

IONIC EQUILIBRIUM

INTRODUCTION

Chemical reactions mostly take place in solutions. Solution chemistry plays a very significant role in chemistry. All chemical substances are made up of either polar units (called ions) or non-polar units. The behaviour of these substances depends upon their nature and conditions of the medium in which they are added. It is therefore necessary to understand the principles that govern their behaviour in solution.

Ionic equilibrium is observed in substances that undergo ionization easily, or in polar substances in which ionization can be induced. Ionic and polar substances are more easily soluble in polar solvents because of the ease of ionization taking place in the solvent medium. With the dissolution of ionic and polar substances in the solvent, these solutions become rich in mobile charge carriers (ions) and thus can conduct electricity. Substances, which are capable of conducting electricity are called **electrolytes** while those substances which are non-conducting are called **non-electrolytes**.

The concepts and principles underlying chemical equilibrium are also applicable for ionic equilibrium. The fundamental concepts of chemical equilibrium, which are useful in ionic equilibrium are :

- The equilibrium are dynamic in nature.
- The equilibrium constant is independent of the initial concentration of reactants.
- The equilibrium constant depends on temperature and nature of reactants and products.
- The equilibrium can be attained from either side.
- The concentration of pure solids, pure liquids and solvents do not appear in the equilibrium constant expression.
- The equilibrium in solutions will only have equilibrium constant.
- The degree of dissociation of a weak electrolyte is the fraction of a mole of electrolyte that underwent dissociation.
- The equilibrium constant for the overall reaction is given by the product of the equilibrium constant of the individual reactions
- In order to predict the direction of equilibrium movement, reaction quotient (Q) should be compared with equilibrium constant, K . If $Q = K$, reaction is at equilibrium, if $Q < K$, reaction will move from right to left to attain equilibrium.
- According to Le Chatelier principle if an external stress is applied to a system at equilibrium, the system will adjust to partially offset the stress.

IMPORTANT TERMS

Electric conductivity

Substance which allow the electric current to pass through them are called electric conductors and this property is called electric conductivity.

On the basis of Electric conductivity, substances are of two types :

- 1 **Non conductors :**
Substance which do not allow the electric current to pass through are called nonconductors. e.g. All covalent compounds & nonmetals.
 - 2 **Conductors :**
Substance which allow the electric current to pass through are called conductors. e.g. all metals, alloys, all acid and bases, salt and graphite etc.
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On the basis of conducting units conductors are of two types :

Metallic or Electric Conductors :

Electricity conduct due to the presence of free and mobile electron which act as electricity conducting unit called metallic or electric conductors. e.g. Metals, Alloys, Graphite, Gas, Carbon etc.

Ionic Conductors or Electrolytes :

Conductors in which the current is passes through due to the presence of free ions are called Ionic Conductors or Electrolyte or Electrolytic conductors.

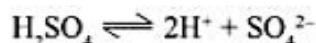
Ionisation :

The process in which molecules of acids bases and salts when melted or dissolve in water dissociate into ions is called ionization.

ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state in solution.

- (i) When an electrolyte is dissolved in a solvent (usually water) or is melted by heating, it spontaneously dissociates into oppositely charged particles called ions, to a considerable extent.



The positively charged ions are called cations and the negatively charged ions are called anions.

- (ii) Since the solution of an electrolyte, as a whole, is electrically neutral, i.e; the total charge on the cations is equal to the total charge on the anions.
- (iii) Electrolytic dissociation or ionization produces equilibrium between unionized molecules and the ions in solution. The degree of dissociation of an electrolyte (α) is the fraction of one mole of an electrolyte that has dissociated under the given conditions.

The value of α depends on

- | | |
|-----------------------------------|-------------------------------|
| (a) the nature of the electrolyte | (b) the nature of the solvent |
| (c) the dilution and | (d) the temperature |
- (a) **Nature of electrolyte :** Some electrolyte , e.g., mineral acid such as H_2SO_4 , HCl and HNO_3 , alkalis such as NaOH and KOH and all salts have a very high degree of ionization (≈ 1) at all reasonable concentration. They are known as strong electrolytes. The number of ions of strong electrolytes is large and thus such solutions have high conductance.

Some electrolytes, e.g., organic acids such as acetic acid and bases like ammonium hydroxide have a low degree of ionization in solution. They are called weak electrolytes. The number of ions in solutions of weak electrolytes is quite small and thus such solutions have low conductance.

- (b) **Nature of the solvent :** A solvent which has a high dielectric constant weakens the attractive force between the cations and anions. Hence a solvent of high dielectric constant favours the dissociation of the electrolyte.

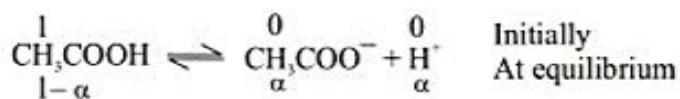
Likewise a solvent which can solvate the ions readily, and can release energy by solvation, favours the dissociation of the electrolyte. Thus the dissociation of acids in water is favoured by the hydration of the hydrogen ions to form hydronium ions. The enthalpy of hydration of the proton has a very high value.

- (c) **Dilution :** For some electrolytes, degree of dissociation increases with dilution as explained by Ostwald's dilution law (explained later)
- (d) **Temperature :** Increase of temperature generally increases ionization.

TYPES OF ELECTROLYTES

There are two types of electrolytes:

- (1) **Strong electrolytes :** These electrolytes are almost completely ionized when dissolved in a polar medium like water. In solution they are excellent conductors, e.g., HNO₃, HCl, KOH, NaOH, etc. Their degree of ionization is high and approaches unity.
- (2) **Weak electrolytes :** These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g., CH₃COOH, H₃PO₄, H₃BO₃, NH₄OH, etc., Equilibrium between ions and unionized molecules is established in solution, e.g.,



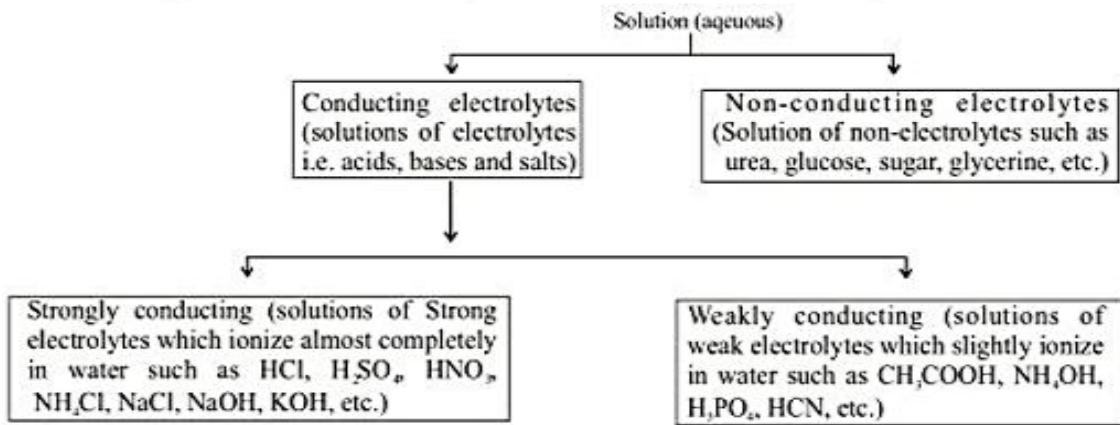
The above equilibrium is termed as ionic equilibrium. Degree of ionization of weak electrolytes is much less than unity. ($\alpha \ll 1$)

Degree of ionization, may be defined as a fraction of total number of molecules of an electrolyte which dissociate into ions.

$$\alpha = \frac{\% \text{ ionization}}{100}$$

$$\text{Degree of Ionization } (\alpha) = \frac{\text{Number of mole dissociated}}{\text{Total number of moles taken}}$$

The following classification of electrolytes is based on their behaviour in a particular solvent, i.e., water.



Note : - Electrolyte may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

Illustration

- Identify the non-electrolyte, strong electrolyte and weak electrolytes in aq. medium of the following substance.

NaOH, HCl, NaCl, NH₂CONH₂(Urea), H₂SO₄, H₃PO₄, HCN, NH₄OH, KOH, C₂H₅COOH, NH₄Cl, HNO₃, C₁₂H₁₂O₁₁(Sugar), C₆H₁₂O₆(glucose)

Sol. Non-electrolyte : NH₂CONH₂, C₁₂H₁₂O₁₁, C₆H₁₂O₆

Weak-Electrolyte : H₃PO₄, HCN, NH₄OH, C₂H₅COOH

Strong-Electrolyte : NaOH, HCl, NaCl, H₂SO₄, KOH, NH₄Cl, HNO₃

OSTWALD'S DILUTION LAW

The application of law of mass action to weak electrolytes is known as ostwald dilution law. There exists dynamic equilibrium between ions and undissociated molecules of the electrolytes in solution and law of mass action can be applied to this. Consider a binary electrolyte AB

AB	\rightleftharpoons	A ⁺ + B ⁻
Initially	C	0 0
Atequilibrium	C(1- α)	C α C α (α = degree of dissociation)

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

K is termed as ionization constant. For a weak electrolyte value of α is very-very small compared to 1 and $(1-\alpha) \approx 1$

$$\therefore K = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha \propto \frac{1}{\sqrt{C}}$$

If V be the volume of the solution containing 1 mole of the solute $C = \frac{1}{V}$.

- Hence $\alpha = \sqrt{KV}$ or $\alpha \propto \sqrt{V}$ as ionic equilibrium is set up in case of weak electrolytes.
- Ostwald's dilution is applicable only in case of weak electrolytes.
- The approximation $(1-\alpha) \approx 1$ can be applied only if $\alpha < 5\%$. If on solving a problem by applying the approximate formula α comes out to be $> 5\%$ the problems may be solved by applying exact formula and α may be calculated applying solution of quadratic equation

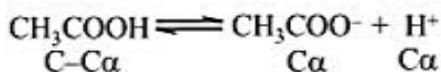
$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{for, } a\alpha^2 + b\alpha + c = 0)$$

Illustration

1. What concentration of acetic acid is needed to give a hydrogen ion concentration of 3.5×10^{-4} M? ($K_a = 1.8 \times 10^{-5}$)
 (A) 3.5×10^{-4} M (B) 6.80×10^{-3} M (C) 4.2×10^{-4} M (D) 7.2×10^{-4} M

Ans. (B)

Sol. Let the concentration of acetic acid be 'C'.



$$K_a = 1.8 \times 10^{-5} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = C\alpha^2$$

$$\text{Now } \alpha^2 = \frac{K_a}{C} \text{ or } \alpha = \sqrt{\frac{K_a}{C}} \text{ or } C\alpha = \sqrt{K_a \cdot C}$$

$$C\alpha = [\text{H}^+] = 3.5 \times 10^{-4} \text{ M} \quad \therefore 3.5 \times 10^{-4} = \sqrt{1.8 \times 10^{-5} C}$$

$$\text{Or } \sqrt{C} = \frac{3.5 \times 10^{-4}}{\sqrt{1.8 \times 10^{-5}}} \text{ or } C = \frac{(3.5 \times 10^{-4})^2}{1.8 \times 10^{-5}} = \frac{12.25 \times 10^{-8}}{1.8 \times 10^{-5}} = 6.80 \times 10^{-3} \text{ mol L}^{-1}$$

Exercise

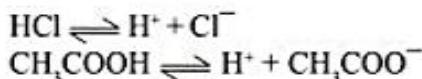
1. Calculate the concentration of $\text{C}_2\text{H}_5\text{COOH}$ that is needed to give a hydrogen ion concentration of 10^{-4} M? ($K_a = 2 \times 10^{-6}$)

Ans. 5×10^{-3} M

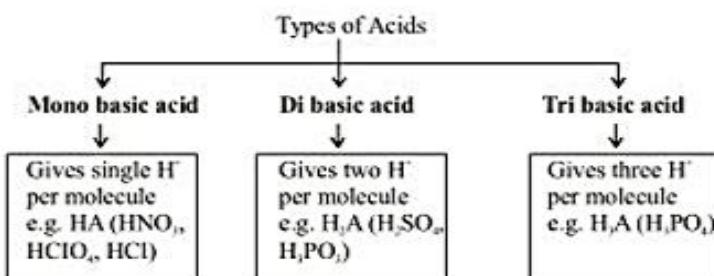
Limitations of Ostwald's dilution law : It holds good only for weak electrolytes and fails completely in the case of strong electrolytes

CONCEPT OF ACIDS AND BASES**(A) The Arrhenius concept****Arrhenius acid :**

An acid is a substance which gives hydrogen ions in aqueous solution as the only cations. e.g.,



Ex. HNO_3 , HClO_4 , HCl , HI , HBr , H_2SO_4 , H_3PO_4 etc.

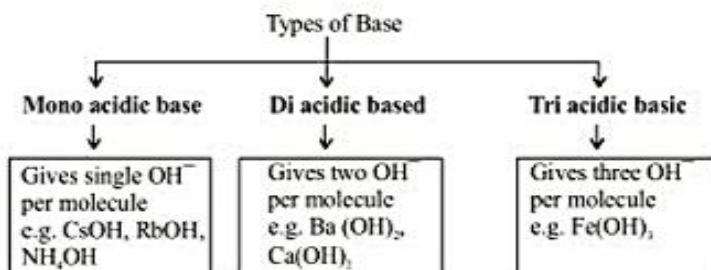
**Note :**

- H_3BO_3 is not an Arrhenius acid.
- H^+ ion in water is extremely hydrated (in form of H_3O^+ , H_5O_2^+ , H_7O_3^+)
- The structure of solid HClO_4 is studied by X-ray, It is found to be consisting of H_3O^+ and ClO_4^-

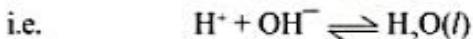
$$\text{HClO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_4^-$$
 (Better representation)

Arrhenius base :

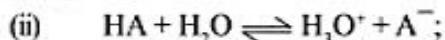
A base is a substance which gives hydroxyl (OH^-) ions in a aqueous solution as the only anions.

**Note :**

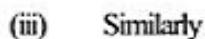
- OH^- ion is present also in hydrated form of H_3O_2^- , H_7O_4^- , H_5O_3^-
- First group elements (except Li) form strong bases
- Neutralization is the combination of H^+ ions of the acid and OH^- ions of the base to form unionized water.

**Strength of acid or base :**

(i) Strength of acid or base depends on the extent of its ionisation. Hence equilibrium constant K_a or K_b respectively of the following equilibria gives a quantitative measurement of the strength of the acid or base.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

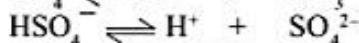
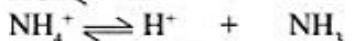
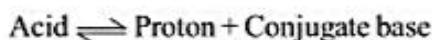


$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Here H_2O is solvent.

(B) The Bronsted-Lowry theory (Protonic concept)

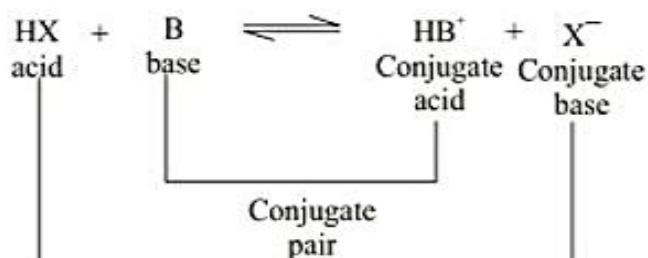
According to this concept, an acid is a substance which has tendency to lose a proton (H^+), i.e. an acid is a proton donor and a base is a substance, which has a tendency to accept a proton, i.e., it is a proton acceptor. When an acid loses a proton, the residue will have a tendency to regain a proton and hence it is referred as conjugate base



The acid and the conjugate base, which differ by a proton, forms a conjugate pair. For example, HCl and Cl^- ions form a conjugate pair, Cl^- is the conjugate base of HCl and HCl is the conjugate acid of Cl^- . From the examples given above, it is clear that acids and bases may be molecules or ions, but at least one of the members of a conjugate pair should be an ion.

Conjugate acid-base pairs

In a typical acid base reaction



* Forward reaction – Here HX being a proton donor is an acid
B being a proton acceptor is a base

Backward reaction – Here HB^+ being a proton donor is an acid
 X^- being a proton acceptor is a base

Acid		Base		Conjugate acid		Conjugate base
HCl	+	H_2O	\rightleftharpoons	H_3O^+	+	Cl^-
HSO_4^-	+	NH_3	\rightleftharpoons	NH_4^+	+	SO_4^{2-}
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	+	H_2O	\rightleftharpoons	H_3O^+	+	$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$

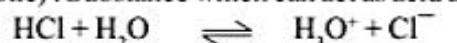
Note :

- Conjugate acid - base pair differ by only one proton.
- Strong acid will have weak conjugate base and vice versa.
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

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	Acid	Conjugate base	Base	Conjugate acid
Ex.	HCl	Cl ⁻	NH ₃	NH ₄ ⁺
	H ₂ SO ₄	HSO ₄ ⁻	H ₂ O	H ₃ O ⁺
	HSO ₄ ⁻	SO ₄ ²⁻	RNH ₂	RNH ₃ ⁺
	H ₂ O	OH ⁻		

Amphoteric (amphiprotic) : Substance which can act as acid as well as base are known as amphoteric



Base



Acid

Behaviour of acids and bases in aqueous solution

- (i) **Acids in water :** Water functions as a weak base and accepts a proton from the acid, thus



A⁻ can be considered as the conjugate base of anion of salt of the acid HA. So an aqueous solution of an acid contains hydronium (H₃O⁺) ions (and not H⁺ ions)

- (ii) **Strong and Weak acids :** (Relationship between a conjugate pair). An acid is considered to be a strong acid, it can give up its proton readily. In an aqueous solution of HCl, there is equilibrium



Since HCl can give up its proton readily, this equilibrium will lie far to the right. Consequently the base Cl⁻ cannot take up the proton from H₃O⁺ readily, i.e., Cl⁻ is a weak base. In general, the conjugate base of a strong acid will be a weak base.

In the case of a weak acid like phenol,



The equilibrium will lie far to the left. So the conjugate base (C₆H₅O⁻) of a weak acid (C₆H₅OH) will be moderately strong. Again there is little ionization in the aqueous solution of a weak acid so the acid is a weak electrolyte and the solution has a low conductance.

Based on studies of acids it is established that,



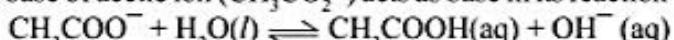
- (iii) Relationship between the ionization constants of acids and their conjugate bases

Let us derive a relationship between the ionization constants of acid, CH₃COOH and its conjugate CH₃COO⁻. The equilibrium reaction of CH₃COOH in water is written as



$$K_{eq} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = K_a \quad \dots\dots(i)$$

The conjugate base of acetic ion (CH₃COO⁻) acts as base in its reaction with water as



$$K'_{eq} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = K_b$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad \dots\dots\text{(ii)}$$

$$\therefore K_b = \frac{[\text{CH}_3\text{COOH}] K_w}{[\text{CH}_3\text{COO}^-][\text{H}^+]}$$

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

Thus, stronger the acid (the larger K_a), weaker will be its conjugate base (the smaller K_b) and vice versa. Therefore, for an acid-conjugate base pair.

$$K_w = K_a \times K_b$$

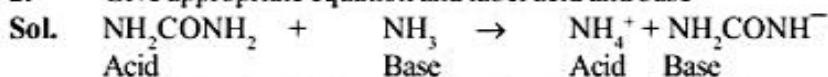
Illustration

1. Which is the strongest Bronsted base in the following anion-
 (A) ClO^- (B) ClO_2^- (C) ClO_3^- (D) ClO_4^-

Ans. (A)

Sol. HClO is weakest acid among HClO , HClO_2 , HClO_3 and HClO_4

2. Give appropriate equation and label acid and base-



In liquid NH_3 solution urea can show weak acidic nature, while in water urea does not dissociate

Exercise

1. Ammonium ion is-
 (A) A Lewis acid (B) Lewis base (C) Bronsted acid (D) Bronsted base

Ans. (C)

2. (a) Write conjugate acids of SO_4^{2-} , NH_2^- , F^-
 (b) Write conjugate base of HNO_2 , H_2CO_3 , HClO_4
 (c) Write conjugate acids and conjugate base of amphoteric species
 HS^- , NH_3 , H_2O , HSO_4^-

Ans. (a) HSO_4^- , NH_3 , HF
 (b) NO_2^- , HCO_3^- , ClO_4^-
 (c) $(\text{H}_2\text{S}, \text{S}^{2-})$ $(\text{NH}_4^+, \text{NH}_2^-)$ $(\text{H}_2\text{SO}_4, \text{SO}_4^{2-})$

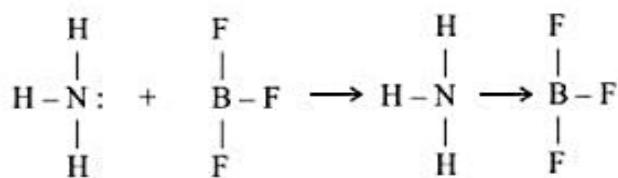
3. Which of the following is the strongest base-
 (A) NH_2^- (B) CH_3COO^- (C) $\text{C}_2\text{H}_5\text{O}^-$ (D) OH^-

Ans. (A)

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(C) Lewis Electronic theory

According to this theory an acid is a molecule or ion, which can accept an electron pair with the formation of a coordinate bond. For example, in BF_3 , the boron atom can accept a pair of electron; so BF_3 is a Lewis acid. A base must therefore be any molecule or ions, which has a lone pair of electron, which it can donate. For example, ammonia molecule has a lone pair of electron; so it is a Lewis base.



Other examples of Lewis acid-base neutralization

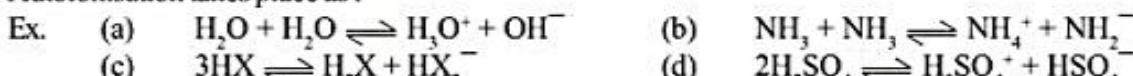
Base	Acid	Products
H_2O	$+\text{HCl}$	$\rightleftharpoons \text{H}_2\text{O} \rightarrow \text{HCl}$ or $\text{H}_3\text{O}^+ + \text{Cl}^-$
CaO	$+\text{CO}_2$	$\rightleftharpoons \text{CaO} \rightarrow \text{CO}_2$ or $\text{Ca}^{2+} + \text{CO}_3^{2-}$
H_2O	$+\text{H}_2\text{O}$	$\rightleftharpoons \text{H}_2\text{O} \rightarrow \text{HOH}$ or $\text{H}_3\text{O}^+ + \text{OH}^-$

Classification of Solvents :

There are two types of solvents : (i) Protic (protic) and (ii) Aprotic

(i) Protic or protic solvent

(a) They are characterized by the presence of a transferable hydrogen and the formation of "Onium" ions
Autoionisation takes place as :



(b) Protic solvents may be

- (a) Acidic (Anhydrous sulphuric acid, liquid HF, Glacial acetic acid etc.)
- (b) Basic (liquid NH_3)
- (c) Amphiprotic (H_2O , proton containing anions)

(c) Aprotic solvents :

Such solvents do not have replaceable hydrogen ion in them. These can be classified into three categories.

(a) Non polar or very weakly polar, nondissociated liquids, which do not solvate strongly.

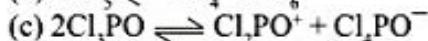
Ex. CCl_4 , hydrocarbons, C_6H_6 , C_6H_{12} etc.

(b) Non-ionised but strongly solvating, generally polar solvents.

Ex. Acetonitrile CH_3CN , DMSO (dimethyl sulfoxide), THF (Tetra hydro furan) and SO_2 .

(c) Highly polar, autoionising solvents.

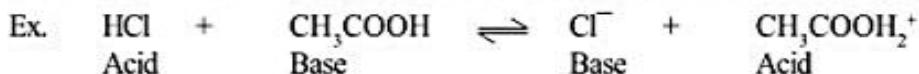
Ex. Inter halogen compounds (BrF , IF_5 , and trichloro phosphine)



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LEVELLING SOLVENTS

- (i) The Bronsted - Lowery theory can be extended to acid-base reactions in non-aqueous solvents. It can be used in differentiating the acid strength of a particular acid and in titration of weak bases.
- (ii) In water solvent, mineral acids appear to be equally strong because of their complete ionisation, so water is called levelling solvent because it levels all the acids to the same strength.
- (iii) If instead of water solvent, we take mineral acids in pure acetic acid solvent (which is poor proton acceptor as compared to water) it is found acids become weak and can be differentiated.



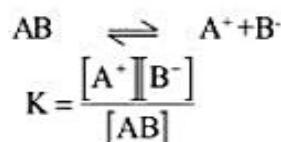
In above example acetic acid and Cl^- ions both compete for protons and the former being a poor proton acceptor does it much less effectively than water. Thus HCl in acetic acid solvent appears to be a much weaker acid than that in water.

- (iv) Mineral acids in acetic acid solvent follow the following order of their strengths.



COMMON ION EFFECT

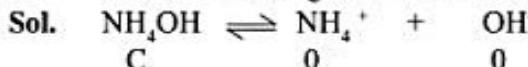
The degree of dissociation of a weak electrolyte is suppressed by the addition of another electrolyte (strong) containing common ion. This is referred to as common ion effect e.g. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of strong acid (H^+ ion as common ion). Let AB be the weak electrolyte, considering its dissociation



The equilibrium constant K has a definite value at a given temperature. If another electrolyte containing A^+ or B^- ions added to the above solution will increase the concentration of A^+ or B^- ions, in order that K remain constant, the concentration of AB must increase, equilibrium will shift to the left side.

Illustration

1. Determine the degree of dissociation of 0.05 M NH_3 at 25°C in a solution of $\text{pH} = 11$



$$\text{Given } \text{pH} = 11 \therefore [\text{H}^+] = 10^{-11}$$

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-11}} = 10^{-3} = C\alpha$$

$$\therefore \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2} \text{ or } 0.2\%$$

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2. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH=2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH=12.0)

Sol. pH of HCl = 2, $\therefore [\text{HCl}] = 10^{-2} \text{ M}$

$$\text{pH of NaOH} = 12, \quad \text{pOH} = 2 \quad \therefore [\text{NaOH}] = 10^{-2} \text{ M}$$

	HCl	+	NaOH	\rightarrow	NaCl	+	H ₂ O
Meq.initial	200×10^{-2}		300×10^{-2}		0		0
	=2		=3				

Meq. final	0		1		2		2
------------	---	--	---	--	---	--	---

$$\therefore [\text{OH}^-] \text{ from NaOH} = \frac{1}{500} = 2 \times 10^{-3} \text{ M}$$

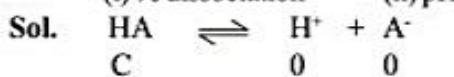
$$\text{pOH} = -\log[\text{OH}^-] = -\log(2 \times 10^{-3})$$

$$\therefore \text{pOH} = 2.6989$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 2.6989 = 11.3010.$$

3. K_a for acid HA is 4.9×10^{-8} . After making the necessary approximation, calculate for its decimolar solution at 25°C.

(i) % dissociation (ii) pH (iii) OH⁻ concentration



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{\text{HA}} \Rightarrow K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

$$\text{i) } \therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9 \times 10^{-8}}{1/10}} \quad (C = 1/10 \text{ M}) \\ = 7 \times 10^{-4} = 0.07 \%$$

$$\text{ii) } [\text{H}^+] = C\alpha = \frac{1}{10} \times 7 \times 10^{-4} = 7 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{iii) } [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10} \text{ mol/Lt.}$$

4. A solution of HCl has a pH = 5. If one ml of it is diluted to 1 liter what will be pH of resulting solution ?

Sol. [HCl] = 10^{-5} M (As pH = 5)

$$\text{Meq of HCl in 1 ml} = 10^{-5} \times 1 = 10^{-5}$$

Let normality after diluting

One ml of HCl (pH=5) to one liter is (N)

Meq of HCl (conc) = Meq of HCl dilute.

$$10^{-5} \times 1 = N \times 100 \Rightarrow N_{\text{HCl (dil.)}} = 10^{-8}$$



10^{-8}	0	0	Initial
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0	10^{-8}	10^{-8}	Final
---	-----------	-----------	-------

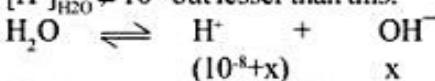
$\therefore [H^+] = 10^{-8}$ but pH = 8 is not possible because solution is acidic. As $(H^+) = 10^{-7} M$ are already present in solution from the dissociation of water and since $10^{-8} < 10^{-7}$ and thus it should not be neglected

$$\therefore [H^+] = 10^{-8} + 10^{-7} = (1.1) \times 10^{-7} M$$

$$\therefore pH = 6.9586.$$

The above solution for pH of the resultant solution has discrepancy, that dissociation of weak electrolyte is also suppressed in presence of HCl due to common ion effect.

$[H^+]_{H_2O} \neq 10^{-7}$ but lesser than this.



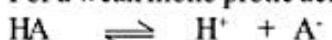
$$K_w = (10^{-8} + x)x \Rightarrow x = 0.95 \times 10^{-7}$$

$$\therefore [H^+] = 10^{-8} + 0.95 \times 10^{-7} = 21.05 \times 10^{-7}$$

$$\therefore pH = 6.9788$$

5. Prove that degree of dissociation of weak acid is given by $\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$. Where K_a is its dissociation constant of weak acid?

Sol. For a weak mono protic acid



$$[H^+] = C\alpha$$

$$K_a = \frac{C\alpha^2}{(1-\alpha)} \quad (\text{Ostwall dilution law})$$

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

$$\therefore [H^+] = \frac{K_a(1-\alpha)}{\alpha^2} \times \alpha = \frac{K_a(1-\alpha)}{\alpha}$$

$$\Rightarrow -\log[H^+] = -[\log K_a + \log(1-\alpha) - \log \alpha]$$

$$\Rightarrow pH = -\log K_a + \log \frac{\alpha}{(1-\alpha)} \Rightarrow pH = pK_a - \log \frac{(1-\alpha)}{\alpha}$$

$$\Rightarrow \log \frac{(1-\alpha)}{\alpha} = (pK_a - pH) \Rightarrow \frac{(1-\alpha)}{\alpha} = 10^{(pK_a - pH)} \Rightarrow \frac{1}{\alpha} - 1 = 10^{(pK_a - pH)}$$

$$\Rightarrow \alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$

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PROPERTIES OF WATER

Amphoteric (amphiprotic) Acid/Base nature :

Water act as an acid as well as a base according to Bronsted - Lowry theory but according to Lewis concept it can only be taken as base only.

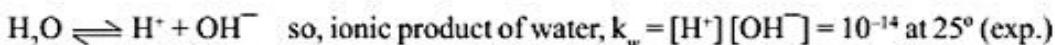
In pure water $[H^+] = [OH^-]$ so it is neutral.

Molar concentration / Molarity of water :

$$\text{Molarity} = \frac{\text{No. of moles/litres}}{18\text{ g / moles}} = \frac{1000\text{ g / litre}}{18\text{ g / moles}} = 55.55 \text{ moles / litre} = 55.55 \text{ M} (\text{density} = 1 \text{ g/cc})$$

Ionic product of water :

According to arrhenius concept



Dissociation of water is endothermic, so on increasing temperature K_w increase.

K_w increases with increase in temperature.

Now $pH = -\log[H^+] = 7$ and $pOH = -\log[OH^-] = 7$ for water at $25^\circ C$ (experimental)

$$\begin{array}{lll} pH = 7 = pOH & \Rightarrow & \text{neutral} \\ pH < 7 \text{ or } pOH > 7 & \Rightarrow & \text{acidic} \\ pH > 7 \text{ or } pOH < 7 & \Rightarrow & \text{basic} \end{array} \left. \right\} \text{ at } 25^\circ C$$

Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

Degree of dissociation of water :

$$H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total no. of moles initially taken}}$$

$$= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7} \%$$

Absolute dissociation constant of water :

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_a = K_b = \frac{[H^+] [OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$\text{So, } pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

Acidity and pH scale :

Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.

So greater the tendency to give H^+ , more will be the acidic strength of the substance.

Basic strength means to give OH^- ions, more will be basic strength of the substance.

The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH is defined as negative logarithm of activity of H^+ ions.

$\therefore \text{pH} = -\log a_{\text{H}^+}$ (where a_{H^+} is the activity of H^+ ions)

Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a solution.

The pH scale was marked from 0 to 14 with central point at 7 at 25°C, taking water as solvent.

If the temperature and the solvent are changed, the pH range of the scale will also change. For example,

0–14	at 25 °C ($K_w = 10^{-14}$)	Neutral point, pH = 7
0–14	at 80 °C ($K_w = 10^{-13}$)	Neutral point, pH = 6.5

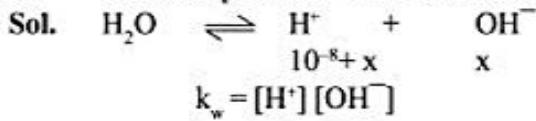
pH CALCULATION OF DIFFERENT TYPES OF SOLUTIONS

(a) Strong acid solution :

- (i) If concentration is greater than 10^{-6} M.
In this case H^+ ions coming from water can be neglected.
so $[H^+] = \text{normality of strong acid solution.}$
 - (ii) If concentration is less than 10^{-6} M but greater than 10^{-8} M
In this case H^+ ions coming from water cannot be neglect.
So $[H^+] = \text{normality of strong acid} + H^+ \text{ ions coming from water in presence of this strong acid.}$
 - (iii) If concentration is less than 10^{-8} M, in this case H^+ ions coming from water is considered only.

Illustration

- 1.** Calculate pH of 10^{-8} M HCl solution.



$$\Rightarrow \frac{10^{-14}}{x^2 + x \times 10^{-8} - 10^{-14}} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401}-1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[\text{H}^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

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

$$\text{pH} = 7 - \log 1.05 \approx 7$$

Exercise

- 1.** Calculate pH of 10^{-10} M HCl solution.

Ans. pH \approx 7

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(b) Strong base solution :

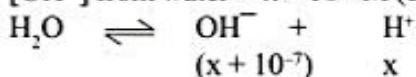
Calculate the $[\text{OH}^-]$ which will be equal to normality of the strong base solution and then use $K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$, to calculate $[\text{H}^+]$

Illustration

1. Calculate pH of 10^{-7} M of NaOH solution

Sol. $[\text{OH}^-]$ from NaOH = 10^{-7}

$[\text{OH}^-]$ from water = $x < 10^{-7}$ M (due to common ion effect)



$$K_w = [\text{H}^+] [\text{OH}^-] = 10^{-14} = x(x + 10^{-7})$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$$

$$[\text{OH}^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$$

$$\text{pOH} = 7 - \log(1.618) = 6.79$$

$$\text{pH} = 14 - 6.79 = 7.21$$

Exercise

1. Calculate pH of a KOH solution having

(a) 5.6 g of KOH mixed in 50 mL water (b) if it is further diluted to make 100 mL

Ans. (a) 14.3 (b) 14

- (c) **pH of mixture of two strong acids :** If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2 , then

$$\text{Number of H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of H}^+ \text{ ions from II-solution} = N_2 V_2$$

If final normality is N and final volume of V , then

$$NV = N_1 V_1 + N_2 V_2$$

[Dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[\text{H}^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

- (d) **pH of mixture of two strong bases :** Similar to above calculation

$$[\text{OH}^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

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

Illustration

1. 500 mL of 10^{-5} M NaOH is mixed with 500 mL of 2.5×10^{-5} M of Ba(OH)₂. To the resulting solution 99 L water is added. Calculate pH.

$$\text{Sol. } [\text{OH}^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000} \quad (\text{Normality of Ba(OH)}_2 = 2 \times 2.5 \times 10^{-5}) \\ = 3 \times 10^{-5} \text{ M}$$

$$M = 3 \times 10^{-5} M_{\odot}$$

$$M_1 = 5 \times 10^{-5} M_\odot$$

$v = 100$

$$V_2 = 100 \text{ L}$$

no. of moles of $\text{[OH}^-]$ initially = no. of moles of $\text{[OH}^-]$, in final solution.

$$3 \times 10^{-5} = M_2 \times 100$$

$$\therefore M_2 = 3 \times 10^{-7} < 10^{-6}$$



$$x = (x + 3 \times 10^{-7})$$

$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left(\frac{\sqrt{13} - 3}{2} \right) \times 10^{-7}$$

$$x = 0.302 \times 10^{-7}$$

$$[\text{OH}^-]_{\text{Net}} = \left[3 + \frac{\sqrt{13} - 3}{2} \right] \times 10^{-7} = \left[\frac{3 + \sqrt{13}}{2} \right] \times 10^{-7} = 3.302 \times 10^{-7}$$

Exercise

- 1.** Calculate the pH for-

- (a) 50 mL of 0.1 M HCl, 25 mL of 0.1 M H_2SO_4 , 25 mL of 0.2 M HNO_3 , + 100 mL of H_2O

- (b) 50 mL of 0.2 M NaOH + 100 mL of 0.1 M RbOH the resulting solution is diluted by 350 mL H₂O.

Ans. (a) 1.123

(b) 12.6

- (e) pH of mixture of a strong acid and a strong base:

Acid base neutralisation reaction will take place.

The solution will be acidic or basic depending on which component is taken in excess.

If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution normality N_2 , then

Number of H^+ ions from I-solution = $N_1 V_1$

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Number of OH^- ions from II-solution = N_2V_2



$$[\text{H}^+] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

Solution will
be acidic in nature

$$[\text{OH}^-] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

Solution will
be basic in nature

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

Illustration

1. Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M $\text{Ba}(\text{OH})_2$) + (400 mL, $\frac{1}{50}$ M HCl) + (200 mL of water)

Sol. $[\text{H}^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$, so pH = $3 - 2 \log 2 = 2.4$

2. What will be resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0)?

Sol. pH of HCl = 2

$\therefore [\text{HCl}] = 10^{-2}$ M

pH of NaOH = 12,	$\text{pOH} = 2$	$\therefore [\text{NaOH}] = 10^{-2}$ M	
Meq. initial	$\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$		
	150×10^{-2}	350×10^{-2}	0
	= 1.5	= 3.5	
Meq. final	0	2	1.5

$\therefore [\text{OH}^-]$ from NaOH = $\frac{2}{500} = 4 \times 10^{-3}$ M

$\text{pOH} = -\log [\text{OH}^-] = -\log (4 \times 10^{-3})$

$\therefore \text{pOH} = 2.3979$

$\therefore \text{pH} = 14 - \text{pOH} = 14 - 2.3979 = 11.6021$

Exercise

1. Calculate pH of mixture 200 mL of 0.2 M H_2SO_4 + 300 mL of 0.2 M NaOH + 200 mL of 0.1 M KOH.

Ans. 7

2. Calculate the pH when 200 mL of 0.25 M H_2SO_4 is mixed with 200 mL of 0.2 M $\text{Ba}(\text{OH})_2$

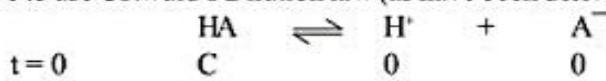
Ans. 1.30

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(f) **pH of a weak acid (monoprotic) solution :**

Weak acid does not dissociate 100% therefore we have to calculate the percentage dissociation using (K_a) dissociation constant of the acid.

We have to use Ostwald's Dilution law (as have been derived earlier)



$$\text{At eq} \quad \frac{\text{c}(1-\alpha)}{\text{Ca}} \quad \frac{\text{Ca}}{\text{C}\alpha} \quad \frac{\text{Ca}}{\text{C}\alpha} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{\text{Ca}^2}{1-\alpha}$$

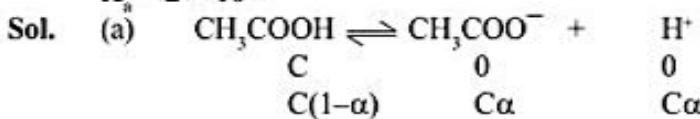
$$\text{If } \alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a = \text{Ca}^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.5)$$

$$[\text{H}^+] = \text{Ca} = \text{C} \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \quad \text{So pH} = \frac{1}{2} (\text{p}K_a - \log C)$$

On increasing the dilution $\Rightarrow \text{C} \downarrow = \alpha \uparrow$ and $[\text{H}^+] \downarrow \Rightarrow \text{pH} \uparrow$

Illustration

1. Calculate pH of (a) 10^{-1} M CH₃COOH (b) 10^{-3} M CH₃COOH
 $K_a = 2 \times 10^{-5}$



$$K_a = \frac{\text{Ca}^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

$$\text{So, } [\text{H}^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$$

$$(b) \alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$$

Since $\alpha > 0.1$, exact calculation is required.

$$K_a = \frac{\text{Ca}^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\%$$

$$[\text{H}^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8$$

Exercise

1. Calculate pH of (a) 10^{-4} M CH₃COOH (b) 10^{-6} M CH₃COOH
 Take $K_a = 2 \times 10^{-5}$

Ans. (a) 4.04 (b) 6.022

Note : At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behaves as strong electrolyte
 $(pH \text{ of } 10^{-6} M HCl = pH \text{ of } 10^{-6} M CH_3COOH = 6)$

(g) pH of a mixture of weak acid (monoprotic) and a strong acid solution :

Weak acid and strong acid both will contribute H^+ ion.

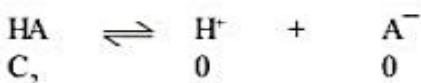
For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If $[SA] = C_1$ and $[WA] = C_2$, then $[H^+]$ from SA = C_1
 the weak acid will dissociate as follows,

(SA = Strong acid)

(WA = Weak acid)



$$C_2(1-\alpha) \quad C_2\alpha + C_1 \quad C_2\alpha \quad K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha \ll 1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$$K_a = (C_2\alpha + C_1)\alpha$$

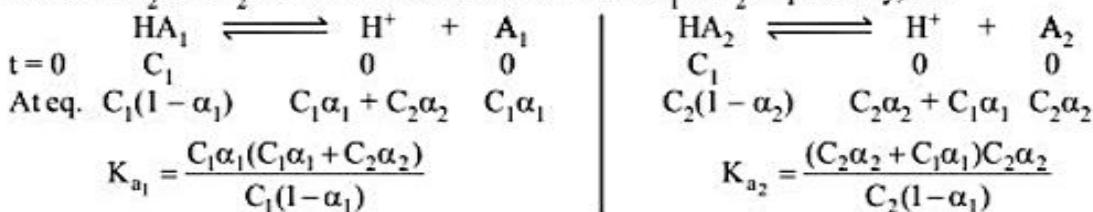
To H^+ ion concentration = $C_1 + C_2\alpha$

If the total $[H^+]$ from the acid is more than $10^{-6} M$, then contribution from the water can be neglected, but if comparable then we take $[H^+]$ from water also.

(h) pH of a mixture of two weak acid (both monoprotic) solution :

- Both acids will dissociate partially

- Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then



(Since α_1, α_2 both are small in comparison to unity)

$$K_{a_1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 : K_{a_2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \Rightarrow \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \Rightarrow [H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So. } [H^+] = C_1\alpha_1 + C_2\alpha_2 = C_1\alpha_1$$

Illustration

1. Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH₃COOH solution given that $K_{a_1} [HOCl] = 2 \times 10^{-4}$

$$K_{a_2} [CH_3COOH] = 2 \times 10^{-5}$$

also calculate OH⁻, OCl⁻, CH₃COO⁻

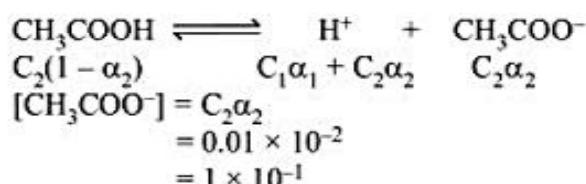
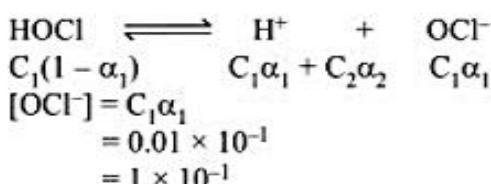
Sol. Final solution volume become double

$$C_1 = 0.01 \quad C_2 = 0.1$$

$$[H^+] = \sqrt{K_{a_1} C_1 + K_{a_2} C_2} = \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$pH = 3 - \log 2 = 3 - 0.3010 = 2.69$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11}$$

$$= 5 \times 10^{-12} M$$

$$HOCl = 10^{-2}(1-0.01) = 9 \times 10^{-3} M$$

$$[CH_3COOH] = 10^{-1}(1-0.01) \approx 10^{-1}$$

Exercise

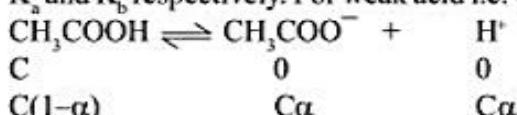
1. Calculate pH of solution obtained by mixing equal vol. of 2 M HOCl & 3 M HA solution given that

$$K_{a_1} [HOCl] = 2 \times 10^{-4}, K_{a_2} [HA] = 2 \times 10^{-5}$$

Ans. 1.4

RELATIVE STRENGTH OF WEAK ACIDS AND BASES

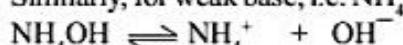
The relative strength of weak acids and bases are generally determined by their dissociation constants K_a and K_b respectively. For weak acid i.e. CH₃COOH



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$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \Rightarrow K_a = C\alpha^2 \quad (\text{if } \alpha \ll 1)$$

Similarly, for weak base, i.e. NH_3OH



$$\begin{array}{ccc} C & 0 & 0 \\ C(1-\alpha) & Ca & Ca \end{array}$$

$$K = C\alpha^2$$

K_a and K_b are just the equilibrium constants and hence depends only on temperature. Greater the value of dissociation constant of the acid (K_a), more is the strength of the acid and greater the value of dissociation constant of the base, more is the strength of the base. For two acids of equimolar concentration,

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly for bases, $\frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$

The modern method is to convert K_a as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit pK_a . Thus, if K_a for acid is equal to 10^{-4} , $pK_a = 4$. So higher pK_a value means lower acid strength.

that is $pK_a = -\log K_a$. Also, $pK_b = -\log K_b$.

Illustration

1. K_a for acid HA is 2.5×10^{-8} calculate for its decimolar solution at 25°C.
 (i) % dissociation (ii) pH (iii) OH^- ion concentration

$$\begin{array}{l} \text{Sol.} \quad \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \\ \quad \quad \quad \text{C} \qquad \qquad \quad 0 \qquad 0 \\ \quad \quad \quad \text{C}(1-\alpha) \qquad \text{C}\alpha \qquad \text{C}\alpha \end{array}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha}{(1-\alpha)} = C\alpha^2$$

$$\textcircled{i} \quad \therefore \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}} \quad (C = 1/10 \text{ M}) \\ = 5 \times 10^{-4} = 0.05\%$$

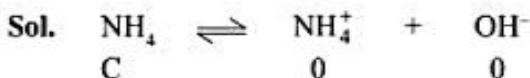
$$(ii) \quad [H^+] = C\alpha = \frac{1}{10} \times 5 \times 10^{-4} \text{ mol/L} \quad \Rightarrow \quad \text{So pH} = 5 - \log 5 = 4.30$$

$$(iii) \quad [H^+] [OH^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{5 \times 10^{-4}} = 2 \times 10^{-10} \text{ mol/L}$$

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2. Determine the degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 10.



Given, pH = 10

$$[\text{H}^+] = 10^{-10}$$

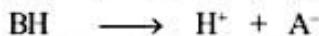
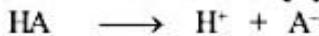
$$[\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$$

$$\therefore \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3} \text{ or } 0.2\%$$

3. Two weak monobasic organic acids HA and HB have dissociation constants as 1.6×10^{-5} and 0.4×10^{-5} respectively at 25°C. If 500 mL of 1 M solutions of each of these two acids are mixed to produce 1 litre of solution, what is the pH of the resulting solution?

Sol. In such cases, we have to consider H^+ from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 0.5 M [equal volumes are mixed] = say 'c'



Let, x = $[\text{H}^+]$ from HA and y = $[\text{H}^+]$ from HB

$$\Rightarrow [\text{H}^+]_{\text{final}} = x + y$$

$$K_{\text{HA}} = \frac{(x+y)x}{C} \quad \text{and} \quad K_{\text{HB}} = \frac{(x+y)y}{C}$$

$$\frac{[\text{H}^+]_{\text{HA}}}{[\text{H}^+]_{\text{HB}}} = \frac{x}{y} = \sqrt{\frac{k_{\text{HA}} \times C}{k_{\text{HB}} \times C}}$$

$$\frac{x}{y} = \sqrt{\frac{1.6 \times 10^{-5}}{0.4 \times 10^{-5}}} = 2$$

$$x = 2y \Rightarrow y = \frac{x}{2}$$

$$\text{Substitute for } y = \frac{x}{2} \text{ in } K_{\text{HA}} = \frac{x^2 + xy}{c}$$

$$1.6 \times 10^{-5} = \frac{2x^2 + x^2}{2 \times 0.5}$$

$$3x^2 = 1.6 \times 10^{-5} \Rightarrow x^2 = 5.33 \times 10^{-6}$$

$$x = 2.30 \times 10^{-3} \text{ M}, \quad y = 1.15 \times 10^{-3} \text{ M}$$

$$[\text{H}^+]_{\text{final}} = x + y = 2.30 \times 10^{-3} + 1.15 \times 10^{-3} = 3.45 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log_{10}(3.45 \times 10^{-3})$$

$$\text{pH} = 2.462$$

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Exercise

1. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSaC . A 8×10^{-4} mole amount of Saccharin is dissolved in 400 cm^3 water of $\text{pH} = 3$. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium.

Ans. $[\text{SaC}^-] = 4 \times 10^{-12} \text{ M}$

2. A solution contains 0.08 M HCl , $0.08 \text{ M CHCl}_2\text{COOH}$ and $0.1 \text{ M CH}_3\text{COOH}$. The pH of this solution is 1. If K_a for acetic acid is 10^{-5} , calculate K_a for CHCl_2COOH .

Ans. $K_a = 3.33 \times 10^{-2}$

ISOHYDRIC SOLUTIONS

- (i) Solution of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solution, there occurs no change in the degree of dissociation of either of the electrolyte.
(ii) Let the isohydric solution is made by HA_1 and HA_2 acids, then $[\text{H}^+]$ of both should be equal i.e.

$$\sqrt{K_{a_1} C_1} = \sqrt{K_{a_2} C_2} \quad \text{or} \quad \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

Illustration

1. The degree of dissociation of pure water at 25°C is found to be 1.8×10^{-9} . Find K_w and K_d at 25°C .
(A) $3.24 \times 10^{-18}; 5.83 \times 10^{-20}$ (B) $1 \times 10^{-14}; 1.8 \times 10^{-15}$
(C) $1.8 \times 10^{-16}; 1 \times 10^{-14}$ (D) $1 \times 10^{-14}; 1 \times 10^{-14}$

Ans. (B)

Sol. Since $\alpha = 1.8 \times 10^{-14}$

$$\text{and for water } C = \frac{1000}{18} = 55.56$$

$$[\text{H}^+] = [\text{OH}^-] = C\alpha = 55.56 \times 1.8 \times 10^{-9} = 1 \times 10^{-7} \text{ M}$$

$$K_w = [\text{H}^+] \times [\text{OH}^-] = (1 \times 10^{-7})^2 = 10^{-14}$$

$$\text{and } K_d = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{K_w}{[\text{H}_2\text{O}]} = \frac{10^{-14}}{55.56} = 1.8 \times 10^{-16}$$

2. When a 0.1 N solution of an acid at 25°C has a degree of ionisation of 4%, the concentration of OH^- present is-
(A) 2.5×10^{-3} (B) 2.5×10^{-11} (C) 2.5×10^{-12} (D) 2.5×10^{-13}

Ans. (C)

$$\text{Sol. } [\text{H}^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3} \text{ M} \quad \text{or} \quad [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 2.5 \times 10^{-12} \text{ N}$$

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Exercise

1. Calculate the molar concentration of a solution of acetic (HOAc) that has a pH of 4.00.
 $(\text{Ka} = 1.8 \times 10^{-5})$
 (A) 1.0×10^{-3} (B) 1.0×10^{-6} (C) 0.057×10^{-2} (D) 0.010
Ans. (C)
2. Select the correct option from the following ?
 (A) pK_w increases with increase of temperature
 (B) pK_w decreases with increase of temperature
 (C) $\text{PK}_w = 14$ at all temperature
 (D) $\text{pK}_w = \text{pH}$ at all temperature
Ans. (B)

SALTS

- (i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.
- (ii) Salts may taste salty, bitter, astringer or sweet or tasteless
- (iii) Solution of salts may be acidic, basic or neutral.
- (iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis
- (v) The salts are generally crystalline solids

1. Classification of salts :

These salts may be classified into four categories.

1.1 Simples salts :

The salts formed by the neutralisation process between acid and base. These are of three types.

(i) Normal salt :

The salt formed by the loss of all possible protons (replaceable H^+ ions)

Ex. NaCl , NaNO_3 , K_2SO_4 , $\text{Ca}_3(\text{PO}_4)_2$, Na_3BO_3 , Na_2HPO_4 , NaH_2PO_4 etc.

(ii) Acids salts :

Salts formed by incomplete neutralisation of polybasic acid. Such salts contain one or more replaceable H atom.

Ex. NaHCO_3 , NaHSO_4 , NaH_2PO_4 , Na_2HPO_4 etc.

Above salts when neutralized by base form normal salts.

(iii) Basic salts :

Salts formed by incomplete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

Ex. Zn(OH)Cl , Mg(OH)Cl , Fe(OH)_2 , Cl_2 , Bi(OH)_2 etc.

Above salt when neutralised by acids form normal salts.

1.2 Double salts :

(i) The addition compounds formed by the combination of two simple salts are termed as double salts.

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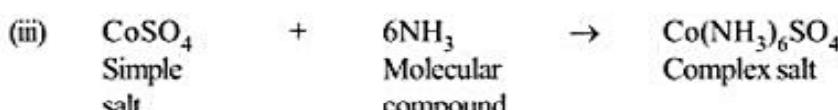
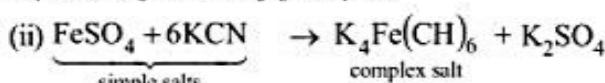
Ex. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Ferrous ammonium sulphate), $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (Alum) and other alums.

- (ii) Above salts are stable in solid state only.
- (iii) When dissolved in water, it furnishes all the ions present in the simple salt form which it has been constituted.
- (iv) The solution of double salt shows the properties of the samples salts from which it has been constituted

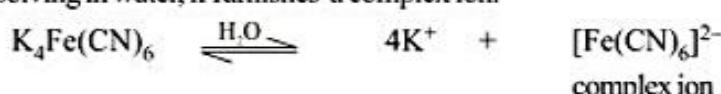
1.3 Complex salts :

- (i) They are formed by combination of simple salt or molecular compounds.

Ex. $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Co}(\text{NH}_3)_6 \text{SO}_4$ etc.



- (iv) These are stable in solid states as well as solutions
- (v) On dissolving in water, it furnishes a complex ion.

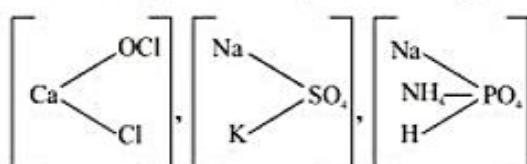


- (vi) The properties of the solution are different from the properties of the substance from which it has been constituted.

1.4 Mixed salts :

- (i) The salt which furnishes more than one cation or more than one anion when dissolved in water is called mixed salt.

Ex. CaOCl_2 , NaKSO_4 , $\text{NaNH}_4\text{HPO}_4$ etc.



HYDROLYSIS OF SALTS

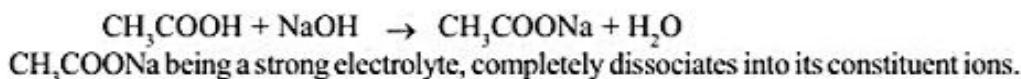
Salts are the product of an acid and a base, other than water. Depending on the nature of an acid or a base there can be four types of salts:

- (i) Salt of a weak acid and a strong base.
- (ii) Salt of a strong acid and a weak base.
- (iii) Salt of a weak acid and a weak base and
- (iv) Salt of a strong acid and a strong base.

We shall first look at what is hydrolysis and then find out how to calculate the pH due to it.

1. Salt of a Weak Acid and Strong Base

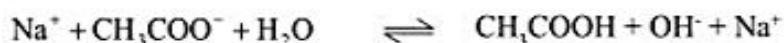
Let us take a certain amount of weak acid (CH_3COOH) and add to it the same amount (equivalents) of a strong base (NaOH). They will react to produce CH_3COONa .



Now, the ions produced would react with H_2O . This process is called hydrolysis.



We know that NaOH is a strong base and therefore it would be completely dissociated to give Na^+ and OH^- ions.



Cancelling Na^+ on both the sides,



We can note here that ions coming from strong bases do not get hydrolysed. We should note here that the solution will be basic. This is because the amount of CH_3COOH produced and OH^- produced are equal. But CH_3COOH will not completely dissociate to give H^+ ions. Therefore $[\text{OH}^-]$ ions will be greater than $[\text{H}^+]$ ions.

Since the reaction is at equilibrium,

$$K_c = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

This equilibrium constant K_c is given a new symbol, K_b

$$\therefore K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

If we multiply and divide the above equation by $[\text{H}^+]$ of the solution, then

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-][\text{H}^+]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}^+]}$$

$$K_b = \frac{K_w}{K_a} \Rightarrow K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a}$$

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	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
Initial	C 0 0
At eq:	$C(1-\alpha)$ $C\alpha$ $C\alpha$

Where α is the degree of hydrolysis of CH_3COO^- ion?

$$\therefore \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{K_w}{K_a}$$

If α is very much less than 1,

$$C\alpha^2 = \frac{K_w}{K_a}, \quad \alpha = \sqrt{\frac{K_w}{K_a C}}$$

$$\text{As } [\text{OH}^-] = C\alpha, [\text{OH}^-] = C \times \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{K_w C}{K_a}}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \sqrt{\frac{K_w K_a}{C}} \quad \text{or} \quad \text{pH} = -\log[\text{H}^+] = -\log\left(\sqrt{\frac{K_w \cdot K_a}{C}}\right) = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

Illustration

1. Find out pH, h and $[\text{OH}^-]$ of milli molar solution of KCN if the dissociation constant of HCN is 10^{-7} .

Sol. (1) $\text{pH} = 7 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C = 7 + \frac{1}{2} \times 7 + \frac{1}{2}\log 10^{-3}$

$$= 7 + \frac{7}{2} - \frac{3}{2}\log 10 = \frac{14+7-3}{2} = \frac{21-3}{2} = 9$$

$$(2) \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14} \times 10^{-3}}{10^{-7}}} = 10^{-5}$$

$$(3) \quad [\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}} = \sqrt{\frac{10^{-14} \times 10^{-3}}{10^{-7}}} = 10^{-5}$$

2. Calculate for 0.01 N solution of sodium acetate

(i) Hydrolysis constant (ii) Degree of hydrolysis (iii) pH

Given K_a of $\text{CH}_3\text{COOH} = 1.9 \times 10^{-5}$

For	$\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NaOH}$
Initial	C 0 0
After	$C(1-h)$ Ch Ch

$$(i) \quad K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$(ii) \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-6} \text{ M}$$

$$(iii) \quad [\text{OH}^-] \text{ from NaOH, a strong base} = Ch = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.64$$

$$\therefore \text{pH} = 14 - 5.64 = 8.36$$

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Exercise

1. Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN, K_a for HCN is 6.2×10^{-11} .

Ans. pH = 11.6

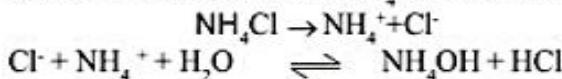
$$\text{Degree of hydrolysis} = 4 \times 10^{-11}$$

2. Calculate the pH after the addition of 90 ml and 100 ml respectively of 0.1 N NaOH to 100 ml 0.1 N CH₃COOH (Given pK_a for CH₃COOH = 4.74)

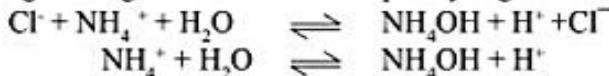
Ans. pH = 8.71

2. Salt of a Weak Base and a Strong Acid

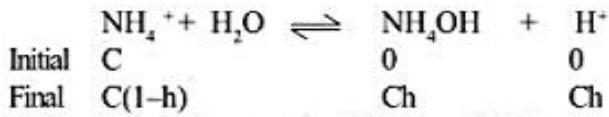
Let the acid be HCl and the base be NH₄OH. Therefore the salt would be NH₄Cl.



HCl being a strong acid dissociates completely to give H⁺ ions and Cl⁻ ions.



We can see that the ion coming from the strong acid does not get hydrolysed. We had previously seen that the ion coming from the strong base also does not get hydrolyzed. Hence, one can conclude that the salt of a strong acid and strong base does not get hydrolyzed. In this hydrolysis, NH₄OH and H⁺ are being produced. This implies that the solution is acidic. To calculate pH,



Where h is the degree of hydrolysis of NH₄⁺.

$$K_b = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

Multiplying and dividing by OH⁻ and rearranging.

$$K_b = \frac{[\text{NH}_4\text{OH}][\text{H}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]} \Rightarrow \frac{[\text{H}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]} = \frac{K_w}{K_b} \quad \therefore K_h = \frac{K_w}{K_b}$$

Now, substituting the concentrations,

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{Ch \cdot Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

$$\text{If } h \leq 0.1, \text{ then } Ch^2 = \frac{K_w}{K_b} \Rightarrow h = \sqrt{\frac{K_w}{K_b C}}$$

$$\text{Since } [\text{H}^+] = Ch, [\text{H}^+] = C \sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{K_w C}{K_b}} \text{ or } \text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

Illustration

1. Find out the K_h of centi normal [10^{-2} N] solution of NH_4Cl (SA-WB) if dissociation constant of NH_4OH is 10^{-6} and $K_w = 10^{-14}$. Find out degree of hydrolysis and also find $[\text{H}^+]$ and pH of solution?
 Given : $K_w = 10^{-14}$; $K_b = 10^{-6}$

$$\text{Sol. (1)} \quad K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$$(2) \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$$

$$(3) \quad [\text{H}^+] = Ch \\ = 10^{-2} \times 10^{-3} \\ = 10^{-5}$$

$$(4) \quad \text{pH} = -\log [\text{H}^+] = -\log [10^{-5}] \\ = +\log [10^{-5}] = +5 \times 1 = 5$$

2. How many grams of NH_4Cl should be dissolved per litre of solution to have a pH of 5.13 ? K_b for NH_3 is 1.8×10^{-5} .

Sol. NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \log C - \text{p}K_b]$$

$$\Rightarrow 10.26 = 14 - \log C - 4.74$$

$$\Rightarrow \log C = 9.26 - 10.26 = -1.0$$

$$\therefore C = 10^{-1} \text{ M}$$

$$[\text{NH}_4\text{Cl}] = 10^{-1} \text{ M}$$

$$W_{\text{NH}_4\text{Cl}} = 10^{-1} \times 53.5 \text{ g L}^{-1} = 5.35 \text{ g L}^{-1}$$

Exercise

1. Find out the K_h at 363 K (90°C) of a salt of [Strong acid - Weak base] if the value of K_b is 10^{-5} [At 90°C $K_w = 10^{-12}$]

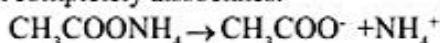
$$\text{Ans. } K_h = \frac{K_w}{K_b} = \frac{10^{-12}}{10^{-5}} = 10^{-7}$$

2. What is the pH of 0.4 M aqueous NaCN solution ? {Given $\text{p}K_b$ of $\text{CN}^- = 4.70$ }

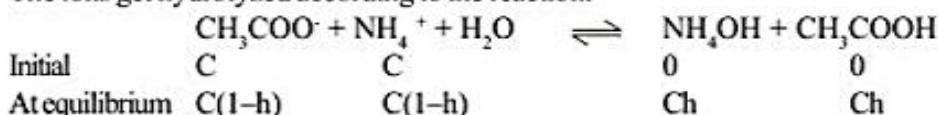
$$\text{Ans. } \text{pH} = 11.45$$

3. **Salt of a Weak Acid and Weak Base**

Let the weak acid be CH_3COOH and the weak base be NH_4OH . Therefore, the salt is $\text{CH}_3\text{COONH}_4$. The salt completely dissociates.



The ions get hydrolyzed according to the reaction.



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}]}{[\text{NH}_4^+][\text{CH}_3\text{COO}^-]}$$

Multiplying and dividing by H^+ & OH^- and rearranging.

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}][\text{H}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{CH}_3\text{COO}^-][\text{H}^+][\text{OH}^-]} \Rightarrow \frac{[\text{H}^+][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}^+]_x [\text{NH}_4^+][\text{OH}^-]} \Rightarrow \frac{K_w}{K_a K_b}$$

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

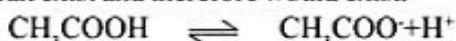
Substituting the concentration terms,

$$K_h = \frac{K_w}{K_a K_b} = \frac{\text{Ch}}{\text{C}(1-h)} \frac{\text{Ch}}{\text{C}(1-h)} \frac{(\text{Ch})^2}{[\text{C}(1-h)]^2} = \frac{h^2}{(1-h)^2}$$

As can be seen in the hydrolysis reaction.

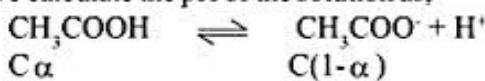


CH_3COOH is present in the solution. This implies that the equilibrium between CH_3COOH , CH_3COO^- and H^+ can exist and therefore would exist.



In fact the equilibrium between NH_4OH , NH_4^+ and OH^- also exists.

Now, we calculate the pH of the solution as,



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{\text{C}(1-\alpha)(\text{H}^+)}{\text{C}\alpha} \quad \therefore [\text{H}^+] = K_a \times \left(\frac{\alpha}{1-\alpha} \right)$$

Substituting $\frac{\alpha}{1-\alpha}$ as $\sqrt{\frac{K_w}{K_a K_b}}$

$$[\text{H}^+] = K_a \times \left(\frac{\alpha}{1-\alpha} \right) = K_a \times \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}}$$

$$\text{or} \quad \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

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Illustration

1. Calculate pH of the mixture (25 mL of 0.1 M NH_4OH + 25 mL of 0.1 M CH_3COOH)
 Given that $K_a : 1.8 \times 10^{-5}$, and $K_b = 1.8 \times 10^{-5}$
- Sol.**
- | | | | | | |
|-----------------------|------------------------|---|--------------------------|---|--|
| Initially milli moles | NH_4OH | + | CH_3COOH | → | $\text{CH}_3\text{COONH}_4 + \text{H}_2\text{O}$ |
| | 25×0.1 | | 25×0.1 | | 0 0 |
| | $= 2.5$ | | $= 2.5$ | | |
| Final milli moles | 0 | | 0 | | 2.5 2.5 |

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$\text{pH} = \frac{\text{pK}_w + \text{pK}_a - \text{pK}_b}{2} = \frac{1}{2} (-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

2. In the following which one has highest/maximum degree of hydrolysis.

- (A) 0.01 M NH_3Cl (B) 0.1 M NH_4Cl
 (C) 0.001 M NH_4Cl (D) Same

Ans. C

Sol.
$$\left(h \sqrt{\frac{K_h}{C}} \text{ if } C \text{ decreases, } h \text{ increases} \right)$$

Exercise

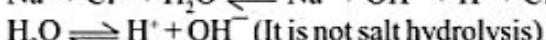
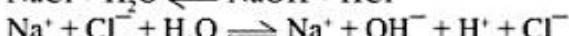
1. In the following which one has lowest value of degree of hydrolysis

- (A) 0.01 M $\text{CH}_3\text{COONH}_4$ (B) 0.1 M $\text{CH}_3\text{COONH}_4$
 (C) 0.001 M $\text{CH}_3\text{COONH}_4$ (D) Same

Ans. D

4. Salt of strong acid and strong base

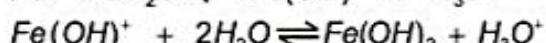
Ex. NaCl , BaCl_2 , Na_2SO_4 , KClO_4 etc.



- (a) No hydrolysis
- (b) Solution is always neutral
- (c) $\text{pH} = 7$ at 25°C

5. Salt of a weak polyprotic acid and strong base

- (i) **Salt containing multivalent cation or anion.** Hydrolysis of multivalent cation or anion takes place in stepwise manner and more than one hydrolytic products are formed. For example the hydrolysis of Fe^{2+} ions will occur in following steps



The hydrolysis constants K_{h_1} and K_{h_2} are

$$K_{h_1} = \frac{[Fe(OH)^+][H_3O^+]}{[Fe^{2+}]} = \frac{K_w}{K_{b_2}}$$

$$K_{h_2} = \frac{[Fe(OH)_2][H_3O^+]}{[Fe(OH)^+]} = \frac{K_w}{K_{b_1}}$$

Where K_{b_1} and K_{b_2} are dissociation constants of $Fe(OH)_2$. Since $K_{b_1} \gg K_{b_2}$ thus $K_{h_1} \gg K_{h_2}$ hence the hydrolysis of $Fe(OH)^+$ in comparison can be neglected and

$$[H_3O^+] = \sqrt{K_{h_1} C}$$

or $pH = 7 - \frac{1}{2} pK_{b_2} - \frac{1}{2} \log C$

- (ii) **Salt containing weak conjugate cation and an amphiprotic cation :** When a salt like $NaHCO_3$, $NaHS$, NaH_2PO_4 , Na_2HPO_4 etc is dissolved in water the amphiprotic anion can either accept a proton from water (Hydrolysis) or can donate a proton to water. The pH of the solution can be calculated as

$$pH = \frac{1}{2}(pK_1 + pK_{a_2})$$

- (iii) **Salt containing strong conjugate cation and an amphiprotic cation :** Examples of such salts are NH_4HCO_3 , NH_4HS etc. The $[H_3O^+]$ of the solution can be calculated as

$$[H_3O^+] = \sqrt{\frac{K_{a_1} K_w}{K_b} - K_{a_1} K_{a_2}}$$

- (iv) **Hydrolysis of amphiprotic anion**

Let us consider hydrolysis of amphiprotic anion only, i.e., when counter cation is not hydrolysed, example of some salts of this category are $NaHCO_3$, $NaHS$, Na_2HPO_4 , NaH_2PO_4 .

Here, $H_2PO_4^-$ and HPO_4^{2-} are amphiprotic anions. pH after their hydrolysis can be calculated as,

$$pH \text{ of } H_2PO_4^- \text{ in aqueous medium} = \frac{pK_{a_1} + pK_{a_2}}{2}$$

$$pH \text{ of } H_2PO_4^- \text{ in aqueous medium} = \frac{pK_{a_2} + pK_{a_1}}{2}$$

Here, $H_2PO_4^{2-}$ is conjugate base of $H_2PO_4^-$ and H_3PO_4 is conjugate acid of $H_2PO_4^-$. Similarly, PO_4^{3-} is conjugate base of HPO_4^{2-} and HPO_4^{2-} is conjugate acid of PO_4^{3-} .

When these salts are dissolved in water, $[H_3O^+]$ concentration can be determined as,

$$[H_3O^+] = \sqrt{K_{a_1} (K_w / k_b + K_{a_2})}$$

$$pH = -\log \sqrt{K_{a_1} (K_w / k_b + K_{a_2})}$$

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Hydrolysis at a Glance

	Salt	Nature	Degree	Hydrolysis Constant	pH
1.	NaCl (Strong acid + Strong Base)	Neutral	No Hydrolysis		
2.	CH ₃ COONa (Weak acid + Strong base)	Base	$h = \sqrt{k_w / C k_a}$	$K_h = k_w / k_a$	$pH = 1/2[pk_w + pk_a + \log C]$
3.	NH ₄ Cl (Strong acid + Weak base)	Acidic	$h = \sqrt{k_w / C k_b}$	$K_h = k_w / C k_b$	$pH = 1/2[pk_w - pk_b - \log C]$
4.	CH ₃ COONH ₄ (Weak acid + Weak base)	*	$h = \sqrt{k_w / (k_a + k_b)}$	$K_h = k_w / (k_a + k_b)$	$pH = 1/2[pk_w + pk_a - pk_b]$

In the case of salt of weak acid and weak base, nature of 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 dilution because there is no concentration term in the expression of degree of hydrolysis.

Note : Degree of hydrolysis always increases with increase in temperature because at elevated temperature increase in K_w is greater as compared to K_a and K_b .

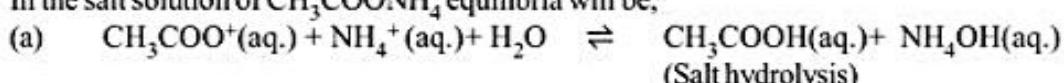
BUFFER SOLUTIONS

- In certain applications of chemistry and biochemistry solutions of constant pH is required. Such solution are called buffer solution.
- A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called buffer solution.
- Buffer solutions are also called solutions of reverse acidity or alkalinity.
- Characteristics of buffer solutions
 - (a) It must have constant pH.
 - (b) Its pH should not be changed on long standing
 - (c) Its pH should not be changed on dilution.
 - (d) Its pH should not be changed to any great extent on addition of small quantity of acid or base.
- Buffer solutions can be classified as follows.
 - (A) Simple buffer
 - (B) Mixed buffer

A. Simple buffer

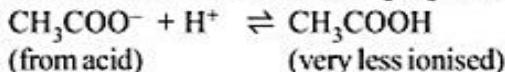
- (i) It is a solution of one compound (salts of WA + WB)
- (ii) Buffer action of such solution can be explained as follows-

In the salt solution of CH₃COONH₄ equilibria will be,

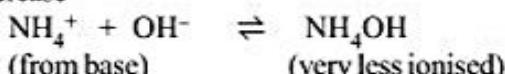


- (b) $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ (weak base)
 (c) $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ (weak acid)
 (d) $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ (feeble ionised)

on addition of small amount of acid the $[H^+]$ in solution will increase and



equilibria will shift in forward direction. Similarly on addition of small amount of base, the $[OH^-]$ in solution will increase



equilibria will shift in forward direction. Hence one can conclude that there will be no change (almost) in the pH of the solution.

- (iii) Simple buffer solutions have very little significance since

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

so solution of desired pH can not be prepared.

B. Mixed buffer

Mixed buffers are solutions of more than one compounds. They can be further classified as

- (a) Acidic buffer (b) Basic buffer

1. Acidic buffer

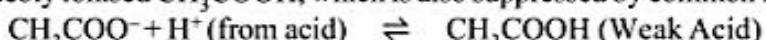
- (i) These are the mixture of a weak acid and its salt with strong base.

e.g.

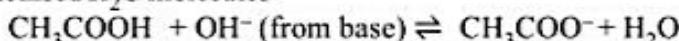
- (a) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 (b) Boric acid (H_3BO_3) + Borax ($\text{Na}_2\text{B}_4\text{O}_7$)

- (ii) Buffer action of acidic buffer can be explained with following equilibria

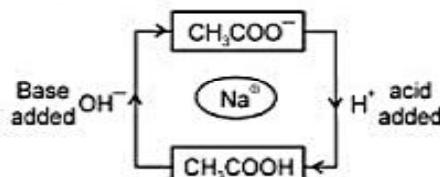
When a strong acid is added in the solution $[H^+]$ increases, which will combine with CH_3COO^- to form feebly ionised CH_3COOH , which is also suppressed by common ion effect.



Again when strong base is added in the solution it will attack on unionised acid CH_3COOH to form feebly ionised H_2O molecules



- (iii) One can remember, buffer action of acidic buffer with the help of following figure -



- (iv) pH calculation for acidic buffer

- (a) $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ (K_s)

- (b) $\text{CH}_3\text{COONa} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COO}^- \text{(aq.)} + \text{Na}^+ \text{(aq.)}$

$\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- (\text{aq.}) + \text{Na}^+ (\text{aq.})$
 CH_3COOH is feebly ionised and its ionisation is also suppressed by presence of common ion (CH_3COO^-).

So one can fairly assume $[CH_3COO^-] = [salt]$ and $[CH_3COOH] = [Acid]$ taken initially in buffer solution.

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

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

$$\log[H^+] = \log K_a + \log[CH_3COOH] - \log[CH_3COO^-]$$

$$-\log[H^+] = -\log K_a - \log[CH_3COOH] + \log[CH_3COO^-]$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

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

Above equation is called Henderson's equation.

Note :

- If we increase the concentration of given salt in acidic buffer, pH will also increases.
- If we increase the concentration of acid in acidic buffer, pH will decreases.
- If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$pH = pK_a + \log \frac{[N_2V_2]}{[N_1V_1]}$$

Where N_2V_2 = conc. & volume of salt

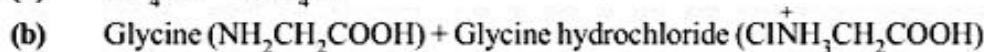
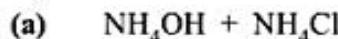
N_1V_1 = conc. & volume of acid

- Mixture of weak acid and strong base solution can also act as an acidic buffer, if value of N_1V_1 of weak acid is greater than the value of N_2V_2 of strong base.

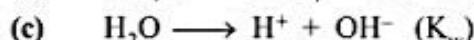
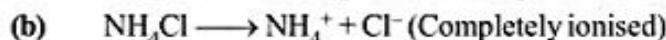
2. Basic Buffer

- (i) These are the mixture of a weak base and its salt with strong acid.

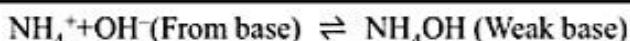
e.g.



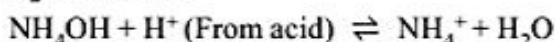
- (ii) Buffer action of basic buffer can be explained with the help of following equilibria



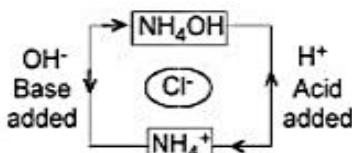
When a strong base is added in the solution $[OH^-]$ increases, which will combine with NH_4^+ to form feebly ionised NH_4OH , which is also suppressed by common ion effect.



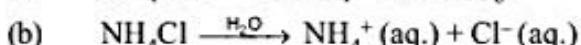
Again when strong acid is added in the solution it will attack on unionised base NH_4OH to form feebly ionised H_2O molecules.



- (iii) One can remember the buffer action of basic buffer with the help of following figure -



- (iv) pH of such basic buffer can be calculated from Henderson - equation as follows.



NH_4OH is feebly ionised and its ionisation is also suppressed by presence of common ion (NH_4^+).

So one can fairly assume $[\text{NH}_4^+] = [\text{Salt}]$ and $[\text{NH}_4\text{OH}] = [\text{Base}]$ taken initially in buffer solution.

$$\text{so} \quad K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\begin{aligned} \text{or} \quad [\text{OH}^-] &= \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} \\ &= \frac{K_b[\text{Base}]}{[\text{Salt}]} \end{aligned}$$

$$\text{or} \quad \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{or} \quad \text{pH} = 14 - \text{pOH}$$

3. Buffer Capacity

- (i) The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.
(ii) Buffer capacity is number of moles of acid or base added in one litre of solution so as to change the pH by unity, i.e.

$$\text{Buffer capacity} (\phi) = \frac{\text{Number of moles of acid or base added/litre solution}}{\text{Change in pH}}$$

- (iii) Higher the buffer capacity, better will be the buffer solution
(iv) For maximum buffer capacity of a given buffer concentration of salt should be equal to the concentration acid/base
(v) A buffer solution work in a buffer range from $\text{pH} = \text{p}K_a \pm 1$
(vi) A buffer solution work between $0.1 < \frac{[\text{Salt}]}{[\text{Acid/Base}]} < 10$

Illustration

1. What will be the pH of the buffer solution containing 0.15 moles of NH_4OH and 0.25 moles of NH_4Cl . K_b for NH_4OH is 1.8×10^{-5} .

(A) 9.08 (B) 10.03 (C) 9.05 (D) 9.03

Ans. D

Sol. Since it is a basic buffer so,

$$\text{pOH} = \text{pK}_b + \log[\text{Salt}]/[\text{Base}]$$

$$\begin{aligned}\text{pOH} &= -\log K_b + \log[\text{Salt}/\text{Base}] \\ &= -\log(1.8 \times 10^{-5}) + \log(0.25/0.15) \\ &= 4.74 + 0.22 = 4.96\end{aligned}$$

$$\text{or pOH} = 4.97$$

$$\begin{aligned}\text{pH} &= 14 - \text{pOH} \\ &= 14 - 4.97 = 9.03\end{aligned}$$

2. Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M NH_3 and 500 cc of 0.5 M NH_4Cl . K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$.

(A) 8.11 (B) 9.81 (C) 8.82 (D) None of these

Ans. C

Sol. Total volume of the buffer solution

$$= 300 \text{ cc} + 500 \text{ cc} = 800 \text{ cc}$$

$$\text{Number of milli moles of } \text{NH}_3 = 300 \times 0.3 = 90$$

$$\text{Molarity of } \text{NH}_3 \text{ (Base) in the buffer} = 90/800 \text{ M}$$

$$\text{Number of milli moles of } \text{NH}_4\text{Cl} = 500 \times 0.5 = 250.0$$

$$\text{Molarity of [salt] in the buffer} = 250/800 \text{ M}$$

Henderson's equation for basic buffer is:

$$\begin{aligned}\text{pOH} &= -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ &= -\log 1.8 \times 10^{-5} + \log \frac{250/800}{90/800} \\ &= 4.74 + \log 250/90 \\ &= 4.74 + 0.44 \\ &= 5.18 \\ \text{pH} &= 14 - \text{pOH} = 14 - 5.18 = 8.82\end{aligned}$$

3. Calculate the pH of a buffer solution prepared by dissolving 10.6 g of Na_2CO_3 in 500 ml of an aqueous solution containing 80 ml of 1M HCl. (K_a for $\text{HCO}_3^- = 6 \times 10^{-11}$)

(A) 8.6 (B) 9.6 (C) 11.6 (D) 12.6

Ans. B

	Na_2CO_3	+	HCl	\rightarrow	NaCl	+	NaHCO_3
Meq. before	$\frac{10.6}{106} \times 1000$		80×1		0		0
Reaction =	100		80		0		0
Meq. After	20		0		80		80

Reaction

The solution Na_2CO_3 and HCO_3^- and thus acts as buffer

$$\text{pH} = -\log K_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = -\log 6 \times 10^{-11} + \log \frac{20}{80} = 9.6$$

4. The concentration of H^+ ion in a 0.2 M solution of HCOOH is 6.4×10^{-3} mole L^{-1} . To this solution HCOONa is added so as to adjust the concentration of HCOONa to one mole per litre. What will be the pH of this solution? K_a for HCOOH is 2.4×10^{-4} and the degree of dissociation of HCOONa is 0.75
 (A) 3.19 (B) 4.19 (C) 5.19 (D) 6.19

Ans.**B**

Sol. Assuming that the addition of HCOONa suppresses the ionization of HCOOH , we can use the expression

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

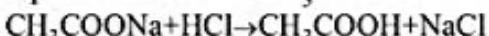
to compute pH of the solution, since salt is 75% dissociated we will get,

$$\begin{aligned}\text{pH} &= -\log(2.4 \times 10^{-4}) + \log \frac{0.75}{0.2} \\ &= 3.62 + 0.57 = 4.19\end{aligned}$$

5. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre.
 (A) 1 : 1 (B) 2 : 1 (C) 1 : 2 (D) 2 : 3

Ans.**C**

Sol. **Case I** - pH when 1 mole CH_3COONa and 1 mole HCl are present



Before reaction	1	1	0	0
After reaction	0	0	1	1

$$[\text{CH}_3\text{COOH}] = 1\text{M}$$

$$\therefore [\text{H}^+] = C \cdot \sqrt{\frac{K_a}{C}} = \sqrt{C \cdot K_a} = \sqrt{K_a}$$

$$\therefore C = 1$$

$$\therefore \text{pH}_1 = -\frac{1}{2} \log K_a$$

Case II - pH when 1 mole CH_3COONa and 1 mole of CH_3COOH , a buffer solution

$$\therefore \text{pH}_2 = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a \quad \because [\text{Salt}] = [\text{Acid}] = 1\text{M}$$

$$\therefore \frac{\text{pH}_1}{\text{pH}_2} = \frac{1}{2} \quad \text{or} \quad \text{pH}_1 : \text{pH}_2 = 1 : 2$$

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6. In which case pH will not change on dilution
 (A) 0.01 M $\text{CH}_3\text{COONa} + 0.01 \text{ M } \text{CH}_3\text{COOH}$ buffer
 (B) 0.01 M $\text{CH}_3\text{COONH}_4$
 (C) 0.01 M NaH_2PO_4
 (D) in all cases

Ans. (D)

Sol. Mixture of Sodium acetate and acetic acid is a buffer of pH value equal to pK_a so its buffer capacity is maximum and hence its pH will not change significantly while $\text{CH}_3\text{COONH}_4$ is a salt of weak acid CH_3COOH and weak base NH_4OH whose magnitude of K_a and K_b are equal. So its pH does not depend upon concentration. Further more, NaH_2PO_4 is, in fact, a single solute buffer.

Exercise

1. Calculate pH of the buffer solution containing 0.15 moles of NH_4OH and 0.25 moles of NH_4Cl . K_b for NH_4OH is 1.98×10^{-5} .
 (A) 7.034 (B) 9.04 (C) 8.043 (D) None of these

Ans. B

2. What volume of 0.1 M HCOONa solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH = 4.0, pK_a of formic acid = 3.7
 (A) 50 ml (B) 40 ml (C) 30 ml (D) 60 ml

Ans. A

3. What amount of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 10.4 using 0.01 mole of NaCN . Given $K_{\text{ion}}(\text{HCN}) = 4.1 \times 10^{-10}$ –
 (A) 8.55×10^{-3} mole (B) 8.65×10^{-3} mole
 (C) 8.75×10^{-3} mole (D) 9.9×10^{-4} mole

Ans. D

4. 20 ml of 0.2 M NaOH is added to 50 ml, of 0.2 M CH_3COOH to give 70ml, of the solution. What is the pH of the solution ? The ionization constant of acetic acid is 2×10^{-5} –
 (A) 4.522 (B) 5.568 (C) 6.522 (D) 7.568

Ans. A

SOLUBILITY (S)

At a constant temperature, the mass of a solute or electrolyte dissolved in the 100 gm of solvent in its saturated solution is called solubility.

Or

Number of gm mole of a solute dissolved in one litre of water at constant temperature is called solubility of that solute.

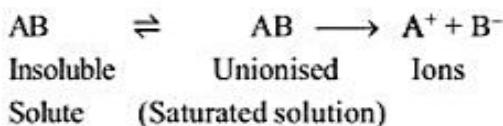
Solubility of a solute in moles / litre

$$= \frac{\text{Solubility of solute in gm/litre}}{\text{molecular weight of the solute}}$$

1. Solubility product (K_{SP}):

It is the product of the ionic concentration of the ions of binary solid electrolyte in saturated state at constant temperature.

- (a) Let solubility of a compound $A_x B_y$ be s moles L^{-1} it means that if more than s moles are dissolved in solvent (one litre) only s moles will be soluble, rest will be insoluble, following equilibrium is established,



Note : In the solubility s moles L^{-1} , moles of only unionised are counted moles of ions and insoluble solute do not have anything to do.

- (b) According to law of mass action -

$$K_1 = \frac{[A^+][B^-]}{[AB]}$$

or $K_1 [AB] = [A^+] [B^-] = K_{SP}$

K_{SP} is called **solubility product**.

- (c) At a certain temperature solubility product of a compound is constant, it means that ions are formed in the manner that product of their concentration is always a constant. However, it becomes clear that if one of ions (A^+ or B^-) is added from outside, it would tend to increase K_{SP} because $[A^+]$ or $[B^-]$ has increased, so that extra ions will react with other ions to convert into insoluble part and it precipitates.
- (d) K_{SP} increases with increase in temperature.
- (e) In a saturated solution.

$$K_{SP} = [A^+][B^-]$$

- (f) In an unsaturated solution of AB

$$K_{SP} > [A^+][B^-]$$

i.e. more solute can be dissolved.

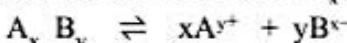
- (g) In a supersaturated solution

$$K_{SP} < [A^+][B^-]$$

i.e. precipitation will start to occur.

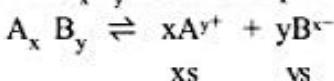
2. Relationship between Solubility and Solubility Product :

The equilibrium for a saturated solution of a salt $A_x B_y$ may be expressed as,



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

Let the solubility of the salt $A_x B_y$ in water at a particular temperature be ' s ' moles per litre then



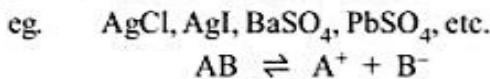
So, $K_{SP} = [xs]^x [ys]^y$

$$K_{SP} = x^x \cdot y^y (s)^{x+y}$$

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S & K_{sp} Relations

(a) 1 : 1 types salts or AB type of salts :

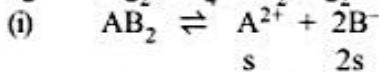


let the solubility of AB is s moles per litre.

$$\text{So, } K_{sp} = [A^+] [B^-] = s \times s = s^2$$

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

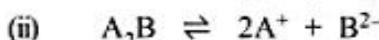
(b) 1 : 2 or 2 : 1 type of salts or AB₂ or A₂B type of salts :



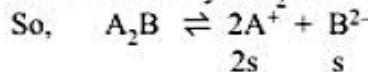
let the solubility of AB₂ is 's' moles per litre

$$\text{So, } K_{sp} = [A^{2+}] [B^-]^2 = s \times (2s)^2 = 4s^3$$

$$s = \left[\frac{K_{sp}}{4} \right]^{1/3}$$



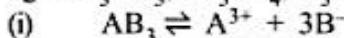
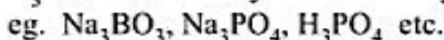
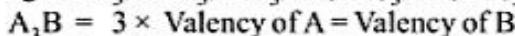
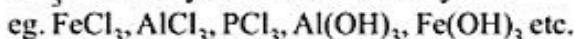
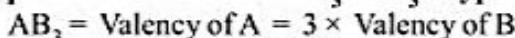
let s the solubility of A₂B



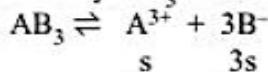
$$K_{sp} = [A^+]^2 [B^{2-}] = (2s)^2 (s) = 4s^3$$

$$s = \left[\frac{K_{sp}}{4} \right]^{1/3}$$

(c) 1 : 3 type of salts or salts of AB₃ or A₃B type of salt -

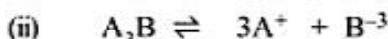


let the solubility of A₃B is 's' mole / litre.

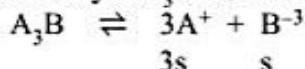


$$K_{sp} = [A^{3+}] [B^-]^3 = s \times (3s)^3 = 27s^4$$

$$s = \left[\frac{K_{sp}}{27} \right]^{1/4}$$



let the solubility of A₃B is 's' moles/litre.

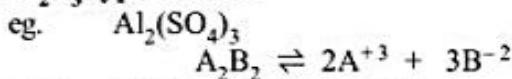


$$K_{sp} = [A^+]^3 [B^{-3}]$$

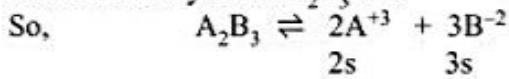
$$= (3s)^3 \times s = 27s^4$$

$$s = \left[\frac{K_{sp}}{27} \right]^{1/4}$$

(d) **2 : 3 or A₂B₃ type of salts :**



let the solubility of salt A₂B₃ is 's' -



$$K_{SP} = [A^{+3}]^2 [B^{-2}]^3 \\ = (2s)^2 \times (3s)^3 = 4s^2 \times 27 s^3$$

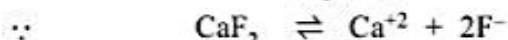
$$K_{SP} = 108 s^5 \quad s = \left[\frac{K_{SP}}{108} \right]^{1/5}$$

Illustration

1. The solubility of CaF₂ in water at 20°C is 15.6 mg per dm³ solution. What will be the solubility product of CaF₂ -
 (A) 4.0×10^{-4} (B) 8.0×10^{-8} (C) 32.0×10^{-12} (D) None

Ans. C

Sol. Solubility in moles per dm³ = $\frac{15.6 \times 10^{-3}}{78 \text{ g/mole}} = 2.0 \times 10^{-4}$



$\therefore [Ca^{+2}] = 2.0 \times 10^{-4}$

and $[F^-] = 2 \times 2.0 \times 10^{-4}$

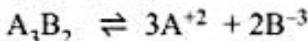
Hence, solubility product K_{SP}
 $= [Ca^{+2}] [F^-]^2 = [2.0 \times 10^{-4}] [4.0 \times 10^{-4}]^2 = 32 \times 10^{-12}$

2. Given the solubility product of F₃B₂ is 2×10^{-30} . What will be the solubility in moles/litre.

(A) $(1.85 \times 10^{-32})^{1/5}$ (B) $\left(\frac{2 \times 10^{-30}}{108} \right)^{1/5}$ (C) $\left(\frac{2 \times 10^{-28}}{5400} \right)^{1/5}$ (D) All

Ans. B

Sol. K_{SP} of A₃B₂ = 2×10^{-30} .



Assume s is the solubility of A₃B₂

then K_{SP} = $(3s)^3 (2s)^2 = 108 s^5$

$$s = 5\sqrt{\frac{K_{SP}}{108}} \quad s = \left(\frac{2 \times 10^{-30}}{108} \right)^{1/5}$$

Exercise

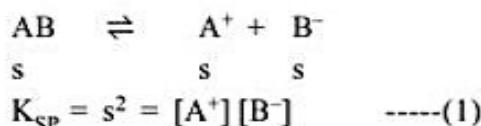
1. How many milligrams of AgBr will dissolve in water to give litres of aqueous solution. Given K_{SP} for AgBr (Mol. wt. 188) = $5.0 \times 10^{-13} M^2$ -
 (A) 7.071×10^{-7} moles per litre (B) 70.71×10^{-7} moles per litre
 (C) 707.1×10^{-7} moles per litre (D) None of these

Ans. A

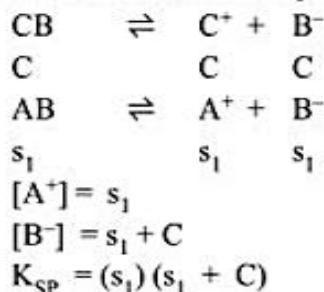
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1. Effect of Common ion on Solubility :

As we saw that for a saturated solution product of concentration of ions should not exceed a constant called solubility product. Now suppose, extra common ions are added to increase concentration of ions it will tend to increase the value of K_{sp} , but it can not increase so ions will react to form molecule and get precipitated e.g. let solubility of AB in water be s moles L^{-1} . It is dissolved in solution CB having a common ion B^- let concentration of CB be C.



(Product should not exceed s^2 otherwise precipitation will start) Now. Let solubility of AB in CB be S_1 .



If $s_1 \ll C$

$$K_{SP} = s_1 C = s^2, \text{ from equation (1)}$$

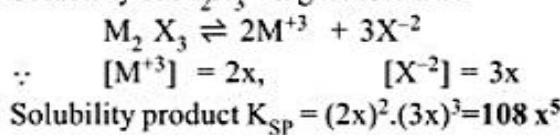
$$\text{or } s_1 = \frac{s^2}{C}$$

So, solubility gets reduced.

Illustration

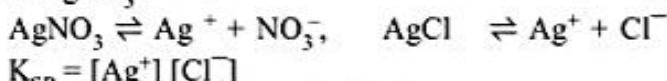
Ans. C

Sol. Solubility of $M_2X_3 = x$ gm mole/litre



Ans. A

Sol. In 0.1 M AgNO_3 ,



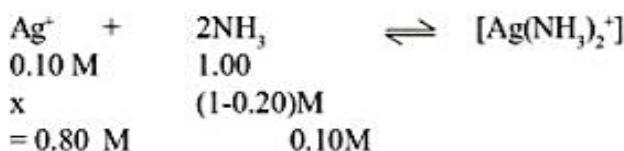
Now $[\text{Ag}^+]$ can be taken as $[\text{AgNO}_3]$

while $[C^-]$ is the solubility of AgCl .

$$\therefore \text{Cl} = \frac{\text{K}_{\text{sp}}}{[\text{Ag}^+]} = \frac{2.8 \times 10^{-10}}{0.1} \quad \therefore \quad \text{Solubility of AgCl} = 2.8 \times 10^{-9} \text{ mole/litre}$$

3. 0.10 mol sample of AgNO_3 is dissolved in one litre of 1.00 M NH_3 . If 0.010 mol of NaCl is added to this solution will AgCl precipitate?

Sol. $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$, $K_f[\text{Ag}(\text{NH}_3)_2]^+ = 1.6 \times 10^7$



It is assumed than all Ag^+ ion has been complexed and only its part x is left

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(0.80)^2}$$

$$\therefore x = 9.8 \times 10^{-9} \text{ M} = [\text{Ag}^+] \text{ undissolved}$$

$$[\text{Cl}^-] = 1.0 \times 10^{-2} \text{ M}$$

$$\therefore [\text{Ag}^+] [\text{Cl}^-] = 9.8 \times 10^{-9} \times 1.0 \times 10^{-2} = 9.8 \times 10^{-11} < 1.8 \times 10^{-10} (K_{sp}(\text{AgCl}))$$

Hence $\text{AgCl}(s)$ will not precipitate.

4. What is the minimum concentration of NH_3 required to prevent $\text{AgCl}(s)$ from precipitating from 1.00 litre of a solution containing 0.10 mol of AgNO_3 and 0.010 mol NaCl ?

$$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$$

$$K_f[\text{Ag}(\text{NH}_3)_2]^+ = 1.6 \times 10^7$$

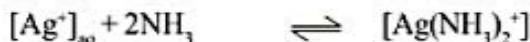
Sol. In order to prevent precipitation of AgCl

$$[\text{Ag}^+] [\text{Cl}^-] \leq K_{sp}$$

$$\Rightarrow [\text{Ag}^+] (0.01) \leq 1.8 \times 10^{-10}, \text{ As } [\text{Cl}^-] = 0.01 \text{ M}$$

$$\therefore [\text{Ag}^+] \leq 1.8 \times 10^{-8} \text{ M}$$

The maximum concentration of free uncomplexed Ag^+ permitted in the solution is 1.8×10^{-8} . That is almost all Ag^+ (0.10M) must be complexed



$$[\text{NH}_3] = ?, \quad [\text{Ag}^+] = 1.8 \times 10^{-8} \text{ M}.$$

$$[\text{Ag}(\text{NH}_3)_2]^+ = 0.10 \text{ M}$$

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+] [\text{NH}_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{(1.8 \times 10^{-8}) [\text{NH}_3]^2}$$

$$\therefore [\text{NH}_3]^2 = 0.3472 \Rightarrow [\text{NH}_3] = 0.589 \text{ M}$$

The concentration calculated above is that of free uncomplexed NH_3 . $[\text{NH}_3]$ required by

$$0.1 \text{ M } \text{Ag}^+ \text{ in the formation of } [\text{Ag}(\text{NH}_3)]^+ = 0.2 \text{ M}$$

$$\text{Hence } [\text{NH}_3] = 0.2 + 0.589 = 0.789 \text{ M}$$

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Exercise

1. The solubility product of chalk is 9.3×10^{-8} . Calculate its solubility in gram per litre –
 (A) 0.3040 gram/litre (B) 0.0304 gram/litre (C) 2.0304 gram/litre (D) 4.0304 gram/litre
Ans. B
2. Given $\text{Ag}^+ (\text{NH}_3)_2 \text{Ag}^+ + 2\text{NH}_3$, $K_c = 6.2 \times 10^{-8}$ and $K_{sp(\text{AgCl})} = 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of complex in 1.0 M aqueous ammonia.
Ans. $[\text{Ag}(\text{NH}_3^+)_2] = 0.539$.

3. Applications of K_{sp} :

- A. **In purification of common salt :** In a saturated solution of NaCl & impurities, by passing HCl gas through it, increase the Cl^- ion concentration which shifts the equilibrium $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$ to left & causes the precipitation of NaCl.
- B. **In preparation of NaHCO_3 by solvay method :** Precipitation of NaHCO_3 from its saturated solution is done by addition of NH_4HCO_3 , HCO_3^- as common ion.
- C. **Predicting precipitation in Ionic reactions :** Precipitation in an ionic reactions could be predicted by comparing K_{sp} to the ionic concentration product of ions.
- D. **Salting out action of Soap :** When NaCl is added to saturated solution of soap (RCOONa) concentration of Na^+ increases & causes to precipitation of soap, it is due to $[\text{Na}^+] [\text{RCOO}^-] > K_{sp}$.
- E. **In qualitative analysis :** Selective precipitation of salt in salt analysis due to suppression of common ion.

THEORY OF INDICATORS

An indicator is a substance which is used to determine the end point in a titration. In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range. The colour change and the pH range of some common indicators are tabulated below:

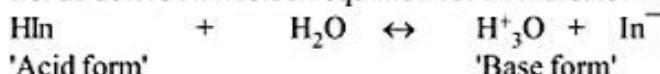
Indicator	pH range	Colour change
Methyl orange	3.2-4.5	Pink to yellow
Methyl red	4.4-6.5	Red to yellow
Litmus	5.5-7.5	Red to blue
Phenol red	6.8-8.4	Yellow to red
Phenolphthalein	8.3-10.5	Colourless to pink

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.

1. Ostwald's Theory

- (a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.
 - (b) The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Let us derive Henderson equation for an indicator



Conjugate acid-base pair

$$K_{In} = [In][H^+][O]/[HIn]; \quad K_{In} = \text{Ionization constant for indicator}$$

$$pH = -\log_{10} [H^+ \cdot O] = -\log_{10}[K_{ln}] - \log_{10}[Hln]/[In^-]$$

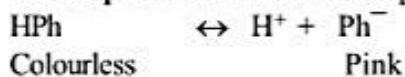
$$\text{pH} = \text{pK}_{\text{In}} + \log_{10}[\text{In}^-]/[\text{HIn}] \quad (\text{Henderson equation for indicator})$$

At equivalence point

$[In^-] = [HIn]$ and $pH = pK_{In}$

Working principle of phenothalene & methyl orange indicators :

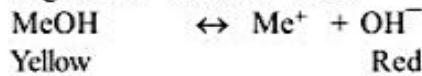
1. Phenolphthalein : It can be represented as HPh. It ionises in solution to a small extent as:



$$K = [H^+] [Ph^-] / [HpH]$$

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 left hand side due to 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 right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

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



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

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

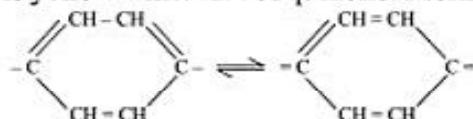
This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution 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.

2. Quinonoid theory:

- (a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium.

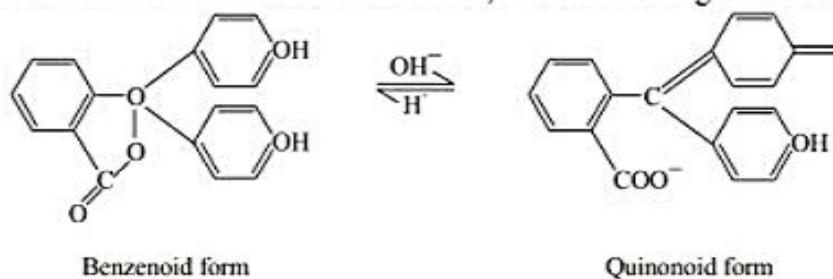
Phenolphthalein has benzoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinonoid form is red.



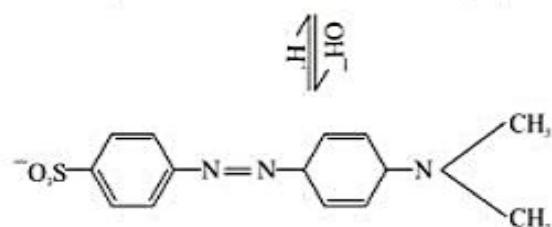
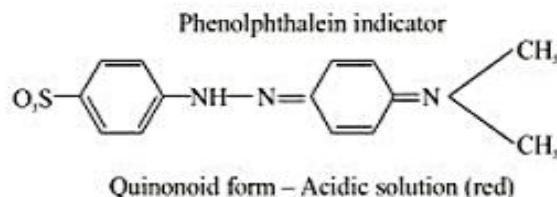
- (b) The two forms have different colors. The color change is due to the interconversion of one tautomeric form into other.
- (c) One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Benzenoid form

Quinonoid form



Methyl orange indicator

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Selection of suitable indicator

In order to choose a suitable indicator, it is necessary to understand the pH changes in different types of titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose.

The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or titration curve.

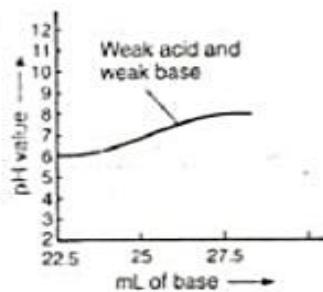
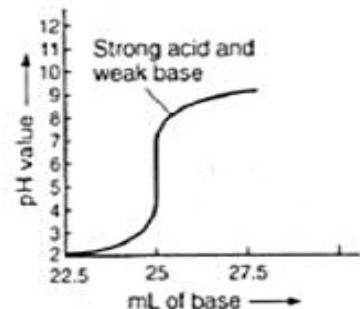
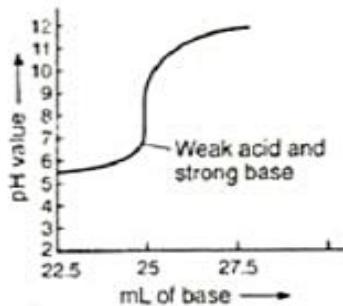
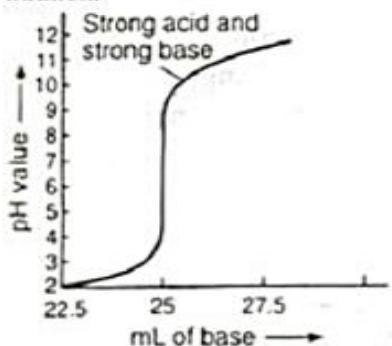
Types of Neutralisation reaction

(i) Strong acid vs. strong base:

pH curve of strong acid (say HCl) and strong base (say NaOH) is vertical over almost the pH range 4-10. So the indicators phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4-6.5) and methyl orange (pH range 3.2-4.5) are suitable for such a titration.

(ii) Weak acid vs. weak base:

pH curve of weak acid (say CH_3COOH of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.



(iii) Strong acid vs. weak base:

pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7. So the indicators methyl red and methyl orange are suitable for such a titration.

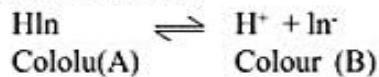
(iv) Weak acid vs. Strong base :

pH curve of weak acid (say CH_3COOH) with a strong base (say NaOH) is vertical over the pH range 7 to 10. So phenolphthalein is suitable indicator for such titration

Illustration

Ans. E

Sol. For acid indicator HIn



$$K_{In} = \frac{[H^+][I_n^-]}{[HI_n]} \text{ when } [I_n^-] = [HI_n] \text{ indicator changes colour.}$$

$$\therefore K_{\text{I}_0} = [\text{H}^+] = 1 \times 10^{-5}$$

Exercise

1. If an acidic indicator HIn ionises as $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$. To which maximum pH value its solution has distinct colour characteristic of HIn .

Ans. B

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SOLVED EXAMPLES

Q.1 For an aqueous solution to be neutral it must have

- (A) pH = 7 (B) [H⁺] = [OH⁻] (C) [H⁺] = $\sqrt{K_w}$ (D) [H⁺] < [OH⁻]

Ans. B

Sol. For neutral solution [H⁺] always must be equal to [OH⁻]

Q.2 If an aqueous solution at 25°C has twice as many OH⁻ as pure water its pOH will be

- (A) 6.699 (B) 7.307 (C) 7 (D) 6.98

Ans. A

Sol. [OH⁻] = 2×10^{-7}

$$\text{pOH} = 14 - \text{pH} \text{ or } -\log [\text{OH}^-]$$

Q.3 The pH of a solution prepared by mixing 50.0 mL of 0.02 M NaOH and 50 mL of 0.04 M CH₃COOH is ($K_a = 1.8 \times 10^{-5}$).

- (A) 4.74 (B) 5.74 (C) 3.74 (D) 7.45

Ans. A

Sol. 50 mL of 0.02 M NaOH contains 1 milli moles of OH⁻

50 mL of 0.04 M CH₃COOH contains 2 millimoles of H⁺

The combination of the two solutions will give 1 milli mole of salt, and 1 milli mole of acid will be left behind. By using Henderson equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \text{ or } \text{pH} = \text{pK}_a + \log \frac{[0.1 \text{ milli mole per 100 mL of soln.}]}{[0.1 \text{ mill mole per 100 mL of soln.}]}$$

$$\text{Or } \text{pH} = -\log K_a = -\log (1.8 \times 10^{-5}) = 4.74$$

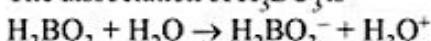
Q.4 The pH of a solution containing 0.10 M H₃BO₃ and 0.18 M NaH₂BO₃ is

(K₁ H₃BO₃ = 7.3×10^{-10})

- (A) 7.5 (B) 12.0 (C) 9.39 (D) 10.43

Ans. C

Sol. The dissociation of H₃BO₃ is



$$K_1 = \frac{[\text{H}_2\text{BO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{BO}_3]} = \frac{(0.18)x}{(0.10)} = 7.3 \times 10^{-10}$$

$$\text{Or } x = [\text{H}_3\text{O}^+] = 4.1 \times 10^{-10} \text{ or } \text{pH} = -\log x = -\log (4.1 \times 10^{-10}) \\ = 9.39$$

Q.5 What molar concentration of ammonia will provide a hydroxyl ion concentration of 1.5×10^{-3} ? (K_b = 1.8×10^{-5})

- (A) 0.125 M (B) 0.12 M (C) 0.13 M (D) 0.14 M

Ans. C

Sol. The reaction is $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.5 \times 10^{-3})(1.5 \times 10^{-3})}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

Equilibrium conc. of ammonia $[NH_3] = 0.125\text{ M}$
 And, total $[NH_3] = 1.5 \times 10^{-3} + 0.125 = 0.13\text{ M}$

- Q.6** A solution of a monoprotic weak acid has acidity constant equal to K_a . The value of minimum concentration C in terms of K_a such that the concentration of undissociated acid can be equated to C within a limit of error of 10% is
 (A) $C = 10 K_a$ (B) $C = 0.9 K_a$ (C) $C = 0.1 K_a$ (D) $C = 90 K_a$

Ans. D

Sol. The reaction is $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ and $K_a = \frac{[H_3O^][A^-]}{[HA]}$

Let C be the minimum initial concentration and x the degree of dissociation. Then

$$K_a = \frac{x^2}{C-x}.$$

Normally, we make the approximation that $C - x \sim C$ within an error of 10%.

Therefore, $C - x = 0.90 C$ or $x = C - 0.90 C = 0.10 C$

$$K_a = \frac{x^2}{C-x} = \frac{(0.10C)^2}{0.90C} = \frac{0.01C^2}{0.90C} = \frac{C}{90} \text{ or } C = 90 K_a$$

- Q.7** If the degree of ionization of water be 1.8×10^{-9} at 298 K. Its ionization constant will be
 (A) 1.8×10^{-16} (B) 1×10^{-14} (C) 1×10^{-16} (D) 1.67×10^{-14}

Ans. A

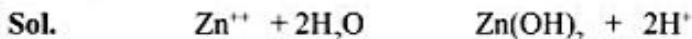
Sol. $K_a = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$

- Q.8** The hydrolysis constant for $ZnCl_2$ will be

$$(A) K_h = \frac{K_{w0}}{K_b} \quad (B) K_h = \frac{K_w^2}{K_b} \quad (C) K_h = \frac{K_w^2}{K_b^2} \quad (D) K_h = \frac{K_b}{K_w^2}$$

Where k_b is effective dissociation constant of base Zn^{++}

Ans. B



$$\therefore K_h = \frac{[Zn(OH)_2][H^+]^2}{[Zn^{++}]} \quad \dots (1)$$



$$\therefore K_b = \frac{[Zn^{++}][OH^-]^2}{[Zn(OH)_2]}, \quad K_{w0} = [H^+][OH^-] \therefore \frac{K_w^2}{K_b} = k_h$$

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- Q.9** The solubility product of Hg_2I_2 is 1.2×10^{-28} . The concentrations of cation and anion in a saturated solution of Hg_2I_2 in water is

 - $\text{Hg}_2^{2+} - 3.1 \times 10^{-10} \text{ M}$ and $\text{I}^- - 6.2 \times 10^{-10} \text{ M}$
 - $\text{Hg}_2^{2+} - 6.2 \times 10^{-10} \text{ M}$ and $\text{I}^- - 12.4 \times 10^{-10} \text{ M}$
 - $\text{Hg}_2^{2+} - 3.1 \times 10^{-14} \text{ M}$ and $\text{I}^- - 6.2 \times 10^{-14} \text{ M}$
 - $\text{Hg}_2^{2+} - 3.6 \times 10^{-12} \text{ M}$ and $\text{I}^- - 1.8 \times 10^{-12} \text{ M}$

Ans. A

$$\text{Sol. } \text{Hg, I}_2 \rightleftharpoons \text{Hg}^{2+} + 2\text{I}^- \quad K_{\text{sp}} = [\text{Hg}^{2+}][\text{I}^-]^2 = 1.2 \times 10^{-28}$$

Let Hg^{2+} be x , then $\text{I}^- = 2x$

$$1.2 \times 10^{-28} = x. [2x]^2 = 4x^3 \text{ or } x = \left[\frac{1.2 \times 10^{-28}}{4} \right]^{\frac{1}{3}}$$

$$\text{Or } x = 3.1 \times 10^{-10} \text{ M} = [\text{Hg}_2^{2+}]$$

$$2x = 6.2 \times 10^{-10} \text{ M} = [I^-]$$

Ans. B

Sol. $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $K_{sp} = 1.2 \times 10^{-11}$

[OH⁻] higher than that contained in a saturated solution will cause precipitation. Therefore, the solution must be at the point of attaining equilibrium and the concentration of ions in solution must be no greater than those required to satisfy the solubility product constant. In this solution, [Mg²⁺] = 0.10 M and [Mg²⁺] [OH⁻]² = 1.2 × 10⁻¹¹

$$[\text{OH}^-]^2 = \frac{1.2 \times 10^{-11}}{0.10} = 1.2 \times 10^{-10} \text{ or } [\text{OH}^-] = 1.1 \times 10^{-5} \text{ or } \text{pOH} = 4.96$$

Or pH = 9.04

- Q.11** Solubility of AgCl in water, 0.01 M CaCl_2 , 0.01 M NaCl and 0.05 M AgNO_3 are S_1, S_2, S_3 and S_4 respectively then.

(A) $S_1 > S_2 > S_3 > S_4$ (B) $S_1 > S_3 > S_2 > S_4$ (C) $S_1 > S_2 = S_3 > S_4$ (D) $S_1 > S_3 > S_4 < S_2$

Ans. B

Sol. AgCl Ag + Cl⁻

In CaCl₂

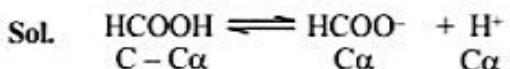
$$\text{CaCl}_2 \quad \text{Ca}^{+2} + 2\text{Cl}^-$$

0.01 0.01 2 x 0.01

In NaCl

NaCl	Na ⁺	+	Cl ⁻
0.01	0.01		0.01
InAgNO ₃			
AgNO ₃	Ag ⁺	+	NO ₃ ⁻
0.05	0.05		0.05
common ion effect is maximum in AgNO ₃			
So, S ₁ > S ₃ > S ₂ > S ₄			

Q.12 Calculate the pH of 0.01 N formic acid solution. The dissociation constant of the acid is 1.77×10^{-4} .



$$\text{and } K_a = C\alpha^2 \text{ or } 1.77 \times 10^{-4} = 0.01 \times \alpha^2$$

$$\text{or } \alpha^2 = \frac{1.77 \times 10^{-4}}{0.01} = 1.77 \times 10^{-2}$$

$$\text{Or } \alpha = 0.1245 \times 10^{-2}$$

$$\text{Or } [\text{H}^+] = C\alpha = 1.245 \times 10^{-3} \text{ and } \text{pH} = -\log(1.245 \times 10^{-3})$$

$$\text{Or } \text{pH} = -(0.015 - 3.00) = -(-2.905) \\ = 2.9$$

Q.13 What will be the pH of a solution formed by mixing 40 mL of 0.10 M HCl with 10 mL of 0.45 M NaOH?

Sol. 40 mL of 0.1 M HCl = $\frac{0.1}{1000} \times 40 = 0.004$ moles of HCl

$$\text{Similarly, 10 mL of 0.45 M NaOH} = \frac{0.45}{1000} \times 10 = 0.0045 \text{ moles of NaOH}$$

Thus, NaOH left unneutralised = 0.0005 moles in a volume of 50 mL

$$\text{Concentration of NaOH} = \frac{1000 \times 0.0005}{50} = 0.01 = 10^{-2} \text{ M}$$

$$\text{Therefore, } [\text{OH}^-] = 10^{-2} \text{ M or } [\text{H}^+] = 10^{-12} \text{ M or } \text{pH} = 12.0$$

Q.14 A solution of HCl contains 0.1920 g of an acid in 0.5 litre of a solution. The degree of dissociation is 95%. The pH of the solution is ?

Sol. Concentration C of HCl solution = $\frac{0.1920}{36.5 \times 0.5} = 0.010 \text{ M}$

The degree of dissociation is 95% i.e., = 0.95

$$\text{Therefore, } [\text{H}^+] = 0.010 \times 0.95 = 0.0095$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.0095) = -[3.9777] = -(-2.02) = 2.0$$

Q.15 A solution of acetic acid is 1.0% ionised. Determine the molar concentration of acid ($K_a = 1.8 \times 10^{-5}$) and also the $[\text{H}^+]$.

Sol. $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ where 'C' is the concn. of the acid and α is the degree of dissociation.

$$K_a = 1.8 \times 10^{-5} = C\alpha^2$$

$$\therefore 1.8 \times 10^{-5} = C \cdot (0.01)^2 \text{ or } C = 1.8 \times 10^{-5} \times 10^4 = 1.8 \times 10^{-1} \text{ M}$$

$$[\text{H}^+] = C\alpha \text{ or } [\text{H}^+] = 1.8 \times 10^{-1} \times 0.01 = 0.18 \times 0.01 = 0.0018 \text{ M or } 1.8 \times 10^{-3} \text{ M}$$

Q.16 A reaction $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$ is at equilibrium. If the concentration of Ca^{2+} is increased four times, what will be the change in F^- concentration as compared to the initial concentration of F^- ?

Sol. The dissociation constant K of the reaction $= \frac{[\text{Ca}^{2+}][\text{F}^-]^2}{[\text{CaF}_2]}$. When the concentration of Ca^{2+} increases and becomes four times, the concentration of F^- must decrease by the same value. This is necessary in order to maintain K as constant. Since the F^- concentration is raised to the power 2 in the expression, the concentration of fluoride ion must decrease by 1/2.

Q.17 An acid solution of $\text{pH} = 6$ is diluted 1000 times, the pH of the final solution is

Sol. $\text{pH} = 6$ means $[\text{H}^+] = 10^{-6} \text{ M}$. After dilution, the hydrogen ion concentration becomes 10^{-9} M . Under such conditions, the hydrogen ions obtained from water cannot be neglected.

$$\begin{aligned}\therefore \text{Total } [\text{H}^+] &= 10^{-9} + 10^{-7} \text{ (approx.)} \\ &= 10^{-7} (10^{-2} + 1) \\ &= 10^{-7} (1.01)\end{aligned}$$

[The contribution of H^+ from water will not be exactly 10^{-7} but still we can make an approximation in an objective problem and take it as 10^{-7}]

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] = -1.01 \times 10^{-7} \\ &= 7 - 0.0043 = 6.9957\end{aligned}$$

Q.18 Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)



The pH of the salt of (weak acid and weak base) is given by

$$\text{pH} = \frac{1}{2} [\text{pK}_a + \text{pK}_b - \text{pK}_b] \Rightarrow \text{pH} = \frac{1}{2} [14 + 3.8 - 4.8] = 6.5$$

Q.19 When 0.100 moles of NH_3 are dissolved in sufficient water to make 1.00 L of solution, the solution is found to have a hydroxide ion concentration of $1.33 \times 10^{-3} \text{ M}$.

(a) What is the pH of this solution?

(b) What will be the pH of the solution when 0.100 mole of NaOH is added to it? Assume no change in volume.

(c) Calculate K_b for ammonia.

(d) How does NaOH added to the solution affect the dissociation of ammonia?

Sol. (a) $[\text{OH}^-] = 1.33 \times 10^{-3} \text{ M} \quad \therefore [\text{H}^+] = \frac{1.00 \times 10^{-14}}{1.33 \times 10^{-3}} = 7.52 \times 10^{-12} \text{ and pH} = 11.12$

(b) When 0.1 mole of NaOH is added, it will completely ionise to give 0.1 mole of OH⁻. Hydroxyl ions obtained from NH₃ are negligible in comparison to those obtained from NaOH. Therefore [OH⁻] = 10⁻¹ M or [H⁺] = 10⁻¹³ M or pH = 13

$$(c) K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.33 \times 10^{-3})^2}{(0.100 - 0.00133)} \quad \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- = 1.79 \times 10^{-5}$$

(d) In the presence of NaOH, the ionisation of ammonia is suppressed.

- Q.20** The pK_b of NH₄OH is 4.75. An aqueous solution of NH₄OH is titrated with HCl. The pH of the solution at a point when half of NH₄OH is neutralised is

Sol. When half of NH₄OH is neutralised

[NH₄OH] = [NH₄Cl]. By using the Henderson equation,

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \text{ or } \text{pOH} = 4.75$$

$$\text{pH} = 14 - 4.75 = 9.25$$

- Q.21** Calculate the pH at the equivalent point of the titration between 0.1 M CH₃COOH (25 ml) with 0.05 M NaOH. Ka (CH₃COOH) = 1.8 × 10⁻⁵.

Sol. We have already seen that even though when CH₃COOH is titrated with NaOH the reaction does not go to completion but instead reaches equilibrium. We can assume that the reaction is complete and then salt gets hydrolysed because, this assumption will help us to do the problem easily and it does not effect our answer.

$$\therefore [\text{H}^+] = \sqrt{\frac{K_w K_a}{C}}$$

First of all we would calculate the concentration of the salt, CH₃COONa. For reaching equivalence point,

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ \therefore 0.1 \times 25 &= 0.05 \times V_2 \\ \Rightarrow V_2 &= 50 \text{ ml} \end{aligned}$$

$$\text{Therefore } [\text{CH}_3\text{COONa}] = \frac{0.1 \times 25}{75} = \frac{0.1}{3}$$

$$\therefore [\text{H}^+] = \sqrt{\frac{10^{-14} \times 1.8 \times 10^{-5}}{0.1/3}} = 2.32 \times 10^{-5} \Rightarrow \text{pH} = -\log 2.32 \times 10^{-5} = 8.63$$

- Q.22** Should Mg(OH)₂ precipitate from a solution that is 0.01M MgCl₂ if the solution is also made 0.10 M in NH₃, [K_{sp}(Mg(OH)₂) = 1.8 × 10⁻¹¹, K_b(NH₄OH) = 1.8 × 10⁻⁵]

Sol. [OH⁻] in 0.10 M NH₄OH = $\sqrt{K_b C}$, (Ostwald's dilution law)

$$= \sqrt{1.8 \times 10^{-5} \times 0.010} = 1.34 \times 10^{-3} \text{ M} \Rightarrow [\text{Mg}^{2+}] = 0.01 \text{ M}$$

$$\text{Ionic product} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.01) \times (1.34 \times 10^{-3})^2 = 1.8 \times 10^{-8} > K_{sp}$$

Ionic product is greater than K_{sp} of Mg(OH)₂, hence precipitation should occur.

- Q.23** The solubility of $\text{Pb}(\text{OH})_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in buffer solution of pH = 8.

Sol. $K_{\text{sp}}^{\text{Pb}(\text{OH})_2} = 4S^3 = 4 \times (6.7 \times 10^{-6})^3$
 $= 1.203 \times 10^{-15}$

The p of buffer solution = 8, pOH = 6

$$\therefore [\text{OH}^-] = 10^{-6}$$

for left solubility of $\text{Pb}(\text{OH})_2$

$$[\text{Pb}^{2+}][\text{OH}^-]^2 = K_{\text{sp}}$$

$$\Rightarrow (s)(2s + 10^{-6})^2 = 1.203 \times 10^{-15}$$

$$\Rightarrow s = \frac{1.203 \times 10^{-15}}{10^{-12}} (2s + 10^{-6} \approx 10^{-6})$$

$$\Rightarrow s = 1.203 \times 10^{-3} \text{ mol/lit}$$

- Q.24** Given the solubility product of $\text{Pb}_3(\text{PO}_4)_2$ is 1.5×10^{-32} . Determine the solubility in gms/litre

Sol. Solubility product of $\text{Pb}_3(\text{PO}_4)_2 = 1.5 \times 10^{-32}$



If x is the solubility of $\text{Pb}_3(\text{PO}_4)_2$

Then $K_{\text{sp}} = (3x)^3(2x)^2 = 108x^5$

$$x = 5 \sqrt[5]{\frac{K_{\text{sp}}}{108}} = \left(\frac{1.5 \times 10^{-32}}{108} \right)^{\frac{1}{5}}$$

$$x = 1.692 \times 10^{-7} \text{ moles/lit}$$

$$\text{Molecular mass of } \text{Pb}_3(\text{PO}_4)_2 = 811$$

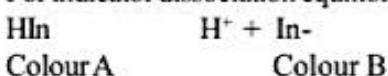
$$x = 1.692 \times 10^{-7} \times 811 \text{ g/lit} = 1.37 \times 10^{-4} \text{ g/lit}$$

Solubility product is

$$K_{\text{sp}} (\text{SrC}_2\text{O}_4) = [\text{Sr}^{2+}][\text{C}_2\text{O}_4^{2-}] = (5.4 \times 10^{-4})^2 = 2.92 \times 10^{-7}$$

- Q.25** Calculate the pH at which an acid indicator with $K_{\text{a}} = 1 \times 10^{-5}$ changes colour when indicator concentration is 1×10^{-3} M. Also report the pH at which coloured ions is 80% present.

Sol. For indicator dissociation equilibrium



$$K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HI}^-]}$$

The mid point of the colour change of an indicator HI_n is the point at which $[\text{In}^-] = [\text{HI}_n]$, $K_{\text{in}} = [\text{H}^+]$

$$= 1 \times 10^{-5} \text{ M}$$

$$\therefore \text{pH} = 5$$

Thus at pH = 5 the indicator will change its colour

$$K_{\text{ind}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HI}^-]} \Rightarrow 1 \times 10^{-5} = \frac{[\text{H}^+] \times 80/100}{20/100}$$

$$\therefore [\text{H}^+] = 0.25 \times 10^{-5}$$

$$\therefore \text{pH} = 5.6020$$