaCN + HCl) of pH 8. 5 using 0. 01 g formula weight of NaCN . K_{HCN} = 4. 1 × $10^{-10?}$ **(JEE MAIN)**

Sol: We are provided with concentration of hydrogen ion and equilibrium constant, so we can find out the concentration by using following expression,

pH = – log K_a + log c

Addition of HCl to NaCN results in a buffer solution, when HCl is added in lesser amount than NaCN, i. e.

$$NaCN + HCl \rightarrow NaCl + HCN$$

	NaCN	HCl	NaCl	HCN
Moles added	0. 01	a	0	0
Moles after reaction	(0. 01 - a)	0	a	a

Thus, buffer solution contains a moles of HCN and (0. 01-a) moles of NaCN

$$\because \ pH = -\log K_a + \log \frac{0.01-a}{a}$$

$$\text{Or } 8.5 = -\log[4.1 \times 10^{-10}] + \log \frac{0.01-a}{a}$$

$\therefore$ a = 8. 85 × 10^{-3} moles of HCl

Illustration 24: Calculate [H^+] and [$CHCl_2CO^-$] in a solution that is 0. 01 M HCl and 0. 0. 1 M in $CHCl_2COOH$. K_a for $CHCl_2COOH$ is 5× 10^{-2} **(JEE MAIN)**

Sol: $CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$

$CHCl_2COOH$	$CHCl_2COO^-$	H^+
c	0	0. 01
$c(1-\alpha)$	$c\,\alpha$	$c\,\alpha$ + 0. 01

$$\therefore K_a = \frac{c\alpha \times (c\alpha + 0.01)}{c(1-\alpha)} = \frac{\alpha(0.01\alpha + 0.01)}{(1-\alpha)} = 5\times10^{-2}$$

$$\text{Or } \frac{0.01\alpha(1+\alpha)}{(1-\alpha)} = 5\times10^{-2}$$

Or $\alpha^2 + 6\alpha - 5 = 0$

$\therefore \alpha$ = 0. 7416

$\therefore$[$CHCl_2COO^-$] = 0. 01 × 0. 7416 = 7. 416 × 10^{-3}M

[H^+] = 7. 416 × 10^{-3} + 0. 01 = 0. 0174 M

Illustration 25: 20 ml of 0. 2 M sodium hydroxide is added to 50 mL of 0. 2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0. 2 M NaOH required to make the pH of solution 4. 74. The ionization constant of acetic acid is 1. 8 × 10^{-5} **(JEE ADVANCED)**

Sol: Fist find out the no of moles NaOH present in 20 ml and Acetic acid present in 50 ml and remaining problem can be solved using Henderson's equation.

No. of moles of NaOH in

$$20 \text{ mL} = \frac{0.2}{1000} \times 20 = 0.004$$

$$\text{No. of moles of acetic acid in 50 mL} = \frac{0.2}{1000} \times 50 = 0.01$$

When NaOH is added, CH_3COONa is formed.

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

1 mole 1 mole 1 mole 1 mole

No. of moles of CH_3COONa in 70 mL solution =0. 004

No. of moles of CH_3COOHin 70 mL solution = (0. 01 – 0. 004) = 0. 006

Applying Henderson’s equation,

$$pH = \log \frac{[Salt]}{[Acid]} - \log k_a = \log \frac{0.004}{0.006} - \log 1.8 \times 10^{-5} = 4.5687$$

On further addition of NaOH, the pH becomes 4. 74.

$$pH = \log \frac{[Salt]}{[Acid]} - \log k_a = \log \frac{[Salt]}{[Acid]} - \log 1.8 \times 10^{-5}$$

$$\text{or } \log = \frac{[Salt]}{[Acid]} = pH + \log 1.8 \times 10^{-5} = (4.74 - 4.7448) = -0.0048$$

$$\text{So,}\log = \bar{1}.9952$$

$$\frac{[Salt]}{[Acid]} = 0.9891$$

Let ‘x’ moles of NaOH be Added

[Salt] = (0. 004 + x) mole

[Acid] = (0. 006 – x) mole

$$\frac{0.004 + x}{0.006 - x} = 0.9891$$

$$x = 0.00097 \text{ moles}$$

Illustration 26: What volume of 0. 10 M sodium formate solution should be added to 50 mL of 0. 05 M formic acid to produce a buffer solution of pH 4. 0? pK_a for formic acid is 3. 80. **(JEE ADVANCED)**

Sol: Let x mL of 0. 10 M sodium formate be added.

No. of moles in x mL of 0. 10 M sodium formate = $\frac{0.10}{1000} \times x$

No. of moles in 50 mL of 0. 05 M formic acid = $\frac{0.05}{1000} \times 50$

$$\frac{[Sod.\ formate]}{[Formic\ acid]} = \frac{\frac{0.10 \times x}{1000}}{\frac{0.05 \times 50}{1000}} = \frac{0.10x}{2.5} = 0.04x$$

Applying the equation,

$$pH = \log \frac{[Salt]}{[Acid]} + pK_a$$

$$4.0 = \log 0.04x + 3.8 = \log 0.04x = 2.0, 0.04x = \text{Antilog } 2.0$$

x = 39. 6 mL

8. SALT HYDROLYSIS

Salt hydrolysis is the phenomenon of interaction of cations and anions of a salt with H_2O in order to produce an acidic nature or an alkaline nature.

Salt + Water $\rightleftharpoons$ Acid + Base

The process of salt hydrolysis is actually reverse the process of neutralization.

Note: The net effect of dissolving a salt (which undergoes hydrolysis) is to break up the water molecules (hydrolysis) to produce a weak acid or weak base or both and thus, phenomenon is always endothermic.

Case I: Salts made up from a Strong Acid and Weak Base

1. Such salts include NH_4Cl, NH_4NO_3, $CuSO_4$, $FeCl_3$, etc.

2. The solution of such salts show acidic character on hydrolysis which may be explained as follows; hydrolysis which may be explained as follows; consider a salt NH_4Cl of this category

$$NH_4Cl + H_2O \rightleftharpoons \underset{\text{(Weak)}}{NH_4OH} + \underset{\text{(Strong)}}{HCl}$$

or $NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$

or $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

The reaction equilibrium suggests that NH_4Cl on dissolution in water shows the interaction of NH_4 to react with H_2O to produce NH_4OH, a weak base having a low degree of dissociation. Furthermore, the dissociation of NH_4OH is also suppressed due to the unhydrolysed NH_4^+ ions and thus, after interaction the (H^+) in the solution increases and the solution acquires an acidic nature.

3. In this category of salt, it is the cation that undergoes hydrolysis.

4. The pH of category of salt is always lesser than 7.

Case II: Salts made up from a Strong Base and Weak Acids

1. This category includes salts such as KCN. CH_3COONa, Na_2S, HCOOK, etc.

2. The solutions of such salts in water show alkaline character on hydrolysis, eg., CH_3COONa.

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^+$

3. In this category of salt, it is the anion that undergoes hydrolysis.

4. The pH of this category of salt is always greater than 7.

Case III: Salts of Weak Acids and Weak Base

1. This category includes salts such as CH_3COONH_4,

$(CH_3COO)_2$ Be, $BeCO_3$, $(NH_4)_3$ PO_4, BeC_2O_4, etc.

2. The solutions of such salts in water shows an almost neutral character on hydrolysis, e.g., CH_3COONH_4.

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

If $K_{CH_3COOH} > K_{NH_4OH}$ solution is acidic,

$K_{CH_3COOH} < K_{NH_4OH}$ solution is alkaline

3. Both the cation and anion of the salt undergo hydrolysis.

4. The pH of this category of salt is nearly equal to 7, this however, depends upon the respective values of the dissociation constants of the acids and bases by which a salt is formed.

Case IV: Salts of Strong Acids and Strong Bases

1. This category includes salts such as KNO_3, NaCl, K_2SO_4, etc .

2. The solution of such salts in water is neutral and this category of salts does not undergo salt hydrolysis.

3. Neither the cation nor anion undergo hydrolysis.

4. The pH of solution is equal to7.

The Hydrolysis Constant and Degree of Hydrolysis

Consider a salt say NH_4 Cl (Case I) in water. Let c mol/litre is concentration of salt and h is its degree of hydrolysis then,

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Before hydrolysis	1	0	0
After hydrolysis	(1 – h)	h	h

$\therefore$ At equilibrium $[NH_4^+] = (1-h)c$, $[NH_4OH] = c \cdot h$, $[H^+] = c \cdot h$

$[H+]=c.\ h$

Therefore, according to law of mass action

$$K = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]} \text{ or } K \times [H_2O] = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$\text{Or } K_H = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad \text{.........(16)}$$

Where K_H is hydrolysis constant of salt NH_4Cl or NH_4^+ ion. Also we have for weak base NH_4OH

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{. . .... . (17)}$$

There, by Eqs. (16) and (17)

$K_H \times K_b = [H^+][OH^-] = k_w$

$$\text{Or } K_H = \frac{K_w}{K_b} \qquad \text{....... . (18)}$$

Also, by Eq. (16)

$$K_H = \frac{ch \cdot ch}{c(1-h)} = \frac{c^2h^2}{c(1-h)} = \frac{ch^2}{(1-h)}$$

Since h is small and thus. 1 – h = 1

$$\therefore K_H = ch^2 \text{ or } h = \sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot c}\right)} \qquad \text{.......... . (19)}$$

Similar equations can be obtained for other case

Now, if we discuss all the cases again;

Case I: Strong acid vs weak base

$$K_H = \frac{K_w}{K_b} \text{ and } h = \sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot c}\right)} \qquad \text{.........(20)}$$

$$[H^+] = ch = c\sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w \cdot c}{K_b}\right)} \quad .... (23)$$

Since pH is decided by free H⁺ given by strong acid

$$\therefore pH = \frac{1}{2}\,[\log K_b - \log K_w - \log c] \quad .... (24)$$

$$= \frac{1}{2}\,[pK_w - \log c - pK_b] \quad .... (25)$$

Case II: Weak acid Vs West Base

$$K_H = \frac{K_w}{K_a} \text{ and } h = c\sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_{w.}c}{K_a}\right)} \quad .... (21)$$

$$[OH^-] = ch = NH_3 + HCl \rightarrow NH_4Cl \quad .... (26)$$

Since pH is decided by free OH⁻ given by strong alkali

$$\therefore pOH = \frac{1}{2}\,[\log K_a - \log K_w - \log c] \quad .... (27)$$

$$= \frac{1}{2}\,[pK_w - \log c - pK_a] \quad .... (28)$$

$$\text{Also, } [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{K_w}{\sqrt{\left(\frac{K_w \cdot c}{k_a}\right)}} = \sqrt{\left(\frac{K_w \times K_a}{c}\right)}$$

$$\therefore pH = \frac{1}{2}\,[\log c - \log K_w - \log K_a] \quad .... (29)$$

$$pH = \frac{1}{2}\,[pK_w + pK_a + \log c] \quad .... (30)$$

Case III: Weak acid Vs weak Base

$$K_H = \frac{K_w}{K_a \cdot K_b} \text{ and } h = \sqrt{K_H} = \sqrt{\left(\frac{K_w}{K_a \cdot K_b}\right)} \quad .... (22)$$

In this case both the acid and alkali formed are weak. Consider the weak acid dissociation.

HA H⁺ + A⁻

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

$$\text{Or } [H^+] = \frac{K_a[HA]}{[A^-]} = \frac{K_a ch}{c(1-h)} = K_a \cdot h$$

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

$$\therefore pH = \frac{1}{2}\,[\log_b - \log K_w - \log K_a] \quad .... (31)$$

$$pH = \frac{1}{2}\,[pK_w + pK_a - pK_b] \quad .... (32)$$

Key Note:

It must be noted here that pH of such salt is independent of their concentration.

Case IV: Hydrolysis of amphichroic anion:

Polyprotic acids and K_a values:

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- ; K_{a_1} = 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} ; K_{a_2} = 6.32 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} ; K_{a_3} = 4.5 \times 10^{-13}$$

$$H_3PO_4 + 3H_2O \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

Ka_1 Ka_2 Ka_3

$$K_{a_1} = \frac{[H_3O^+]\left[H_2PO_4^-\right]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$K_{a_2} = \frac{[H_3O^+]\left[HPO_4^{2-}\right]}{[H_2PO^-_4]} = 6.32 \times 10^{-8}$$

$$K_{a_2} = \frac{[H_3O^+]\left[PO_4^{3-}\right]}{[HPO^{2-}_4]} = 4.5 \times 10^{-13}$$

pH of $H_2PO^{2-}{}_4$ in aq. medium $= \dfrac{pka_1 + pka_2}{2}$

pH of $HPO^{2-}{}_4$ in aq medium $= \dfrac{pka_2 + pka_3}{2}$

Table 6.4: Hydrolysis at a Glance

Salt	**Nature**	**Degree**	**Hydrolysis Constant**	**pH**
1. NaCl (Strong acid + Strong base	Neutral Basic Acidic	No hydrolysis		
2. CH_3COONa (Weak acid + Strong base)		$h = \sqrt{\frac{K_w}{CK_a}}$	$K_h = \frac{K_w}{K_a}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
3. NH_4Cl (Strong acid + Weak base)		$h = \sqrt{\frac{K_w}{CK_b}}$	$K_h = \frac{K_w}{K_b}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
4. CH_3COONH_4 (Weak acid + Weak base)		$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$K_h = \frac{K_w}{K_a \times K_b}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

In the case of the salt of the weak acid and weak base, the nature of the medium after hydrolysis is decided in the following manner:

(i) If $K_a = K_b$, the medium will be neutral.

(ii) If $K_a > K_b$, the medium will be acidic,

(iii) If $K_a < K_b$, the medium will be basic.

The degree of hydrolysis of salts of weak acids and weak bases is unaffected by the dilution because there is no concentration term in the expression of degree of hydrolysis.

[**Note:** Degree of hydrolysis always increases with the increase in temperature because at an elevated temperature, the increase in K_w is greater as compared to K_a and K_b]

Illustration 27: A student prepared solutions of NaCl, Na_2CO_3 and NH_4Cl. He put them separately. In three test tubes. He forgot to label them. All solutions were colourless. How should he proceed to know the solutions present in the three test tubes?

Sol: He can test the solutions with blue and red litmus solutions. NaCl solution is neutral. It will neither turn blue litmus red nor red litmus blue. NH_4Cl solution is acidic. It will turn blue litmus red but will have no effect on red litmus. Na_2CO_3 solution is basic, it will turn red litmus blue but will have no effect on blue litmus.

Illustration 28: Calcium lactate is a salt of weak acid and represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.13 mole of salt in 0. 50 litre solution. The pOH of this is 5. 60 Assuming complete dissociation of salt, calculate K_b of lactic acid. **(JEE MAIN)**

Sol: $[Ca\ (LaC)_2] = \dfrac{0.13}{0.5} = 0.\ 26\ M$

$\because$ 1 Mole Ca $(LaC)_2$ gives 2 mole (LaC)

$\therefore$ [LaC] = 0. 26 × 2 = 0. 52 M

$LaC^- + H_2O \rightleftharpoons HLaC + OH^-$

$$\therefore [OH^-] = c\cdot h = c\sqrt{\frac{K_H}{c}} = \sqrt{(K_H\cdot c)} = \sqrt{\frac{K_w\cdot c}{K_a}}$$

where, c is the conc. of anion which undergoes hydrolysis

$$\text{or } 10^{-5.60} = \sqrt{\frac{10^{-14}\times 0.52}{K_a}} \quad \therefore K_a = 8.25\times 10^{-4}$$

Illustration 29: Calculate the pH at the equilibrium point when a solution of 0. 1 M acetic acid is titrated with a solution of 0. 1 M NaOH. K_a for acid = 1.9×10^{-5}. **(JEE MAIN)**

Sol: Calculate the concentration of sodium acetate formed during the reaction between acetic acid and NaOH. Hydroxide ion concentration can be calculated using Ostwald's dilution law as $[OH^-] = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \times c}{K_a}}$

Now from $[OH^-]$ we can determine pOH as,

$pOH = -\log [OH^-]$

pH can be calculated by using following expression,

$pH = 14 - pOH$

Suppose V mL of 0. 1 N acid and 0. 1 N NaOH are used at equivalence point

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

mm before reaction $\quad 0.\,1 \times V \; 0. \quad 1 \times V \quad 0 \quad 0$

$\therefore$ $[CH_3COONa] = \dfrac{0.1\times V}{2V} = \dfrac{0.1}{2} = 0.\,05$ M

For hydrolysis of CH_3COO^-

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$1 \quad 0 \quad 0$

$(1 - h) \quad h \quad h$

$$[OH^-] = c{\cdot}h = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \times c}{K_a}} = \sqrt{\frac{10^{-14}\times 0.05}{1.9\times 10^{-5}}} = 5.\,12 \times 10^{-6}$$

$\therefore$ pOH = 5. 29 $\qquad \therefore$ pH = 8. 71

Illustration 30: Calculate change in pH upon ten-fold dilution of the following solutions:

(a) 0. 1 HCl (b) 0. 1 M acetic acid (c) 0. 1 MNH_4Cl

K_a $CH_3COOH = 1.\,8 \times 10^{-5}$, $K_bNH_3 = 1.\,8 \times 10^{-5}$ **(JEE ADVANCED)**

Sol: (a) HCl is a strong acid. It is completely ionised in solution.

$HCl \rightleftharpoons H^+ + Cl^-$

$[H^+] = 0.\,1 = 10^{-1}$

$pH = -\log[H^+] = -\log(10^{-1}) = 1$

After dilution, $[H^+] = 0.\,01 = 10^{-2}$ M

$pH = -\log[H^+] = -\log 10^{-2} = 2$

pH change from 1 to 2.

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

$(0.\,1 - x) \quad x \quad x$

(CH_3COOH is a weak acid)

$\dfrac{x^2}{0.1} = 1.\,8 \times 10^{-5}$ or $x^2 = 1.\,8 \times 10^{-6}$ or $x = 1.34\times 10^{-3}$

$pH = -\log x = -\log(1.\,34 \times 10^{-3}) = 2.\,87$

After dilution,

$\dfrac{x_1^2}{0.01} = 1.\,8 \times 10^{-5}$ or $x_1^2 = 18 \times 10^{-8}$ or $x_1 = 4.\,24 \times 10^{-4}$ M

$pH = -\log x = -\log 4.\,24 \times 10^{-4} = 3.\,37$

pH change from 2. 87 to 3. 37.

(c) NH_4Cl is a salt of weak base and strong acid

$$\underset{(0.1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$$

$\dfrac{h^2}{0.1} = K_h$ or $h^2 = 0.\,1 \times K_h$

$$\left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.55\times10^{-10}\right] = 0.1 \times 5.55 \times 10^{-10}$$

$h = 7.45 \times 10^{-6} = [H^+]$

$pH = -\log(7.45 \times 10^{-6}) = 5.128$

After dilution, $h^2 = 0.01 \times K_h = 0.01 \times 5.55 \times 10^{-10}$

$h = 2.35 \times 10^{-6}$

$pH = -\log 2.35 \times 10^{-6} = 5.627$

pH change from 5. 128 to 5. 627.

Illustration 31: How much must a 0. 2 M solution of sodium acetate be diluted at 25 °C in order to double the degree of hydrolysis? **(JEE ADVANCED)**

Sol: Let h be the initial degree of hydrolysis

$K_h = Ch^2 = 0.2 \times h^2$ .... (i)

Let the concentration be C_1 when degree of hydrolysis is 2h.

$K_h = C_1(2h)^2$ .... (ii)

Dividing both the equations, $1 = \frac{0.2\times(h^2)}{4C_1\times(h)^2}$

$C_1 = \frac{0.2}{4} = 0.05$ M

Applying, $M_1V_1 = M_2V_2$

$0.2V_1 = 0.05\times V_2$

$V_2 = \frac{0.2}{0.05}V_1 = 4V_1$

The solution be diluted four times.

9. THEORY OF INDICATORS

Theory of acid-base Indicators: Following theories have been given to explain working of acid-base indicators.

1. Ostwald theory

According to this theory

(i) Indicators are either weak acids or weak bases.

(ii) Their unionised molecules possess different colours from those of the ions which are part of the solution.

(iii) An indicator having acidic nature yields a coloured anion while an indicator having basic nature yields a coloured cation in the solution.

(iv) Since the indicators are weak electrolytes, they are not sufficiently ionised in the solution. But in presence of strong acid or alkali, their degree of ionisation is considerably increased and they produce a large number of coloured ions.

(v) An indicator changes colour when the concentration of hydrogen ion (in mol per litre) in the solution is equal to the dissociation constant of the indicator, i. e., indicator is 50% dissociated, e.g. Some of the common acid base indicators are:

Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as:

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons H^+ + \underset{\text{Pink}}{ph^-}$$

Applying law of mass action, $K = \frac{[H^+][Ph^-]}{[HPh]}$

The undissociated molecules of phenolphthalein are colourless while Ph^- ions are pink in colour. In presence of an acid, the ionisation of HPh is practically negligible as the equilibrium shifts to the left hand side due to a high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to the right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart a pink colour to the solution.

Let as derive Henderson's equation for an indicator

$$HIn \quad + \quad H_2O \qquad\qquad H_3^+O \quad + \quad In^-$$

'Acid form' **Base form'**

Conjugate acid - base pair

$K_{In} = \frac{[In^-][H_3^+O]}{[HIn]}$; (K_{In} = Ionization constant of indicator)

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionised in the solution to give Me^+ and OH^- ions.

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

Applying law of mass action,

$K = \frac{[Me^+][OH^-]}{[MeOH]}$

In the presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to the right hand side. Thus, sufficient Me^+ ions are produced which imparts red colour to the solution. On the addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to the left hand side, i. e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionized methyl orange molecules, i. e., yellow.

MASTERJEE CONCEPTS

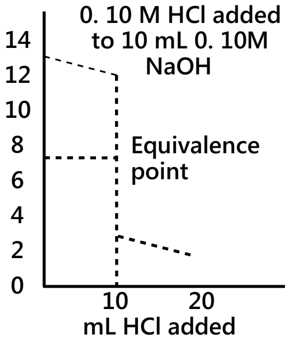
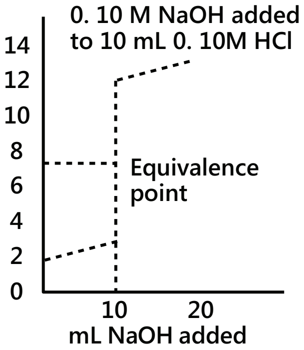
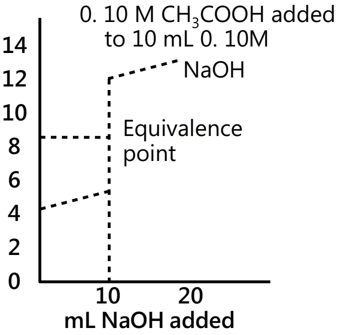
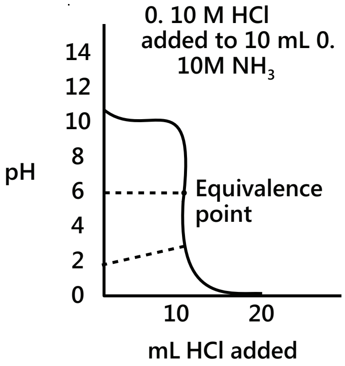
This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i. e., pH is not reached to 8. 3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

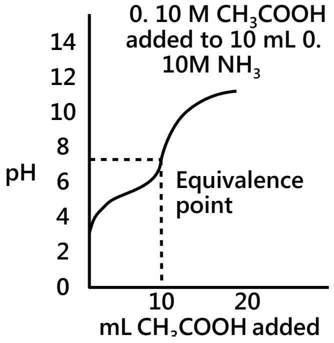
- Phenolphthalein and thymophthalein are suitable indicators for weak acids and strong base titrations.
- Methyl orange, bromocresol green and methyl red are suitable indicators for strong acid and weak base titrations.
- Bromothymol blue, phenolphthalein and methyl orange are suitable indicators for strong acid and strong base titrations.

Vaibhav Krishnan (JEE 2009, AIR 22)

10. TITRATIONS

Table 6.5: Typical titration curves for different types of solutions

General Type	Typical Titration Curve	Features of Curve
Strong Acid and Strong Base $NaOH + HCl \rightarrow NaCl + H_2O$		Curve begins at high pH typical of strong base and ends at low pH typical of strong acid. There is a large rapid change in pH near the equivalence point (pH = 7)
Strong Base and Strong acid $NaOH + HCl \rightarrow NaCl + H_2O$		Curve begins at low pH typical of strong acid, and ends at high pH typical of strong base. There is a large rapid change in pH near the equivalence point (pH = 7)
Weak Acid and Strong Base $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$		Curve begins at a higher acidic pH and ends at high basic pH. The pH change at the equivalence point (pH > 7) is not so great.
Weak Base and Strong Acid $NH_3 + HCl \rightarrow NH_4Cl$		Curve begins at low pH and ends at a less high basic pH. The pH change at the equivalence point (pH > 7) is similar to that for a strong Base and Weak Acid.

General Type	Typical Titration Curve	Features of Curve
Weak Acid and Weak Base $CH_3COOH + HN_3 \rightarrow CH_3COONH_4$		Curve begins at a higher acidic pH and ends at low basic pH. There is no great pH change at the equivalence point (pH~7) making this is a very difficult titration to perform.

Tirations of a weak polyprotic acid

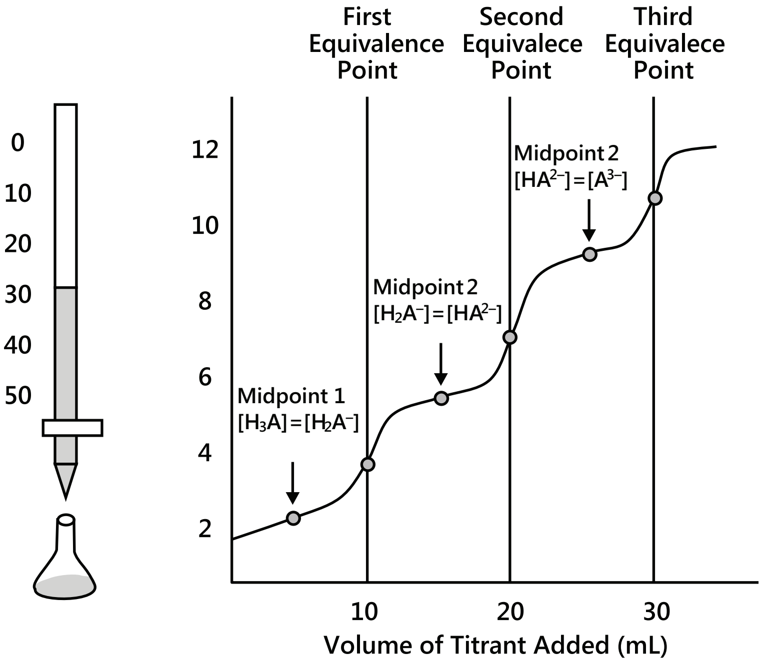


Figure 6.3 Titration of a Weak Polyprotic Acid.

The final equivalence point is attained by adding another 10 ml, or a total of 30 ml, of the titrant to the weak polyprotic acid. Image created by Heather Yee.

- The curve starts at a higher pH than a titration curve of a strong base
- There is a steep climb in pH before the first midpoint
- Gradual increase of pH until past the midpoint.
- Right before the equivalence point there is a sharp increase in pH
- pH steadies itself around the midpoint because the solutions at this point in the curve are buffer solutions, which means that adding small increments of a strong base will only barely change the pH
- Increase in pH near the equivalence point