

General Chemistry

Chapter 4: Ionic Equilibrium in aqueous Solutions

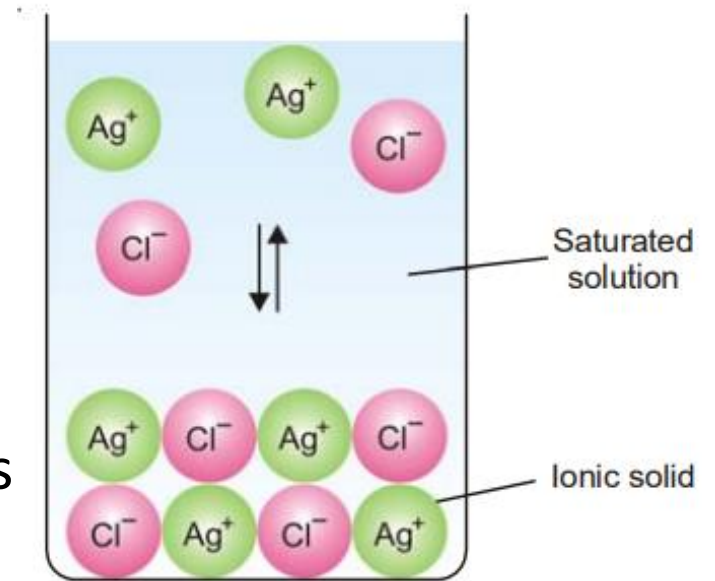
Ionic equilibria in aqueous solutions

Readily soluble salts:

- Dissolves easily in the aqueous solution
- For example, NaCl, KCl, Mg Cl₂, Na₂SO₄, C₁₂H₂₂O₁₁, CuSO₄, FeSO₄ etc.

Sparingly soluble ionic salts:

- Very slightly soluble in the aqueous solution
- Some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions
- For example, AgCl, BaF₂, CaF₂, CaSO₄, BaCO₃, Ca₃(PO₄)₂ etc.



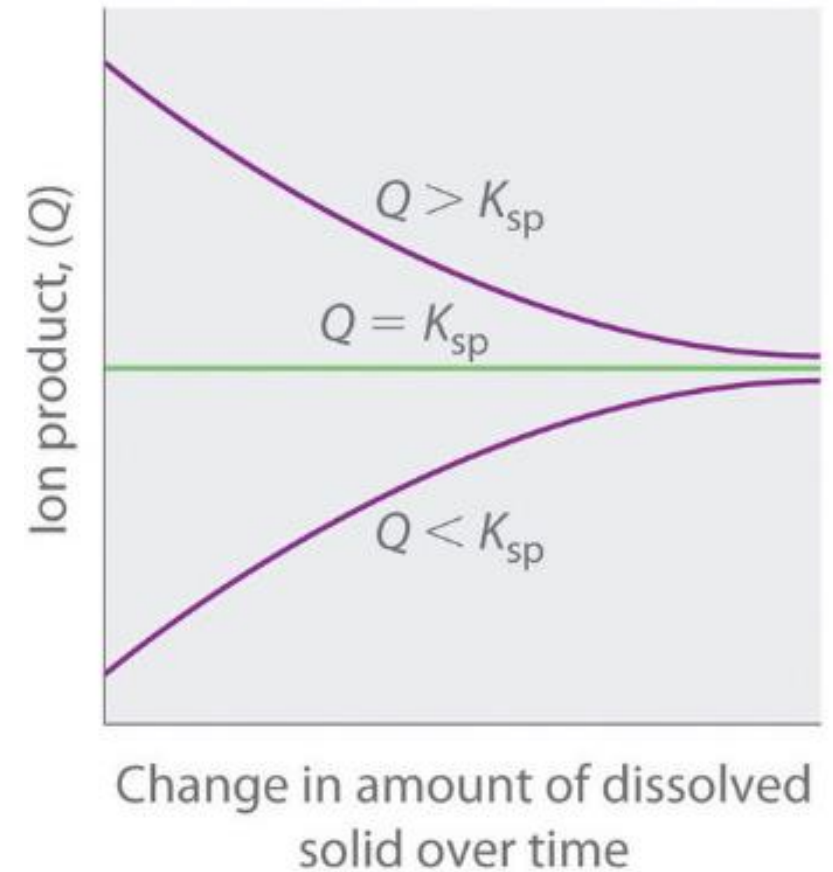
The Solubility Product (K_{sp})

- Suppose a **sparingly soluble salt** AgCl. The dissolution of solid AgCl in water can be represented as an equilibrium equation as follows:
- $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+_{\text{(aq)}} + \text{Cl}^-_{\text{(aq)}} \dots\dots\dots\text{(i)}$
- At equilibrium, solution is said to be **saturated** i.e. dissolved and undissolved solute are in equilibrium. **Solubility**- concentration in the saturated solution. (**Solubility for AgCl is 1.67×10^{-5} mole/L**)
- The equilibrium constant expression for the dissolution of silver chloride is therefore, **$K = [\text{Ag}^+][\text{Cl}^-] / [\text{AgCl}]$ or $K \cdot [\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$**
- Finally, the equilibrium expression becomes: **$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \dots\dots\dots\text{(ii)}$**
- So, **K_{sp}** may be stated as the product of the concentration of ions (mol/l) in the saturated solution which is constant at a given temperature
- The **ion product (Q)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression.

contd....

As summarized in Fig. there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.



Solubility product expression



• $K_{\text{sp}} = [\text{Ca}^{++}] [\text{F}^{-}]^2$



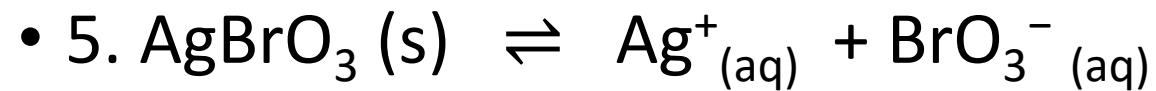
• $K_{\text{sp}} = [\text{Ag}^{+}]^2 [\text{CrO}_4^{--}]$



• $K_{\text{sp}} = [\text{Ca}^{++}]^3 [\text{PO}_4^{-3}]^2$



• $K_{\text{sp}} = [\text{La}^{+3}] [\text{OH}^{-}]^3$



• $K_{\text{sp}} = [\text{Ag}^{+}] [\text{BrO}_3^{-}]$

Numerical Problems based on Solubility and Solubility product

1. Calculation of solubility product constant (Ksp) from Solubility

- Let sparingly soluble salt be AgCl. Then the equilibrium reaction is given by,
$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$$
- If 'S' mol/l be the solubility of AgCl, the equilibrium concentrations of Ag^+ and Cl^- are : $[\text{Ag}^+] = S \text{ mol/l}$ and $[\text{Cl}^-] = S \text{ mol/l}$. Then, Ksp expression takes the form,
- $\text{Ksp} = [\text{Ag}^+] [\text{Cl}^-] = [S \text{ mol/l}] [S \text{ mol/l}] = S^2 \text{ mol}^2/\text{L}^2$ i.e. **$\text{Ksp} = S^2 \text{ mol}^2/\text{L}^2$**
- **Q.** The solubility of CuBr is found to be $2.0 \times 10^{-4} \text{ mol/L}$ at 25°C . Calculate Ksp value for CuBr.
- **[Ans. $4.0 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$]**

contd....

2. Calculation of Solubility from solubility product (Ksp)

- Let sparingly soluble salt be CaF_2 . Then the equilibrium reaction is given by,
$$\text{CaF}_2 (\text{s}) \rightleftharpoons \text{Ca}^{++} (\text{aq}) + 2\text{F}^- (\text{aq})$$
- If 'S' mol/l be the solubility of CaF_2 , the equilibrium concentrations of Ca^{++} and F^- are : $[\text{Ca}^{++}] = S \text{ mol/l}$ and $[\text{F}^-] = 2S \text{ mol/l}$. Then, Ksp expression takes the form,
- $\text{Ksp} = [\text{Ca}^{++}] [\text{F}^-]^2 = [S \text{ mol/l}] [2S \text{ mol/l}]^2 = 4 S^3 \text{ mol}^3/\text{L}^3$ i.e. $S^3 = \text{Ksp}/4$
- **Q.** Calculate the solubility of Ag_2CrO_4 . The Ksp value for Ag_2CrO_4 is 1.9×10^{-12} .
- **[Ans. $7.8 \times 10^{-5} \text{ mol/L}$]**

contd....

3. Calculation of solubility in presence of a common ion

Let sparingly soluble salt be Ag_2CrO_4 . Then it dissolves in pure water as the equilibrium reaction given , $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+_{(\text{aq})} + \text{CrO}_4^{2-}_{(\text{aq})}$

- If ' S ' mol/l be the solubility of Ag_2CrO_4 in pure water then we may mention that,
 $S \text{ mol/L Ag}_2\text{CrO}_4 \longrightarrow 2S \text{ mol/L Ag}^+ + S \text{ mol/L CrO}_4^{2-}$
- In presence of 0.1 M solution of AgNO_3 i.e. having common ion to that in Ag_2CrO_4 . Now, the equilibrium concentrations in terms of S are
- **$[\text{Ag}^+] = 2S + \text{Ag}^+ \text{ contributed by } \text{AgNO}_3$ and $[\text{CrO}_4^{2-}] = S$.** Then, Ksp expression takes the form, $K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = [2S + 0.1]^2 [S]$ **(Since S is very small compared to 0.100 M, the factor $2S^2$ is ignored).** Then, **$S = K_{\text{sp}} / [0.1]^2$**
- **Q.** Calculate the solubility of Ag_2CrO_4 in a 0.1 M solution of AgNO_3 .
Ksp value for Ag_2CrO_4 is 1.9×10^{-12} . **[Ans. $1.9 \times 10^{-10} \text{ mol/L}$]**

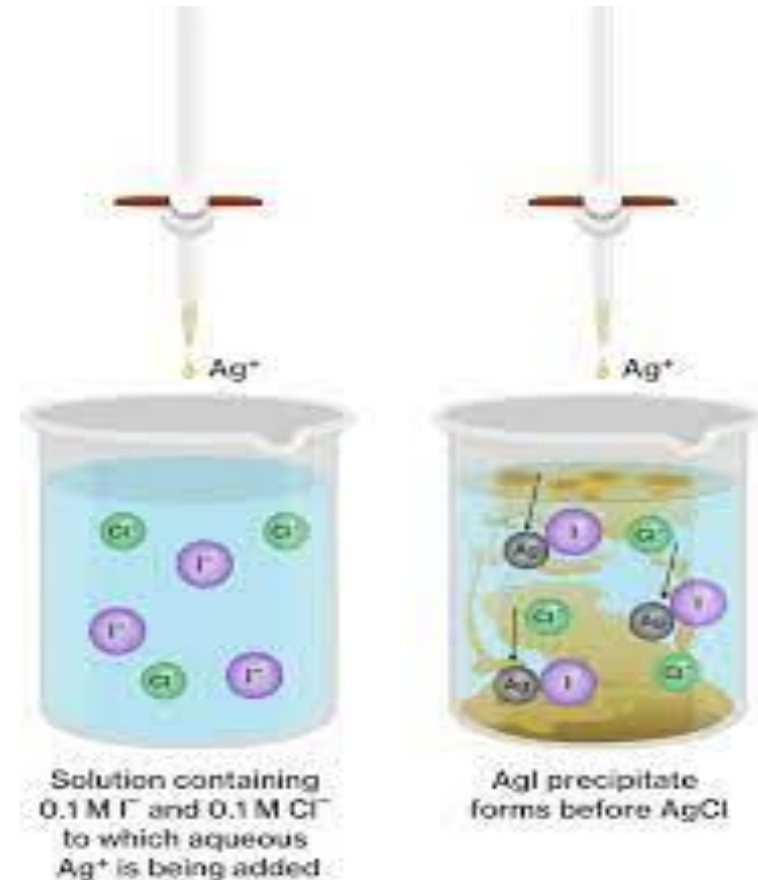
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4. Whether precipitation will occur on mixing solutions (**Predicting the precipitation**)

- The precipitation will take place if $Q > K_{sp}$.
- If $Q < K_{sp}$, no precipitation will occur.
- **Q.** A 200 ml of 1.3×10^{-3} M AgNO_3 is mixed with 100 ml of 4.5×10^{-5} M Na_2S solution. Will precipitation occur? ($K_{sp} = 1.6 \times 10^{-49}$)
- $2\text{Ag}^+_{(aq)} + \text{S}^{2-}_{(aq)} \rightleftharpoons \text{Ag}_2\text{S (s)}$ While, $Q = [\text{Ag}^+]^2 [\text{S}^{2-}]$
- **Molar concentrations of Ag^+ and S^{2-} ions:** $[\text{Ag}^+] = [1.3 \times 10^{-3} \times 200]/300 = 8.7 \times 10^{-4} \text{M}$
- $[\text{S}^{2-}] = [4.5 \times 10^{-5} \times 100]/300 = 1.5 \times 10^{-5} \text{M}$. Now, $Q = [\text{Ag}^+]^2 [\text{S}^{2-}] = 1.13 \times 10^{-11}$
- Therefore, $Q > K_{sp}$ and precipitation will occur.
- [Ans. Precipitation will occur]

Selective Precipitation

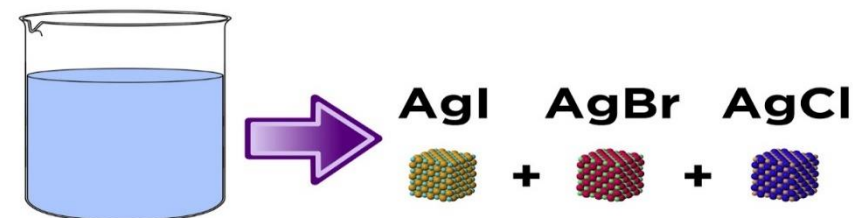
- **Selective precipitation** is a technique of separating ions in an aqueous solution by using a reagent that **precipitates** one or more of the ions at a time, while leaving other ions in solution.
- Calculation **using solubility products** can tell us when a separation of this type is possible.
- This technique is useful both **in Qualitative and Quantitative Analysis**.
- The best example of the selective precipitation is separation of the Basic ions into Groups I to VI using the reagent like dil. HCl, H₂S, NH₄OH etc
- In this way ions are precipitated from solution one by one.



AgCl
 1.8×10^{-10}

AgBr
 7.7×10^{-13}

AgI
 1.5×10^{-16}



Practical example of Selective Precipitation

- **Q.** What will happen when Ag^+ ion is added slowly to the solution of 0.1M Cl^- and 0.01M CrO_4^{--} ? $K_{\text{sp}} = [\text{Ag}^+].[\text{Cl}^-] = 2.8 \times 10^{-10}$; $K_{\text{sp}} = [\text{Ag}^+]^2.[\text{CrO}_4^{--}] = 1.9 \times 10^{-12}$ i.e. both are sparingly soluble salts.
- The system will not be at equilibrium and precipitation of AgCl must occur if $[\text{Ag}^+].[\text{Cl}^-] > 2.8 \times 10^{-10}$
- No precipitation of **AgCl** will occur until the **Ag^+ concentration becomes high enough** so that $[\text{Ag}^+].[\text{Cl}^-] = K_{\text{sp}}$.
- No precipitation of **AgCl** will occur until the **concentration of Ag^+ is ;**
$$[\text{Ag}^+] = K_{\text{sp}} / [\text{Cl}^-] = 2.8 \times 10^{-10} / 0.1 = 2.8 \times 10^{-9} \text{ M.}$$
- No precipitation of **Ag_2CrO_4** will occur until the **concentration of Ag^+ is ;**
$$[\text{Ag}^+]^2 = K_{\text{sp}} / [\text{CrO}_4^{--}] = 1.9 \times 10^{-12} / 0.01 = 1.9 \times 10^{-10} \text{ M.}$$

contd...

- From above calculation, it shows that **no solid** will form until the concentration of Ag^+ ion reaches **$2.8 \times 10^{-9} \text{ M}$** . **The first precipitation of AgCl will occur after this point.**
- Further addition of Ag^+ will cause more **precipitation of AgCl but no precipitation of Ag_2CrO_4 will occur until Ag^+ ion concentration rises to $1.4 \times 10^{-5} \text{ M}$.**
- In order to obtain the **complete precipitation of Cl^- ion before first precipitation of Ag_2CrO_4 begins**, the **Cl^- ion concentration** must be;

$$[\text{Cl}^-] = K_{\text{sp}} / [\text{Ag}^+] = 2.8 \times 10^{-10} / 1.4 \times 10^{-5} = \mathbf{2.0 \times 10^{-5}}.$$

contd...

- **Q.** Consider a solution containing both Zn^{++} and Fe^{++} at 0.1 M concentration. What will happen when H_2S is passed over it? $K_{\text{sp}} = [\text{Zn}^{++}][\text{S}^{--}] = 4.5 \times 10^{-24}$; $K_{\text{sp}} = [\text{Fe}^{++}][\text{S}^{--}] = 1 \times 10^{-19}$
- From solubility product value of zinc sulfide and iron sulfide , zinc sulfide is less soluble than iron sulfide. We can start the precipitation of ZnS only, leaving all the Fe^{++} in the solution.
- From the solubility product of FeS , we can calculate that to precipitate ZnS avoiding precipitation of FeS , $[\text{S}^{--}]$ ion concentration must be less than;
 - $[\text{S}^{--}] = K_{\text{sp}} / [\text{Fe}^{++}] = 1 \times 10^{-19} / 0.1 = 1 \times 10^{-18} \text{ M}$.
- For safe precipitation of ZnS , $[\text{S}^{--}]$ ion concentration may be taken to 10^{-19} M .
- **At a $[\text{S}^{--}]$ ion concentration of 10^{-19} M , the concentration of Zn^{++} remaining in the solution is ;**
- $\text{Zn}^{++} = K_{\text{sp}} / [\text{S}^{--}] = 4.5 \times 10^{-24} / 1 \times 10^{-19} = 4.5 \times 10^{-5} \text{ M}$

Different concepts of Acids and Bases

- **There are three concepts of acids and bases.** Each has its own peculiar advantages. These three concepts are :
 1. **Arrhenius concept**
 2. **Bronsted-Lowry concept**
 3. **Lewis concept**
- These concepts of Acids and Bases are illustrated considering as:
 - i. **Definition**
 - ii. **Example**
 - iii. **Strength of acid and base**
 - iv. **Neutralization**
 - v. **Limitation**

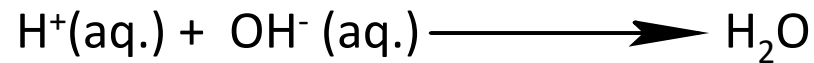
1. Arrhenius concept of acid and base:

- **Acid** : Latin, acidus = sour ; acetum= vinegar
- **Alkalis**: Arabic, alkali = ashes of plant (First suggested)
- According to this concept,
 - A substance which can produce **hydrogen ion** (proton, H^+ ion) when dissolved in water (aqueous solution), is called **acid**. Example H_2SO_4 , HCl , CH_3COOH etc.
 - A substance which can produce **hydroxyl ion** (OH^- ion) when dissolved in water (aqueous solution), is called **base**. Example $NaOH$, KOH , $Ca(OH)_2$, $Mg(OH)_2$ etc
- For example, **HCl** is an Arrhenius acid and **NaOH** is an Arrhenius base.



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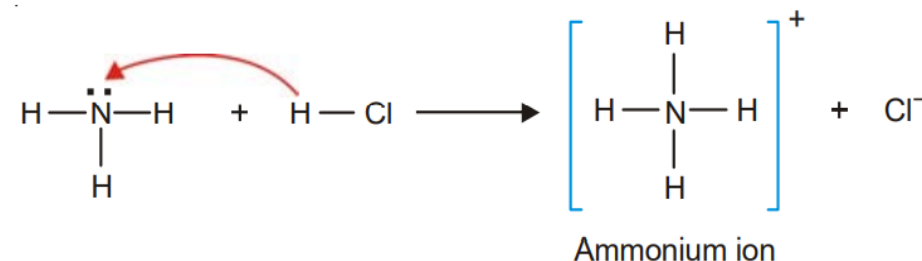
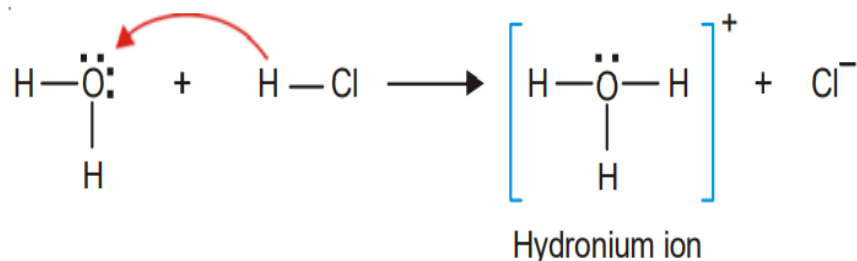
- Different ***strength*** of acid and base are the result of ***Arrhenius ionic dissociation***
- Chemical activity and electrical conductivity of solution of acid and base is due to **consequence of their reversible dissociation into ions** , one of which is H^+ and OH^-
- **Neutralization**, combination of H^+ ion and OH^- ion to give water.



- **Limitations**
- Nature of hydrogen ion in aqueous solution. i.e. **stable form is H_3O^+** , hydronium ion
- **Limited scope only water** as solvent, but not for other solvent.
- Acid and base with or without H^+ ion and OH^- ion. **CO_2 as acid; NH_3 , Na_2CO_3 base**

2. Lowry-Bronsted concept of acid and base:

- A more powerful and general concept of acid and base.
- According to this concept,
 - A substance having tendency to donate a proton is called **acid**.ie. **proton donor**. Example H_2SO_4 , HCl , CH_3COOH etc.
 - A substance having tendency to accept a proton is called **base**.ie. **proton acceptor**. Example NH_3 , H_2O etc.
- Examples of Bronsted acids and bases



HCl is a proton donor and hence a Bronsted acid, while NH_3 is a proton acceptor and a Bronsted base

contd...

- *Bronsted-Lowry concept is superior to Arrhenius concept*
 - Much wider scope
 - Not limited to aqueous solutions
 - Release of OH^- not necessary to qualify as a base
- **Conjugate Acid-Base pairs**
 - The pair of acid and base which differs by only one proton (H^+) is called conjugate acid –base pair.

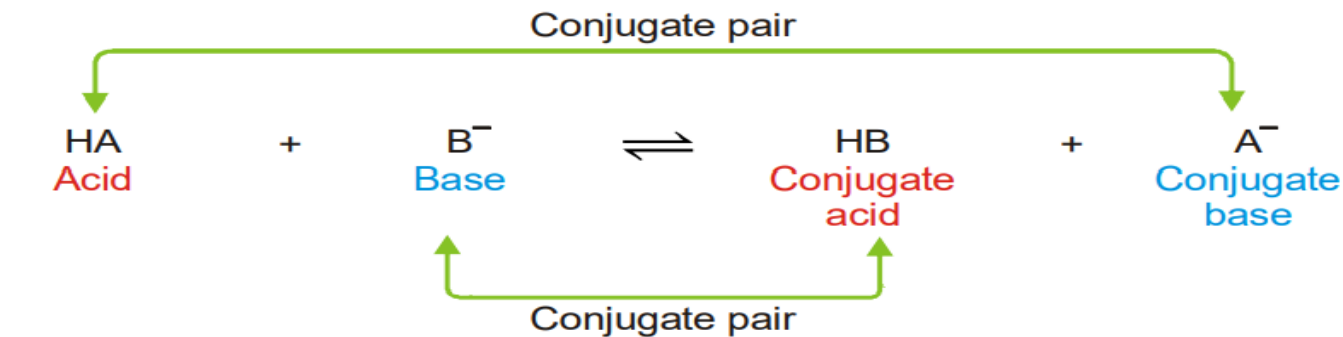
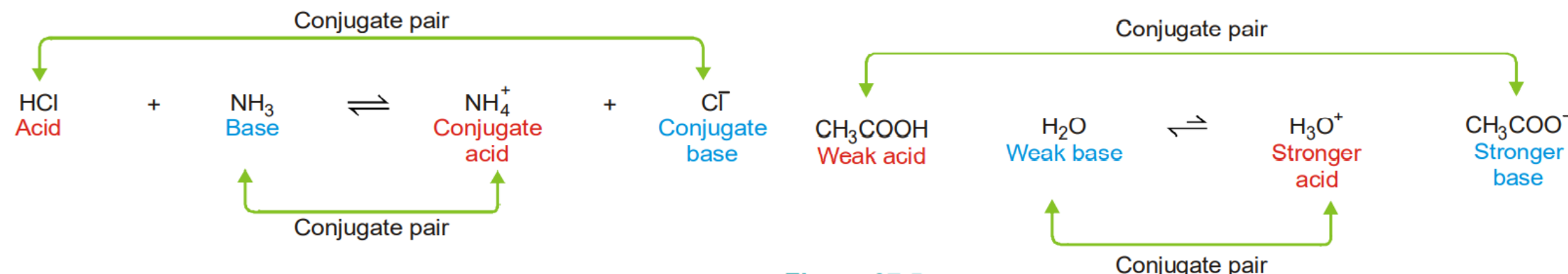


Illustration of conjugate pairs

- A weak acid has its strong conjugate base and vice-versa.
- A weak base has its strong conjugate acid and vice-versa.

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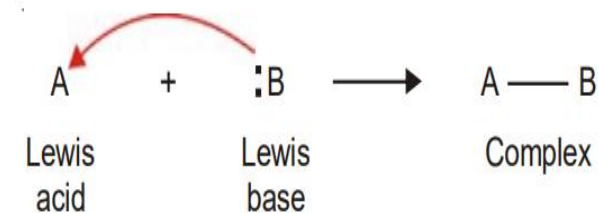
- Examples of Conjugate Acid-base pairs



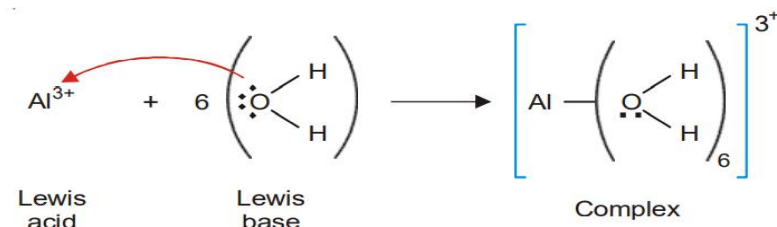
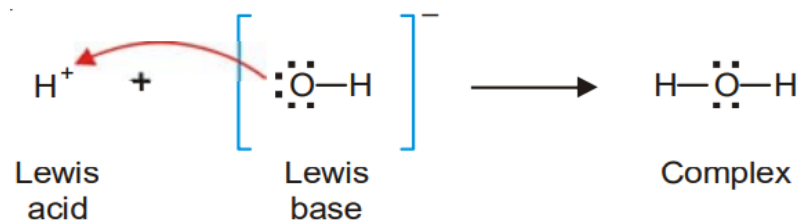
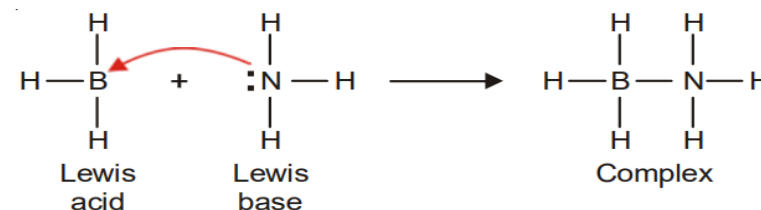
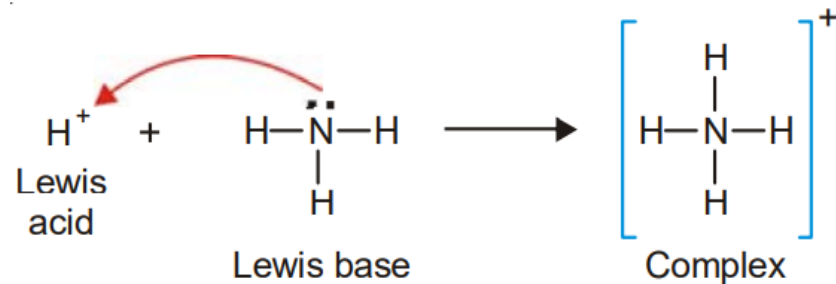
- **Neutralization:** Formation of conjugate acid-base pairs
- **Limitations**
 - Acid oxides like, CO_2 , SO_3 etc.
 - Basic oxides like MgO , CaO
 - Acidic behavior, AlCl_3 , FeCl_3 , BCl_3

3. Lewis concept of acid and base:

- According to this concept,
 - An acid is an **electron –pair acceptor** (electrophile)
 - An base is an **electron –pair donor** (nucleophile)



- Examples of Lewis reactions (Neutralization)



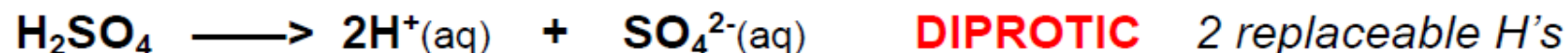
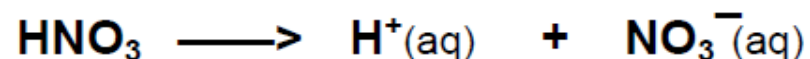
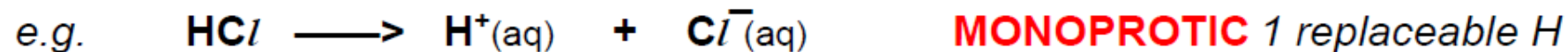
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- **Limitations:**

- Formation of co-ordinate covalent bond which is not common in acid base reaction.
- Most of acid base reactions are very fast but to form co-ordinate covalent bond, it should be is very slow.
- It cannot calculate the strength of acid and base.

THE STRENGTH OF ACIDS

Strong acids **completely dissociate** (split up) into ions in aqueous solution



Weak acids **partially dissociate** into ions in aqueous solution eg ethanoic acid

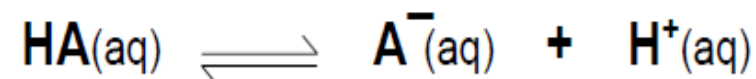


Theory When a weak acid dissolves in water an **equilibrium** is set up



The **water** is essential as it **stabilises**

the resulting ions. However to make calculations easier the dissociation is usually written in a shorter way



The **weaker** the acid

- the **less** it dissociates
- the **more** the equilibrium lies to the left

The relative strengths of acids can be expressed as K_a or $\text{p}K_a$ values (see later).

The **dissociation constant** for weak acid HA is

$$K_a = \frac{[\text{H}^{+}_{(\text{aq})}] [\text{A}^{-}_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]} \text{ mol dm}^{-3}$$

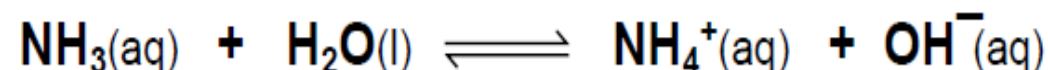
(see later for a fuller discussion)

THE STRENGTH OF BASES

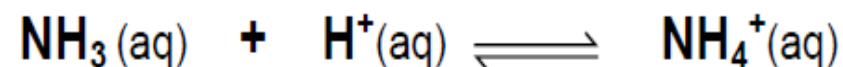
Strong **completely** dissociate into ions in aqueous solution $\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$

Weak **partially** react to give ions in aqueous solution

When a weak base dissolves in
water an equilibrium is set up



as in the case of acids
it is more simply written



The **weaker the base**

- the **less** it dissociates
- the **more** the equilibrium lies to the left

Dissociation constants of acids

Acid	Reaction	K (25°C)
Acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}
Formic acid	$\text{HCOOH} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HCOO}^-$	1.8×10^{-4}
Hydrogen cyanide	$\text{HCN} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CN}^-$	4.8×10^{-10}
Hydrogen sulfate ion	$\text{HSO}_4^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	1.2×10^{-2}
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{F}^-$	6.8×10^{-4}
Nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{NO}_2^-$	4.5×10^{-4}
Chloroacetic acid	$\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CH}_2\text{ClCOO}^-$	1.4×10^{-3}
Carbonic acid	$\text{CO}_2 + 2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HCO}_3^-$	4.2×10^{-7}
Bicarbonate ion	$\text{HCO}_3^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$	4.8×10^{-11}
Hydrogen sulfide	$\text{H}_2\text{S} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HS}^-$	1.1×10^{-7}
Hydrogen sulfide ion	$\text{HS}^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{S}^{2-}$	1×10^{-14}
Phosphoric acid	$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	7.5×10^{-3}
Dihydrogen phosphate ion	$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	6.2×10^{-8}
Hydrogen phosphate ion	$\text{HPO}_4^{2-} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$	1×10^{-12}

HYDROGEN ION CONCENTRATION

- Introduction*
- hydrogen ion concentration determines the acidity of a solution
 - hydroxide ion concentration determines the alkalinity
 - for strong acids and bases the concentration of ions is very much larger than their weaker counterparts which only partially dissociate.

pH hydrogen ion concentration can be converted to pH **$\text{pH} = -\log_{10} [\text{H}^+(\text{aq})]$**

to convert pH into hydrogen ion concentration **$[\text{H}^+(\text{aq})] = \text{antilog} (-\text{pH})$**

pOH An equivalent calculation for bases converts the hydroxide ion concentration to pOH **$\text{pOH} = -\log_{10} [\text{OH}^-(\text{aq})]$**

in the above, **[]** represents the concentration in mol dm^{-3}

Ionic Product of Water. . . K_w

Formula Despite being covalent, water conducts electricity to a very small extent.

It is due to the slight ionisation ... $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$

or $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

Applying the Equilibrium Law
$$K_c = \frac{[\text{H}^+(\text{aq})] [\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]}$$

[] is the equilibrium concentration in mol dm^{-3}

As the **dissociation is small**, the water concentration is very large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be regarded as constant.

This “constant” is combined with (K_c) to get a new constant (K_w).

$$\begin{aligned} K_w &= [\text{H}^+(\text{aq})] [\text{OH}^-(\text{aq})] \text{ mol}^2 \text{ dm}^{-6} \\ &= 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \quad (\text{at } 25^\circ\text{C}) \end{aligned}$$

The relationship between pH and pOH

Because H^+ and OH^- ions are produced in equal amounts when water dissociates their concentrations will be the same.

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$$

- take the equation for K_w

$$[\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

- take logs of both sides

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

- multiply by minus

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

- change to pH and pOH

$$\text{pH} + \text{pOH} = 14 \quad (\text{at } 25^\circ\text{C})$$

N.B. As they are based on the position of equilibrium and that varies with temperature, the above values are only true if the temperature is 25°C (298K)



















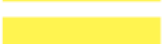


Neutral solutions are best described as those where $[\text{H}^+] = [\text{OH}^-]$

Therefore a neutral solution is pH 7 only at a temperature of 25°C (298K)

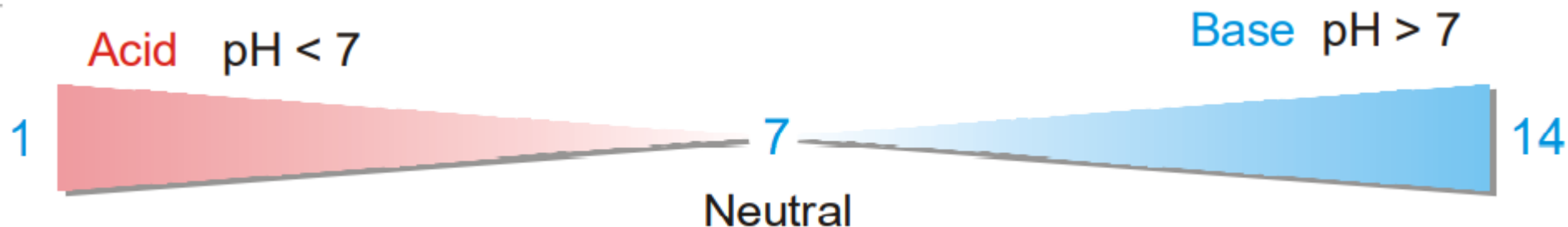
The value of K_w is constant for any aqueous solution at the stated temperature

$[H^+]$	1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} 10^{-11} 10^{-12} 10^{-13} 10^{-14}
$[OH^-]$	10^{-14} 10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1
pH	<div> <div>0 1 2</div> <div>← strongly acidic</div> </div> <div> <div>3 4 5 6</div> <div>← weakly acidic</div> </div> <div> <div>7</div> <div>neutral</div> </div> <div> <div>8 9 10 11</div> <div>← weakly alkaline</div> </div> <div> <div>12 13 14</div> <div>← strongly alkaline</div> </div>



Substance	pH		Substance	pH	
Hydrochloric Acid 10M	-1.0		Milk	6.5	
Battery acid	0.5		Pure Water	7.0	
Gastric acid	1.5 – 2.0		Healthy human saliva	6.5 – 7.4	
Lemon juice	2.4		Blood	7.34 – 7.45	
Cola	2.5		Seawater	7.7 – 8.3	
Vinegar	2.9		Hand soap	9.0 – 10.0	
Orange or apple juice	3.5		Household ammonia	11.5	
Beer	4.5		Bleach	12.5	
Acid Rai	<5.0		Household lye	13.5	
Coffee	5.0		Caustic Soda	13.9	
Tea or healthy skin	5.5				

The scale on which pH values are computed is called the pH scale.



CALCULATING THE pH AND pOH OF STRONG ACIDS AND BASES

- This is relatively easy because the species have completely dissociated
- Only needs to **know the original concentration** of the acid or base

Example 1 Calculate the pH of 0.1M hydrochloric acid.

HCl (strong monoprotic acid) is fully dissociated. $\text{HCl} \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

The $[\text{H}^+]$ is therefore the same as the original concentration of HCl i.e. 0.1M.

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} (10^{-1}) = 1 \quad \text{ANS. 1}$$

Example 2 Calculate the pH of 0.001M sodium hydroxide.

NaOH (a strong base) is fully dissociated. $\text{Na}^+\text{OH}^- \longrightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$[\text{OH}^-]$ is therefore the same as the original concentration of NaOH i.e. 0.001M.

$$\begin{aligned} \text{pOH} &= -\log_{10} [\text{OH}^-] = -\log_{10} (10^{-3}) = 3 \\ \text{and } \text{pH} &= 14 - \text{pOH} = 14 - 3 = 11 \quad \text{ANS. 11} \end{aligned}$$

What will be the pH value of 0.02M H_2SO_4 solution?

- H_2SO_4 dissociates into 2H^+ and SO_4^{2-} . Thus each H_2SO_4 molecule gives two H^+ ions.
- So, 0.02M of H_2SO_4 will give $2 \times 0.02\text{M}$ H^+ ions.
- Hence pH of the solution is given as-
 $\text{pH} = -\log[2 \times 0.02]$
 $\text{pH} = -\log[0.04]$
- Hence $\text{pH} = 1.4$

Calculate the pH value in 10^{-8}M NaOH solution.

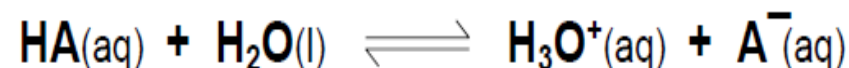
- NaOH is strong base and fully dissociated as: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$
- So, $[\text{OH}^-] = 10^{-8}\text{M} + 10^{-7} = 1.1 \times 10^{-7}$
- $\text{pOH} = -\log[\text{OH}^-] = -\log[1.1 \times 10^{-7}] = 6.9586$
- $\text{pH} + \text{pOH} = 14$
- $\text{pH} = 14 - 6.9586$
- $\text{pH} = 7.0413$

CALCULATING THE pH AND pOH OF WEAK ACIDS AND BASES

- can't be calculated by just knowing the concentration
- need to know... the extent of the ionisation (from K_a) *and* the original concentration

The dissociation constant for a weak acid (K_a)

A weak monobasic acid (HA) dissociates in water thus.



Applying the equilibrium law we get

$$K_c = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})][\text{H}_2\text{O}(\text{aq})]}$$

[] is the equilibrium concentration in mol dm⁻³

For a weak acid (little dissociation) in dilute solution, the concentration of water is large compared with the dissociated ions and any changes to its value are insignificant so its concentration can be regarded as 'constant'.

$[H_2O_{(l)}]$ is 'constant'

Combine this 'constant' with (K_c) to get a new one (K_a).

$$\text{where } K_a = K_c [H_2O_{(l)}]$$

$$K_a = \frac{[H_3O^+_{(aq)}] [A^-_{(aq)}]}{[HA_{(aq)}]} \text{ mol dm}^{-3}$$

A **simpler way** to write it all out is



The dissociation constant K_a is then

$$K_a = \frac{[H^+_{(aq)}] [A^-_{(aq)}]}{[HA_{(aq)}]} \text{ mol dm}^{-3}$$

The weaker the acid

- the less it dissociates
- the fewer ions you get
- the smaller K_a

The stronger the acid

- the more the equilibrium lies to the right
- the larger K_a

pKa

- very weak acids have very small K_a values
- it is easier to compare the strength as pK_a values

The conversion is carried out thus...

$$pK_a = -\log_{10} K_a$$

To convert pK_a into K_a

$$K_a = \text{antilog} (-pK_a)$$

Calculating the pH of a weak acid

Theory Weak monobasic acid (HA) dissociates in water $\text{HA(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$

the dissociation constant (K_a) is
$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA(aq)}]} \quad \text{mol dm}^{-3}$$

Assumptions The equation shows that, on dissociation, ions are formed in equimolar amounts.

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

The **acid is weak**, so **dissociation is small**.
The **equilibrium concentration of HA** can be **approximated to be its original** value.

the equation can be re-written ...

$$[\text{H}^+(\text{aq})]^2 = K_a [\text{HA(aq)}]$$

and

$$[\text{H}^+(\text{aq})] = \sqrt{K_a [\text{HA(aq)}]}$$

The pH can then be calculated ...

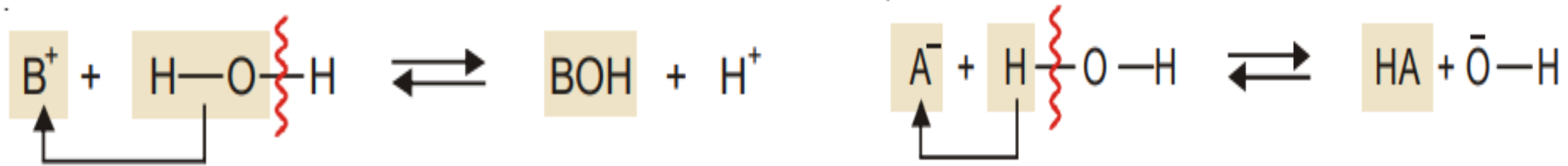
$$\text{pH} = -\log_{10} [\text{H}^+(\text{aq})]$$

Some Problems

- The hydrogen ion concentration of a fruit juice is 3.3×10^{-2} M. What is the pH of the juice ? Is it acidic or basic ? [**pH=1.48, acidic**]
- If a solution has a pH of 7.41, determine its H^+ concentration. [**3.9×10^{-8} M**]
- Calculate the pH of 0.001 M HCl. [**$H^+ = 0.001$ M; pH of 0.001 M HCl is 3**]
- Determine the pH of 0.10 M NaOH solution. [**pH of 0.10 M NaOH is 13**]
- Calculate the pH of 0.1 M CH_3COOH . The dissociation constant of acetic acid is 1.8×10^{-5} [**0.1 M CH_3COOH solution is 2.87**]
- Calculate the pH of 0.1 M NH_3 solution. The ionization constant, K_b , for NH_3 is 1.8×10^{-5} [**pH of 0.1 M NH_3 solution is 11.1**]
- What is the pH of 0.01 M sulfuric acid H_2SO_4 solution at $25^\circ C$? [**1.69**]

Hydrolysis (hydro= water; lysis = analysis):

- Let, B^+ and A^- be the cation and anion from the any salt, then the interaction between ions and water can be represented as:



- The interaction of cation or anion of salt with water followed by cleavage of O-H bond to produce acidic or basic solution, is called hydrolysis. It is the reverse process of neutralization.
- The first is known as **cationic hydrolysis**, there is excess of H^+ ions which makes the solution slightly acidic ($pH < 7$).
- The second is known as **anionic hydrolysis**, the solution becomes slightly basic ($pH > 7$).

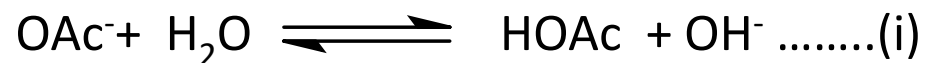
Hydrolysis of different salt is categorized as:

- Hydrolysis of salt of *weak acid* and *strong base*.
- Hydrolysis of salt of *strong acid* and *weak base*.
- Hydrolysis of salt of *weak acid* and *weak base*.
- Hydrolysis of salt of *strong acid* and *strong base*.

Quantitative Aspect of Hydrolysis

Q.1. Deduce the relation, $K_h = \frac{K_w}{K_a}$. (or Establish a quantitative relation that a weaker the acid, stronger is its conjugate base, and vice versa)

- We know that **a weak acid and its anion** are a **conjugate acid-base pair** and if an acid is weak, its conjugate base is strong.
- For example, **CH₃COOH is a moderately weak acid**, so **acetate ion is a moderately strong base**. Let the salt of weak acid and strong base (AcONa).
- Thus, OAc⁻ ion will accept the proton in aqueous solution and the hydrolysis reaction is represented by;



- Here, this reaction represents the **hydrolysis of the acetate ion**. The equilibrium constant for the *above* reaction is; $K_h = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} \dots\dots(ii)$
- Where, **K_h** is **hydrolysis constant**.

Contd...

- K_h (often not tabulated value) can be evaluated easily from **Ka (ionization constant)** of corresponding acid. Therefore we, multiply equation (ii) by $\frac{H_3O^+}{H_3O^+}$ to get,
- $K_h = \frac{[HOAc] [OH^-] [H_3O^+]}{[OAc^-] [H_3O^+]} \dots\dots\dots (iii)$
- In the numerator of above equation, we can obtain $[OH^-] [H_3O^+] = K_w$ (**ionic product constant**).
- Then equation (iii) takes the form;
- $K_h = \frac{[HOAc] [K_w]}{[OAc^-] [H_3O^+]} \dots\dots\dots (iv)$ (**While, $K_a = \frac{[OAc^-] [H_3O^+]}{[HOAc]}$ or $1/K_a = \frac{[HOAc]}{[OAc^-] [H_3O^+]}$**)
- Then, $K_h = \frac{K_w}{K_a} \dots\dots\dots (v)$
- It is clear from (v) that the hydrolysis constant (K_h) of the salt varies inversely as the dissociation constant K_a of the weak acid. Therefore, weaker the acid greater is the hydrolysis constant of the salt. i.e. **weaker the acid, stronger is its conjugate base, and vice versa**

Contd...

Q. What is the pH of a solution prepared by dissolving one mole of sodium acetate (CH_3COONa) in enough water to make one liter of solution. K_a for $\text{CH}_3\text{COOH} = 1.85 \times 10^{-5}$?

[Calculation of Hydrolysis Constant; Calculation of pH (From the hydrolysis reaction). $[\text{OH}^-] = 2.3 \times 10^{-5} \text{ M}$ **Ans. pH = 9.36**]

Q. What is the pH of a 0.2 M solution of NaCN ? K_a for $\text{HCN} = 4.0 \times 10^{-10}$?

[Calculation of Hydrolysis Constant; Calculation of pH (From the hydrolysis reaction). $[\text{OH}^-] = 2.24 \times 10^{-3}$ **Ans. pH = 11.35**]

Q. What is the pH of a 0.625 M solution of CH_3COONa ? K_a for $\text{CH}_3\text{COOH} = 1.85 \times 10^{-5}$?

[Calculation of Hydrolysis Constant; Calculation of pH (From the hydrolysis reaction). $[\text{OH}^-] = 1.84 \times 10^{-5}$ **Ans. pH = 9.26**]

Q.2. Deduce the relation, $K_h = \frac{K_w}{K_b}$. (or Establish a quantitative relation that a weaker the base, stronger is its conjugate acid, and vice versa)

- We know that **a weak base and its cation** are a **conjugate acid-base pair** and if an **base is weak**, its conjugate acid is strong.
- For example, **NH₄OH is moderately a weak base**, so **ammonium ion is moderately a strong acid**. Let the salt of weak base and strong acid (NH₄Cl).
- Thus, NH₄⁺ will donate the proton in aqueous solution and the hydrolysis reaction is represented by;



- Here, this reaction represents the **hydrolysis of the ammonium ion**. The equilibrium constant for the *above* reaction is;

$$K_h = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \text{(ii)}$$

- Where, **K_h** is **hydrolysis constant**.

Contd...

- K_h (often not tabulated value) can be evaluated easily from **K_b (ionization constant)** of corresponding base. Therefore we, multiply equation (ii) by $\frac{OH^-}{OH^-}$ to get,
- $K_h = \frac{[NH_3][H_3O^+][OH^-]}{[NH_4^+][OH^-]} \dots\dots\dots (iii)$
- In the numerator of above equation, we can obtain $[OH^-][H_3O^+] = K_w$ (**ionic product constant**).
- Then equation (iii) takes the form;
- $K_h = \frac{[NH_3][K_w]}{[NH_4^+][OH^-]} \dots\dots\dots (iv)$ (**While, $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$ or $1/K_b = \frac{[NH_3]}{[NH_4^+][OH^-]}$**)
- Then, $K_h = \frac{K_w}{K_b} \dots\dots\dots (v)$
- It is clear from (v) that the hydrolysis constant (K_h) of the salt varies inversely as the dissociation constant K_b of the weak base. Therefore, weaker the base greater is the hydrolysis constant of the salt. i.e. **weaker the base, stronger is its conjugate acid, and vice versa**

Contd...

Q. Calculate the pH of a 0.10 M solution of ammonium chloride, $K_b = 1.8 \times 10^{-5}$.

[Calculation of Hydrolysis Constant; Calculation of pH (From the hydrolysis reaction). $[H_3O^+]] = 7.5 \times 10^{-6}$ M **Ans. pH = 5.12]**

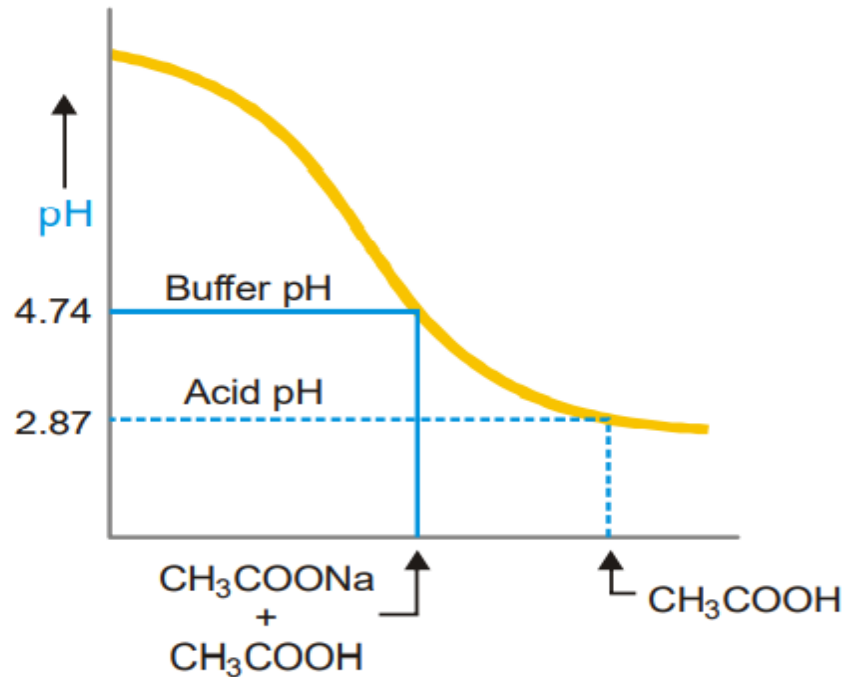
Q. Calculate the pH of a 0.20 M solution of ammonium chloride, $K_b = 1.8 \times 10^{-5}$.

[Calculation of Hydrolysis Constant; Calculation of pH (From the hydrolysis reaction). **Ans. pH = 4.9775]**

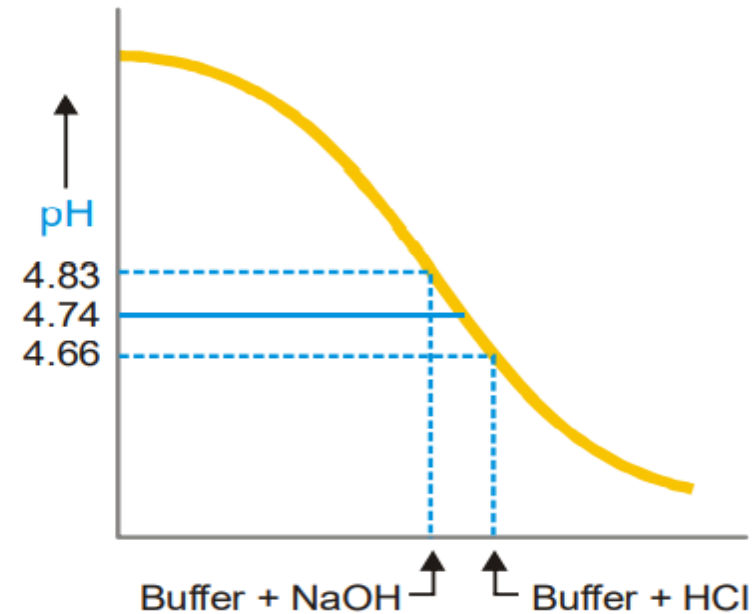
Buffer Solutions

- A buffer solution is one which **maintains its pH fairly constant** even upon the addition of **small amounts of acid or base**.
- Simply, a **buffer solution resists (or buffers) a change in its pH**
- **To maintain a certain pH of a solution in laboratory and industrial processes.**
- **Types of Buffer solution**
 - Two common types of buffer solutions are :
 1. **Acidic Buffer solution:** A **weak acid** together with a **salt of the same acid with a strong base**. For example, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.
 2. **Basic Buffer solution:** a **weak base** and its salt with a strong acid. For example, $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

Contd...



- The buffer solution ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) has a higher pH than the acid itself.



The pH of buffer changes only slightly upon addition of an acid (0.01 moles) or base (0.01 mole NaOH).

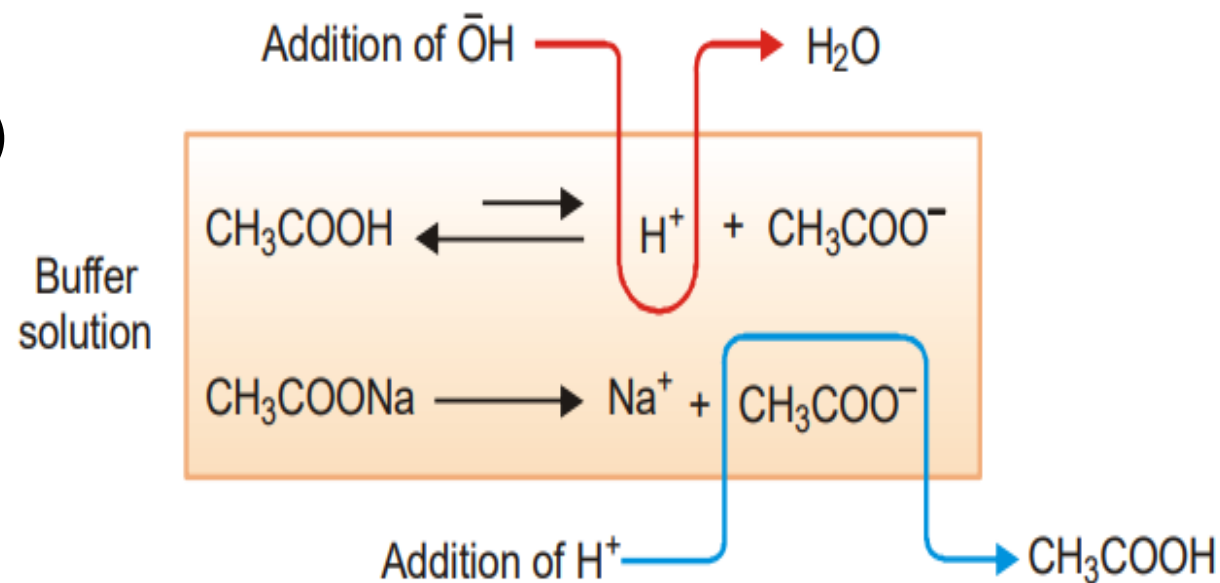
Mechanism of Buffer action (How A Buffer Operates?)

1. Buffer action of an acid buffer:

- The pH of the buffer is governed by the equilibrium.



- Large excess of Acetate ions due to complete ionization of $\text{CH}_3\text{COONa} \longrightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ \text{(ii)}$
- On Addition of HCl:**
- Marginal decrease of pH of the buffer solution on addition of HCl.
- On Addition of NaOH:**
- $[\text{H}^+]$ is also slightly less and pH slightly higher than the buffer pH values.



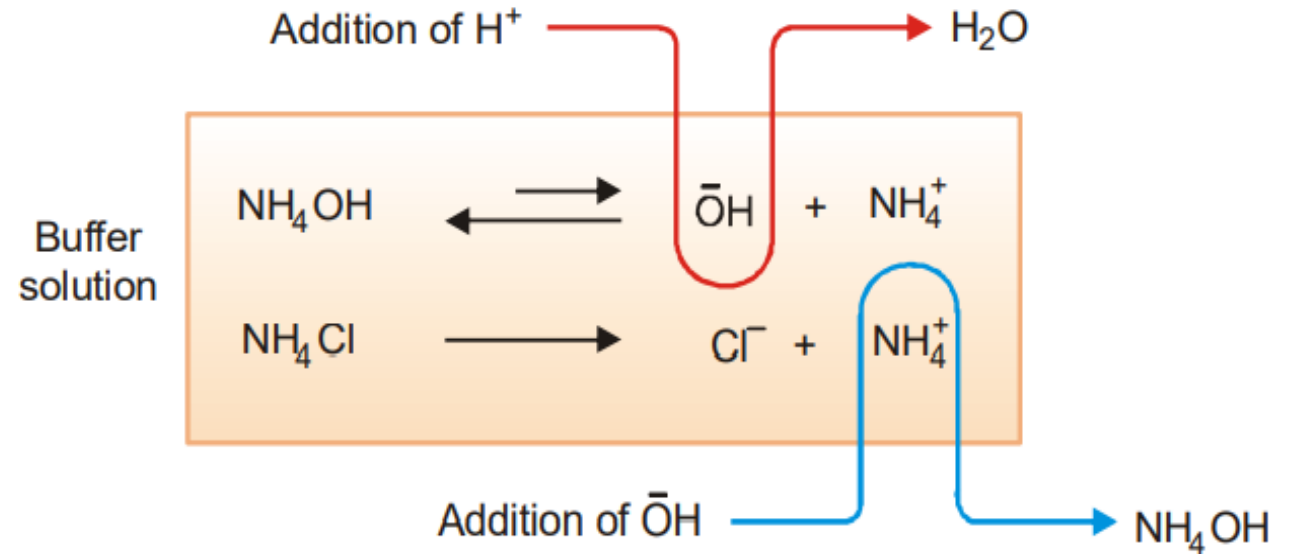
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2. Buffer action of a basic buffer:

- The buffer solution is governed by the equilibrium.



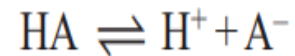
- Large excess of ammonium ions due to complete ionization of $\text{NH}_4\text{Cl} \longrightarrow \text{NH}_4^+ + \text{Cl}^- \dots\dots(ii)$
- On Addition of HCl:**
 - The eqm. is shifted to right side till H^+ neutralized and original buffer pH restored.
- On Addition of NaOH:**
 - OH^- ions associate with excess of NH_4^+ ions to form unassociated NH_4OH and pH of the buffer is maintained approximately constant.



Henderson equation (Calculation Of The pH of Buffer Solutions)

- The **pH of an acid buffer** can be calculated from the **dissociation constant, K_a** , of the weak acid and the **concentrations of the acid and the salt used**

The dissociation expression of the weak acid, HA, may be represented as



and

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

or

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \quad \dots(1)$$

- The **weak acid is only slightly dissociated** and its dissociation is further **depressed by the addition of the salt (Na^+A^-)** which provides A^- ions (Common ion effect).
- As a result the **equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid**.
- The **equilibrium concentration $[\text{A}^-]$ is presumed to be equal to the initial concentration of the salt added since it is completely dissociated**.
- Thus we can **write the equation (1) as-**

contd..

$$[\text{H}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \quad \dots(2)$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used.

Taking negative logs of both sides of the equation (2), we have

$$-\log[\text{H}^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]} \quad \dots(3)$$

But $-\log[\text{H}^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$

Thus from (3) we have

$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Hence

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

This relationship is called the **Henderson-Hasselbalch equation** or simply **Henderson equation**.

In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as :

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Significance of the Henderson-Hasselbalch equation

1. The **pH of a buffer solution can be calculated** from the initial concentrations of the weak acid and the salt provided K_a is given.
2. **The dissociation constant of a weak acid (or weak base) can be determined** by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.
3. **A buffer solution of desired pH can be prepared** by adjusting the concentrations of the salt and the acid added for the buffer.

Some Numericals

Q. Find the pH of a buffer solution containing 0.20 mole per litre CH_3COONa and 0.15 mole per litre CH_3COOH . K_a for acetic acid is 1.8×10^{-5} . [**Ans. 4.8697**]

Q. Estimate the pH at 25°C containing 0.10 M sodium acetate and 0.03 M acetic acid pK_a for $\text{CH}_3\text{COOH} = 4.57$. [**Ans. 5.09**]

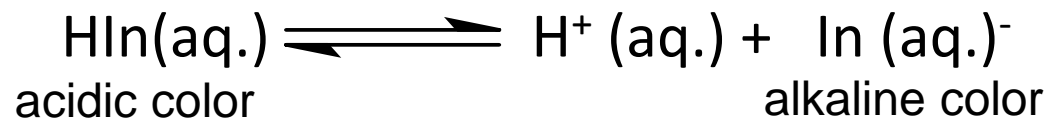
Q. Calculate the pH of a buffer solution that is 0.250 M in formic acid, HCOOH , and 0.100 M in sodium formate, HCOONa . K_a for formic acid is 1.8×10^{-4} . [**Ans. 3.3468**]

Q. A buffer solution contains 0.015 mole of ammonium hydroxide and 0.025 mole of ammonium chloride. Calculate the pH value of the solution. Dissociation constant of NH_4OH at the room temperature is 1.80×10^{-5} . [**Ans. 9.0335**]

Q. A buffer solution contains 0.25 M NH_3 and 0.40 M NH_4Cl . Calculate the pH of the solution. K_b for ammonia = 1.8×10^{-5} . [**Ans. 9.055**]

Acid-Base indicators:

- **Acid-base Indicator** is a substance which indicates the **end point** (or **equivalence point**) in a titration by undergoing a **sharp change in its color**.
- An **acid-base** indicator is an **organic dye** and the color of such dye molecule depends on the concentration of H_3O^+ . Finally it indicates the **completion of reaction** by **sharp change in its color**.
- These indicators are themselves **weak acids or bases** whose **conjugate acid-base** forms are **of different color**.
- **Theory of Indicators**
 - The ionized and unionized forms of indicators have different colors.
 - If **90 %** or more of a **particular form (ionised or unionised)** is **present**, then its color can be distinctly seen.
 - In general, for an indicator which is weak acid, partially dissociates in aqueous as;













Contd..

- $K_I = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \dots\dots\dots(\text{i})$
- $\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_I}{[\text{H}_3\text{O}^+]} \dots\dots\dots(\text{ii})$
- The ratio of ionized to unionized form can be determined from , $\text{pH} = \text{pKa} + \log [\text{HIn}]/[\text{In}^-]$. Here, dissociation of the indicator will not affect the concentration of H_3O^+ at all. But the concentration of $[\text{H}_3\text{O}^+]$ in the solution determines the ratio of $[\text{In}^-]$ to $[\text{HIn}]$ by the equation (ii).
- **In acidic solution, $[\text{H}^+(\text{aq})]$ increases.** According to Le Chatelier's principle, the position of the above **equilibrium shifts to the left. $[\text{In}^-(\text{aq})]$ decreases and the dissociation of HIn is suppressed.** i.e. $[\text{HIn}] > [\text{In}^-]$ **The colour of HIn (acidic color) predominates.**
- **In alkaline solution, the increased $\text{OH}^-(\text{aq})$ ions combine with $\text{H}^+(\text{aq})$ ions.** According to Le-Chatelier's principle, **equilibrium position shifts to the right to replace the $\text{H}^+(\text{aq})$.**i.e. $[\text{In}^-] > [\text{HIn}]$. The intensity of the **alkaline colour due to the anion In^- increases**

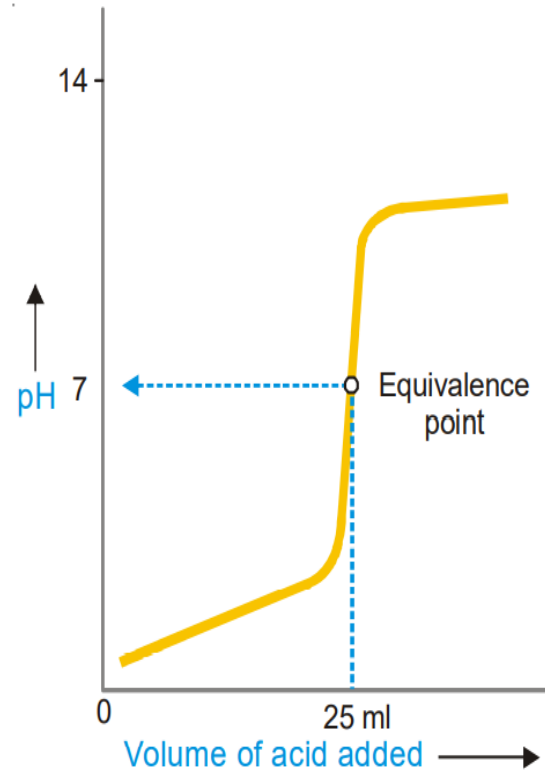
pH range of indicators

- Most indicators do not change colour at a particular pH. They do so over a range of pH from two to three units.
- This is called the pH range which is different for various indicators.

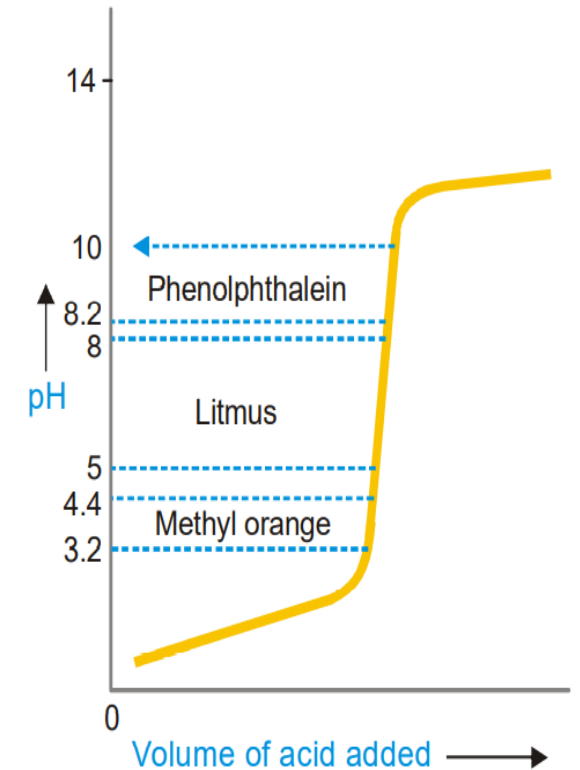
Indicator	Colour change (acid-base)		pH range
Methyl orange	red-orange	 → 	3.1–4.4
Methyl red	red-yellow	 → 	4.4–6.0
Litmus	red-blue	 → 	5.0–8.0
Bromothymol blue	yellow-blue	 → 	6.0–7.6
Phenolphthalein	colourless-pink	 → 	8.3–10.0

pH curves and Indicator range

- A **suitable indicator** for a given titration may be defined as one which has as **narrow a pH range as possible** that lies **entirely on the upright part of the titration curve**.
- For example, **phenolphthalein**, litmus and **methyl orange** may be used as indicators for **acid-base titrations**.



pH curve for titration of a strong base with strong acid.

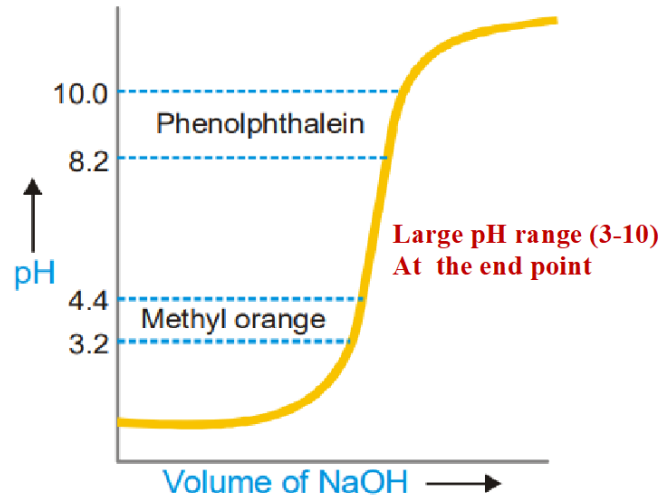


Indicator ranges for phenolphthalein, litmus and methyl orange.

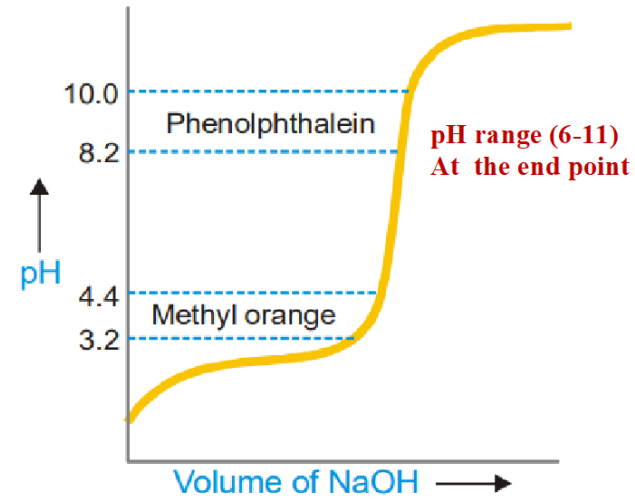
Choice of A Suitable Indicator

- The choice of a **suitable indicator for a particular acid-base titration** depends on the **nature of the acid and the base** involved in the titration.
- We have following types of the titration :
 - I. A strong acid with a strong base
 - II. A weak acid with a strong base
 - III. A strong acid with a weak base
 - IV. A weak acid with weak base
- **Which indicator is suitable** for a given titration, can be found by **examining the titration curve of that particular titration.**

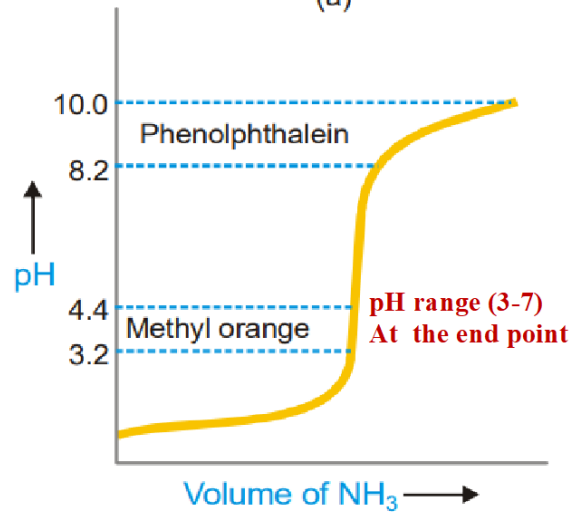
Contd....



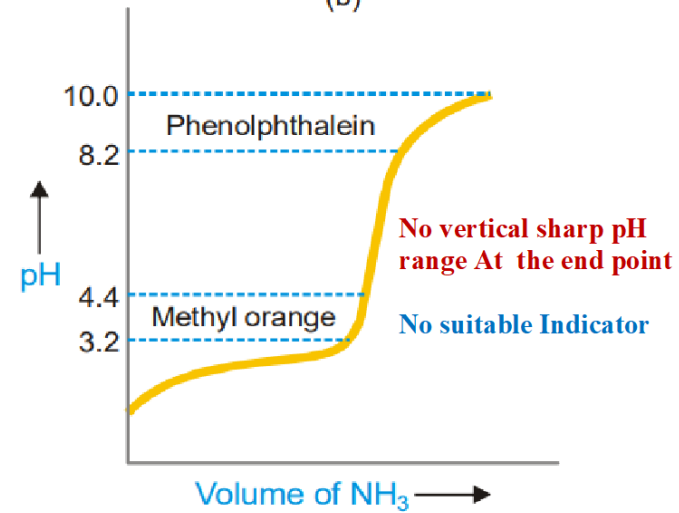
(a)



(b)

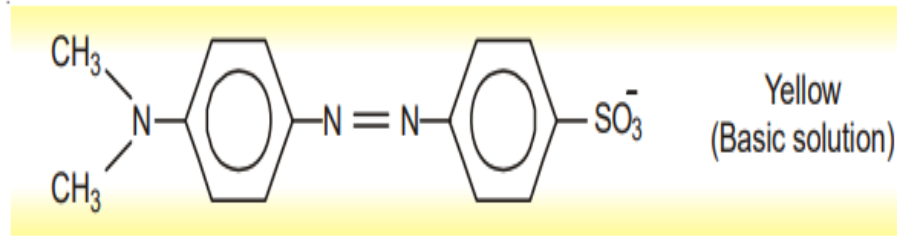


(c)



(d)

(a) Strong acid and strong base (b) Weak acid and strong base (c) Strong acid and weak base and (d) Weak acid and weak base.



Methyl Orange

