IONIC EQUILIBRIUM
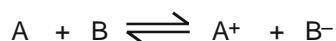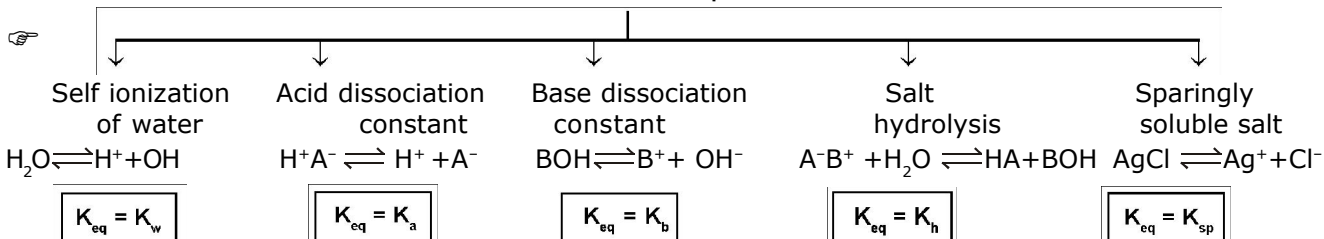
An ionic Equilibrium exists between the unionised electroyte molecules and the ions that result from ionisation

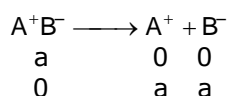$$A + B \rightleftharpoons A^+ + B^-$$

★ **Types of k_{eq}**

☞

Self ionization of water	Acid dissociation constant	Base dissociation constant	Salt hydrolysis	Sparingly soluble salt
$H_2O \rightleftharpoons H^+ + OH$	$H^+A^- \rightleftharpoons H^+ + A^-$	$BOH \rightleftharpoons B^+ + OH^-$	$A^-B^+ + H_2O \rightleftharpoons HA + BOH$	$AgCl \rightleftharpoons Ag^+ + Cl^-$
$K_{eq} = K_w$	$K_{eq} = K_a$	$K_{eq} = K_b$	$K_{eq} = K_h$	$K_{eq} = K_{sp}$

★ **Concept of electrolyte**

☞

Strong electrolyte

$$A^+B^- \longrightarrow A^+ + B^-$$
$$\begin{array}{ccc} a & 0 & 0 \\ 0 & a & a \end{array}$$

Weak electrolyte

$$A B \rightleftharpoons A^+ + B^-$$
$$\begin{array}{ccc} a & 0 & 0 \\ a(1-\alpha) & a\alpha & a\alpha \end{array}$$

☞ 100% disssociation ($\alpha = 1$) $\alpha < 1$

☞ no equilibrium   equilibrium
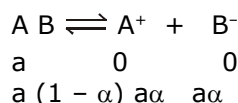
☞ it is irreversible   it is reversible process.
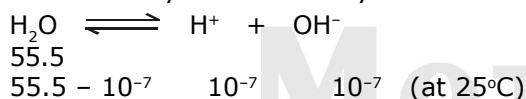
★ **Self ionization of water**

Concentration of H_2O ($[H_2O]$) = $\dfrac{1000/18}{1}$ = 55.5 M

Water is very weak electrolyte
$$H_2O \rightleftharpoons H^+ + OH^-$$
55.5
$55.5 - 10^{-7}$ 10^{-7} 10^{-7} (at 25°C)

☞ $k_{eq} = \dfrac{[H^+][OH^-]}{[H_2O]}$

            Constant

☞ $K_w = k_{eq}[H_2O] = [H^+][OH^-]$

☞   **$K_w = [H^+][OH^-]$,** at 25°C, $[H^+] = [OH^-] = 10^{-7}$
        K_w (25°C)   = 10^{-14}
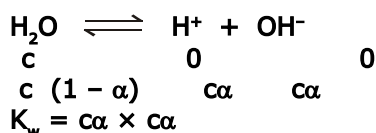   ↓
        Self ionization constant of water

        let, K_{w_1} at temperature T_1 , K_{w_2} at temperature T_2

☞ $\log \dfrac{K_{w_2}}{K_{w_1}} = \dfrac{\Delta H}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$, $T \uparrow \Rightarrow K_w \uparrow$

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☞ **For calculation of α :**

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

c   0   0

c (1 − α)   cα   cα

$K_w = c\alpha \times c\alpha$

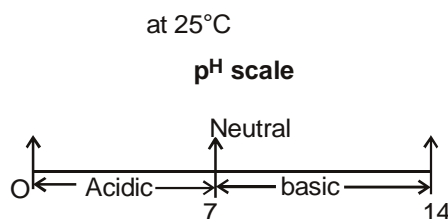☞ $\alpha = \dfrac{\sqrt{k_w}}{c}$ c = 5 5.56 M   ☞ $\alpha = 1.8 \times 10^{-2}\sqrt{K_w}$

(pH) (pH scale is given by Sorension)

☞ potent
⇓
strength → Hydrogen ion

at 25°C

★ pH = − log [H⁺]
p OH = − log [OH⁻]
p K_w = − log K_w
at any temperature :
      [H⁺] = [OH⁻]
      [H⁺] [OH⁻] = K_w

p^H scale

Neutral

O ← Acidic → ← basic →
7   14

☞ − log [H⁺] − log [OH⁻] = − log [K_w]

☞ **pH + pOH = p K_w**

at 25°C   at 80°C
$K_w = 10^{-14}$ $K_w = 10^{-12}$
pH + pOH = 14   pH + pOH = 12
25°C   90°C
pH + pOH = 14   pH + pOH = 12

Some concept regarding pH calculation

☞ **Concept 1 :**   ☞ **Concept 2:**
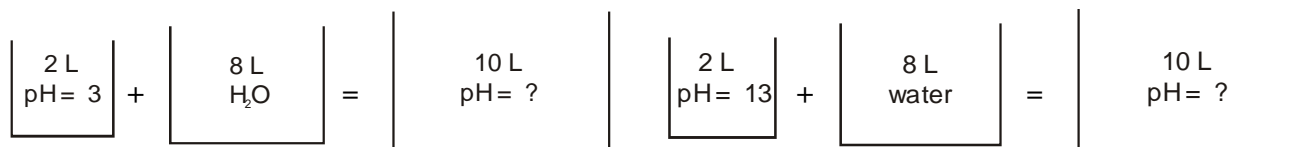
| 5 L pH= 3 | ⇒ | 1 L pH= ? |

| 3 L pH= 3 | + | 2 L pH= 3 | ⇒ | 5 L pH= ? |

☞ **Concept 3:**   ☞ **Concept 4:**

| 2 L pH= 3 | + | 8 L H_2O | = | 10 L pH= ? |

| 2 L pH= 13 | + | 8 L water | = | 10 L pH= ? |

☞ **Note :** ← Calculate pH ——— 7 pH (i) Calculate pOH (ii) pH = 14- pOH

☞ **Concept 5:**

$$\boxed{pH = 3}_{2} \quad + \quad \boxed{pH = 4}_{1} \quad = \quad \boxed{pH = ?}$$

☞ **Note :** The final pH of solution after mixing two solution is in between the previous solution pH.
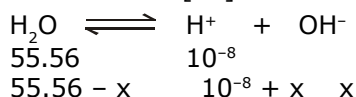
☞ **Concept 6:** ☞ **Concept 7:**

$$\boxed{\begin{array}{c}V\\pH= 3\end{array}} + \boxed{\begin{array}{c}V\\pH= 11\end{array}} \Rightarrow \boxed{\begin{array}{c}2\,V\\pH= ?\end{array}}$$

$$\boxed{\begin{array}{c}10^{-8}\ M\ HCl\\pH= ?\end{array}}$$

☞ **Note :**

When $[H^+] > 10^{-5} \Rightarrow [H^+]_{water}$ neglected
When $[H^+] < 10^{-5} \Rightarrow [H^+]_{water}$ considered

$H_2O \quad \rightleftharpoons \quad H^+ \quad + \quad OH^-$
55.56 $\qquad$ 10^{-8}
55.56 – x $\qquad$ $10^{-8} + x \quad x$

☞ $x (10^{-8} + x) = 10^{-14} \qquad \Rightarrow \qquad x = .94 \times 10^{-7}$

☞ $[H^+] = 10^{-8} + .94 \times 10^{-7} \qquad\qquad = 1.04 \times 10^{-7}$

☞ $pH = 7 - \log (1.04)$

☞ **Concept 8:**

$$\boxed{\begin{array}{c}10^{2}\ M\ HCl\\pH= ?\end{array}} \qquad \boxed{\textbf{pH = – log [Active mass]}}$$

✯ **Dissociation of weak acid :**

$H^+ A^- \quad \rightleftharpoons \quad H^+ \quad + \quad A^-$
c
$c (1- \alpha) \qquad\qquad c\alpha \qquad c\alpha$
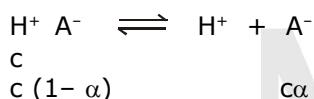
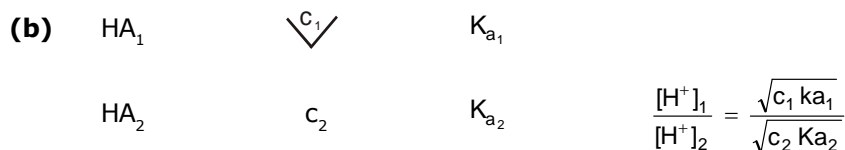$K_a = \dfrac{c\alpha^2}{1-\alpha} \qquad$ for weak acid $\alpha << 1 \qquad K_a = c\alpha^2$

☞ $\boxed{\alpha = \sqrt{\dfrac{K_a}{c}}}$

$[H^+] = c\alpha = \sqrt{c\,K_a}, \quad pH = -\log \sqrt{c\,K_a}, \quad$ for bases $\quad [H^+] = \dfrac{K_w}{\sqrt{c \times K_b}}$

☞ **Note :**

(a) $HA_1 \qquad\qquad c \qquad\qquad K_{a_1}$

$\qquad\qquad\qquad || \qquad\qquad \wedge$

$HA_2 \qquad\qquad c \qquad\qquad K_{a_2} \qquad\qquad \therefore \quad \dfrac{[H^+]_1}{[H^+]_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$

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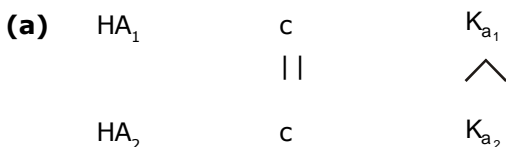
☞ So HA_2 is stronger acid than HA_1

(b) HA_1 $\overset{c_1}{\vee}$ K_{a_1}

HA_2 c_2 K_{a_2} $\dfrac{[H^+]_1}{[H^+]_2} = \dfrac{\sqrt{c_1\, ka_1}}{\sqrt{c_2\, Ka_2}}$
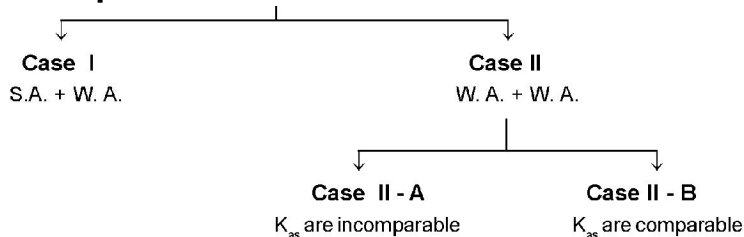
☞ The acidic strength of two weak acid can be compared by K_a value only in the case when their concentration are same. Otherwise the procedure of case (b) should be followed .
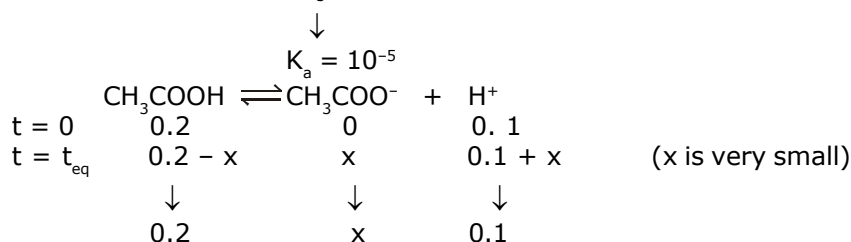
★
<center>pH of mixture of two acids</center>

Case I S.A. + W. A.	**Case II** W. A. + W. A.

☞

Case II - A K_{as} are incomparable	**Case II - B** K_{as} are comparable

★ <center>Case (I) (Strong acid + weak acid)</center>

Question :   HCl (0.1 M) + CH$_3$COOH (0.2 M)

$$\downarrow$$
$$K_a = 10^{-5}$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

t = 0   0.2   0   0. 1

t = t$_{eq}$ 0.2 – x   x   0.1 + x   (x is very small)

        $\downarrow$ $\downarrow$ $\downarrow$
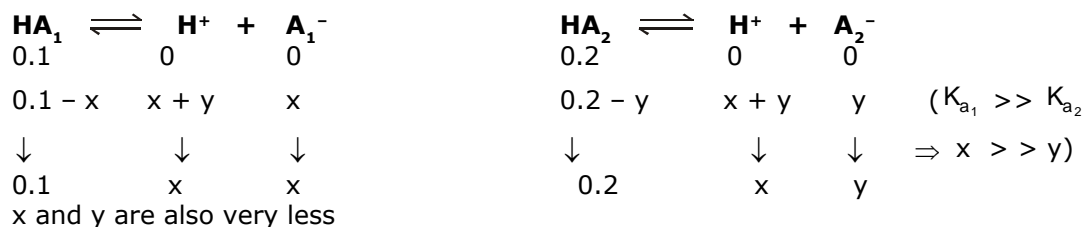
        0.2   x   0.1

$\Rightarrow$ pH = – log (0.1) = 1 $\Rightarrow$ $[CH_3COO^-]$ = ? $\Rightarrow$ $10^{-5} = \dfrac{x \times 0.1}{0.2} \Rightarrow [CH_3COO^-] = 2 \times 10^{-5}$

★ <center>Case (II-A) (weak acid + weak acid) (k$_{as}$ are incomparable)</center>

Question : HA_1 (0.1 M, $K_{a_1} = 10^{-5}$)

         HA_2 (0.2 M, $K_{a_2} = 10^{-9}$)

$HA_1 \rightleftharpoons$	H^+	$+$	A_1^-		$HA_2 \rightleftharpoons$	H^+	$+$	A_2^-	
0.1	0		0		0.2	0		0	
0.1 – x	x + y		x		0.2 – y	x + y		y	($K_{a_1} >> K_{a_2}$
$\downarrow$	$\downarrow$		$\downarrow$		$\downarrow$	$\downarrow$		$\downarrow$	$\Rightarrow$ x > > y)
0.1	x		x		0.2	x		y	

x and y are also very less

$10^{-5} = \dfrac{x.x}{10^{-1}}$ $[H^+] = x = 10^{-3}$, $\Rightarrow$ pH = 3 $[A_1^-] =$ $[A_2^-] =$

★ <center>Case (II-B) (weak acid + weak acid) (k$_{as}$ are comparable)</center>

☞ **Question :** HA_1 (0.1) $\qquad K_{a_1} = 10^{-5}$

$\qquad\qquad HA_2$ (0.2) $\qquad K_{a_2} = 10^{-6}$

$HA_1 \rightleftharpoons$	H^+	+	A_1^-		$HA_2 \rightleftharpoons$	H^+	+	A_2^-
0.1	0		0		0.2	0		0
0.1 – x	x + y		x		0.2 – y	x + y		y
0.1	x + y		x		0.2	x + y		y

$\Rightarrow \qquad$ now $\qquad K_{a_1} = \dfrac{x\,(x+y)}{0.1}$

$\Rightarrow \qquad\qquad K_{a_1} = \dfrac{x\,(x+y)}{c_1} \qquad , \qquad K_{a_2} = \dfrac{(x+y)\,y}{c_2}$

$\Rightarrow$

$$x\,(x+y) = c_1\,K_{a_1} \qquad\qquad y\,(x+y) = c_2\,K_{a_2}$$

$$(x+y)^2 = c_1\,K_{a_1} + c_2\,K_{a_2}$$

$\Rightarrow \qquad [H^+] = x + y = \sqrt{c_1\,K_{a_1} + c_2\,K_{a_2}}$

☞ weak polyprotic acids or bases
$(H_2S, H_3PO_4, NH_2 - NH_2, H_2CO_3)$

(a) $\quad H_2S \rightleftharpoons H^+ + HS^- \qquad K_{a_1} \qquad\qquad HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_{a_2}$

(b) $\quad NH_2 - NH_2 + H^+ \rightleftharpoons NH_2 - NH_3^+ \quad K_{b_1} \qquad NH_2 - NH_3^+ + H^+ \rightleftharpoons \overset{+}{N}H_3 - \overset{+}{N}H_3 \quad K_{b_2}$

Cases

Case I	Case II	Case III
Dibasic weak acids	Dibasic W. A. + S. A.	Tribasic W. A.

☞ **Case I :** H_2S (0.1 M $\quad K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-9}$)

$\Rightarrow$

$H_2S \rightleftharpoons$	H^+	+	HS^-		$HS^- \rightleftharpoons$	H^+	+	S^{2-}
0.1	0		0		x	x		0
0.1 – x	x + y		x – y		x – y	x + y		y
↓	↓		↓		↓	↓		↓
0.1	x		x			x		x

$K_{a_1} >> K_{a_2} \qquad\qquad x >> y$

$10^{-4} = \dfrac{x^2}{0.1} \Rightarrow x = \sqrt{10^{-5}} \qquad \dfrac{x \times y}{x} = 10^{-9}$

$[H^+] = x = \qquad [HS^-] = x = \qquad [S^{2-}] = y =$

✯ **Case II :**

HCl $\rightleftharpoons$	H^+	+	Cl^-
0.2	0		0
0	0.2		0.2

$\Rightarrow$

$H_2S \rightleftharpoons$	H^+	+	HS^-		$HS^- \rightleftharpoons$	H^+	+	S^{2-}
0.1	0.2		0		x	0.2 + x		0
0.1 – x	0.2 + x + y		x		x – y	0.2 + x + y		y
↓	↓		↓		↓	↓		↓
0.1	0.2		x		x	0.2		y

$[H^+] = 0.2 \Rightarrow pH = - \log (0.2)$

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☞   **Note :** Strong acid controls the pH.

☞   Now , $[H^+] = 0.2$

★   **Case III :** H_3PO_4 (0.1 M) $K_{a_1} = 10^{-5}$, $K_{a_2} = 10^{-8}$, $K_{a_3} = 10^{-11}$

⇒ $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$
        0.1   0   0   x   x
        0.1 − x   x + y + z   x − y   x − y   x + y   y
        ↓   ↓   ↓   ↓   ↓   ↓
        0.1   x   x   x   x   y

⇒ $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$
        y   y + x
        y − z   x + y + z   z
        ↓   ↓   ↓

        y   x   z   ⇒ $\dfrac{x^2}{0.1} = 10^{-5} \Rightarrow x = 10^{-3} \Rightarrow pH = 3$
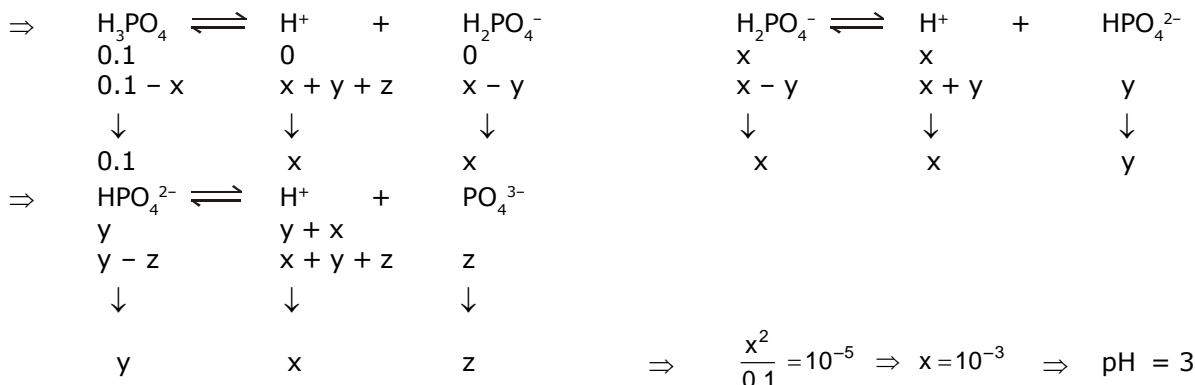
★   **Buffer**
☞   Any solution which resist the change in pH is called Buffer solution.
★   **Requirement of Buffer**
☞ **(1)** Must have acidic and basic components so that it can consume H^+, OH^- added to the buffer.

☞ **(2)** Acidic and basic components should not react with each other.

          $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
          acid   conjugate base
            ↓   ↓
        acidic component   basic component
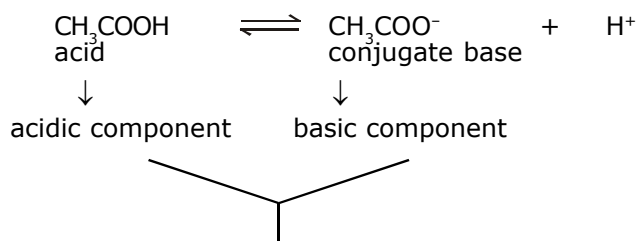
        do not react with each other.

☞ **(3)**   Buffers can be prepared by following two ways

★   **Buffer**

        CH_3COOH / CH_3COONa NH_4OH / NH_4Cl
        W. A / Conjugate Base   W. B / Conjugate acid
        ⇒ acidic buffer   ⇒ basic buffer
        ⇒ 0 < pH < 14   ⇒ 0 < pH < 14

☞   **Acidic buffer**   **Basic buffer**
          CH_3COOH / CH_3COONa NH_4OH / NH_4Cl
        K_a c_1 c_2 K_b c_1 c_2
        $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $NH_4OH \rightleftharpoons NH_4^+ + OH^-$
          c_1 c_2 0 c_1 c_2 0
        $c_1 - x$ $c_2 + x$ x $c_1 - x$ $c_2 + x$ x
          ↓   ↓   ↓   ↓   ↓   ↓
          c_1 c_2 x c_1 c_2 x
        in presence of CH_3COO^- dissociation
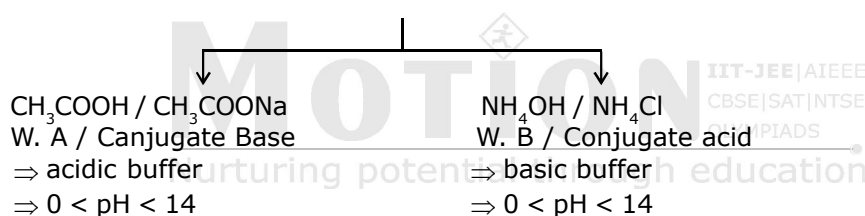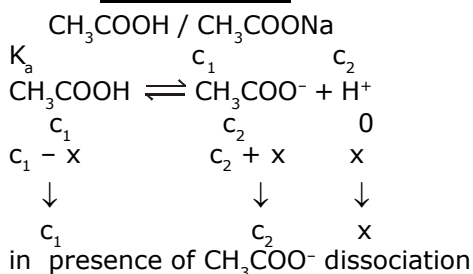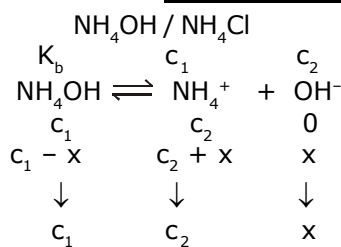
        of CH_3COOH is supressed. $K_b = \dfrac{c_2 . x}{c_1}$

So x is very small

$$x = K_b \, \frac{c_1}{c_2}$$

$$K_a = \frac{c_2 \, x}{c_1}$$

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

$$\Rightarrow x = \frac{K_a \, c_1}{c_2} \qquad pH = pK_a + \log \frac{c_2}{c_1} \qquad pH = pK_a + \log \frac{[salt]}{[acid]}$$

★ **Buffer action**

☞

Acidic	**Basic**
$CH_3COOH \, / \, CH_3COONa$	$NH_4OH \, / \, NH_4Cl$
$c_1 \qquad\quad c_2$	$c_1 \qquad\quad c_2$

$$pH = pK_a + \log \frac{c_2}{c_1} \qquad\qquad pOH = pK_b + \log \frac{[c_2]}{[c_1]}$$

(salt ↗ , acid ↙)

☞ **(a)** NaOH is added $(x \, M)$ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ **(a)** HCl is added $(x \, M)$

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

c_1	x	c_2		c_1	x	c_2
$c_1 - x$	0	$c_2 + x$		$c_1 - x$	0	$c_2 + x$
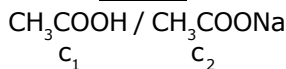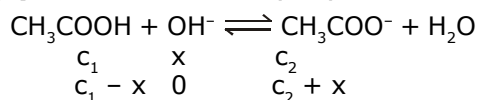
$$pH = pK_a + \log \frac{c_2 + x}{c_1 - x} \qquad\qquad pOH = pK_b + \log \frac{c_2 + x}{c_1 - x}$$

☞ **(b)** HCl is added $(x \, M)$ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ **(b)** NaOH is added $(x \, M)$

$CH_3COOH \rightleftharpoons CH_3COO^- + HCl$ ‎ ‎ ‎ ‎ $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

c_1	c_2	x		c_1	c_2	x
$c_1 + x$	$c_2 - x$	0		$c_1 + x$	$c_2 - x$	0
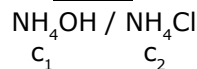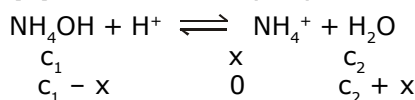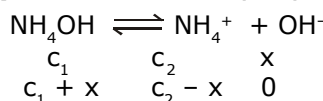
$$pH = pK_a + \log \frac{c_2 - x}{c_1 + x} \qquad\qquad pOH = pK_b + \log \frac{c_2 - x}{c_1 + x}$$

★ **How to prepare buffer**

Acidic buffer	**Basic buffer**
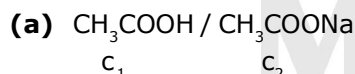
☞ **(a)** $CH_3COOH \, / \, CH_3COONa$ ‎ ‎ ‎ ‎ ‎ ‎ **(a)** $NH_4OH \, / \, NH_4Cl$

‎ ‎ ‎ $c_1 \qquad\qquad c_2$ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ ‎ $c_1 \qquad\quad c_2$

$$pH = pK_a + \log \frac{c_2}{c_1} \qquad\qquad pOH = pK_b + \log \frac{c_2}{c_1}$$

☞ **(b)** $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$ ‎ ‎ **(b)** $NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$

a	x			a	x	0
$a - x$	0	x		$a - x$	0	x

$$pH = pK_a + \log \frac{x}{a - x} \qquad\qquad pOH = pK_b + \log \frac{x}{a - x}$$

☞ **(c)** $CH_3COONa + HCl \rightleftharpoons CH_3COOH + NaCl$ ‎ ‎ **(b)** $NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl$

a	x	0		a	x	
$a - x$	0	x		$a - x$	0	x

$$pH = pK_a + \log \frac{a - x}{x} \qquad\qquad pOH = pK_b + \log \frac{a - x}{x}$$

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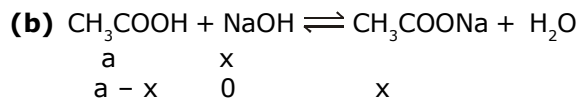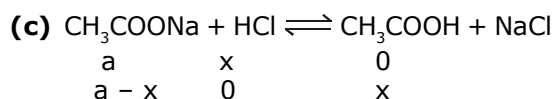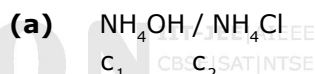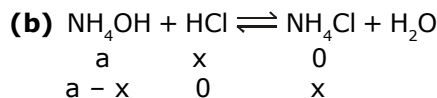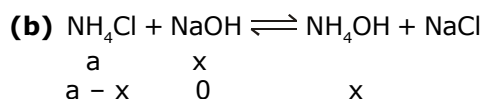
✯ **Parameters of buffer**

☞

Buffer range	**Requirement of good buffer**

Buffer range

The range of pH a buffer can work nicely is called buffer range

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

after buffer action

$$pH = pK_a + \log \frac{c_2 - x}{c_1 + x}$$

min. ratio $\left(\frac{[salt]}{[acid]} \right) = 0.1$

$$pH = pK_a - 1$$

pK$_a$ − 1   pK$_a$ pK$_a$ + 1
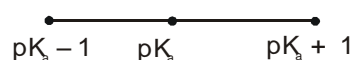
Requirement of good buffer

(1)   pH = pKa

resist both OH⁻ and H⁺ in equal amount

(2) $pH = pK_a + \log \dfrac{c_2}{c_1}$

max. ratio $\left(\dfrac{[salt]}{[acid]} \right) = 10$

$\Rightarrow pH = pK_a + 1$

both will be approximately same when

c_1 and c_2 are very large

$c_1 , c_2 >> x$

$\Rightarrow pH = pK_a + \log \dfrac{c_2}{c_1}$

✯ **Buffer capacity**

☞ $$Buffer\,Capacity = \frac{number\ of\ mol\ of\ H^+\ added/L\ of\ solution}{Change\ in\ pH\ of\ buffer}$$

✯ **Buffer of polyprotic acid**

$H_2CO_3 / NaHCO_3$

	c_1	c_2

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad K_{a_1}$

$c_1 \qquad\quad c_2 \qquad\quad 0$
$c_1 - x \qquad c_2 + x - y \quad x + y$
↓ ↓ ↓
$c_1 \qquad\quad c_2 \qquad\quad x$

$$pH = pK_{a_1} + \log \frac{c_2}{c_1}$$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad K_{a_2}$

$c_2 + x \qquad x \qquad 0$
$c_2 + x - y \qquad y + x \quad y$
↓ ↓ ↓
$c_2 \qquad\quad x \qquad y$
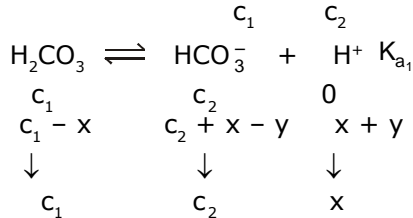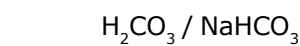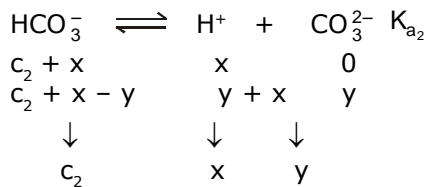
$$pH = pK_{a_2} + \log \frac{y}{c_2}$$

✯ **Salt Hydrolysis**

Acid + Base $\longrightarrow$ Salt + H_2O neutralization

Salt + H_2O $\longrightarrow$ Acid + Base $\longrightarrow$ reverse of neutralization $\Rightarrow$ Salt hydrolysis

since salt hydrolysis is an endothermic reaction hence on increasing the temperature, the extent of hydrolysis increases.

✯ **Types of salt**

Case I	**Case II**	**Case III**	**Case IV**
W. A + S. B	S. A. + W. B.	W. A + W. B.	S. A. + S. B.
e.g. CH_3COONa	**e.g.** NH_4Cl	**e.g.** CH_3COONH_4	**e.g.** $NaCl$
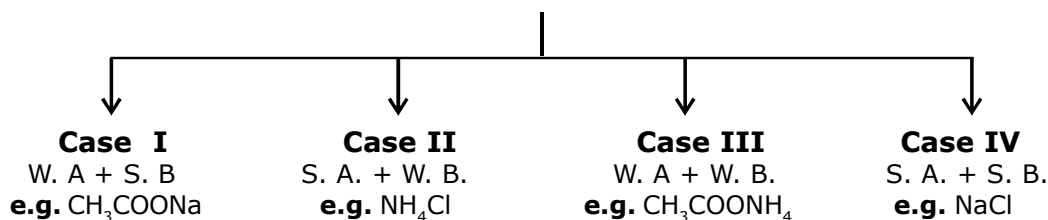
☞**Case : (I)   Hydrolysis of WA + SB :**

$$CH_3COONa \longrightarrow \quad CH_3COO^- \quad + \quad \boxed{Na^+} \quad \rightarrow \text{ spectator ion}$$

↓   ↓

Very strong   Very weak
Conjugate base   Conjugate acid

↓ ←—— H – OH ——→ ↓

CH$_3$COOH   NaOH

⇅   ⇅

CH$_3$COO$^-$ + H$^+$ Na$^+$ + OH$^-$

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

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

_____

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

_____
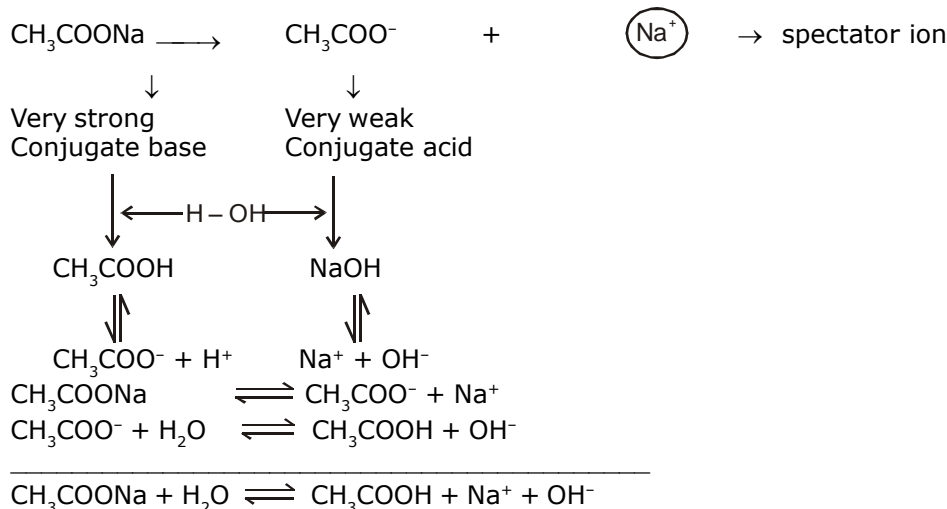
Note : (1)   Only weaker part of salt undergoes hydrolysis.   **(2)**   This solution becomes basic.

☞**Case : (II)   S.A. + W.B. (NH$_4$Cl) :**

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$, This solution becomes acidic

☞**Case : (III)   W.A. + W.B. $\rightleftharpoons$ (CH$_3$COONH$_4$) :**

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
  a   x
  a – x
$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$
  a   y
  a – y
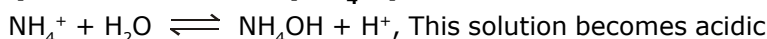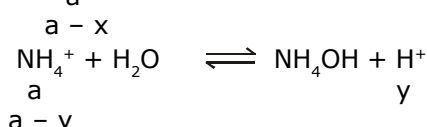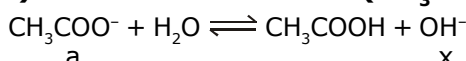
Can be acidic, basic or neutral

⇒ $K_a > K_b \Rightarrow$ acidic $K_a = K_b \Rightarrow$ neutral $K_a < K_b \Rightarrow$ basic

☞**Case : (IV)   S. A + S. B (NaCl) :**
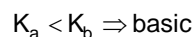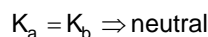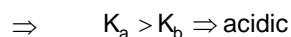
⇒   No hydrolysis   ⇒   Solution will be neutral
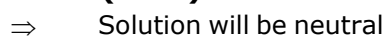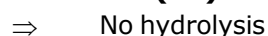
✯   **Relationship between K$_a$, K$_b$, and K$_h$**

☞**Case (I) : W. A. + S.B. (CH$_3$COONa)**

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
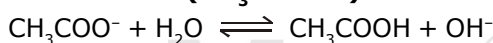
⇒ $K_{eq} = \dfrac{[CH_3COOH][OH^-]}{[H_2O][CH_3COO^-]}$ ⇒ $K_h = K_{eq}[H_2O] = \dfrac{[CH_3COOH][OH^-] \times [H^+]}{[CH_3COO^-] \times [H^+]}$ $K_h = \dfrac{K_w}{K_a}$

☞**Case (II) :   S. A. + W. B. (NH$_4$OH)**

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

⇒ $K_h = \dfrac{[NH_4OH][H^+]}{[NH_4^+]}$ ⇒ $K_h = \dfrac{[NH_4OH][H^+] \times [OH^-]}{[NH_4^+] \times [OH^-]}$ ⇒ $K_h = \dfrac{K_w}{K_b}$

☞**Case (III)   W. A. + W. B. (CH$_3$COO NH$_4$)**

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

_____

$CH_3COO^- + NH_4^+ + \cancel{2}H_2O \rightleftharpoons NH_4OH + CH_3COOH + \cancel{H^+} + \cancel{OH^-}$

_____
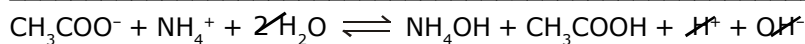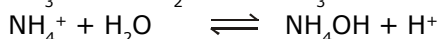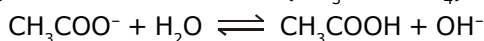
⇒ $K_h = \dfrac{[NH_4OH][CH_3COOH]}{[CH_3COO^-][NH_4^+]}$ ⇒ $K_h = \dfrac{[NH_4OH]}{[NH_4^+][OH^-]} \dfrac{[CH_3COOH][OH^-][H^+]}{[CH_3COO^-][H^+]}$ ⇒ $K_h = \dfrac{K_w}{K_a \cdot K_b}$

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★   **pH calculation**

☞**Case (I) :** W. A. + S. B. ($CH_3COONa \Rightarrow c, K_a$)   ,   h → degree of hydrolysis.

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

c   0   0
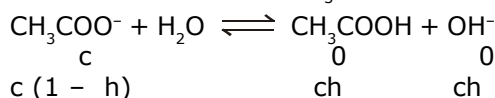
c (1 − h)   ch   ch

$$\Rightarrow \quad K_h = \frac{(ch)^2}{c\,(1-h)} = \frac{ch^2}{1-h} \quad h << 1 \quad \Rightarrow \quad K_h = ch^2 \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{c}}$$

$$\Rightarrow [OH^-] = c \times h = \sqrt{c.\,K_h} = \sqrt{c.\frac{K_w}{K_a}} \Rightarrow pOH = \frac{1}{2}[pK_w - pK_a - \log c] \Rightarrow pH = \frac{1}{2}[pK_w + pK_a + \log c]$$

☞**Case (II) :** S. A. + W. B. ($NH_4Cl \Rightarrow c, K_b$)

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

c   0   0

c   (1 − h)   ch   ch
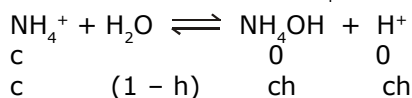
$$\Rightarrow \quad K_h = \frac{ch^2}{1-h} \quad\quad h << 1 \quad\quad \Rightarrow K_h = ch^2 \quad\quad \Rightarrow \quad h = \sqrt{\frac{K_h}{c}}$$

$$\Rightarrow \quad [H^+] = c.h = \sqrt{c \times K_h} = \sqrt{c \times \frac{K_w}{K_b}} \quad \Rightarrow pH = \frac{1}{2}[pK_w - pK_b - \log c] \quad \Rightarrow p^{OH} = \frac{1}{2}\left[p^{k_w} + p^{k_b} + \log c\right]$$

☞**Case (III)** W. A. + W. B. ($CH_3COONH_4 \rightarrow K_a, K_b, c$)

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

    c   c

c (1 − h)   c (1 − h)   ch   ch
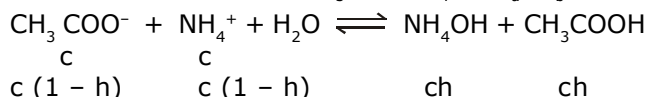
$$\Rightarrow \quad K_h = \frac{c^2h^2}{c^2\,(1-h)^2} = \frac{h^2}{(1-h)^2} \quad \Rightarrow K_h = h^2 \quad 1-h \approx 1 \quad \Rightarrow h = \sqrt{K_h}$$

$$\Rightarrow \quad h = \sqrt{\frac{K_w}{K_a\,K_b}} \quad\quad\quad - - - - - \quad (1)$$

$$\Rightarrow \quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \Rightarrow K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]} \quad \Rightarrow [H^+] = K_a\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$\Rightarrow \quad = K_a \times \frac{ch}{c\,(1-h)} \quad (h << 1) \quad \Rightarrow [H^+] = K_a . h \quad \Rightarrow [H^+] = K_a \cdot \sqrt{\frac{K_w}{K_a.K_b}} \quad (from\ 1)$$

$$\Rightarrow \quad [H^+] = \sqrt{K_w \cdot \frac{K_a}{K_b}} \quad\quad \Rightarrow pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

$\Rightarrow$ **If** , $K_a > K_b \Rightarrow pK_a < pK_b \Rightarrow$ acidic, $K_a = K_b \Rightarrow$ neutral, $K_a < K_b \Rightarrow$ basic
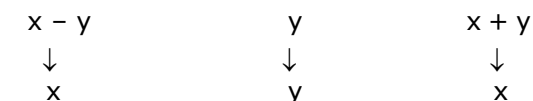
★   **Summary of hydrolysis**
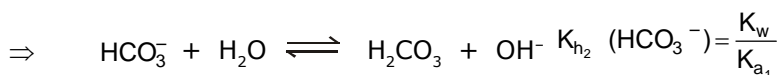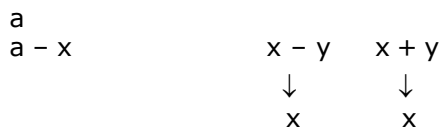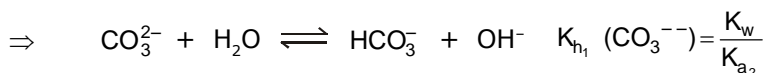
1.   **W. A. + S. B.** $K_h = \frac{K_w}{K_a}$ $pH = \frac{1}{2}[pK_w + pK_a + \log c]$

2.   **W. B. + S. A.** $K_h = \frac{K_w}{K_b}$ $pH = \frac{1}{2}[pK_w - pK_b - \log c]$

3.   **W. A. + W. B.** $K_h = \frac{K_w}{K_a . K_b}$ $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

✶ **Hydrolysis of salt of polyprotic acid / base (Na_2CO_3)**

⇒ $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ $K_{h_1}\ (CO_3^{--}) = \dfrac{K_w}{K_{a_2}}$

a
a − x   x − y   x + y
                  ↓   ↓
                  x   x

⇒ $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ $K_{h_2}\ (HCO_3^-) = \dfrac{K_w}{K_{a_1}}$

  x − y   y   x + y
    ↓   ↓   ↓
    x   y   x

$K_{a_1} >> K_{a_2}$ ⇒ $K_{h_1} >> K_{h_2}$ ⇒   Mainly hydrolysis is governed by CO_3^{2-}.

⇒ $[OH^-] = \sqrt{c \times K_{h_1}} = \sqrt{\dfrac{c \times K_w}{K_{a_2}}}$,   ⇒ $[HCO_3^-] = [OH^-] = \sqrt{\dfrac{c \times K_w}{K_{a_1}}}$,   ⇒ $\dfrac{K_w}{K_{a_1}} = \dfrac{x \times y}{x}$ ⇒ $[H_2CO_3] = \dfrac{K_w}{K_{a_1}}$

✶ **Solubility of sparingly soluble salt**

$AgCl\,(s) \xrightarrow{\text{Solubility}} AgCl\,(aq.) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$
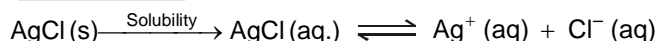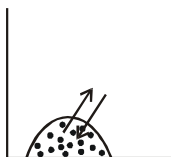
⇒ In ionic equilibrium all the components of equilibrium should be in same phase.
⇒ In case of solubility equilibrium of sparingly soluble salt equilibrium is a heterogeneous equilibrium.

☞**Example (1) :**   Solubility of AgCl
        $AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
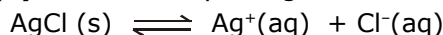
        $K_{eq} = \dfrac{[Ag^+][Cl^-]}{[AgCl]}$

⇒ **$K_{sp} = K_{eq} \cdot [AgCl] = [Ag^+][Cl^-]$**

⇒ It is a endothermic reaction on increasing temperature T ↑ ⇒ solubility ↑

⇒ $\log \dfrac{K_{sp_2}}{K_{sp_1}} = \dfrac{\Delta H}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

☞**Example (2) :**   Solubility of Ag_2CO_3 $Ag_2CO_3(s) \rightleftharpoons 2\,Ag^+ + CO_3^{2-}$

⇒ **$K_{sp} = [Ag^+]^2\ [CO_3^{2-}]$,**   ⇒ In general , if salt is $M_x N_y$ type, $M_x N_y \rightleftharpoons x\,M^{y+} + y\,N^{x-}$

⇒ **$K_{sp} = [M^{y+}]^x\ [N^{x-}]^y$**

let , $Q = [M^{y+}]^x\ [N^{x-}]^y$ Q = ionic product
If , $Q = K_{sp}$ ⇒ Equilibrium (Saturated solution) $Q > K_{sp}$ ⇒ PPt (Super saturated)
        $Q < K_{sp}$ ⇒ Unsaturated solution.

✶ **Various case in solubility**

☞ **Case (1) :** Ag_2SO_4 (S = 10^{-3} mol/L)

$Ag_2SO_4 \rightleftharpoons 2\,Ag^+ + SO_4^{2-}$
  S   0   0
  0   2 S   S $K_{sp} = [Ag^+]^2\ [SO_4^{--}] = (2S)^2\,(S) = 4\,S^3$
   = 4 × $(10^{-3})^3$

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☞   **Case (2) :**   S (moL / L) $\xrightarrow{}$ S (gm / L)

         10^{-3}

         $S_{Ag_2SO_4}$ (gm/L) = $10^{-3} \times (108 \times 2 + 96)$

☞   **Case (3) :** K_{sp} given , Solubility = ?

         $Ag_2 SO_4 \rightleftharpoons 2 Ag^+ + SO_4^{2-}$

           S   0   0

           0   2 S   S

⇒ $4 S^3 = K_{sp}$ ⇒ $S = \sqrt[3]{\dfrac{K_{sp}}{4}}$ **mol/L**

☞   **Case (4) :**   70% of the dissolved salt ionizes .

         $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

           S   0   0

         S – 0.7S   2 × 0.7S   0.7S

⇒ $K_{sp} = (1.4S)^2 (0.7S)$ ⇒ $S = \sqrt[3]{\dfrac{K_{sp}}{0.98}}$

☞   **Case (5) :**   Solubility of Ag_2SO_4 in 0.1 M $AgNO_3$

         $AgNO_3 \longrightarrow Ag^+ + NO_3^-$

          0.1   0   0

          0   0.1   0.1

   Ag_2SO_4 (solid) $\rightleftharpoons Ag_2 SO_4$ (aq) $\rightleftharpoons 2 Ag^+ + SO_4^-$

                   S   0.1

                   0   0.1 + 2S   S

⇒ $K_{Sp} = (0.1 + 2S)^2 (S)$ ⇒ $K_{sp} \approx (0.1)^2 \times S$ ⇒ $S = \dfrac{K_{sp}}{0.01}$

☞   **Case (6) :**   Solubility of Ag_2SO_4 in 0.1M $Na_2 SO_4$

         $Na_2SO_4 \rightleftharpoons 2 Na^+ + SO_4^{2-}$

          0.1   0   0

          0   0.2   0.1

     Ag_2SO_4 (S) $\rightleftharpoons Ag_2 SO_4$ (aq) $\rightleftharpoons 2 Ag^+$ (aq) + SO_4^{2-} (aq.)

                   S   0   0.1

                   0   2 S   0.1 + S

⇒ $K_{Sp} = (2 S)^2 (S + 0.1)$ ⇒ $\approx 4S^2 \times 0.1$ ⇒ $S = \sqrt{\dfrac{K_{sp}}{0.4}}$

☞   **Case (7) :**   100 ml 0.01 M $AgNO_3$ + 400 ml 0.02 M Na_2SO_4, K_{sp} ($Ag_2 SO_4$) = 4×10^{-9}

     (a)   Will any ppt or not ?
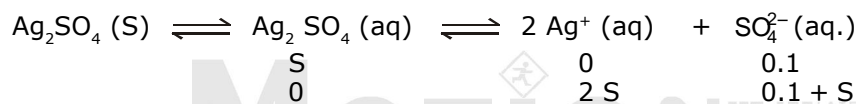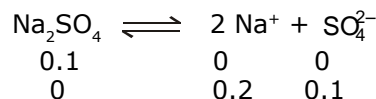
         $Q = [Ag^+]^2 [SO_4^{2-}]$ $Q = (1/500)^2 \left[\dfrac{8}{500}\right] = 6.4 \times 10^{-8}$ $Q > K_{sp}$ ⇒ ppt

     (b)   After ppt $[Ag^+]$ = ? ; $[SO_4^{2-}]$ = ?

at equilibrium
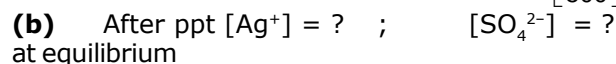
         $4S^3 = 4 \times 10^{-9}$ S = 10^{-3}

Number of moles of (Ag_2SO_4) = 500×10^{-3} = 0.5 m mole

   $2 Ag^+ + SO_4^{2-} \rightleftharpoons Ag_2SO_4$

     1   8

   1 – 2x   8 – x   x

   ■ $\left(\dfrac{y}{500}\right)^2 \times \left(\dfrac{7.5}{500}\right) = K_{sp} = 4 \times 10^{-9}$

   y   7.5   0.5   y = ?