

CHAPTER:4IONIC EQUILIBRIUM# Readily Soluble Salts

The salts that easily dissolves in the aqueous solution is called readily soluble salts.

Eg: NaCl , KCl , MgCl_2 , Na_2SO_4 , $\text{Ca}(\text{H}_2\text{O})_2$, etc.

Sparingly Soluble Ionic Salts

The salts that is slightly soluble in the aqueous solution is called sparingly soluble ionic salts.

Some of the salts dissolves to form a solution, which establishes an equilibrium between the pure solid and a solution of its ions.

Eg: AgCl , BaF_2 , CaSO_4 , $\text{Ca}_3(\text{PO}_4)_2$, etc.

Solubility product constant (K_{sp})

K_{sp} is defined as "the product of molar concentration of the ions in a saturated solution of the salt each raised to the power equal to the stoichiometric coefficient of the species in the balanced chemical equation at a given temperature."

Ionic product constant (Q)

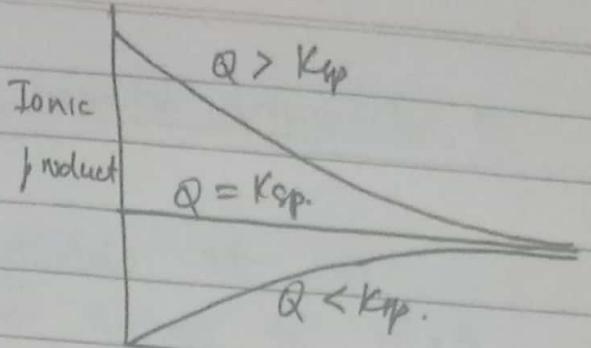
Q is defined as the product of the concentrations of the ions in solution raised to the same power equal to the stoichiometric coefficient of balanced chemical equation."

Cases:

(i): $Q > K_{sp}$, supersaturated and ionic solid will precipitate.

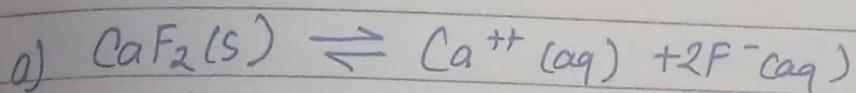
(ii) $Q = K_{sp}$, saturated and at equilibrium.

(iii) $Q < K_{sp}$, unsaturated and no precipitation occurs.

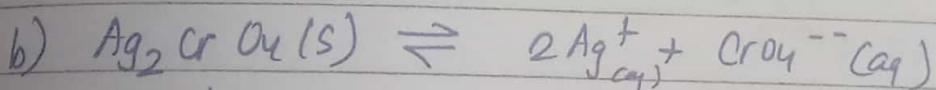


Change in amount of dissolved solid over time

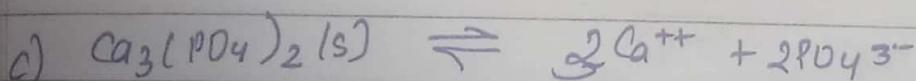
* Writing K_{sp} :



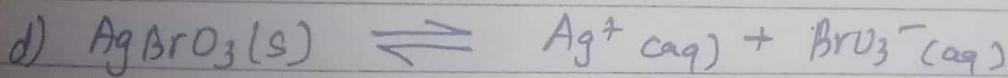
$$K_{sp} = [\text{Ca}^{++}][\text{F}^-]^2$$



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



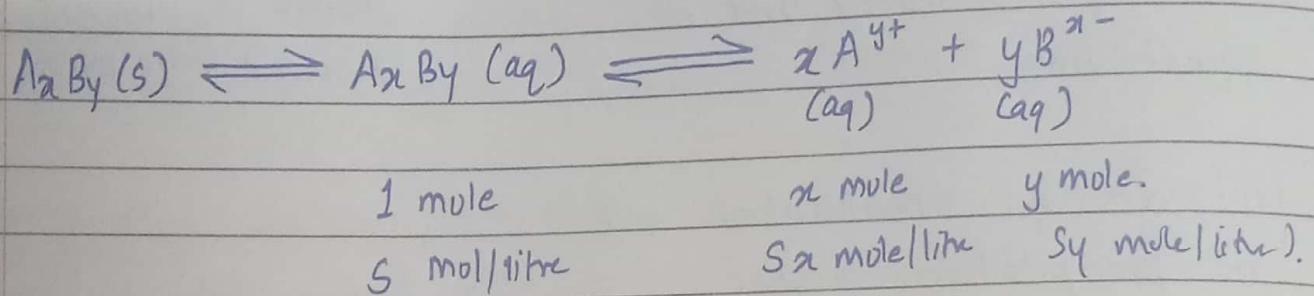
$$\therefore K_{sp} = [\text{Ca}^{++}]^3 [\text{PO}_4^{3-}]^2$$



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

Relationship between solubility and solubility constant

Let the solubility of a sparingly soluble salt $A_x B_y$ at certain temperature be 's' mole/litre, then,



Here so,

$$a_q [A^{y+}] = x s \text{ mol L}^{-1} \quad a_q [B^{x-}] = y s \text{ mol L}^{-1}$$

We have,

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

$$= [xs]^x [ys]^y$$

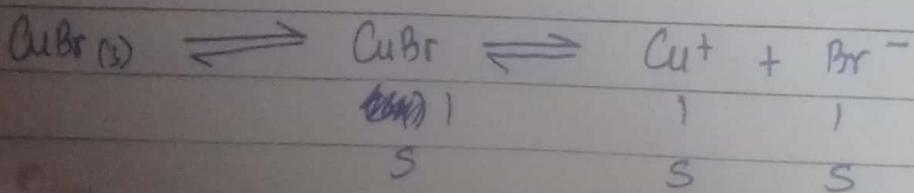
$$= x^x y^y s^{(x+y)}$$

$$\text{or, } K_{sp} = x^x y^y s^{(x+y)}$$

$$\therefore s = \left(\frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{(x+y)}}$$

Q7: The solubility of $CuBr$ is found to be 2.0×10^{-4} mol/L at $25^\circ C$. Calculate K_{sp} for $CuBr$.

SOLN:



We know,

$$\begin{aligned} K_{sp} &= [S][S] \quad (\text{for } \text{Ag}_2\text{CrO}_4) \\ &\Rightarrow K_{sp} = [\text{Ag}^+][\text{Br}^-] \\ &= S \times S \\ &= (2.0 \times 10^{-4})^2 \end{aligned}$$

$$\therefore K_{sp} = 4 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$$

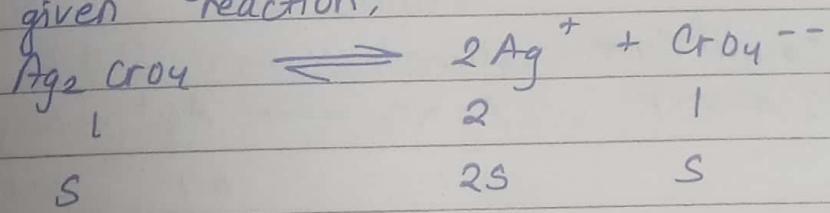
Q7: Calculate the solubility of Ag_2CrO_4 . The K_{sp} value for Ag_2CrO_4 is 1.9×10^{-12} .

So S :

Given,

$$\text{K}_{sp} \text{ value of } \text{Ag}_2\text{CrO}_4 = 1.9 \times 10^{-12}$$

The given reaction,



Now,

$$\begin{aligned} K_{sp} &= [2\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ \alpha, 1.9 \times 10^{-12} &= [2S]^2 [S] \end{aligned}$$

$$\text{on } 1.9 \times 10^{-12} = 4S^3$$

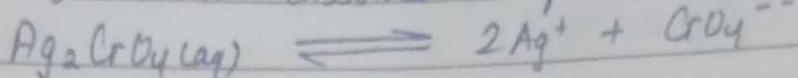
$$\text{or, } S = \left(\frac{1.9 \times 10^{-12}}{4} \right)^{\frac{1}{3}}$$

$$\therefore S = 7.8 \times 10^{-5} \text{ mol/L.}$$

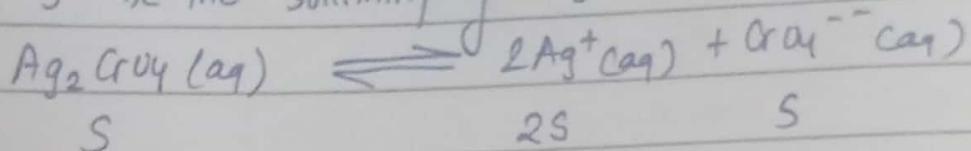
Calculation Solubility in presence of a common ion

Let us consider a sparingly soluble salt be Ag_2CrO_4 .

When it dissolves in pure water,



Let 'S' be the solubility of Ag_2CrO_4 . So,



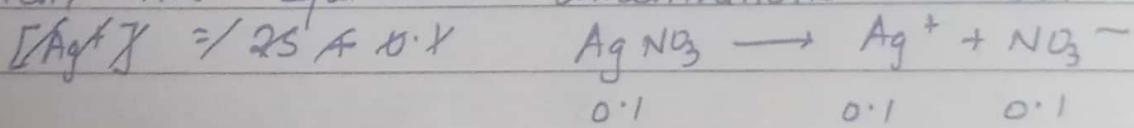
Here,

$$[\text{Ag}^+]_{\text{aq}} = 2S$$

$$[\text{CrO}_4^{2-}] = S$$

If Ag_2CrO_4 is dissolved in 0.1 M solution of AgNO_3 i.e., Ag^+ is a common ion.

Then, the equilibrium concentrations will be.



So,

$$[\text{Ag}^+] = 2S + 0.1$$

$$[\text{CrO}_4^{2-}] = S$$

So,

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

$$= [2S + 0.1]^2 [S]$$

$$= [4S^2 + 4S(0.1)^2] S$$

$$= 4S^3 + 4S^2 + 0.016S$$

In comparison to 0.1 M, the factor $\frac{S^n}{(0.1)^2} \quad n \geq 2$ can be ignored. Then, $K_{\text{sp}} = S [0.1]^2$.

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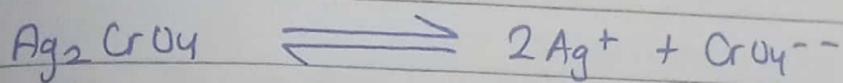
(Q): Calculate the solubility of Ag_2CrO_4 in 0.1 M soln of AgNO_3 . $K_{\text{sp}} \text{ of } \text{Ag}_2\text{CrO}_4 = 1.9 \times 10^{-12}$.

Soln:

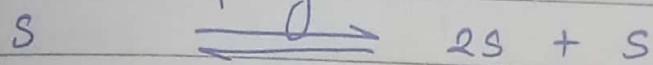
Given,

$K_{\text{sp}} \text{ of } \text{Ag}_2\text{CrO}_4 = 1.9 \times 10^{-12}$
concentration of $\text{AgNO}_3 = 0.1 \text{ M}$

For reaction;



Let s be solubility of Ag_2CrO_4 .

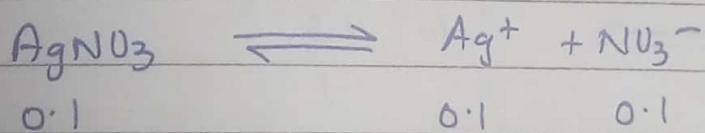


Here,

$$[\text{Ag}^+] = 2s$$

$$[\text{CrO}_4^{2-}] = s$$

When dissolved in 0.1 M AgNO_3 ,



Hence, concentration of

$$[\text{Ag}^+] = 2s + 0.1$$

$$[\text{NO}_3^-] = [\text{CrO}_4^{2-}] = s$$

We know,

$$K_{\text{sp}} = [2s + 0.1]^2 [s]$$

$$\text{So, } K_{\text{sp}} = [0.1]^2 s \quad [\because 0.1 \gg 2s, \text{ hence, } 2s \text{ is neglected}]$$

$$\therefore s = \frac{K_{\text{sp}}}{[0.1]^2} = \frac{1.9 \times 10^{-12}}{0.1}$$

$$\therefore s = 1.9 \times 10^{-10} \text{ mol/L}$$

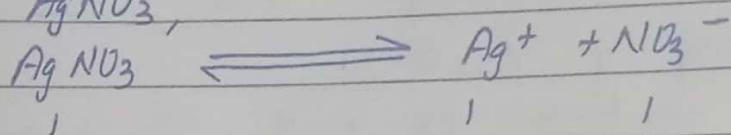
Checking for Precipitation

- i) $Q > K_{sp}$, precipitation occurs
- ii) $Q < K_{sp}$, no precipitation occurs.

Q7: 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 Ag_2S precipitate out?
 $[K_{sp} \text{ of } \text{Ag}_2\text{S} = 1.6 \times 10^{-49}]$

Soln:

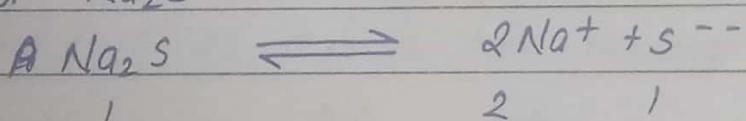
For AgNO_3 ,



Here,

$$\text{concentration of } [\text{Ag}^+] = \frac{200 \times 1.3 \times 10^{-3}}{(200+100)} = 8.67 \times 10^{-4} \text{ M}$$

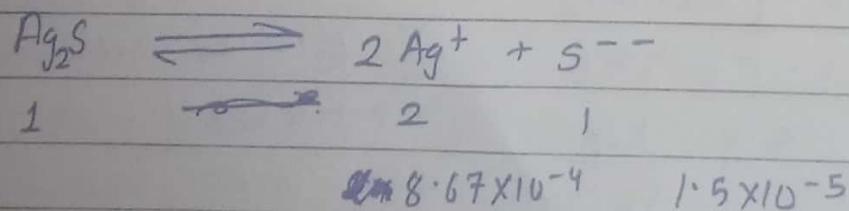
For Na_2S .



Here,

$$\text{concentration of } [\text{S}^{--}] = \frac{100 \times 4.5 \times 10^{-5}}{(200+100)} = \frac{4.5 \times 10^{-4}}{1.5 \times 10^{-5}} \text{ M}$$

For Ag_2S :



Now,

$$Q = [2\text{Ag}^+]^2 [\text{S}^{2-}]$$
$$= [2 \times 8.67 \times 10^{-4}]^2 [1.5 \times 10^{-5}]$$

$$\therefore Q = 1.13 \times 10^{-11}$$

Here, $Q > K_{\text{sp}}$.

∴ Ag_2S 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.

We use solubility product to determine selective precipitation.

Best example of selective precipitation is separation of the basic ions into group I to VI using various reagent.

Hence, ions are precipitated from solution one by one.

(Q): What will happen when Ag^+ ion is added slowly to the solution of 0.1 M Cl^- and $0.01 \text{ M CrO}_4^{2-}$?

$$K_{\text{sp}} \text{ of } \text{AgCl} = 2.8 \times 10^{-10}$$

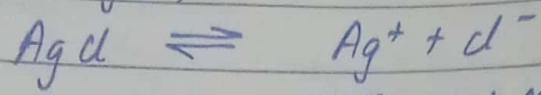
$$K_{\text{sp}} \text{ of } \text{Ag}_2\text{CrO}_4 = 1.9 \times 10^{-12}$$

80 M :

$$\text{Given, } K_{\text{sp}} \text{ of } \text{AgCl} = 2.8 \times 10^{-10}$$

$$K_{\text{sp}} \text{ of } \text{Ag}_2\text{CrO}_4 = 1.9 \times 10^{-12}$$

for AgCl ,



~~atm~~ 0.1 M

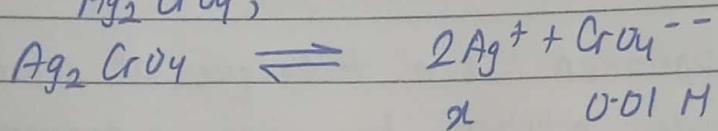
Let x be the concentration of $[\text{Ag}^+]$

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

$$\therefore \text{or, } 2.8 \times 10^{-10} = x \times 0.1$$

$$\therefore x = 2.8 \times 10^{-9} \text{ mol L}^{-1}$$

For Ag_2CrO_4 ,



x 0.01 M

$$K_{\text{sp}} \text{ of } \text{Ag}_2\text{CrO}_4 = [\text{Ag}^+]^2 \times 0.01$$

$$\therefore 1.9 \times 10^{-12} = x^2 \times 0.01$$

$$\therefore x = 3.61 \times 10^{-6} \text{ mol L}^{-1}$$

$$\therefore x = 1.38 \times 10^{-5} \text{ mol L}^{-1}$$

Conclusion:

No precipitation of $[\text{Ag}^+]$ occurs until concentration of $[\text{Ag}^+]$ reaches $2.8 \times 10^{-9} \text{ mol L}^{-1}$.

when conc. of Ag^+ , increases from 2.8×10^{-9} to $1.38 \times 10^{-5} \text{ mol L}^{-1}$, AgCl precipitation occurs but $\text{Ag}_2\text{CrO}_4^{2-}$ precipitation doesn't occur.

After concentration of $[\text{Ag}^+]$ increases from $1.38 \times 10^{-5} \text{ mol L}^{-1}$, the precipitation of $\text{Ag}_2\text{CrO}_4^{2-}$ begins

For complete precipitation of Cl^- before Ag_2CrO_4 precip.,
 $[\text{Cl}^-]$ must be,

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

$$\frac{2 \cdot 8 \times 10^{-10}}{2 \cdot 8 \times 10^{-3}} = 1 \cdot 38 \times 10^{-5}$$

$$\therefore [\text{Cl}^-] = 2 \cdot 02 \times 10^{-15} \text{ mol L}^{-1}$$

~~$\text{Ag}_2\text{CrO}_4 > 2 \cdot 02 \times 10^{-15}$, Ag₂O and AgCl too~~

(Q7): Consider a solution containing both Zn^{++} and Fe^{++} at 0.1 M concentration.

What will happen when H_2S is passed over it?

$$K_{\text{sp}} \text{ of } \text{ZnS} = 4 \cdot 5 \times 10^{-24}$$

$$K_{\text{sp}} \text{ of } \text{FeS} = 1 \times 10^{-19}$$

Sol D:

Given,

$$K_{\text{sp}} \text{ of } \text{ZnS} = 4 \cdot 5 \times 10^{-24}$$

$$K_{\text{sp}} \text{ of } \text{FeS} = 1 \times 10^{-19}$$

Here,

$$K_{\text{sp}} \text{ of } \text{ZnS} \leftarrow K_{\text{sp}} \text{ of } \text{FeS}.$$

Firstly, ZnS precipitates out and then FeS precipitates out.

For ZnS

$$K_{\text{sp}} = [\text{Zn}^{++}][\text{S}^{--}]$$

$$\text{or, } 4 \cdot 5 \times 10^{-24} = 0 \cdot 1^n \times [\text{S}^{--}]$$

$$\therefore n = 4 \cdot 5 \times 10^{-23}$$

Here, K_{sp} of FeS \gg K_{sp} of ZnS , so ~~firstly~~ ZnS precipitates out.

For FeS ,

$$\begin{aligned} K_{\text{sp}} \text{ of } \text{FeS} &= [\text{Fe}^{2+}][\text{S}^{2-}] \\ \text{or, } 1 \times 10^{-19} &= 0.1 \times [\text{S}^{2-}] \\ \therefore [\text{S}^{2-}] &= 1 \times 10^{-18} \text{ M.} \end{aligned}$$

If 10^{-19} concentration of sulphur is taken for safe precipitation of ZnS

$$\begin{aligned} K_{\text{sp}} \text{ of } \text{ZnS} &= [\text{Zn}^{2+}][\text{S}^{2-}] \\ \text{or, } 4.5 \times 10^{-24} &= [\text{Zn}^{2+}] \times 10^{-19} \\ \therefore [\text{Zn}^{2+}] &= 4.5 \times 10^{-5} \text{ M} \end{aligned}$$

Also,

$$\begin{aligned} K_{\text{sp}} \text{ of } \text{ZnS} &= [\text{Zn}^{2+}][\text{S}^{2-}] \\ \text{or, } 4.5 \times 10^{-24} &= \end{aligned}$$

Conclusion:

Here, when 10^{-18} M H_2S is passed, ~~FeS is~~ ~~ZnS precipitates out first~~ as $K_{\text{sp}} \text{ of } \text{FeS} > K_{\text{sp}} \text{ of } \text{ZnS}$.
~~ii. FeS is more soluble.~~
~~If 10^{-19} M H_2S passed for safe precipitation, 4.5×10^{-5} M $[\text{Zn}^{2+}]$ remains in the solution.~~

Conclusion:

Since K_{sp} of $\text{ZnS} < K_{\text{sp}}$ of FeS , ZnS precipitation occurs first.

ZnS precipitates till ~~$[10^{-18}]$~~ $[\text{S}^{2-}] = 10^{-18}$ M. To safely precipitate ZnS , 10^{-19} M ~~$[\text{S}^{2-}]$~~ is taken.
 Doing this,

4.5×10^{-5} M $[\text{Zn}^{2+}]$ is left in solution.

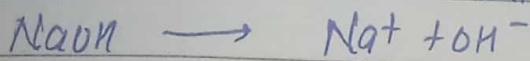
Arrhenius Concept of Acid / Base

(*) Acid: A substance which can produce H^+ ion ie, proton when dissolved in water is called acid.

Eg: HCl, H_2SO_4 , CH_3COOH , etc.



(*) Base: A substance which can produce OH^- ion ie, hydroxyl ion when dissolved in water is called base. Eg: NaOH, $Ca(OH)_2$, etc.

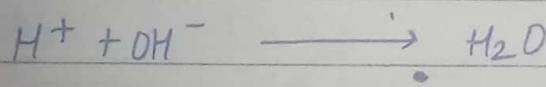


(*) Strength:

The strength of acid or base are the result of Arrhenius ionic dissociation.

(*) Neutralization:

Combination of H^+ and OH^- to give water is the neutralization.



(*) Limitations:

→ Nature of H^+ in aq. soln ie, stable form H_3O^+ ie, hydronium ion.

→ It has limited scope ie, only for water as solvent

→ Doesn't explain acid & base without H^+ and OH^- ion.

Lowry-Bronsted concept:

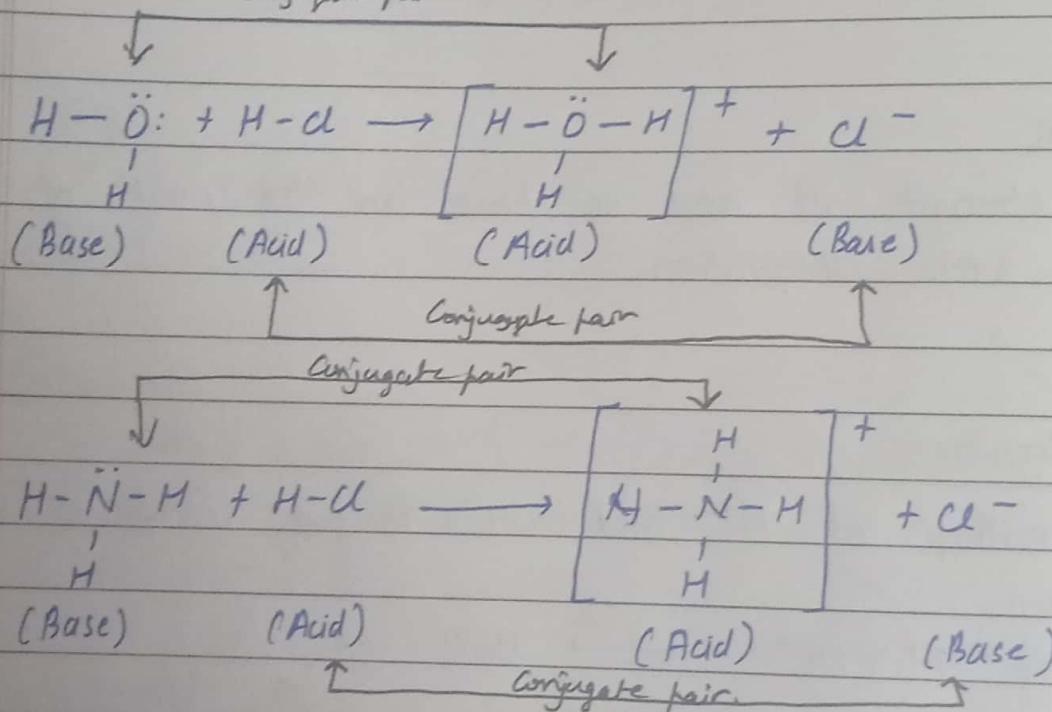
* Acid: A substance having tendency to donate a proton i.e., proton donor is called acid.

Eg: H_2SO_4 , HCl , CH_3COOH , etc.

* Base: A substance having tendency to accept a proton i.e., proton acceptor is called base.

Eg: NH_3 , H_2O , etc.

Conjugate pair

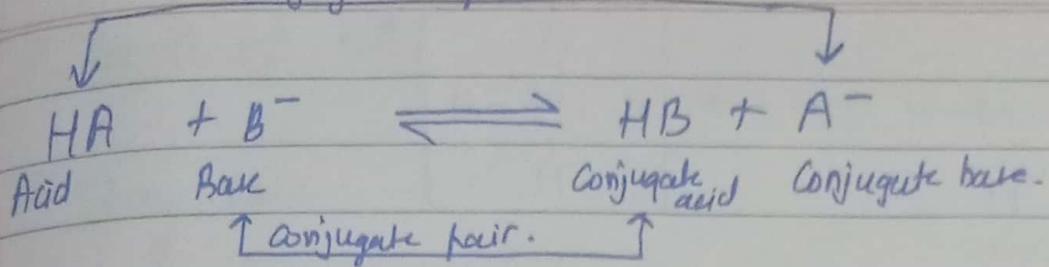


(*) Conjugate Acid-Base Pair

The pair of acid-base which differs by only one proton (H^+) is called conjugate acid-base pair.

A weak acid has strong conjugate base and strong acid has weak conjugate base i.e., same for bases.

Conjugate pair



* Superiority to previous concept:

- i) Not limited to aqueous solution.
- ii) Release of OH^- not necessary to be base.

* Neutralization:

Formation of conjugate acid-base pairs.

* Limitations:

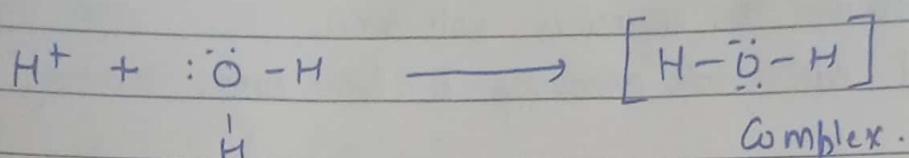
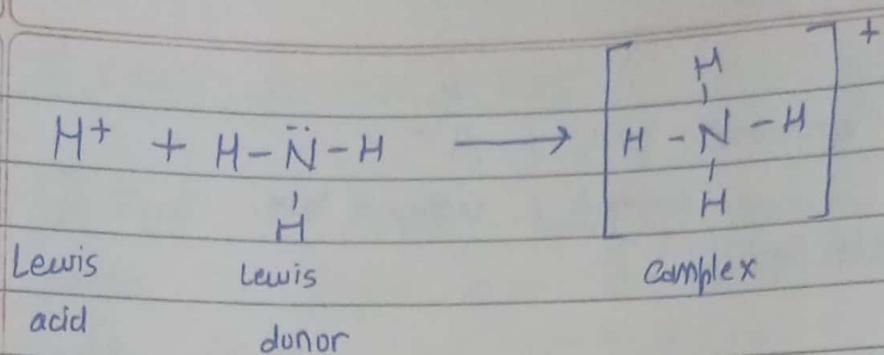
- (i) Doesn't explain acidic and basic oxides.
- (ii) Doesn't explain acidic nature of AlCl_3 , BCl_3 , FeCl_3 , etc.

Lewis Concept of Acid/Base:

* Acid: A substance that accepts electron-pair, ie, electrophile is called acid.

* Base: A substance that donates electron-pair ie, nucleophile is called base.

* Neutralization: Lewis acid + base combine to form a complex.



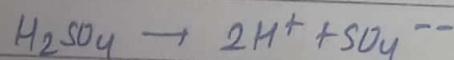
* Limitations :

- (i) Doesn't explain formation of coordinate covalent bond
- (ii) It can't calculate strength of acid and base.

Strength of Acids

* Strong acid:

It completely dissociates into ions in aqueous solution.



* Weak acids :

If partially dissociates into ions in aqueous solution.
 Eg: $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

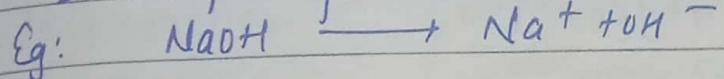
The weaker the acid, it dissociates less

equilibrium shifts more towards left.

Strength of Base

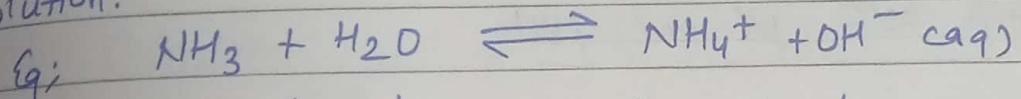
(*) Strong base:

It completely dissociates into its ions in aq. solution.



(*) Weak base:

It partially dissociates into its ions in aqueous solution.



The weaker the base, it dissociates less.

equilibrium shifts more towards left.

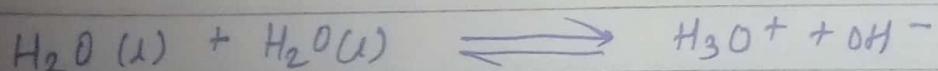
Hydrogen & Hydroxyl Ion Concentration

For the strong acid and base, the concentration of ions is larger than their weaker counterparts.

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

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

(*) Ionic product of water: (K_w) = $10^{-14} \text{ mol}^2 \text{ dm}^{-6}$



Applying equilibrium sto law,

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Since the dissociation of water is small, in comparison to dissociated ions, the water concentration and any changes to it is ~~constant~~ insignificant.

$$K_c \times [H_2O] = [H^+][OH^-]$$

$$\text{or } K_w = 10^{-7} \times 10^{-7}$$

$$\therefore K_w = 10^{-14} \text{ mol}^{1/2} \text{ dm}^{-6}$$

Relationship b/w pH and pOH

We know,

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

and

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

In water, the following equilibrium exists.

$$K_w = [H^+][OH^-]$$

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

Taking log on both sides, we get.

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

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

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

$$\therefore \boxed{pH + pOH = 14}$$

* In neutral sol¹⁰ : $[H^+] = 10^{-7}$

In acidic sol¹⁰ : $[H^+] > 10^{-7}$

In acidic sol¹⁰
basic : $[H^+] < 10^{-7}$ */

* In neutral sol¹⁰ : $[OH^-] = 10^{-7}$

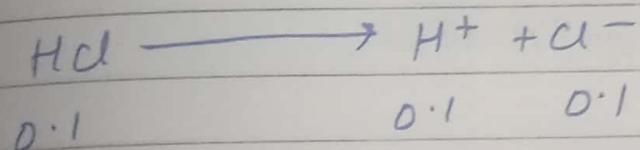
In acidic sol¹⁰ : $[OH^-] < 10^{-7}$

In basic sol¹⁰ : $[OH^-] > 10^{-7}$ */

(Q7): Calculate pH of 0.1 M HCl.

Sol¹⁰:

Here, HCl is strong acid so it completely dissociates.



Sol₁:

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

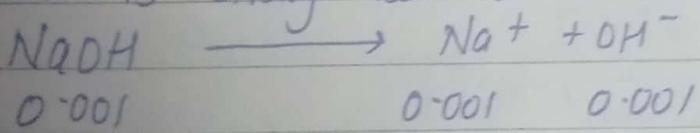
$$= -\log [0.1]$$

$$\therefore pH = 1.$$

(Q8): Calculate pH of 0.001 M NaOH.

Sol²:

Here, NaOH is strong base so it completely dissociates.

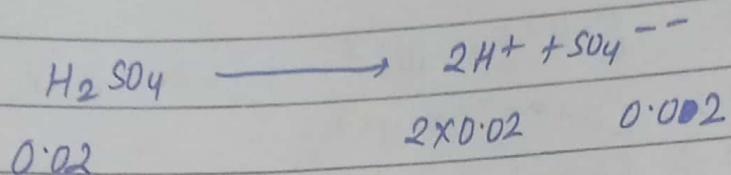


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$$\begin{aligned} p[OH] &= 14 + \log [OH^-] & = 14 + \log [0.001] \\ && \therefore pH = 11 \end{aligned}$$

(Q): Calculate pH of 0.02 M H_2SO_4 soln.

Here, H_2SO_4 is strong acid.



Here,

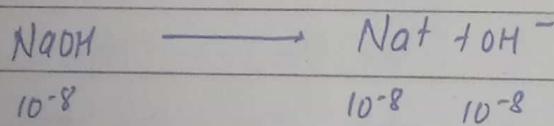
$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log [0.04] \\ \therefore pH &= 1.4 \end{aligned}$$

(Q): Calculate pH of 10^{-8} M NaOH.

Soln:

Here,

NaOH completely dissociates as it is strong base.



For base, $[OH^-] > 10^{-7}$

Here, water is mixed with the solution.

$$[OH^-] = 10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$$

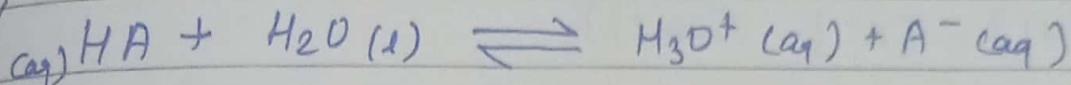
$$\begin{aligned} \therefore p[H] &= 14 - p[OH^-] \\ &= 14 + \log [1.1 \times 10^{-7}] \\ \therefore pH &= 7.84 \end{aligned}$$

Dissociation Constant for Weak Acid (K_a)

We know,

A weak monoprotic acid (HA) dissociates in water.

Thus,



Applying the equilibrium law, we get.

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

Here, $[\text{H}_2\text{O}]$ is taken as constant as change in $[\text{H}_2\text{O}]$ is insignificant in comparison to dissociated ions.

So,

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

Also

$$K_a = K_c [\text{H}_2\text{O}]$$

Hence,

K_a can be written as;

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

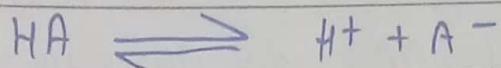
For weaker acids, it dissociates very less, we get fewer ions and smaller K_a .

So,

$$\text{p}K_a = -\log(K_a)$$

↳ it helps us compare strength.

(*) Calculating pH:



Here,

$$[\text{H}^+] = [\text{A}^-] \quad \text{--- (i)}$$

And we know,

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

Using in eqn (i);

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

$$\therefore [\text{H}^+] = \sqrt{K_a [\text{HA}]}$$

Thus, pH

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

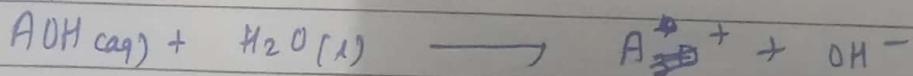
$$\therefore \text{pH} = -\log \left[\sqrt{K_a [\text{HA}]} \right]$$

Dissociation constant for weak base.

We know,

A weak monovalent base (AOH) dissociates in water.

Thus,



Applying equilibrium law,

$$K_c = \frac{[\text{A}^+][\text{OH}^-]}{[\text{AOH}][\text{H}_2\text{O}]}$$

Here, $[H_2O]$ is taken as constant as change in $[H_2O]$ is insignificant in comparison to dissociated ions

So,

$$K_c \propto [H_2O] = \frac{[A^+][OH^-]}{[AOH]}$$

$$\therefore K_b = \frac{[A^+][OH^-]}{[AOH]} \text{ mol dm}^{-3}$$

For weaker base, we get few ions and smaller K_b value

So,

$$pK_b = -\log(K_b) \rightarrow \text{easier to compare strength.}$$

* Calculating pOH:



$$\text{Here, } [A^+] = [OH^-] - (i).$$

We know,

$$K_a = \frac{[A^+][OH^-]}{[AOH]}$$

Using eqn (i),

$$K_a = \frac{[OH^-]^2}{[AOH]}$$

$$\therefore [OH^-] = \sqrt{K_a [AOH]}$$

Thus,

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

$$\therefore pOH = -\log(\sqrt{K_b [AOH]})$$

<Q>: The hydrogen ion concentration of a fruit juice is 3.3×10^{-2} . What is the pH of the juice?

Sol D:

Given,

$$[H^+] = 3.3 \times 10^{-2} \text{ M}$$

We know,

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log [3.3 \times 10^{-2}] \\ \therefore \text{pH} &= 1.48 \end{aligned}$$

<Q>: If pH is 7.41, determine H^+ concentration.

Sol D:

Given,

$$\text{pH} = 7.41$$

We know,

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

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

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

$$\text{or, } [H^+] = 10^{-7.41}$$

$$\therefore [H^+] = 3.89 \times 10^{-8} \text{ M}$$

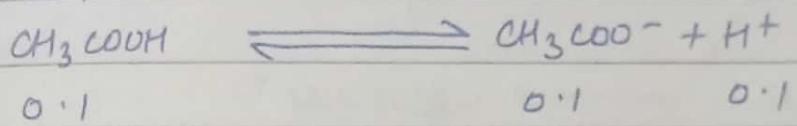
Q7: Calculate pH of 0.1 M CH_3COOH . The dissociation constant of acetic acid is 1.8×10^{-5} .

Solⁿ

Given,

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

We know,



Now,

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= -\log (\sqrt{K_a} [\text{CH}_3\text{COOH}]) \\ &= -\log (\sqrt{1.8 \times 10^{-5}} \times 0.1) \\ \therefore \text{pH} &= 2.87 \end{aligned}$$

Q7: Calculate the pH of 0.1 M LiNH_3 . The ionization constant (K_b) for NH_3 is 1.8×10^{-5} .

Solⁿ,

Given,

$$K_b = 1.8 \times 10^{-5}$$

and

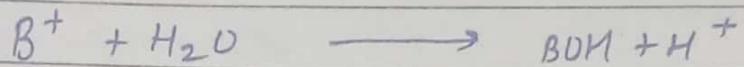
$$[\text{NH}_3] = 0.1$$

Now,

$$\begin{aligned} \text{pH} &= -\log [\text{OH}^-] \\ &= -\log [\sqrt{K_b [\text{NH}_3]}] \\ &= -\log [\sqrt{(1.8 \times 10^{-5}) \times 0.1}] \\ \therefore \text{pH} &= 11.1 \end{aligned}$$

Hydrolysis:

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



The interaction of cation and anion of salt with water followed by cleavage of ~~OFF~~ O-H bond to produce acidic or basic solution is called hydrolysis.

It is the reverse process of neutralization.

(*) Cationic hydrolysis:

The interaction of cation of salt with water followed by cleavage of O-H bond to produce acidic solution is called cationic hydrolysis.

Hence, there ~~is~~ is excess of H^+ ions which makes solution slightly acidic of $pH < 7.0$.

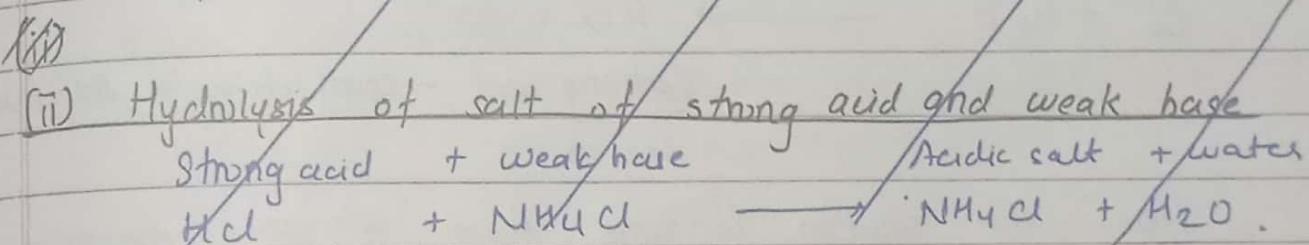
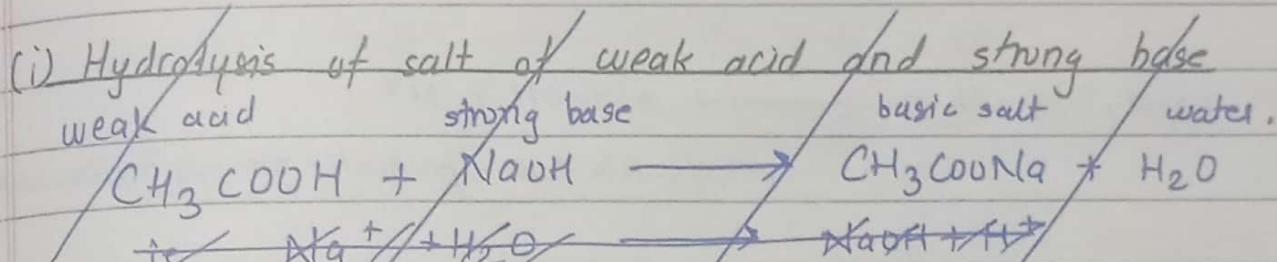
(*) Anionic hydrolysis

The interaction of anion of salt with water followed by cleavage of O-H bond to produce basic solution is called anionic hydrolysis.

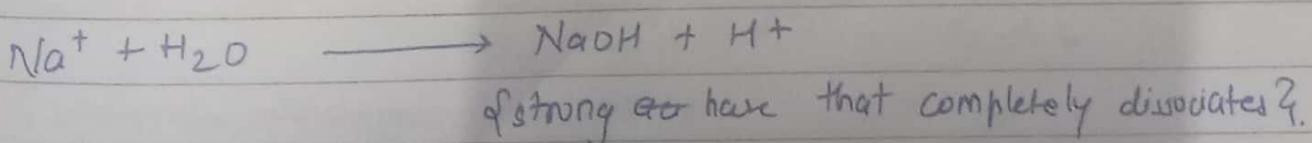
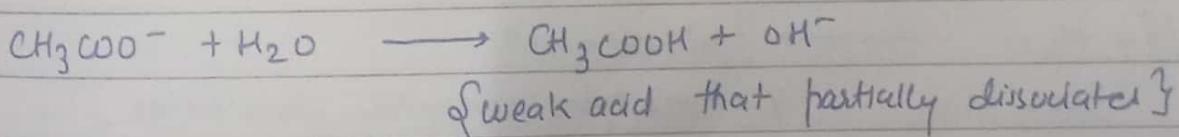
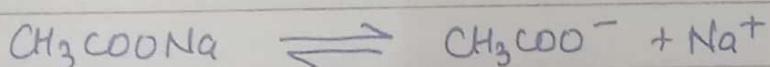
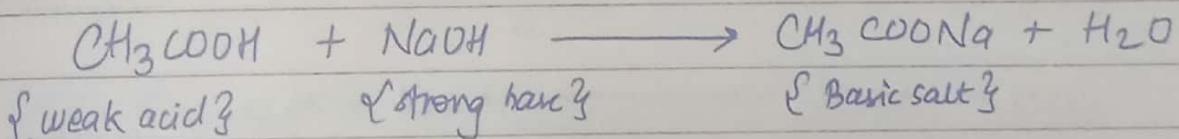
Hence, there is excess of OH^- ions which makes solution slightly basic of $pH > 7.0$.

Hydrolysis of different salt is categorized as

- Weak acid and strong base
- Strong acid and weak base
- Weak acid and weak base
- Strong acid and strong base.

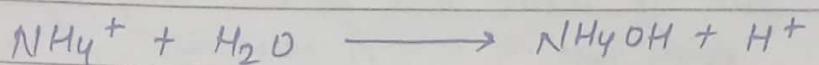
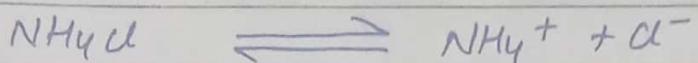
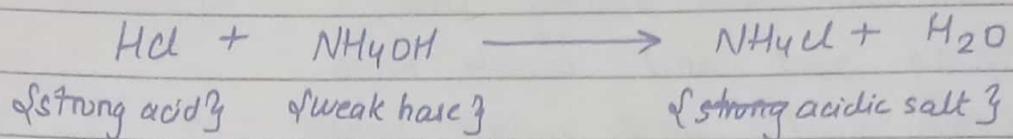


(iii) (i) Hydrolysis of salt of weak acid and strong base

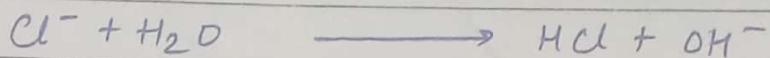


So, here, the solution contains more OH^- ions hence giving basic solution.

(ii) Hydrolysis of salt of strong acid and weak base.



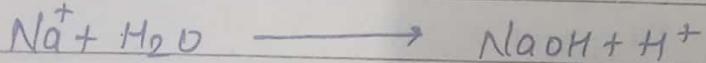
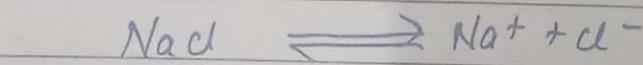
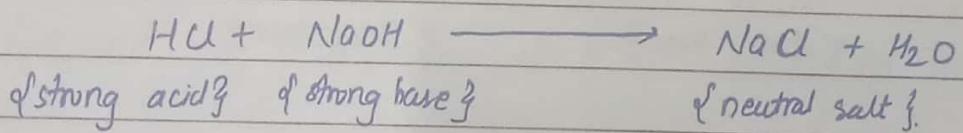
(weak base - partially ionizes) dissociates



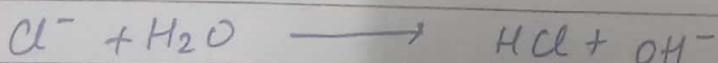
(strong acid - completely dissociates)

Here, the solution contains more H^+ ions meaning the solution is acidic.

(iii) Hydrolysis of salt of strong acid and strong base



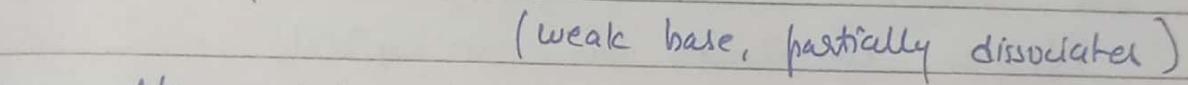
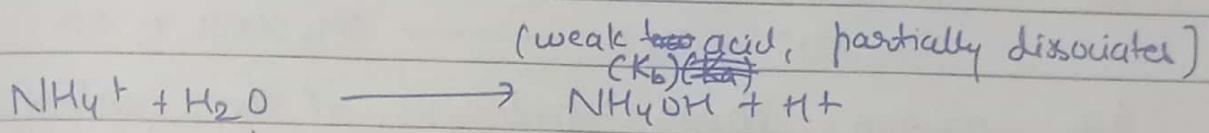
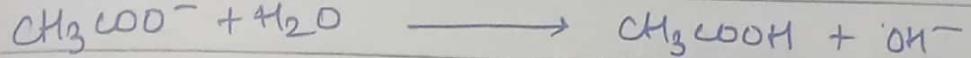
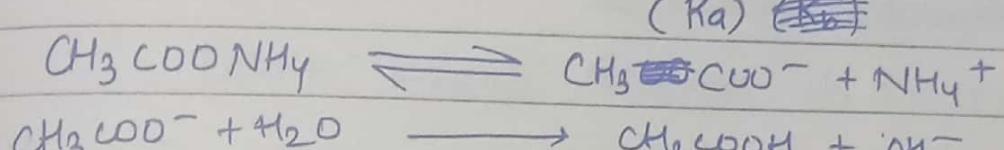
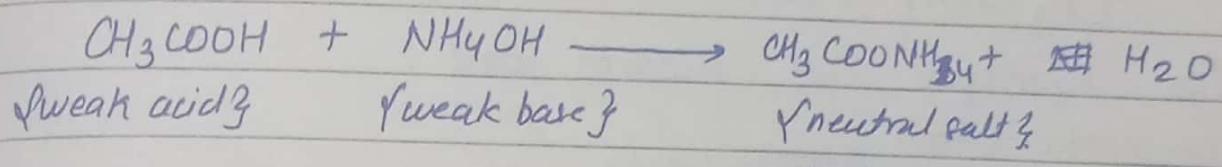
(strong base, completely dissociates)



(strong acid, completely dissociates)

Here, the solution contains almost equal number of H^+ & OH^- ions meaning solution is neutral.
thus, strong acid and strong base don't hydrolyse.

(iv) Hydrolysis of salt of weak acid and weak base:



Here, the solution

if $K_a > K_b$, the solution is acidic.

$K_a = K_b$, the solution is neutral

$K_a < K_b$, the solution is alkaline.

Quantitative Aspect of Hydrolysis

Q7: Deduce the relation $K_h = \frac{K_w}{K_a}$. or,

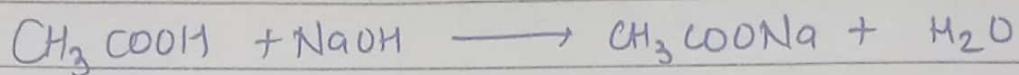
establish a quantitative relation that a weak acid, stronger is its conjugate and vice-versa.

Solⁿ:

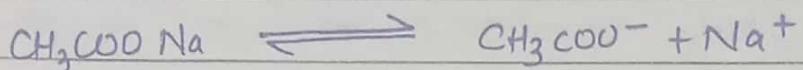
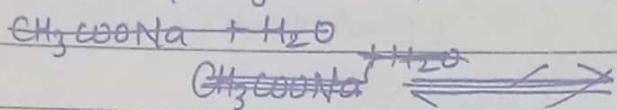
let us consider a moderately strong weak acid CH_3COOH . So that acetate ion is moderately strong ~~base~~.



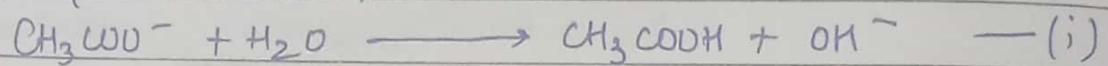
Also, consider a moderately strong base. NaOH . which combines with CH_3COOH .



The hydrolysis of acetate salt;



The hydrolysis reaction,



This reaction shows hydrolysis of the acetate ion.

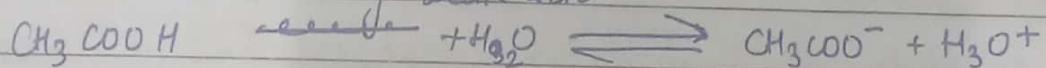
Applying equilibrium law on eqn (i);

$$K_{\text{ac}} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}_2\text{O}]}$$

$$\text{or, } K_{\text{H}} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \text{--- (ii)}$$

Here K_{H} is hydrolysis constant.

We know, dissociation of weak acid



So,

$$K_{\text{a}} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{--- (iii)}$$

In eqn (ii);

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

$$K_H = \frac{1}{K_a} \times [OH^-][H_3O^+] \quad [\because \text{Using eqn (iii)}]$$

$$\therefore K_H = \frac{K_w}{K_a} \quad \text{--- (iv)}$$

This eqn (iv) shows that $K_H \propto \frac{1}{K_a}$.

For weaker acid, hydrolysis constant of salt is larger.

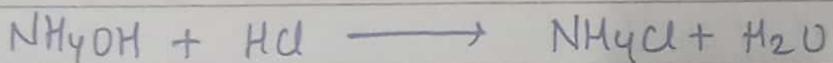
This proves that weaker the acid, stronger is the conjugate base and vice-versa.

Q7: Deduce the relation, $K_H = \frac{K_w}{K_b}$ or,

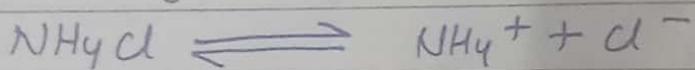
establish a quantitative relation, weaker the base, stronger is conjugate base and vice-versa.

Solⁿ:

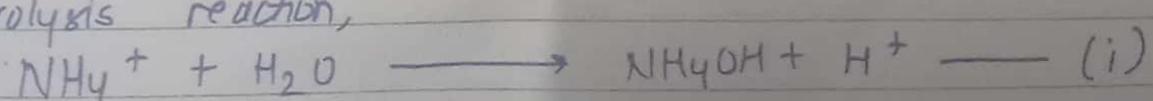
let us consider a moderately weak base NH_4OH which combines with considerably strong acid HCl .



The hydrolysis of ammonium salt;



The hydrolysis reaction,



This reaction shows hydrolysis of the ~~the~~ ammonium ion.

Applying equilibrium law in eqⁿ(i);

$$K_c = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+][\text{H}_2\text{O}]}$$

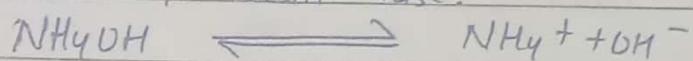
$$\text{or, } K_c \times [\text{H}_2\text{O}] = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

$$\text{or } K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{--- (ii)}$$

Here, K_h is hydrolysis constant.

We know,

dissociation of weak base.



So,

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

In eqⁿ(ii);

$$K_h = \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+][\text{OH}^-]} \times [\text{H}^+][\text{OH}^-]$$

$$\text{or } K_h = \frac{1}{K_b} \times [\text{H}^+][\text{OH}^-] \quad [:\text{ From eqn (iii)}]$$

$$\therefore K_h = \frac{K_w}{K_b} \quad \text{--- (iv)}$$

This equation (iv) shows $K_h \propto \frac{1}{K_b}$.

For weaker base, hydrolysis constant of salt is larger.

This proves that, weaker the base ~~and~~ stronger is the conjugate acid and vice-versa.

(Q7): What is the pH of solution prepared by dissolving one mole of sodium acetate (CH_3COONa) in enough water to make one litre solution. ($K_a = 1.85 \times 10^{-5}$)

Soln:

Given,

$$K_a = 1.85 \times 10^{-5}$$

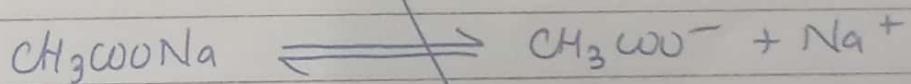
$$K_w = 10^{-14}$$

Now,

$$K_H = \frac{K_w}{K_a} = \frac{10^{-14}}{1.85 \times 10^{-5}}$$

$$\therefore K_H = 5.4 \times 10^{-10}$$

Now,

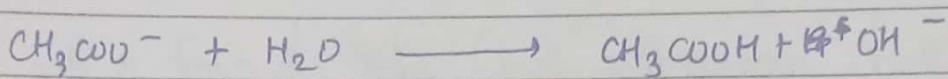
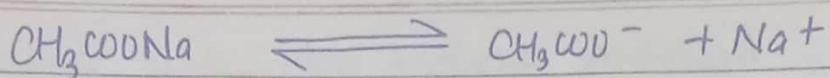


~~$$R \quad K_H = K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$~~

Let $[\text{H}^+]$ concentration be x .

~~$$\text{or, } 1.85 \times 10^{-5} = \frac{x^2}{1-x}$$~~

~~$$\text{or, } x^2 + 1.85 \times 10^{-5}x - 1.85 \times 10^{-5} = 0$$~~



Let L M CH_3COO^- hydrolyses to give $\alpha \text{ M}$
 CH_3COOH and $\alpha \text{ M}$ ~~OH^-~~

So,

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

$$\text{or } 5.40 \times 10^{-10} = \alpha^2$$

$$\therefore \alpha = 2.32 \times 10^{-5} \text{ M}$$

$$\text{So, } [\text{OH}^-] = 2.32 \times 10^{-5} \text{ M}$$

$$\begin{aligned} \therefore p\text{H} &= 14 + \log [\text{OH}^-] \\ &= 14 + \log [2.32 \times 10^{-5}] \\ \therefore \text{pH} &= 9.37 \end{aligned}$$

<Q>: What is the pH for 0.2 M solution of NaCN?
 K_a for HCN = 4.0×10^{-10} .

So,

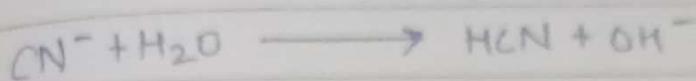
Given,

$$K_a \text{ of HCN} = 4.0 \times 10^{-10}$$

$$K_w = 10^{-14}$$

So,

$$K_H = \frac{K_w}{K_a} = \frac{10^{-14}}{4 \times 10^{-10}} \quad \therefore K_H = 2.5 \times 10^{-5}$$



We know,

$$K_H = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$\text{or, } 2.5 \times 10^{-5} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

Let 0.2 M CN⁻ hydrolyses to give x M HCN and
x M OH⁻.

So,

$$2.5 \times 10^{-5} = \frac{x \times x}{0.2}$$

$$\text{or, } 2.5 \times 10^{-5} \times 0.2 = x^2 \\ \therefore x = 2.23 \times 10^{-3} \text{ M}$$

$$\text{So, } [\text{OH}^-] = 2.23 \times 10^{-3} \text{ M}$$

$$\begin{aligned} \therefore \text{pH} &= 14 + \log [\text{OH}^-] \\ &= 14 + \log [2.23 \times 10^{-3}] \\ \therefore \text{pH} &= 11.348 \end{aligned}$$

Q7: What is the pH of a 0.625 M solution of CH_3COONa ? K_a of $\text{CH}_3\text{COOH} = 1.85 \times 10^{-5}$;
Soln.:

Given,

$$K_a = 1.85 \times 10^{-5}$$

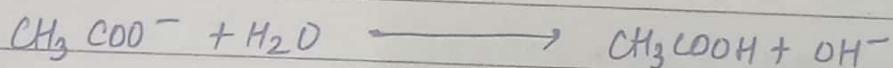
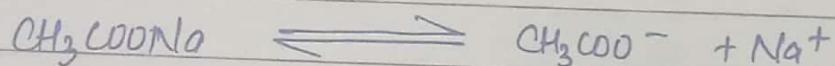
$$K_w = 10^{-14}$$

Hence,

$$\begin{aligned} K_H &= \frac{K_w}{K_a} \\ &= \frac{10^{-14}}{1.85 \times 10^{-5}} \end{aligned}$$

$$\therefore K_H = 5.40 \times 10^{-10}$$

Now,



Sol.

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

Let 0.625 M of CH_3COO^- hydrolyses x M of OH^- and x M of CH_3COOH .

So,

$$K_H =$$

$$5.40 \times 10^{-10} = \frac{x^2}{0.625}$$

$$\text{or, } x = \sqrt{0.625 \times 5.40 \times 10^{-10}} \quad \therefore x = 1.83 \times 10^{-5} \text{ M}$$

$$\therefore [\text{OH}^-] = 1.83 \times 10^{-5} \text{ M}$$

Now,

$$\begin{aligned}\therefore \text{pH} &= 14 + \log [\text{OH}^-] \\ &= 14 + \log [1.83 \times 10^{-5}]\end{aligned}$$

$$\therefore \text{pH} = 9.26$$

(Q7): Calculate the pH of a 0.10 M solution of ammonium chloride. K_b of NH_4Cl = 1.8×10^{-5} .

Given,

$$K_b \text{ of } \text{NH}_4\text{Cl} = 1.8 \times 10^{-5}$$

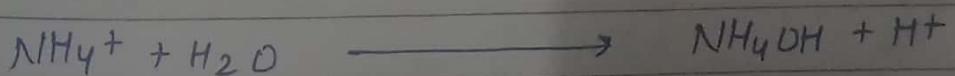
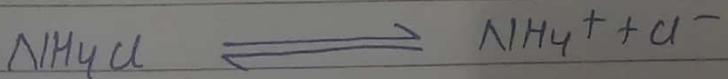
$$\text{We know, } K_w = 10^{-14}$$

So,

$$K_H = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$$\therefore K_H = 5.56 \times 10^{-10}$$

Now,



So,

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

Let 0.10 M of NH_4^+ hydrolyses x M of $[\text{H}^+]$ and x M of $[\text{NH}_4\text{OH}]$

$$\text{or } \frac{1.8 \times 10^{-5} \times 5.56 \times 10^{-10}}{0.1} = x^2$$

$$\therefore \sqrt{5.56 \times 10^{-10} \times 0.1} = x$$

$$\therefore x = 7.45 \times 10^{-6} \text{ M}$$

$$\therefore [\text{H}^+] = 7.45 \times 10^{-6} \text{ M}$$

Now,

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= -\log [7.45 \times 10^{-6}] \end{aligned}$$

$$\therefore \text{pH} = 5.12.$$

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

Soln.

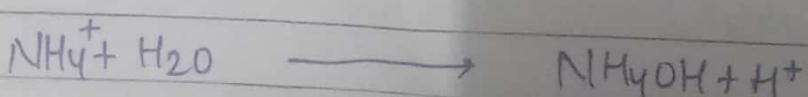
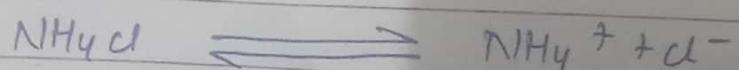
Given,

$$K_b = 1.8 \times 10^{-5}$$

$$\text{We know, } K_w = 10^{-14}$$

$$\therefore K_H = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} \quad \therefore K_H = 5.56 \times 10^{-10}$$

Now,



So,

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

or, $5.56 \times 10^{-10} \propto$

Let 0.20 M of NH_4^+ hydrolyses $x \text{ M}$ of $[\text{H}^+]$
and $[\text{NH}_4\text{OH}] = x$.

or $5.56 \times 10^{-10} \times 0.2 = x^2$

$$\therefore x = 1.05 \times 10^{-5}$$

So,

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log [1.05 \times 10^{-5}] \\ \therefore \text{pH} &= 4.97\end{aligned}$$

Buffer Solutions

A solution which maintains its pH fairly constant even upon the addition of small amounts of acid or base is called buffer solution.

A buffer solution resists a change in its pH.

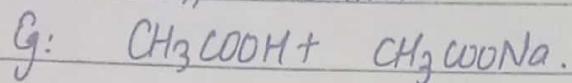
* Types of Buffer solutions

The two types of buffer solutions are as follows:

- i) Acidic buffer solution
- ii) Basic buffer solution.

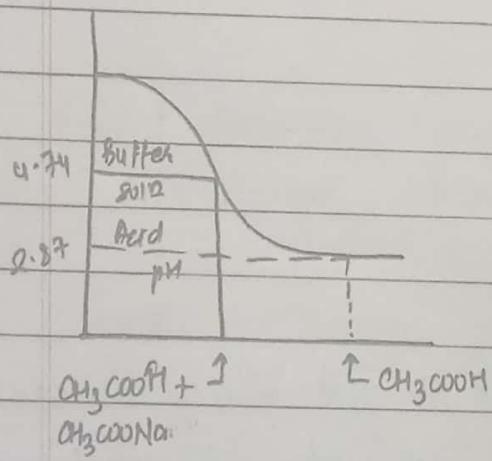
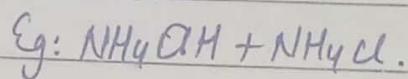
i) Acidic Buffer Solution:

A weak acid together with a salt of the same acid with a strong base is called acidic buffer solution.

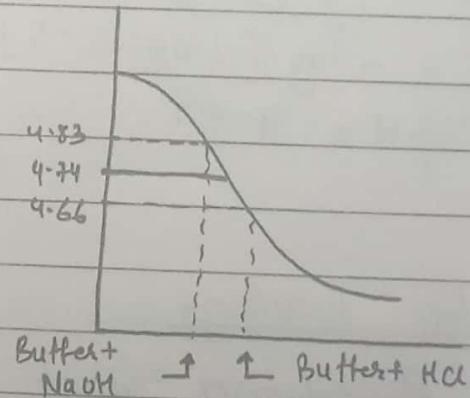


ii) Basic buffer solution:

A weak base together with a salt of the same base with a strong base is called basic buffer solutions.



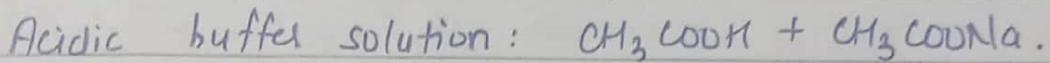
The buffer soln.
of $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
has higher pH than
acid itself.



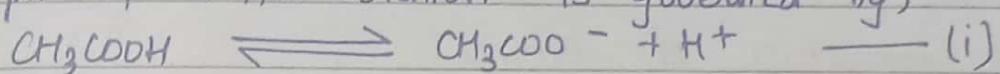
The pH of buffer changes only
slightly upon addition of
an acid or base (0.01 moles).

Mechanism of Buffer Solution

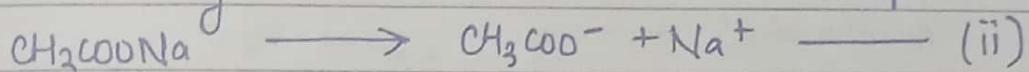
(a): Buffer action of an Acid Buffer:



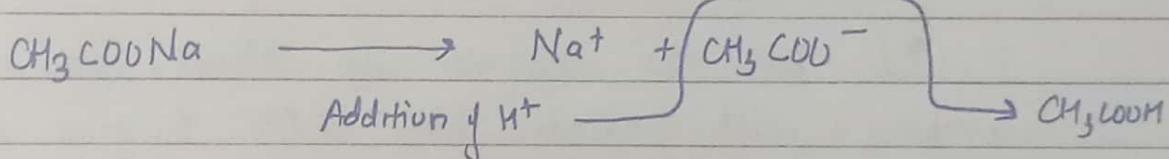
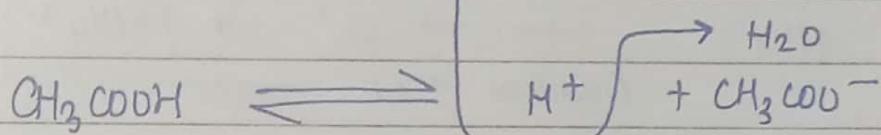
The pH of buffer solution is governed by;



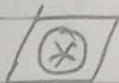
Large number of Acetate ions is due to complete ionization of



Addition of OH^-



Addition of H^+



Upon the addition of HCl to buffer solution, the H^+ ions from HCl, combines with excess acetate ions to give unionized CH_3COOH which neutralizes added H^+ ions. and pH is virtually unchanged.

As CH_3COOH concentration increases, equilibrium shifts towards right in eqn (i) which decreases pH marginally.



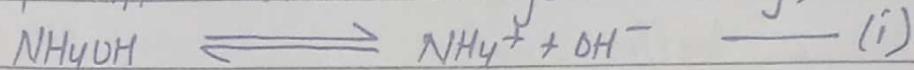
Upon the addition of NaOH to buffer solution, the OH^- ions from NaOH, combines with H^+ ions to give H_2O which neutralizes added OH^- ions and pH is virtually unchanged.

As H_2O concentration increases, eq the H^+ concentration in buffer solution decreases which marginally decreases pH.

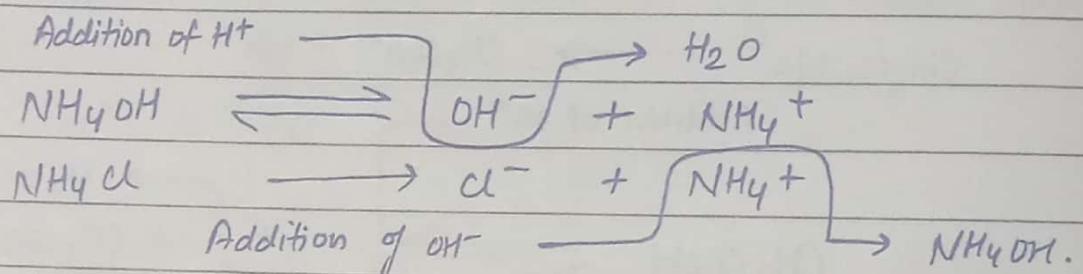
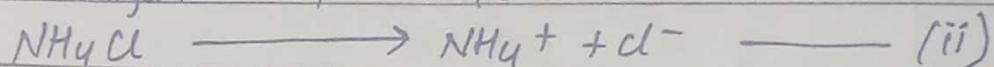
(b) Buffer action of an Basic Buffer:

Basic buffer action: $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

The pH of buffer solution is governed by;



Large excess of ammonium ions due to complete ions due to complete ionization of NH_4Cl .



Upon the addition of NaOH , OH^- ions from NaOH combines with excess NH_4^+ ions to give unionized NH_4OH . Thus, the added OH^- are neutralized and pH of solution is virtually unchanged.

As NH_4OH concentration increases, equilibrium of (i) shifts towards right and increases OH^- ions increasing the pH of solution marginally.

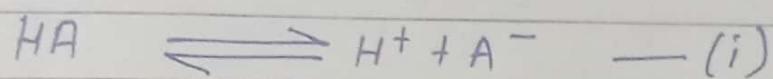
Upon the addition of HCl , H^+ ions from HCl , combines with OH^- ions to give H_2O which neutralizes added H^+ ions and pH is virtually unchanged.

As H_2O concentration increases, the OH^- ion concentration decreases due to which pH of the solution marginally decreases.

Henderson Equation / Calculate pH of Buffer soln

The pH of an acid buffer is calculated from dissociation constant (K_a) of weak acid and concentrations of acid and salt used.

The dissociation expression of weak acid HA,



So,

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

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

The weak acid is only slightly dissociated which is ~~further depressed~~ only dissociated by the addition of salt ($Na^+ A^-$) which provides A^- ions through common ion effect.

So, the equilibrium concentration of the unionized acid \approx the initial concentration of the acid.

and

the equilibrium concentration of $[A^-] \approx$ initial concentration of the salt added since it is completely dissociated.

So,

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

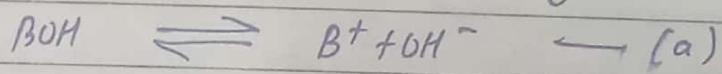
Taking log negative log of both sides in eqⁿ (iii), we get.

$$-\log [H^+] = -\log K_a - \frac{\log [\text{acid}]}{[\text{salt}]}$$

$$\text{or, } pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \quad - (\text{iv})$$

Here, eqⁿ(iv) is Henderson - Hasselbalch equation. for acidic buffer.

The pOH of an basic buffer can be calculated from the dissociation constant K_b of the weak base and concentrations of the acid and the salt used. The dissociation constant of weak base BOH,



and,

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

$$\text{or } [\text{OH}^-] = K_b \frac{[\text{BOH}]}{[\text{B}^+]} \quad - (\text{b})$$

The weak base is only slightly dissociated which is only disso further depressed by the addition of salt (B^+d^-) which provides B^+ ions through common ion effect.

So, the equilibrium concentration of the unionized base \approx the initial concentration of base.

and

the equilibrium concentration of $[\text{B}^+]$ \approx the initial concentration of salt

added since it is completely dissociated.
So,

$$[\text{OH}^-] = K_b \times \frac{[\text{base}]}{[\text{salt}]} \quad (\text{c})$$

Taking negative log on both sides of eqn(c),

$$-\log [\text{OH}^-] = -\log K_b - \log \left(\frac{\text{base}}{\text{salt}} \right)$$

$$\text{or, } \text{pH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} \quad (\text{d})$$

Here eqn (d) is Henderson-Hasselbalch equation for basic buffer.

* Significance

- (i) The pH of the buffer solution can be calculated.
- (ii) The dissociation constant of a weak acid / base can be determined by measuring the pH of buffer solution containing equimolar concentrations of acid / base and the salt.
- (iii) A buffer solution of desired pH can be prepared.

(Q7): Find the pH of a buffer solution containing 0.20 moles L⁻¹ CH₃COONa and 0.15 moles L⁻¹ CH₃COOH. K_a for acetic acid = 1.8 × 10⁻⁵.

Soln:

Given,

$$\text{K}_a \text{ of acetic acid} = 1.8 \times 10^{-5}$$

$$[\text{CH}_3\text{COONa}] = 0.20 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.15 \text{ M}$$

$$\text{pH} = ?$$

We know, the Henderson equation,

$$\begin{aligned} \text{pH} &= -\log [\text{K}_a] + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= -\log [1.8 \times 10^{-5}] + \log \frac{0.20}{0.15} \end{aligned}$$

$$\therefore \text{pH} = 4.8697.$$

(Q7): 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 of HCOOH = 1.8 × 10⁻⁴.

Soln:

Given,

$$\text{K}_a \text{ of HCOOH} = 1.8 \times 10^{-4}$$

$$[\text{HCOOH}] = 0.250 \text{ M}$$

$$[\text{HCOONa}] = 0.100 \text{ M}$$

$$\text{pH} = ?$$

We know, from Henderson equation,

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

$$= -\log [K_a] + \log \frac{[0.100]}{[0.250]}$$

$$= -\log [1.8 \times 10^{-5}] + \log \frac{[0.100]}{[0.250]}$$

$$\therefore pH = 3.34$$

(Q): A buffer solution contains 0.015 mole of ammonium hydroxide and 0.025 mole of ammonium chloride. Calculate the pH value of solution. $K_b = 1.80 \times 10^{-5}$.

Given,

$$K_b = 1.80 \times 10^{-5}$$

$$[\text{NH}_4\text{OH}] = 0.015$$

$$[\text{NH}_4\text{Cl}] = 0.025$$

$$pH = ?$$

We know, from Henderson equation,

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

$$\text{or, } pH = 14 - \left[\log K_b + \log \frac{[\text{salt}]}{[\text{base}]} \right]$$

$$= 14 - \left[-\log [1.80 \times 10^{-5}] + \log \left(\frac{0.025}{0.015} \right) \right]$$

$$\therefore pH = 9.033$$

<Q7: 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} .

Given:

$$K_b = 1.8 \times 10^{-5}$$

$$[\text{NH}_3] = 0.25 \text{ M}$$

$$[\text{NH}_4^+] = 0.40 \text{ M}$$

$$\text{pH} = ?$$

We know, from Henderson equation,

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

$$\text{or } \text{pH} = 14 - \left[\text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]} \right]$$

$$= 14 - \left[-\log (1.8 \times 10^{-5}) + \log \left(\frac{0.40}{0.25} \right) \right]$$

$$\therefore \text{pH} = 9.05$$

Acid-Base Indicators

Indicators is a substance which indicates the end point in a titration by undergoing a sharp change in its colour.

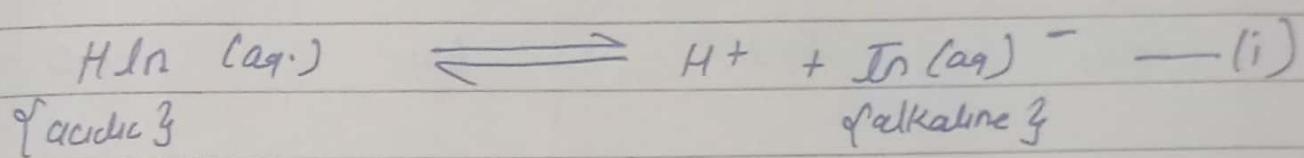
and

An acid-base indicator is an organic dye and the colour of dye depends on concentration of H_3O^+ .

and indicates the completion of reaction by sharp colour change.

④ Theory of Indicators

In general, an indicator is a weak acid which partially dissociates in aqueous solution.



$$K_I = \frac{[\text{H}_3\text{O}^+] [\text{In}^-]}{[\text{HIn}]} \quad \text{--- (ii)}$$

or,

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_I}{[\text{H}_3\text{O}^{\oplus}]} \quad \text{--- (iii).}$$

The concentration of $[\text{H}_3\text{O}^{\oplus}]$ ~~remains~~ in solution determines the ratio of $[\text{In}^-]/[\text{HIn}]$ in eqⁿ (ii).

In acidic solution, $[\text{H}^+]$ increases. Here, the equilibrium shifts towards left i.e., $[\text{In}^-]$ decreases and dissociation of HIn decreases suppressed. i.e., $[\text{HIn}] > [\text{In}^-]$. The acidic colour of HIn predominates.

In alkaline solution, $[\text{OH}^-]$ increases i.e., $[\text{H}^+]$ ions decrease. Here, the equilibrium shifts towards right i.e., $[\text{In}^-]$ increases and dissociation of HIn enhances. i.e., $[\text{HIn}] < [\text{In}^-]$. The basic colour of HIn predominates.

② Indicators, Colours and pH range:

Indicator	Colour in acid	Colour in 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

Selection of Indicators

The curve obtained by plotting the graph of pH vs. the volume of alkali / acid added is called titration curve.

In acid-base titration, the indicators are selected in such a way that the pH range of indicator must lie with pH range of the solution at the end point.

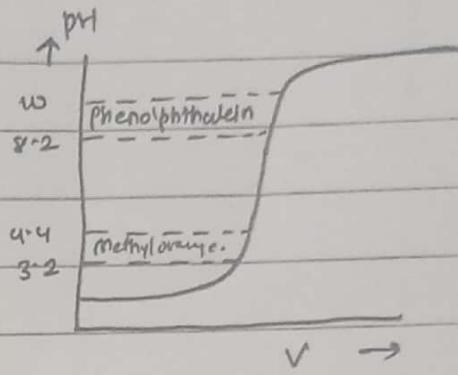
(a) Titration of Strong Acid and Strong Base.

pH jump at end point = 3.1 - 4.4.

Suitable indicators:

$$\text{methyl orange} = (3.1 - 4.4)$$

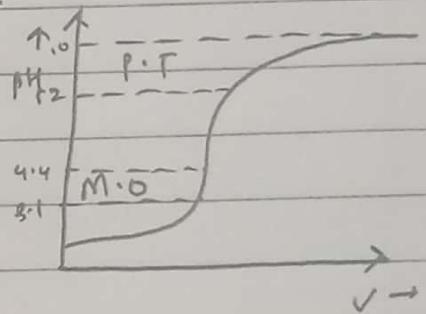
$$\text{phenolphthalein} = (8.2 - 10)$$

(b) Titration of Strong acid and Weak base

pH jump at end point = 3 - 8

Suitable indicators:

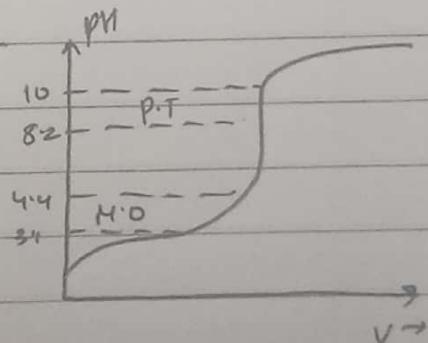
$$\text{Methyl orange} = (3.1 - 4.4)$$

(c) Titration of Weak Acid and Strong base

pH jump at end point = 6 - 11

Suitable indicators:

$$\text{Phenolphthalein} = 8.2 - 10$$

(d) Titration of weak acid and weak base.

pH jump at end point = 6 - 8

No suitable indicators.

