

# IONIC EQUILIBRIUM

**Electrolytes:** Whose aqueous solution conduct electricity.

Electrolytes are classified into two groups.

- Strong Electrolytes:** Are those whose ionization is almost 100%, in aqueous solution generally all ionic compounds are strong electrolytes e.g. NaCl, NaNO<sub>3</sub>, HCl, KCl.
- Weak Electrolytes:** Whose degree of dissociation is < 10-15%. Generally covalent compounds are weak electrolytes. e.g. NH<sub>4</sub>OH, CH<sub>3</sub>COOH.

Strong and Weak electrolytes is a value term it only depends upon degree of ionization. Some times covalent compounds acts as a strong electrolytes in highly diluted solution.

$$K_a = C\alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a V} \quad \alpha = \frac{\text{ionized molecules}}{\text{Total molecules}}$$

“The fraction of total no. of molecules of electrolytes dissolved, that ionizes at equilibrium is called degree of ionization or degree of dissociation.”

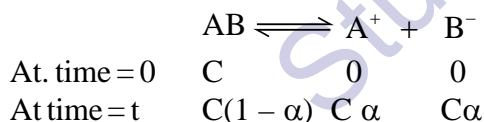
For: unionized molecules  $\rightleftharpoons$  ionized molecules  $\alpha \ll 1$

Generally strong and weak electrolyte property depends upon nature of solvent NaCl in H<sub>2</sub>O acts strong electrolyte whereas CH<sub>3</sub>COOH is weak electrolyte in water. But in liquid NH<sub>3</sub>, the dissociation of NaCl and CH<sub>3</sub>COOH both are same.

## 1. Ostwald's Dilution Law

Ostwald pointed out that like chemical equilibrium, in ionic equilibrium we can apply law of mass action. An equilibrium between ionized and unionized molecules.

Consider a binary electrolyte having conc. C and degree of dissociation is  $\alpha$ .



$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}, \text{ for a weak electrolyte } 1-\alpha \cong 1$$

$$K_{eq} = C\alpha^2, \alpha = \sqrt{\frac{K_{eq}}{C}}$$

If 1 mole of AB is present in 'V' litre of solution.

$$C = \frac{1}{V} \quad \Rightarrow \quad \alpha = \sqrt{K_{eq} \times V}$$

$$\text{Conc. of } [A^+] = \text{Conc. } [B^-] = C\alpha = C\sqrt{\frac{K_{eq}}{C}} = \sqrt{K_{eq} C}$$

### Limitation

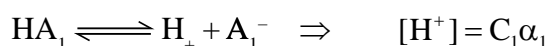
- (i) This is only for weak electrolytes not for strong electrolytes.
- (ii) This law is not applicable for strong electrolytes because strong electrolytes are almost completely ionized at all dilution and hence  $\frac{\lambda^c}{\lambda^\infty}$  does not give accurate results.

## 2. Relative strength of Acids and Bases

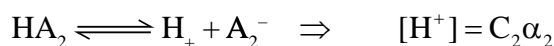
### For weak acids

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

For Acids  $\text{HA}_1$  if concentration is  $C_1$  and degree of dissociations  $\alpha_1$



For  $\text{HA}_2$  if concentration is  $C_2$  and degree of dissociation is  $\alpha_2$



$$\text{Then, Relative strength} = \frac{[\text{H}^+] \text{ furnished by I acid}}{[\text{H}^+] \text{ furnished by II acid}} = \frac{C_1\alpha_1}{C_2\alpha_2}$$

$$\text{R.S.} = \frac{C_1}{C_2} \times \sqrt{\frac{K_{a_1} C_2}{K_{a_2} C_1}} = \sqrt{\frac{K_{a_1} C_1}{K_{a_2} C_2}}$$

If  $C_1$  and  $C_2$  are same, then

$$\text{R.S.} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

### Illustration 1:

**Calculate the degree of ionization of 0.01 M solution of HCN,  $K_a$  of HCN is  $4.8 \times 10^{-10}$ . Also calculate hydronium ion concentration.**

### Solution:

The ionization of HCN may be represented as,



If degree of ionization of HCN is  $\alpha$  then equilibrium concentration of various species are

$$[\text{HCN}] = C(1 - \alpha), \quad [\text{CN}^-] = C\alpha, \quad [\text{H}_3\text{O}^+] = C\alpha$$

where  $C$  = concentration of HCN.

Applying law of chemical equilibrium

$$K_a = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]} = \frac{(C\alpha)(C\alpha)}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

Since  $\alpha$  is very small as compared with unity therefore,  $1 - \alpha$  in the denominator may be taken as 1.

$$K_a = C\alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.8 \times 10^{-10}}{0.01}} = 2.2 \times 10^{-4}.$$

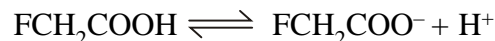
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$$[\text{H}_3\text{O}^+] = C\alpha = 0.01 \times 2.2 \times 10^{-4} = 2.2 \times 10^{-6} \text{ mol L}^{-1}.$$

### Illustration 2:

*Calculate the concentration of fluoroacetic acid which is required to get  $[\text{H}^+] = 1.50 \times 10^{-3} \text{ M}$ .  $[K_a \text{ of acid} = 2.6 \times 10^{-3}]$ .*

### Solution:



$$[\text{FCH}_2\text{COO}^-] = [\text{H}^+] = 1.5 \times 10^{-3}$$

$$\therefore 2.6 \times 10^{-3} = \frac{(1.5 \times 10^{-3})^2}{C - 1.5 \times 10^{-3}} \Rightarrow C - 1.5 \times 10^{-3} = 8.65 \times 10^{-4} \therefore C = 2.365 \times 10^{-3}$$

## 3. Common ion effect

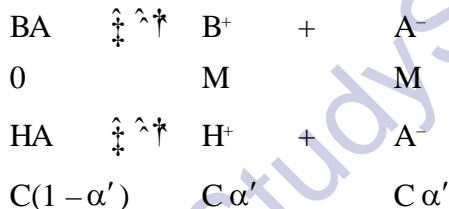
The degree of dissociation of a weak electrolyte is suppressed by the addition of another electrolyte containing the common ion.

### Quantitative Aspect

$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$  its degree of dissociation be  $\alpha$ .

$$\alpha = \sqrt{\frac{K_a}{C}}$$

BA (another electrolyte) added whose molarity is  $M$ , due to this the new degree of dissociation becomes  $\alpha'$ .



$$K_a(\text{HA}) = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[C\alpha'][C\alpha' + M]}{[C(1 - \alpha')]}$$

$$K_a(\text{HA}) = C\alpha'^2 + M\alpha' \qquad 1 - \alpha' \cong 1$$

$$C\alpha'^2 \text{ Neglecting because } \alpha' < 1$$

$$\alpha' = \frac{K_a}{M}$$

As a result of common ion effect, the conc. of the ion, which is not common changes to make the  $K_a$  constant, because  $K$  only depends upon temperature not on concentration.

**Note:** The use of this phenomenon is made in quantities analysis to adjust the conc. of  $\text{S}^{2-}$  ions in second group (reagent  $\text{H}_2\text{S}$  and  $\text{HCl}$ ) and  $\text{OH}^-$  ion conc. in third group ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ).

### Illustration 3:

*Calculate the degree of ionization of 0.02 M acetic acid if its  $K_a = 1.8 \times 10^{-5}$ . What would be the degree of ionization if the solution also contains 0.01 M sodium acetate ?*

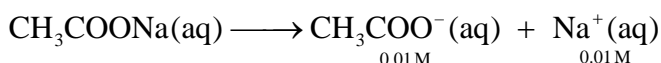
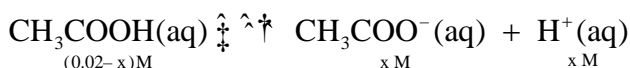
### Solution:



The degree of ionization of this weak acid can be calculated by the approximate relation :

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.02}} = 0.03 = 3 \times 10^{-2}.$$

Now let us calculate the degree of ionization when the solution also contains 0.01 M sodium acetate. Sodium acetate being a strong electrolyte would be completely ionized in solution. Let  $x \text{ mol L}^{-1}$  of acetic acid be ionized.



$$[\text{H}^+] = x \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{COO}^-] = (x + 0.01) \text{ mol L}^{-1} \approx 0.01 \text{ mol L}^{-1}$$

[Q  $x$  is very small as compared to 0.01]

$$[\text{CH}_3\text{COOH}] = (0.02 - x) \text{ mol L}^{-1} \approx 0.02 \text{ mol L}^{-1}$$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \Rightarrow 1.8 \times 10^{-5} = \frac{(x)(0.01)}{(0.02)}$$

$$x = \frac{1.8 \times 10^{-5} \times 0.02}{0.01} = 3.6 \times 10^{-5} \text{ M}$$

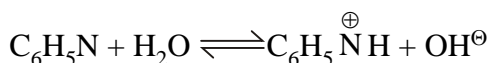
$$\text{Degree of ionization, } \alpha = \frac{x}{0.02} = \frac{3.6 \times 10^{-5}}{0.02} = 1.8 \times 10^{-3}$$

Thus, it may be noted that the degree of ionization of acetic acid has decreased from  $3 \times 10^{-2}$  to  $1.8 \times 10^{-3}$  due to the presence of sodium acetate.

#### Illustration 4:

Calculate the degree of ionization of pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) in its 0.1 M solution  $K_b$  for pyridine is  $1.5 \times 10^{-9}$ . What would be the degree of ionization of pyridine if the solution also contain 0.1 M in NaOH?

#### Solution:



$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.5 \times 10^{-9}}{0.1}} = 1.23 \times 10^{-4}$$

In presence of 0.1 M NaOH solution, common ion effect operates hence  $\text{OH}^-$  ions are produced only by NaOH

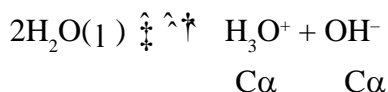
$$\therefore 1.5 \times 10^{-9} = \frac{(0.1\alpha)(0.1)}{(0.1)}$$

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$$\alpha = 1.5 \times 10^{-8}$$

### 4. Ionization of Water

Water is a weak electrolyte. It does not dissociate completely, the undissociated water and the dissociated  $\text{H}^+$ ,  $\text{OH}^-$  remain in the equilibrium. Let us take pure water whose density is 1 gram/c.c. and hence its concentration would be  $(1000/18 = 55.55 \text{ M})$ . Let the degree of dissociation of water be  $\alpha$ .



$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K_{\text{eq}}[\text{H}_2\text{O(l)}] = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Since conc. of pure water remain constant

$$K_{\text{eq}}k = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$k_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$K_w$  = dissociation constant of water at  $25^\circ\text{C}$ ,  $K_w$  comes out to be  $1 \times 10^{-14}$ .

$K_w$  depends upon temperature dissociation of water gives equal no. of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions.

$$1 \times 10^{-14} = [\text{H}_3\text{O}^+]^2 = [\text{OH}^-]^2$$

So  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mole/litre}$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [10^{-7}] = 7.$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 10^{-7} = 7.$$

**Note:** In case of water

$$[\text{H}_3\text{O}^+]_w [\text{OH}^-]_w = 10^{-14}.$$

But in case of acidic or basic solution.

$[\text{H}_3\text{O}^+]_T [\text{OH}^-]_T = 10^{-14}$ , where  $[\text{H}_3\text{O}^+]_T$  and  $[\text{OH}^-]_T$  are the conc. of  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  totally present in the solution.

### 5. pH Calculation

The pH of a solution is the negative logarithm (to the base 10) of the concentration (in moles per litre) of hydrogen ions which it contains.

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

$$\text{p}K_w = -\log_{10} [K_w]$$

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

taking  $-\log_{10}$  both side

$$-\log K_w = -\log [\text{H}_3\text{O}^+] + [-\log (\text{OH}^-)]$$

$$\text{p}K_w = \text{pH} + \text{pOH}$$

$$\text{at } 25^\circ\text{C}, K_w = 1 \times 10^{-14}, \text{p}K_w = 14$$

$$\text{pH} + \text{pOH} = 14$$

$K_w$  is also called as auto protolysis constant, it increases with temperature.

Since with increase in temperature dissociation of water increases, therefore the value of  $K_w$  increases

as the temperature is increased, however at all temperature  $[H_3O^+]$  remain equal to  $[OH^-]$  in pure water.

**Illustration 5:**

The  $K_w$  for  $2H_2O \rightleftharpoons H_3O^+ + OH^-$  changes from  $10^{-14}$  at  $25^\circ C$  to  $9.62 \times 10^{-14}$  at  $60^\circ C$ . What is pH of water at  $60^\circ C$ ? What happens to its neutrality?

**Solution:**

$K_w$  for  $H_2O$  at  $25^\circ C = 10^{-14}$

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

$$(Q \ K_w = [H^+][OH^-])$$

$$\therefore [H^+] = 10^{-7} \text{ M} \quad \therefore \text{pH} = 7$$

Now  $K_w$  for  $H_2O$  at  $60^\circ C = 9.62 \times 10^{-14}$

$$\therefore [H^+] = [OH^-] = 9.62 \times 10^{-14}$$

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

$$\therefore [H^+]^2 = 9.62 \times 10^{-14}$$

$$\therefore [H^+] = \sqrt{9.62 \times 10^{-14}} = 3.10 \times 10^{-7} \text{ M}$$

$$\therefore \text{pH} = -\log H^+ = -\log 3.10 \times 10^{-7}$$

$$\text{pH} = 6.51$$

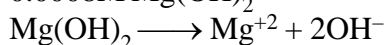
Thus, pH of water becomes 6.51 at  $60^\circ C$  but the nature is neutral since calculation for pure water has been made, i.e., pH scale at  $60^\circ C$  becomes in between 0 to 13.02.

**Illustration 6:**

Calculate pH for (a)  $0.0008 \text{ M Mg(OH)}_2$ , (b)  $0.01 \text{ N Ca(OH)}_2$

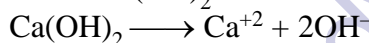
**Solution:**

(a)  $0.0008 \text{ M Mg(OH)}_2$



$$\therefore [OH^-] = 2 \times 8 \times 10^{-4} = 1.6 \times 10^{-3} \Rightarrow \text{pOH} = 2.8 \quad \therefore \text{pH} = 11.2$$

(b)  $0.01 \text{ N Ca(OH)}_2$



$$[OH^-] = 0.01 \text{ N} \quad (\square \text{ equivalents are always same})$$

$$\therefore [OH^-] = 0.01 \text{ M} \Rightarrow \text{pOH} = 2 \Rightarrow \text{pH} = 12$$

## 6. pH determination for Weak Acids

Weak acids do not dissociate completely in the water their % degree of dissociation is very less. e.g. let's take  $\text{CH}_3\text{COOH}$  (C mole/litre and having degree dissociation  $\alpha$ ).



$$\text{C}(1-\alpha) \qquad \qquad \text{C}\alpha \qquad \qquad \text{C}\alpha$$

$$K_{a(\text{CH}_3\text{COOH})} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{\text{C}\alpha \cdot \text{C}\alpha}{\text{C}(1-\alpha)}$$

$$K_a = \frac{\text{C}\alpha^2}{1-\alpha}$$

if  $\alpha \leq 0.1$ , then we can neglect  $1-\alpha \cong 1$

$$K_a = \text{C}\alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_a}{\text{C}}}$$

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

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$$\text{pH} = -\log [\text{H}^+] = -\log_{10} [\sqrt{K_a C}]$$

**Note:** For calculating the pH of a weak acid first of all we calculate  $\alpha$  from the equation  $K_a = \frac{C\alpha^2}{1-\alpha}$ , if  $\alpha$  comes out to be  $\leq 0.1$  then  $1-\alpha$  will be taken as one and we use formula  $K_a = C\alpha^2$  otherwise we would use the formula

$$K_a = \frac{C\alpha^2}{1-\alpha} \text{ for all calculation.}$$

### Illustration 7:

- (a) *pH of a solution is 10 in NaOH solution. What is concentration of NaOH ?*  
 (b) *What is molar concentration of  $\text{Ca(OH)}_2$  if its solution has pH of 12 ?*

#### Solution:

- (a)  $[\text{H}^+] = 10^{-\text{pH}}$   
 $[\text{OH}^-] = 10^{-\text{pOH}}$   
 NaOH is strong base, hence  $[\text{OH}^-] = [\text{NaOH}]$   
 In  $\text{pH} = 10$ ,  $\text{pOH} = 4$   
 $\therefore [\text{OH}^-] = 10^{-4} = [\text{NaOH}]$   
 (b)  $\text{pH of } \text{Ca(OH)}_2 = 12 \quad \therefore \quad \text{pOH} = 2 \quad \therefore \quad [\text{OH}^-] = 10^{-2} \text{ M}$   
 $\therefore [\text{Ca(OH)}_2] = \frac{10^{-2}}{2} \text{ M} = 0.5 \times 10^{-2} \text{ M}$   
 [Every  $\text{Ca(OH)}_2$  gives two  $\text{OH}^-$  ions]

### Illustration 8:

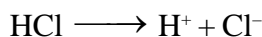
*A solution of HCl has a pH = 5. If one mL of its is diluted to 1 litre, what will be pH of resulting solution ?*

#### Solution:

- $\text{pH} = 5 \quad \Rightarrow \quad [\text{H}^+] = 10^{-5} \quad \therefore \quad [\text{HCl}] = 10^{-5} \text{ M}$   
 now using dilution formula,  $M_1 V_1 = M_2 V_2$   
 $10^{-5} \times 1 = M_2 \times 1000 \Rightarrow M_2 = 10^{-8} \text{ M}$   
 At this low concentration,  $\text{H}^+$  ions are also produced from water  
 $\therefore [\text{H}^+] = 1.05 \times 10^{-7} \Rightarrow \text{pH} = 6.978$

## 7. Determination of pH of acids or bases

For strong acid



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

If conc. of HCl is less than  $10^{-6} \text{ M}$  than we take conc. of  $\text{H}^+$  from water into accounts i.e.  $10^{-7}$ . Otherwise we would neglect the conc. of  $\text{H}^+$  from water.

e.g. **find the pH of  $10^{-8} \text{ M HCl}$**

According to rule

$$\text{pH} = -\log [\text{H}^+] = -\log [10^{-8}] = 8$$

But pH of an acid can't be 8 so we have to take contribution of  $\text{H}^+$  from water

Total  $\text{H}^+$  ion in solution =  $\text{H}^+$  (from HCl) +  $\text{H}^+$  (from  $\text{H}_2\text{O}$ ) =  $10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$  mole/litre and hence

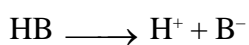
$$\text{pH} = -\log [\text{H}^+] = -\log [1.1 \times 10^{-7}] = 7 - \log 1.1 = 7 - 0.0414$$

$$\text{pH} = 6.9586 \text{ (Acidic).}$$

Same rule applies for pH of  $10^{-8}$  M NaOH.

## 8. pH for the mixture of Weak Acid and Strong Acid

Let strong acid be HB whose conc. is  $C_1$



and weak acid whose conc. is  $C_2$  and degree of dissociation is  $\alpha$



$$\text{Total } (\text{H}^+) \text{ conc.} = C_1 + C_2\alpha$$

$$\text{pH} = -\log [C_1 + C_2\alpha]$$

$$K_{a(\text{HA})} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[C_1 + C_2\alpha][C_2\alpha]}{[C_2(1-\alpha)]}$$

**Illustration 9:**

*What concentration of  $\text{HCOO}^-$  is present in a solution of 0.015 M  $\text{HCOOH}$  and 0.02 M  $\text{HCl}$ ?*

$$K_a \text{ for } \text{HCOOH} = 1.8 \times 10^{-4}.$$

**Solution:**

$$\text{Given, } [\text{HCOOH}] = 0.015\text{M} \Rightarrow [\text{HCl}] = 0.02\text{M} \quad \therefore [\text{H}^+] \text{ in solution} = 0.02\text{M}$$

The dissociation of  $\text{HCOOH}$  is suppressed due to common ion effect in presence of  $\text{HCl}$ . The  $[\text{H}^+]$  is provided by  $\text{HCl}$  in solution.



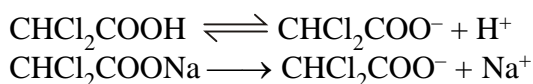
$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$1.8 \times 10^{-4} = \frac{[0.02][\text{HCOO}^-]}{[0.015]} \quad \therefore [\text{HCOO}^-] = 1.35 \times 10^{-4} \text{ M}$$

**Illustration 10:**

*Calculate  $[\text{H}^+]$  in a 0.20 M solution of dichloroacetic acid ( $K_a = 5 \times 10^{-2}$ ) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.*

**Solution:**



$$\begin{aligned} \therefore K_a &= \frac{[\text{CHCl}_2\text{COO}^-][\text{H}^+]}{[\text{CHCl}_2\text{COOH}]} \Rightarrow 5 \times 10^{-2} = \frac{(0.1+0.2\alpha)(0.2\alpha)}{0.2(1-\alpha)} \Rightarrow \frac{1}{2} = \frac{(1+2\alpha)\alpha}{1-\alpha} \\ &\Rightarrow 1 - \alpha = 2\alpha + 4\alpha^2 \end{aligned}$$

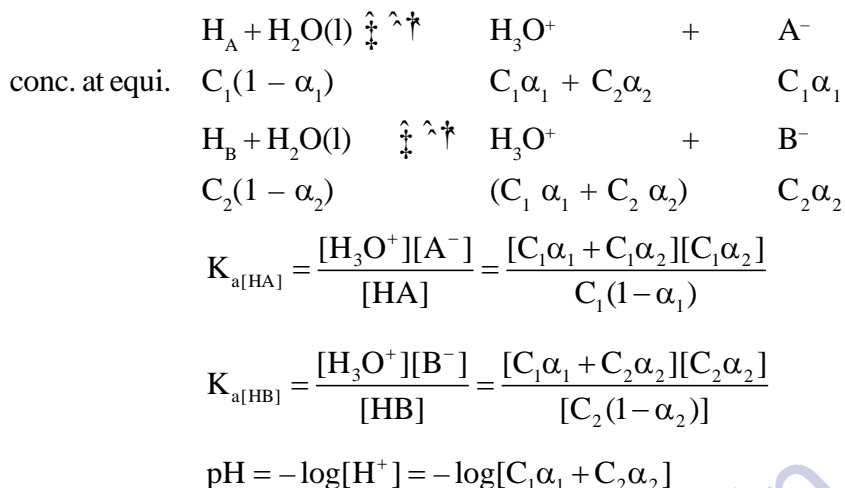
$$\therefore 4\alpha^2 + 3\alpha - 1 = 0 \Rightarrow \alpha = \frac{-3 \pm \sqrt{9+16}}{8} = \frac{-3+5}{8} = \frac{2}{8} = 0.25$$

$$\therefore [\text{H}^+] = 0.2\alpha = 0.2 \times 0.25 = 0.05$$



## 9. pH calculation of solution of a mixture of two weak Acids in water

Let two weak acids be HA and HB and their conc. are  $C_1$  and  $C_2$ ,  $\alpha_1$  is the degree of dissociation of HA in presence of HB (due to common ion effect) and  $\alpha_2$  be degree of dissociation of HB in presence of HA. In aqueous solution of HA and HB following equilibrium exists.

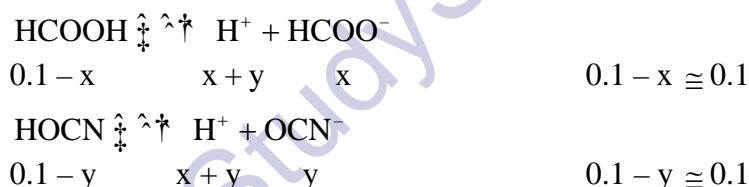


### Illustration 11:

**Calculate  $[\text{H}^+]$  in a solution containing 0.1 M HCOOH and 0.1 M HOCN.  $K_a$  for HCOOH and HOCN are  $1.8 \times 10^{-4}$  and  $3.3 \times 10^{-4}$ .**

### Solution:

In this problem both the acids contribute for  $[\text{H}^+]$  due to appreciable dissociation. Thus,



Because  $[\text{H}^+]$  will remain common in solution. Thus,

$$K_{\text{HCOOH}} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.8 \times 10^{-4} \quad \dots (1)$$

$$K_{\text{HOCN}} = \frac{[\text{H}^+][\text{OCN}^-]}{[\text{HOCN}]} = 3.3 \times 10^{-4} \quad \dots (2)$$

or 
$$K_{\text{HCOOH}} = \frac{(x + y)x}{0.1} = 1.8 \times 10^{-4} \quad \dots (3)$$

$$K_{\text{HOCN}} = \frac{(x + y)y}{0.1} = 3.3 \times 10^{-4} \quad \dots (4)$$

Thus, by eqs. (3) and (4)

$$\frac{x}{y} = \frac{1.8}{3.3} \quad \text{or} \quad y = 1.83x \quad \dots (5)$$

From Eq. (3)  $(x + 1.83x) \cdot x = 1.8 \times 10^{-5}$

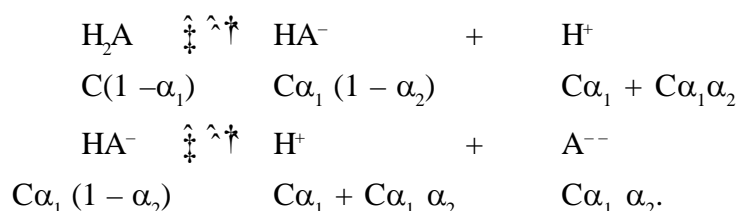
$$\therefore x = 2.52 \times 10^{-3}$$

$$\text{Therefore, } y = 4.61 \times 10^{-3}$$

$$\text{Thus, } [H^+] = x + y = 2.52 \times 10^{-3} + 4.61 \times 10^{-3} = 7.13 \times 10^{-3} \text{ M}$$

## 10. pH of a dibasic Acids and Polyprotic Acid

Let's take the eg. of a dibasic acid  $H_2A$ . Assuming both dissociation is weak. Let the initial conc. of  $H_2A$  is  $C$  and  $\alpha_1$  and  $\alpha_2$  be degree of dissociation for first and second dissociation.



$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]}$$

$$K_{a1} = \frac{[C\alpha_1(1 - \alpha_2)][C\alpha_1 + C\alpha_1\alpha_2]}{C(1 - \alpha_1)}$$

$$K_{a2} = \frac{[H^+][A^{--}]}{[HA^-]} = \frac{[C\alpha_1 + C\alpha_1\alpha_2][C\alpha_1\alpha_2]}{[C\alpha_1(1 - \alpha_2)]}$$

After solving for  $\alpha_1$  and  $\alpha_2$ . We can calculate the  $H^+$  conc.

$$[H^+] = C\alpha_1 + C\alpha_1\alpha_2$$

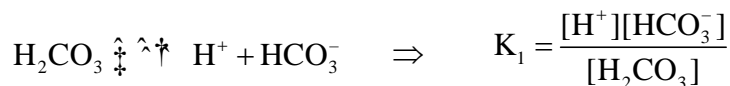
$$pH = -\log [C\alpha_1 + C\alpha_1\alpha_2]$$

### Illustration 12:

*Find the concentrations of  $H^+$ ,  $HCO_3^-$  and  $CO_3^{2-}$  in a 0.01 M solution of carbonic acid if the pH of solution is 4.18.  $K_1 = 4.45 \times 10^{-7}$ ,  $K_2 = 4.69 \times 10^{-11}$ .*

**Solution:**

$$\text{Given, } pH = 4.18 = -\log [H^+] \quad \therefore [H^+] = 6.61 \times 10^{-5} \text{ mol litre}^{-1}$$



$$\text{or } 4.45 \times 10^{-7} = \frac{[6.61 \times 10^{-5}][HCO_3^-]}{[0.01]} \quad \text{or } [HCO_3^-] = 6.73 \times 10^{-5} \text{ mol litre}^{-1}$$

Again for dissociation of  $HCO_3^-$ , we have



$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad \text{or } 4.69 \times 10^{-11} = \frac{[6.61 \times 10^{-5}][CO_3^{2-}]}{[6.73 \times 10^{-5}]}$$

$$\therefore [CO_3^{2-}] = 4.78 \times 10^{-11} \text{ mol litre}^{-1}$$

## 11. pH of mixture

Let one litre of an acidic solution of pH 2 be mixed with two litre of other acidic solution of pH 3. The resultant pH of the mixture can be evaluated in the following way.

### Sample 1

$$\text{pH} = 2$$

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

$$V = 1 \text{ litre}$$

$$M_1 V_1 + M_2 V_2 = M_R (V_1 + V_2)$$

$$10^{-2} \times 1 + 10^{-3} \times 2 = M_R (1 + 2)$$

$$\frac{12 \times 10^{-3}}{3} = M_R$$

$$4 \times 10^{-3} = M_R \text{ (Here, } M_R = \text{Resultant molarity)}$$

$$\text{pH}_R = -\log[4 \times 10^{-3}] = 2.3980$$

### Sample 2

$$\text{pH} = 3$$

$$[\text{H}^+] = 10^{-3} \text{ M}$$

$$V = 2 \text{ litre}$$

### Illustration 13:

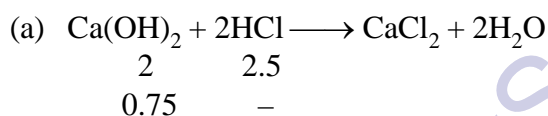
*Calculate the pH of the resultant mixture*

(a) 10 mL of 0.2 M  $\text{Ca}(\text{OH})_2$  + 25 mL of 0.1 M  $\text{HCl}$

(b) 10 mL of 0.01 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.01 M  $\text{Ca}(\text{OH})_2$

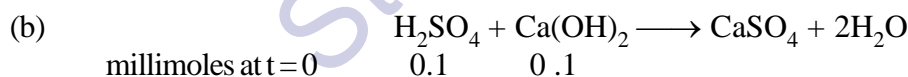
(c) 10 mL of 0.01 M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.1 M  $\text{KOH}$ .

**Solution:**

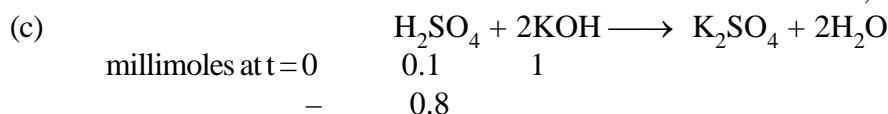


$$\therefore [\text{Ca}(\text{OH})_2] = \frac{0.75}{35} \Rightarrow [\text{OH}^-] = 2 \times \frac{0.75}{35} = \frac{1.5}{35}$$

$$\therefore \text{pOH} = 1.37 \Rightarrow \text{pH} = 12.63$$



hence both will neutralise each other so solution will be neutral, So pH = 7



$$\therefore [\text{KOH}] = \frac{0.8}{20} = 0.04 \Rightarrow [\text{OH}^-] = 0.04 \Rightarrow \text{pOH} = 1.4$$

$$\therefore \text{pH} = 12.6$$

### $\text{pK}_a$ and $\text{pK}_b$ for a conjugate acid-base pair

For an acid HX



$$\therefore K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} \quad \dots (\text{A})$$

For conjugate base  $\text{X}^-$  of acid HX



$$K_b = \frac{[HX][OH^-]}{[X^-]} \quad \dots (B)$$

By eqs. (A) and (B),

$$K_a \times K_b = [H^+][OH^-] = K_w$$

or  $pK_a + pK_b = pK_w = 14$

- Note :**
- Stronger is acid, weaker is its conjugate base.**
  - Higher is the value of  $pK_a$  of an acid, lower is acid strength and higher is basic strength of its conjugate base.**

## 12. Buffer Solution

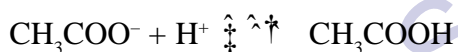
A Buffer solution is that which resist the pH change by addition of small quantity of acid or alkali.

There are three types of buffer

- (i) Acidic Buffer                      (ii) Basic Buffer                      (iii) Salt Buffer

### Mechanism of Buffer Action:

Let us see why  $CH_3COONH_4$  is a Buffer while  $NaCl$  is not.  $CH_3COONH_4$  exists almost entirely in form of its ion  $CH_3COO^-$  or  $NH_4^+$  if an acid is added to that solution, the  $H^+$  ion furnished by the acid combine with  $CH_3COO^-$  ions to form feebly dissociated molecule of  $CH_3COOH$ .



Since most of the  $H^+$  ions added are taken up by  $CH_3COO^-$  to form  $CH_3COOH$  which itself slightly dissociated, the pH of  $CH_3COONH_4$  changes only slightly.

Now, suppose a base is added to  $CH_3COONH_4$  solution the  $OH^-$  furnished by the base will be taken up by  $NH_4^+$  ion to form feebly dissociated  $NH_4OH$ .



Since most of the  $OH^-$  ions are taken up by  $NH_4^+$  ions to form feebly dissociated  $NH_4OH$ . Due to this very little change in the pH of  $CH_3COONH_4$  solution occurs.

Now let us see why a solution of  $NaCl$  is not a Buffer. In aqueous solution it is almost entirely dissociated into  $Na^+$  and  $Cl^-$ . If  $H^+$  ions are added to this solution the  $H^+$  combines with  $Cl^-$  to form  $HCl$  which completely dissociated due to strong electrolyte hence pH falls.

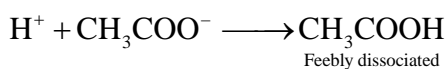
If  $OH^-$  ions are added to the solution, it will combine with  $Na^+$  to form  $NaOH$  which will almost completely dissociated. Hence pH will rise.

## 13. Acid Buffer

A very common acidic buffer is prepared by mixing equimolar solutions of acetic acid and sodium acetate. Acetic acid is very slightly dissociated while sodium acetate, being a salt, is almost completely dissociated. The mixture thus contains  $CH_3COOH$  molecules as well as  $CH_3COO^-$  and  $Na^+$  ions. Let us consider the buffer action of this mixture.

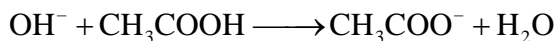
Suppose a strong acid is added to the above mixture. The  $H^+$  ions added will be taken up immediately by  $CH_3COO^-$  ions to form very slightly dissociated  $CH_3COOH$  :

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Thus, the  $\text{H}^+$  ions added are neutralized by the acetate ions present in the mixture. There is very little change in the pH of the mixture.

If, on the other hand, a strong base is added, the  $\text{OH}^-$  ions added are neutralized by the acetic acid present in the mixture :



Thus, again, there is very little change in the pH of the mixture.

## 14. Calculation of pH of Acidic Buffer Solution

e.g. Mixture of  $(\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa})$



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

Since most of  $\text{CH}_3\text{COO}^-$  comes from salt ( $\text{CH}_3\text{COONa}$ ) and hence conc. of  $\text{CH}_3\text{COO}^-$  will be conc. of  $\text{CH}_3\text{COONa}$ .

$$K_a = \frac{[\text{Salt}][\text{H}^+]}{[\text{Acid}]} \Rightarrow [\text{H}^+] = \frac{K_a[\text{Acid}]}{[\text{Salt}]}$$

Taking  $(-ve)$  log both side

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

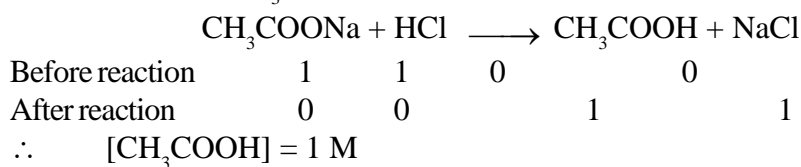
$$\text{Handerson's equation } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

### Illustration 14:

*Calculate the ratio of pH of a solution containing 1 mole of  $\text{CH}_3\text{COONa}$  + 1 mole of  $\text{HCl}$  per litre and of other solution containing 1 mole  $\text{CH}_3\text{COONa}$  + 1 mole of acetic acid per litre.*

### Solution:

**Case I:** pH when 1 mole  $\text{CH}_3\text{COONa}$  and 1 mole  $\text{HCl}$  are present.



$$\therefore [\text{H}^+] = C \cdot \alpha = C \sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a \cdot C)} = \sqrt{(K_a)} \quad \text{Q } C = 1$$

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

**Case II:** pH when 1 mole  $\text{CH}_3\text{COONa}$  and 1 mole of  $\text{CH}_3\text{COOH}$ ; a acidic buffer solution forms

Q  $[\text{Salt}] = 1 \text{ M}, [\text{Acid}] = 1 \text{ M}$

$$\begin{aligned}\therefore \text{pH}_2 &= -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ \text{pH}_2 &= -\log K_a \\ \therefore \frac{\text{pH}_1}{\text{pH}_2} &= \frac{1}{2}\end{aligned}$$

**Illustration 15:**

*Calculate pH change when 0.01 mol  $\text{CH}_3\text{COONa}$  solution is added to one litre of 0.01 M  $\text{CH}_3\text{COOH}$  solution.*

$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ,  $\text{p}K_a = 4.74$ .

**Solution:**

On addition of  $\text{CH}_3\text{COONa}$  to  $\text{CH}_3\text{COOH}$  solution resulting solution will be a buffer solution hence on using Handerson eq. for acidic buffer.

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= 4.74 + \log \frac{0.01}{0.01} = 4.74\end{aligned}$$

$$\therefore \text{For initial pH, } [\text{H}^+] = \sqrt{K_a \times C} = \sqrt{1.8 \times 10^{-5} \times 0.01} = 4.24 \times 10^{-4}$$

$$\begin{aligned}\therefore \text{pH} &= 3.37 \\ \Delta\text{pH} &= 4.75 - 3.37 = 1.37\end{aligned}$$

## 15. Basic Buffer

A mixture containing equimolar solutions of ammonium hydroxide and its almost completely dissociated salt, ammonium chloride, constitutes another good basic buffer. The mixture contains undissociated  $\text{NH}_4\text{OH}$  as well as  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions. The buffer action of this mixture may now be considered. If a strong acid is added, the  $\text{H}^+$  ions added are neutralized by the base  $\text{NH}_4\text{OH}$  :



If a strong base is added, the  $\text{OH}^-$  ions added are neutralized by  $\text{NH}_4^+$  ions forming very slightly dissociated  $\text{NH}_4\text{OH}$  .

## 16. Calculation of pH of Basic Buffer Solution

e.g. Mixture of  $(\text{NH}_4\text{OH} + \text{NH}_4\text{Cl})$



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

Since most of  $\text{NH}_4^+$  ions comes from salt ( $\text{NH}_4\text{Cl}$ ) so we take  $\text{NH}_4^+$  conc. as conc. of salt ( $\text{NH}_4\text{Cl}$ ).

$$K_b = \frac{[\text{Salt}][\text{OH}^-]}{[\text{Base}]}$$

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$$[\text{OH}^-] = \frac{K_b \times [\text{Base}]}{[\text{Salt}]}$$

Taking  $(-\log_{10})$  both side

$$-\log [\text{OH}^-] = -\log 10 K_b - \log \frac{[\text{Base}]}{[\text{Salt}]}$$

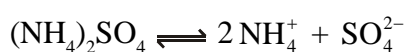
$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Hence  $\text{pH} = 14 - \text{pOH}$  at  $14^\circ\text{C}$ ,  $K_w = 1 \times 10^{-14}$  mol/litre

### Illustration 16:

*A buffer of pH 9.26 is made by dissolving  $x$  moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If  $\text{p}K_b$  of ammonia is 4.74, calculate value of  $x$ .*

**Solution:**



Thus, every one mole of  $(\text{NH}_4)_2\text{SO}_4$  gives two moles of  $\text{NH}_4^+$ .

$$\therefore \text{millimoles of } \text{NH}_3, (\text{NH}_4\text{OH}) = 100 \times 0.1 = 10 \text{ millimol}$$

$$\text{millimoles of } (\text{NH}_4)_2\text{SO}_4 = 100 \times x = 100x \text{ millimol}$$

$$\text{millimoles of } \text{NH}_4^+ = 200 \times x = 200x \text{ millimol}$$

$$\therefore \text{pH} = 9.26 \quad \therefore \text{pOH} = 14 - 9.26 = 4.74$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$4.74 = 4.74 + \log \frac{200x}{10}$$

$$\log 20x = 0 \quad \Rightarrow \quad 20x = 1 \quad \Rightarrow \quad x = \frac{1}{20} = 0.05.$$

### Illustration 17:

*50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M  $\text{NH}_4\text{Cl}$  to make a basic buffer. If  $\text{p}K_a$  of  $\text{NH}_4^+$  is 9.26, Calculate pH.*

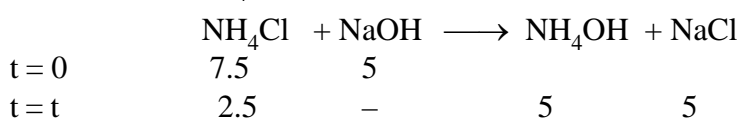
**Solution:**

Using Handerson equation for basic buffer

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

$$\square \quad \text{For } \text{NH}_4\text{OH}, (\text{p}K_a)_{\text{NH}_4^+} + (\text{p}K_b)_{\text{NH}_4\text{OH}} = 14$$

$$\therefore (\text{p}K_b)_{\text{NH}_4\text{OH}} = 14 - 9.26 = 4.74$$



$$\therefore \text{pOH} = 4.74 + \log \frac{2.5}{5} = 4.44 \quad \therefore \text{pH} = 14 - 4.44 = 9.56$$

## 17. Salt Buffer

A salt buffer is a solution of a salt which itself can act as a buffer. Such salt is the salt of a weak acid and weak base.



When an acid is added, it reacts with  $\text{CH}_3\text{COO}^-$  to produce  $\text{CH}_3\text{COOH}$  and when a base is added, it reacts with  $\text{NH}_4^+$  to produce  $\text{NH}_4\text{OH}$ .

## 18. Buffer capacity or Buffer Index

Buffer capacity of a solution is defined in terms of buffer index which is the change in the concentration of Buffer acid (or base) required for change of its pH value by one, keeping  $(C_{\text{salt}} + C_{\text{acid}})$  or  $(C_{\text{base}} + C_{\text{salt}})$  constant.

Let there be a buffer solution of volume 1 litre with 'x' mole of acid and 'S' moles of 'salt'.

$$\text{pH} = \text{pK}_a + \log_{10} \frac{S}{x - S}$$

$$\text{pH} = \text{pK}_a + \frac{1}{2.303} \log_e \frac{S}{x - S}$$

$$\frac{\partial(\text{pH})}{\partial S} = \frac{1}{2.303} \left[ \frac{1}{S} + \frac{1}{x - S} \right]$$

$$\frac{\partial(\text{pH})}{\partial S} = \frac{1}{2.303} \left[ \frac{x - S + S}{S(x - S)} \right]$$

$$\frac{\partial S}{\partial(\text{pH})} = \frac{1}{2.303} \left[ \frac{S(x - S)}{x} \right]$$

### Maximum value of Buffer Index

$$\text{B.I} = \frac{1}{2.303} \frac{S(x - S)}{x}$$

$$\frac{d}{dS} (\text{B.I}) = \frac{1}{2.303} \left[ \frac{1}{x} [x - 2S] \right]$$

for maximum value of Buffer index

$$\frac{d}{dS} (\text{B.I}) = 0$$

After solving  $S = x/2$

$$\text{Thus } \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{S}{x - S} = \frac{x/2}{x - x/2} = 1$$



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Hence max. value of Buffer index occurs when  $\frac{[\text{Salt}]}{[\text{Acid}]} = 1$ ,

### 19. Buffer Range

It is difficult to give an exact limit upto which a buffer can be used it is generally accepted that a solution has useful buffer capacity provided that the value of  $[\text{Salt}]/[\text{Acid}]$  lie within the range of 10 to 0.1. Hence from Henderson equation

$$\text{pK}_a + \log 0.1 < \text{pH} < \text{pK}_a + \log_{10} 10$$

$$\text{pK}_a - 1 < \text{pH} < \text{pK}_a + 1$$

Outside this range the Buffer capacity is too small to be of any practical application.

### 20. Hydrolysis of Salt

Salts are strong electrolytes when dissolved in water, they dissociated almost completely into cations or anions. If anion reacts with water it is called as anionic hydrolysis.



If cation reacts with water it is called as cationic hydrolysis.



“The phenomenon of the interaction of anions and cations of the salt with  $\text{H}^+$  and  $\text{OH}^-$  ions furnished by water yielding acidic or alkaline solution is known as salt hydrolysis.

For the study of hydrolysis salts are divided into 4 groups.

#### Hydrolysis of salt of strong Acid or weak base:

$\text{NH}_4\text{Cl}$  is a salt of weak base ( $\text{NH}_4\text{OH}$ ) and strong acid ( $\text{HCl}$ ). After hydrolysis resultant solution will be acidic due to presence of strong acid  $\text{HCl}$ .



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

#### Relation B/w $K_h$ , $K_b$ and $K_w$ :



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots (1)$$



$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots (2)$$

Dividing (2)  $\div$  (1)

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

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

### Degree of hydrolysis



$$K_h = \frac{Ch \cdot Ch}{C(1-h)} = Ch^2 \quad (1-h \approx 1)$$

$$h = \sqrt{\frac{K_h}{C}} \Rightarrow h = \sqrt{\frac{K_w}{K_b C}}$$

$$[H^+] = Ch = C \sqrt{\frac{K_w}{K_b C}} \Rightarrow [H^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

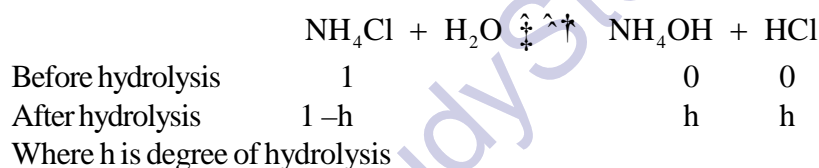
Taking  $-\log_{10}$  both side

$$pH = \frac{1}{2}[pK_w - pK_b - \log C] \Rightarrow pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

### Illustration 18:

Calculate degree of hydrolysis and pH of 0.2 M solution of  $NH_4Cl$ . Given  $K_b$  for  $NH_4OH$  is  $1.8 \times 10^{-5}$ .

**Solution:**



$$h = \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot C}\right)} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.2}} = 5.27 \times 10^{-5}$$

From HCl, strong acid

$$\therefore [H^+] = C.h = C \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{(K_h \cdot C)} = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)} = \sqrt{\left(\frac{10^{-14} \times 0.2}{1.8 \times 10^{-5}}\right)} = 1.054 \times 10^{-5}$$

$$\therefore pH = -\log[H^+] = -\log 1.054 \times 10^{-5} = 4.9771$$

### Illustration 19:

Find out the amount of  $NH_4Cl$  dissolved in 500 mL to have  $pH = 4.5$ .  $K_b$  for  $NH_4OH$  is  $1.8 \times 10^{-5}$ .

**Solution:**

Using salt hydrolysis formula

$$pH = 7 - \frac{pK_b}{2} - \frac{\log c}{2} \Rightarrow 4.5 = 7 - \frac{4.74}{2} - \frac{\log c}{2} \Rightarrow \log c = 0.26$$

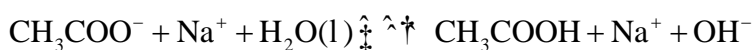
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$$\therefore c = 1.82 \text{ M}$$

$$\therefore W_{\text{NH}_4\text{Cl}} = \frac{1.82}{2} \times 53.5 = 48.7 \text{ gm}$$

### Hydrolysis of salt of weak acid and strong base:

$\text{CH}_3\text{COONa}$  is a salt of weak acid ( $\text{CH}_3\text{COOH}$ ) and strong base ( $\text{NaOH}$ ). After hydrolysis resultant solution will be basic due to presence of strong base ( $\text{NaOH}$ ).



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

Relation between,  $K_h$ ,  $K_w$  and  $K_a$



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots (1)$$

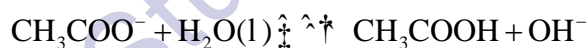


$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots (2)$$

Dividing equation (2)  $\div$  (1)

$$\frac{K_w}{K_a} = \frac{[\text{H}^+][\text{OH}^-] \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = K_h$$

### Degree of Hydrolysis



at time = 0	$C$	$0$	$0$
at time = t	$C(1-h)$	$Ch$	$Ch$

$$K_h = \frac{Ch \cdot Ch}{C(1-h)} = Ch^2 \quad (1-h \cong 1) \text{ } h \text{ should be smaller than } 0.1 \text{ than } 1-h = 1.$$

$$h = \sqrt{\frac{K_h}{C}} \Rightarrow h = \sqrt{\frac{K_w}{K_a C}}$$

$$\text{OH}^- = Ch \Rightarrow \text{OH}^- = C \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{K_w C}{K_a}}$$

$$\text{H}_3\text{O}^+ = \frac{K_w}{[\text{OH}^-]} = K_w \sqrt{\frac{K_a}{K_w C}} = \sqrt{\frac{K_a \times K_w}{C}}$$

Taking (–ve) log both side

$$-\log[\text{H}^+] = \frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log C = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log C$$

pH will be more than 7, hence resultant solution will be basic in nature.

**Illustration 20:**

*Calcium lactate is a salt of weak organic acid and strong base, represented as  $\text{Ca}(\text{Lac})_2$ . A saturated solution of  $\text{Ca}(\text{Lac})_2$  contains 0.13 mole of this salt in 0.50 L solution. The pOH of this solution is 5.60. Assuming a complete dissociation of the salt, calculate  $K_a$  of lactic acid.*

**Solution:**

Formula of calcium lactate suggests that lactic acid is dibasic acid. Each mole of salt furnishes two moles of lactate ion



0.50 L solution contains = 0.13 mol of salt = 0.26 mol of lactate ion

$\therefore$  1 L of solution contains = 0.52 mol of lactate ion

[lactate] = 0.52 M.

given pOH = 5.6

$\therefore$  pH = 8.4

using equation of pH for salt of weak acid and strong base

$$\text{pH} = 7 + \frac{\text{pK}_a}{2} + \frac{\log C}{2}$$

$$8.4 = 7 + \frac{\text{pK}_a}{2} + \frac{\log 0.52}{2} = 7 + \frac{\text{pK}_a}{2} - 0.14$$

$$\text{pK}_a = 3.08$$

$$K_a = 10^{-3.08} = 8.3 \times 10^{-4}.$$

**Illustration 21:**

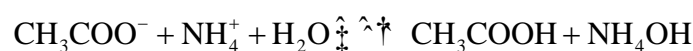
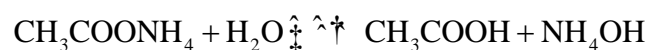
*What is the pH of a 0.5 M aqueous NaCN solution?  $\text{pK}_b$  of  $\text{CN}^-$  = 4.70.*

**Solution:**

$$\text{pH} = \frac{1}{2} [14 + \text{pK}_a + \log c] = \frac{1}{2} [14 + 9.3 + \log 0.5] = 11.5$$

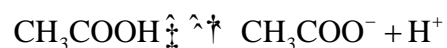
**Hydrolysis of salt of Weak Acid and Weak Base:**

Let's take the salt  $\text{CH}_3\text{COONH}_4$  made of salt of weak acid ( $\text{CH}_3\text{COOH}$ ) and Weak base ( $\text{NH}_4\text{OH}$ ).



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

Relation between,  $K_h$ ,  $K_w$ ,  $K_a$  &  $K_b$



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots (1)$$

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$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots (2)$$

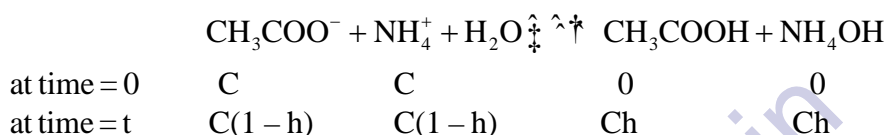


$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots (3)$$

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

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

### Degree of Hydrolysis



$$K_h = \frac{\text{Ch} \cdot \text{Ch}}{\text{C}(1-h)\text{C}(1-h)} = \frac{h^2}{(1-h)^2}$$

if  $h \leq 0.1, \quad 1-h \cong 1$

$$\frac{h}{1-h} = \sqrt{\frac{K_w}{K_a K_b}}$$

The acetic acid formed would partially decompose to give  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$ . But because of common ion effect (that is, due to the unhydrolysed  $\text{CH}_3\text{COO}^-$ ) it is possible to neglect the acetate ion coming from  $\text{CH}_3\text{COOH}$ .



$$K_a = \frac{C\alpha}{C(1-\alpha)} = \frac{C(1-\alpha)[\text{H}^+]}{C\alpha}$$

$$K_a = \frac{[\text{H}^+]}{\alpha} \quad (1-\alpha \cong 1)$$

$$[\text{H}^+] = K_a \alpha = K_a \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}} \quad \text{or} \quad \text{pH} = \frac{1}{2} \text{p}K_w + \text{p}K_a - \text{p}K_b$$

This expression is independent of conc. of the salt.

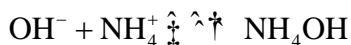
- (i) if  $K_a = K_b$ , pH = 7 solution will be neutral
- (ii) if  $K_a > K_b$ , pH < 7, acidic solution
- (iii) if  $K_a < K_b$  then pH > 7, alkaline solution

In the hydrolysis of salt of weak acid and a weak base such as  $\text{NH}_4\text{CN}$ ,  $\text{CH}_3\text{COONH}_4$ . Both the ions are hydrolysed, if we assume  $K_a \cong K_b$ , then the hydrolysis of the cation and anion of the salt occur approximately to equal extent for a salt which has  $K_a < K_b$ , it would be expected at the first

glance that  $\text{CN}^-$  ions hydrolysed to a much greater extent than  $\text{NH}_4^+$  ions. However, the hydrolysis of  $\text{CN}^-$  ions produced  $\text{OH}^-$  ions according to the equation.



which can react with  $\text{NH}_4^+$  ions as



This latter reaction causes equilibrium in the former reaction to be displaced to the right. Because  $\text{OH}^-$  ions are removed from the solution. Also the production of  $\text{OH}^-$  by the former reaction displaces the latter reaction to the right. Therefore the hydrolysis of one ion drags the hydrolysis of the other ion along so that both the hydrolysis are fairly extensive not too far in extent from each other so it is fairly safe to assume that  $[\text{HCN}] = [\text{NH}_4\text{OH}]$ , even in the case of the salt where  $K_a \neq K_b$ .

**Illustration 22:**

*The dissociation constants for aniline, acetic acid and water at 25°C are  $3.83 \times 10^{-10}$ ,  $1.75 \times 10^{-5}$  and  $1.008 \times 10^{-14}$  respectively. Calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report the pH.*

**Solution:**

Q	Aniline <sup>+</sup>	+ Acetate	+ H <sub>2</sub> O	$\rightleftharpoons$	Aniline	+ Acetic acid
Before hydrolysis	1	1			0	0
After hydrolysis	1-h	1-h			h	h

Let concentration of salt be C mol litre<sup>-1</sup>

$$\therefore K_h = \frac{[\text{Aniline}][\text{Acetic Acid}]}{[\text{Aniline}^+][\text{Acetate}^-]} = \frac{C \cdot h \cdot C \cdot h}{C \cdot (1-h) \cdot C \cdot (1-h)}$$

$$\therefore K_h = \frac{h^2}{(1-h)^2}$$

$$\therefore \frac{h}{1-h} = \sqrt{K_h} \Rightarrow \frac{h}{1-h} = \sqrt{\left( \frac{K_w}{K_a \cdot K_b} \right)} = \sqrt{\left( \frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}} \right)}$$

$$\therefore h = 54.95\%$$

**Illustration 23:**

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

**Solution**

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

## 21. Case IV : Salts of strong Acid + Strong Base

e.g., NaCl, KNO<sub>3</sub>, ... etc.

This category of salts does not undergo salt hydrolysis

## 22. Solubility and solubility Product

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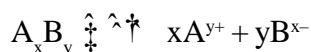
A solution which remain in contact with excess of the solute is said to be saturated. The amount of a solute, dissolved in a given volume of a solvent (in 1 litre) to form a saturated solution at a given temperature, it termed as the solubility of the solute in the solvent at that temperature.

### Molar Solubility:

No. of moles of solute dissolved in per litre of solution

### Solubility Product:

In a saturated solution of a salt, there exists a dynamic equilibrium between the excess of the solute and ions furnished by that parts of the solute which has gone in solution. The solubility product of a sparingly soluble salt is given as product of the conc. of the ions raised to the power equal to the no. of times the ion occur in the equation after the dissociation of the electrolyte.



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

Let the solubility of  $A_x B_y$  is  $S$  then

$$K_{sp} = [xS]^x [yS]^y$$

$$K_{sp} = x^x \cdot y^y [S^{x+y}]$$

The principle of solubility product is applicable for sparingly soluble salt.

## 23. Common-ion Effect on Solubility

The common ion present in the solution decrease the solubility of a given compound e.g. The solubility of  $BaSO_4$  in  $Na_2SO_4$  solution is smaller than that in an aqueous solution.

Consider saturated solution of  $AgCl$ . If a salt having either of the ion common to  $AgCl$  say  $KCl$  is added to it, then



For  $AgCl$   $K_{sp} = [Ag^+][Cl^-]$

$[Cl^-]$  Increases in solution due to presence of  $KCl$  and thus to have  $K_{sp}$  constant,  $[Ag^+]$  will decrease or  $AgCl$  will precipitate out from solution, i.e., solubility of  $AgCl$  will decrease with increasing concentration of  $KCl$  in solution.

Let  $0.1 M KCl_{(aq.)}$  solution with  $AgCl_{(aq.)}$ . If solubility of  $AgCl$  is  $s \text{ mol litre}^{-1}$ , then,

For  $AgCl$   $K_{sp} = [Ag^+][Cl^-]$

$$K_{sp} = s(s + 0.1)$$

$s$  being small in comparison to  $0.1$  and thus may be neglected therefore,

$$K_{sp} = s \times 0.1 \text{ or } s_{AgCl} = \frac{K_{sp}}{0.1}$$

where  $s$  is solubility of  $AgCl$  in presence of  $0.1 M KCl_{aq.}$

## 24. Ionic Product

For a solution of a salt at a specified concentration, the product of the concentration of the ions, each

raised to the proper power, is called as the ionic product for a saturated solution in equilibrium with excess of solid, the ionic product is equal to solubility product.

At equilibrium, ionic product = solubility product

If ionic product is less than solubility product it means solution is unsaturated means more salt can be dissolve in it.

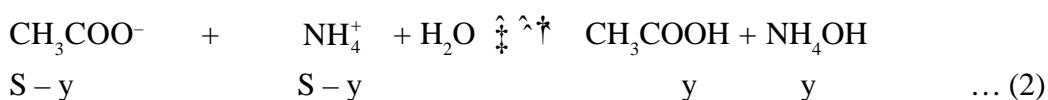
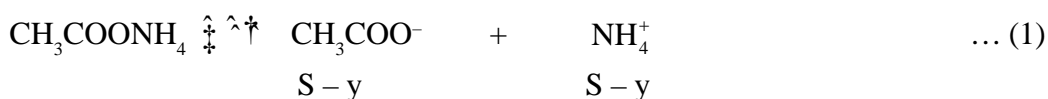
If ionic product greater than solubility it means solution is holding more salt than can dissolve in it, therefore ppt started till, until or unless ionic product becomes equal to  $K_{sp}$ .

## 25. Preferential Precipitation of Salts

Frequently, a solution contains more than one ion capable of forming a ppt. with another ion which is added to the solution. e.g., in a solution containing  $Cl^-$ ,  $Br^-$  and  $I^-$ , if  $Ag^+$  ions are added then out of the three, the least soluble silver salt is ppt first. If the addition of  $Ag^+$  ions is continued, eventually a stage is reached when the next lesser soluble salt starts ppt along with the least soluble salt and so on if the stoichiometry of the ppted salts is the same, then the salt with the minimum  $K_{sp}$  or minimum solubility will ppted first followed by higher  $K_{sp}$ .

If the stoichiometry of the ppted salts is not the same, then with  $K_{sp}$  alone, we can't predict which ion will ppted first. e.g. a solution containing  $Cl^-$  and  $CrO_4^{2-}$  both of these ions form ppt with  $Ag^+$  though the  $K_{sp}(AgCl) > K_{sp}(Ag_2CrO_4)$ . Yet it is  $AgCl$  (less soluble) which ppted first when  $Ag^+$  ions added to the solution. In order to predict which ion ( $Cl^-$  or  $CrO_4^{2-}$ ) ppt first. We have to calculate the conc. of  $Ag^+$  ion needed to start ppt through the  $K_{sp}$  and given conc. of  $Cl^-$  and  $CrO_4^{2-}$  if the conc. of  $Ag^+$  ions needed to start the ppt of  $CrO_4^{2-}$  is larger than that of  $Cl^-$ . Hence as  $AgNO_3$  is added to the solution, the minimum of the two conc. of  $Ag^+$  to start the ppt will be reached first and thus the corresponding ion ( $Cl^-$  in this case) will be ppted in preference to the other. During the course of ppt conc. of  $Cl^-$  decreases and conc. of  $Ag^+$  increases when its conc. become equals to the conc. required (of  $Ag^+$ ) for  $CrO_4^{2-}$ . At this stages the whole of  $Cl^-$  ions have been ppted the addition of more of  $AgNO_3$  causes the ppt of both the ions together.

- (i) **Solubility of a salt of weak acid and strong base in Basic Buffer suppresses than pure water due to common ion effect. But in acidic buffer solution solubility increase than pure water.**
- (ii) **Solubility of salt of weak acid and weak base in pure water:** Let the solubility of salt be  $S$ , and  $y$  mol/litre is the amount of salt getting hydrolysed.



$$K_{sp} = (S - y)(S - y) = (S - y)^2$$

Due to hydrolysis of salt from equation (2)

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{y \cdot y}{(S - y)(S - y)}$$

$$K_h = \left( \frac{y}{S - y} \right)^2$$



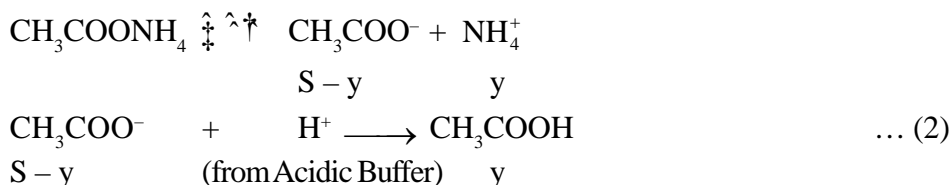
## IONIC EQUILIBRIUM

and we also know that

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

### 26. Solubility of a salt of weak acid and weak base in acidic buffer

Let the solubility of salt be  $S$  and  $y$  be the amount of weak acid being formed.



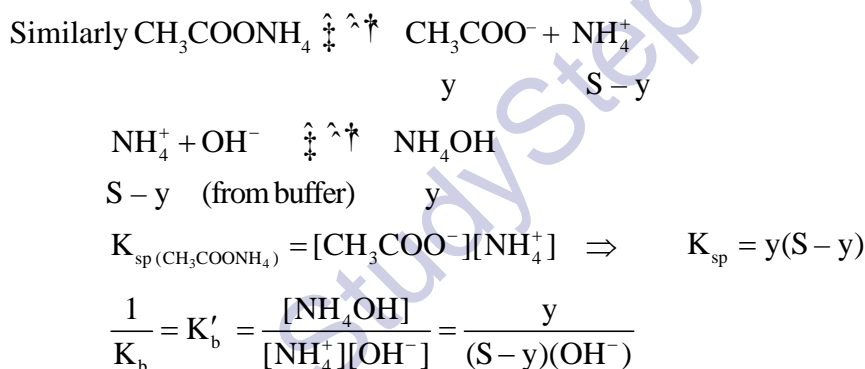
$$K_{sp} = [\text{CH}_3\text{COO}^-][\text{NH}_4^+] = [S - y][y] = y[S - y]$$

for equation (2)

$$\frac{1}{K_{a(\text{CH}_3\text{COOH})}} = K'_a = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} = \frac{y}{(S - y)(\text{H}^+)}$$

Solubility of  $\text{CH}_3\text{COONH}_4$  in acidic buffer would be higher than in pure water

### 27. Solubility of a salt of weak acid and weak base in basic buffer

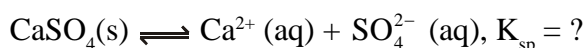


The solubility of  $\text{CH}_3\text{COONH}_4$  in basic buffer would be higher than pure water.

#### Illustration 24:

A 100.0 mL sample is removed from a water solution saturated with  $\text{CaSO}_4$  at  $25^\circ\text{C}$ . The water is completely evaporated from the sample and a deposit of 0.24 g  $\text{CaSO}_4$  is obtained. What is  $K_{sp}$  for  $\text{CaSO}_4$  at  $25^\circ\text{C}$ ?

#### Solution:



Data shows that the solubility of  $\text{CaSO}_4$  is 0.24 g per 100 mL.

$$\therefore [\text{CaSO}_4] = \frac{0.24}{100} \times \frac{1000}{136} \text{ mol L}^{-1} = 0.01765 \text{ M}$$

$$\therefore [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 0.01765 \text{ M}.$$

$$\therefore K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (0.01765)^2 = 3.115 \times 10^{-4}.$$

#### Illustration 25:

**Zn salt is mixed with  $(\text{NH}_4)_2\text{S}$  of molarity 0.021 M. What amount of  $\text{Zn}^{2+}$  will remain unprecipitated in 12 mL of the solution?  $K_{\text{sp}}$  of  $\text{ZnS} = 4.51 \times 10^{-24}$ .**

**Solution:**

$$(i) \quad K_{\text{sp}} = [\text{Zn}^{2+}] [\text{S}^{2-}]$$

$$4.51 \times 10^{-24} = [\text{Zn}^{2+}] \times 0.021 \Rightarrow [\text{Zn}^{2+}] = 2.15 \times 10^{-22} \text{ M}$$

$$\therefore \text{amount} = 2.15 \times 10^{-22} \times 65.4 \times \frac{12}{1000} = 1.68 \times 10^{-22} \text{ g}$$

**Illustration 26:**

**Calculate the solubility of  $\text{AgCN}$  in a buffer solution of  $\text{pH} = 3$ . Given  $K_{\text{sp}}$  of  $\text{AgCN} = 1.2 \times 10^{-16}$  and  $K_a$  for  $\text{HCN} = 4.8 \times 10^{-10}$ .**

**Solution:**



From (1),  $x(x - y) = 1.2 \times 10^{-16}$

From (2)  $\frac{10^{-14}}{4.8 \times 10^{-10}} = \frac{y \times 10^{-11}}{(x - y)}$

Multiplying both,  $xy \times 10^{-11} = \frac{1.2 \times 10^{-16} \times 10^{-14}}{4.8 \times 10^{-10}}$

$$\therefore xy = 2.5 \times 10^{-11}$$

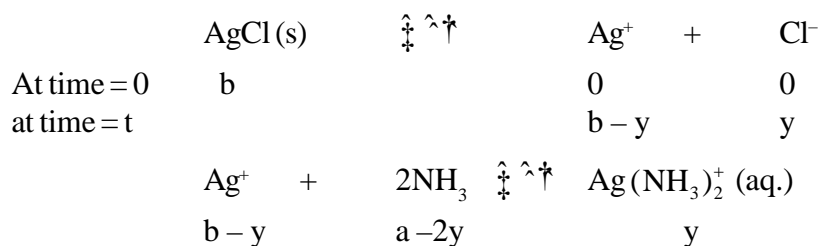
now  $x^2 - xy = 1.2 \times 10^{-16} \Rightarrow x^2 = 1.2 \times 10^{-16} + 2.5 \times 10^{-11}$

$$\therefore x^2 = 2.5 \times 10^{-11}$$

$$x = 1.58 \times 10^{-5} \text{ M}$$

## 28. Solubility of $\text{AgCl}$ in an aqueous solution containing $\text{NH}_3$

Let the amount of  $\text{NH}_3$  initially be 'a' M. if the solubility of salt be 'b' mole/ litre.



where y is the amount of  $\text{Ag}^+$  which reacted with  $\text{NH}_3$ .

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (b - y)y$$

$$K_{\text{f}} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{y}{(b - y)(a - 2y)}$$

After knowing the value of  $K_{\text{sp}}$  and  $K_{\text{f}}$  the value of solubility can be calculated.

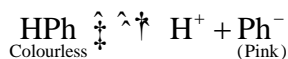
## 29. Acid-base Indicators

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An acid & base indicator are substance which changes its colour within limits with variation in pH of the solution to which it is added. Indicators, in general are either organic weak acid or weak bases with a characteristics of having different colours in the ionized and unionized form e.g. phenolphthalein is a weak acid (ionized form is pink and unionized form is colourless).

### Acidic Indicator Action (e.g. HPh)

HPh (Phenolphthalein) is a colourless weak acid



$$K_{\text{IN}} = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]}$$

If the solution is acidic, the  $\text{H}^+$  by the acid increases and since  $K_{\text{in}}$  is constant and it does not depend upon the concentration so  $\text{HPh}$  also increases mean equilibrium will shift towards left means solution remain colourless. By addition of alkali,  $\text{OH}^-$  will be furnished and that  $\text{OH}^-$  will combines with  $\text{H}^+$  of HPh to form water and equilibrium will moves towards right and therefore solution becomes pink. Thus HPh appears colourless in acidic and pink in alkaline solution pH range of HPh is (8.3 – 10).

$$\text{pH} = \text{pK}_{\text{in}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

The colour of the indicator changes from colour A to colour B at a particular point known as end point of indicator. At this point  $[\text{HIn}] = [\text{In}^-]$  means  $\text{pH} = \text{pK}_{\text{in}}$  (at this point half of indicator is in the acid form and half in the form of its conjugate form).

## 30. Indication (Basic) action of MeOH (Methyl Orange)

When MeOH is dissolved in water and undergoes dissociation to a small extent. The undissociated molecules are yellow while dissociated  $\text{Me}^+$  are red in colour.



If the solution is acidic, the  $\text{H}^+$  furnished by the acid combines with  $\text{OH}^-$  ions furnished by the indicators to form undissociated water. This shifts the equilibrium towards right giving red coloured solution. Therefore in acid solution, this indicator gives red colour. In the presence of alkali,  $\text{OH}^-$  increases and due to common ion effect the dissociation of MeOH suppress means equilibrium will shifts towards left. Hence the solution in alkaline medium remains yellow in colour.

Colour of solution depends upon relative amount of ionized form to unionized form (ratio of  $\text{Me}^+/\text{MeOH}$ ).

In general pH range of indicator lies B/w  $\text{pK}_{\text{in}} - 1$  to  $\text{pK}_{\text{in}} + 1$

**Case 1 :**  $\text{pH} = \text{pK}_{\text{in}} - 1$

$$\text{Means } \frac{[\text{In}^-]}{[\text{HIn}]} = 0.1 = 10\%$$

Percentage ionization of indicator would be

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100\% = \frac{0.10 \text{ HIn}}{0.10 \text{ HIn} + (\text{HIn})} \times 100\%$$

$$= \frac{1}{11} \times 100 = 9.1\%$$

In fact,  $\text{pH} = \text{pK}_{\text{In}} - 1$  is the maximum pH upto which the solution has a distinct colour characteristic of HIn. At pH smaller than this value, more of the indicator is present in the unionized form.

Thus at  $\text{pH} \leq \text{pK}_{\text{In}} - 1$ , the solution has a colour characteristic of HIn.

**Case 2 :** at  $\text{pH} = \text{pK}_{\text{In}} + 1$

$$\text{Mean } \frac{[\text{In}^-]}{[\text{HIn}]} = 10$$

Percentage of ionization of indicator is

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100\% = \frac{10 [\text{HIn}]}{10 [\text{HIn}] + [\text{HIn}]} \times 100\% = \frac{1000}{11} = 91\%$$

Thus most of the indicator is present in the ionized form  $\text{In}^-$  and solution gets the colour characteristic.

In fact  $\text{pH} = \text{pK}_{\text{In}} + 1$  is the minimum pH upto which the solution has a distinct characteristic of  $\text{In}^-$ .

At pH greater than this value, still more of the indicator is present in the ionized form. Thus at  $\text{pH} \geq \text{pK}_{\text{In}} + 1$ , the solution has a colour characteristics of  $\text{In}^-$ .

**Illustration 27:**

*An indicator is a weak acid and pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the centre of the hydrogen ion concentrations corresponding to the given pH range, calculate the ionization constant of the indicator.*

**Solution:**

$$\text{pH} = -\log [\text{H}_3\text{O}^+], \text{ or } \log [\text{H}_3\text{O}^+] = -\text{pH}$$

$$\therefore [\text{H}_3\text{O}^+] = \text{antilog of } (-\text{pH})$$

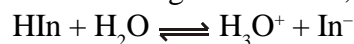
$$\text{for pH} = 3.1 \quad [\text{H}_3\text{O}^+]_1 = \text{antilog of } (-3.1) = \text{antilog of } (\bar{4}.9) = 7.94 \times 10^{-4}$$

$$\text{for pH} = 4.5 \quad [\text{H}_3\text{O}^+]_2 = \text{antilog of } (-4.5) = \text{antilog of } (\bar{5}.5) = 3.16 \times 10^{-5}$$

Since neutral point lies at the centre of the hydrogen ion concentration in the given pH range, hence  $[\text{H}_3\text{O}^+]$  at the neutral point

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{[\text{H}_3\text{O}^+]_1 + [\text{H}_3\text{O}^+]_2}{2} \\ &= \frac{7.94 \times 10^{-4} + 3.16 \times 10^{-5}}{2} = 4.13 \times 10^{-4} \text{ M} \end{aligned}$$

Let indicator be HIn behaving as weak acid, then



$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad [\text{ionization constant of indicator is } K_{\text{In}}]$$

$$= [\text{H}_3\text{O}^+] \{ \text{since at neutral point } [\text{In}^-] = [\text{HIn}] \} = 4.13 \times 10^{-4}.$$

**Illustration 28:**

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

**Solution:**

## IONIC EQUILIBRIUM

$$\text{pH} = \text{pK}_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

For colour change,  $\frac{[\text{In}^-]}{[\text{HIn}]} = 1$

$\therefore \text{pH} = \text{pK}_{\text{In}} = -\log (1 \times 10^{-5}) = 5$

now  $[\text{In}^-] = 80, [\text{HIn}] = 20$

$\therefore \text{pH} = 5 + \log \frac{80}{20} = 5.6$

### 31. Ostwald's Theory

According to this theory:

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

Considering two important indicators phenolphthalein (a weak acid) and methyl orange (a weak base), Ostwald theory can be illustrated as follows:

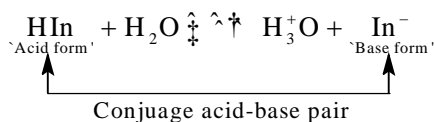
**Phenolphthalein:** It can be represented as HPh. It ionizes in solution to a small extent as:



Applying law of mass action,

$$K = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]}$$

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



$$K_{\text{In}} = \frac{[\text{In}^-][\text{H}_3\text{O}^+]}{[\text{HIn}]}; K_{\text{In}} = \text{Ionization constant of indicator}, [\text{H}_3\text{O}^+] = K_{\text{In}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

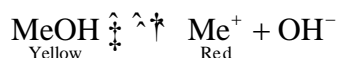
$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} [K_{\text{In}}] - \log_{10} \frac{[\text{HIn}]}{[\text{In}^-]}$$

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

At equivalence point;

$$[\text{In}^-] = [\text{HIn}] \text{ and } \text{pH} = \text{pK}_{\text{In}}$$

**Methyl orange:** It is a weak base and can be represented as MeOH. It is ionized in solution to give  $\text{Me}^+$  and  $\text{OH}^-$  ions.



Applying law of mass action

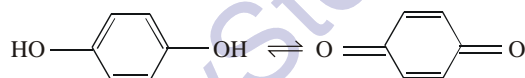
$$K = \frac{[\text{Me}^+][\text{OH}^-]}{[\text{MeOH}]}$$

In presence of an acid,  $\text{OH}^-$  ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient  $\text{Me}^+$  ions are produced which impart red colour to the solution. On addition of alkali, the concentration of  $\text{OH}^-$  ions increases in the solution and the equilibrium shifts to left hand side (due to common ion effect), i.e., the ionization of MeOH is practically negligible. Thus, the solution acquires the colour of unionized methyl orange molecules, i.e., yellow.

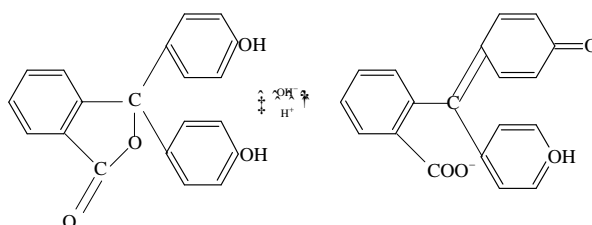
This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The  $\text{OH}^-$  ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

**Quinonoid Theory:** According to this theory:

- (a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

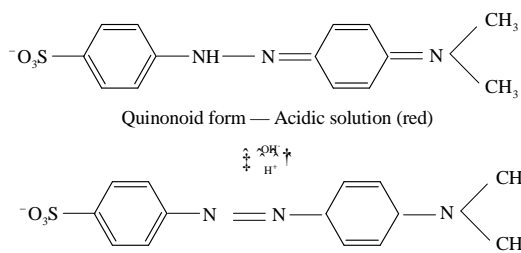


- (b) The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other.
- (c) One form mainly exists in acidic medium and the other in alkaline medium. Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs. Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



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

## IONIC EQUILIBRIUM



## 1. Daily Practice Problem Sheet

### Dissociation of acids and base

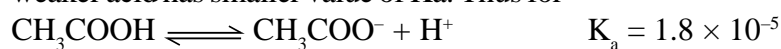
- I.** For a weak acid HA
- $$HA \rightleftharpoons H^+ + A^- \quad K_a = 10$$
- When the concentration of acid is 10 M, then
- Q.1** The degree of dissociation of acid is -  
 (A) 1 (B) 0.618 (C) 0.309 (D) 0.418
- Q.2** With respect to Q. 1 what will be the concentration of  $H^+$  ion -  
 (A) 6.18 M (B) 10 M (C) 3.09 M (D) 4.18 M
- Q.3** When the concentration of acid is reduced to 1 M, then degree of dissociation will be  
 (A) 0.6 (B) 3.16 (C) 0.916 (D) 0.8
- Q.4** With Respect to Q. 3 the concentration of  $H^+$  ion will be -  
 (A) 0.916 (B) 3.16 (C) 0.6 (D) 0.8
- Q.5** Now the concentration of acid is further reduced to 0.1 M, then its degree of dissociation now be -  
 (A) 0.916 (B) 10 (C) 0.6 (D) 0.99
- Q.6** With respect to Q. 5 now the concentration of  $H^+$  ion is -  
 (A) 0.0916 (B) 0.1 (C) 0.06 (D) 0.099
- II.** Degree of dissociation of a weak acid having concentration  $10^{-3}$  M is 0.1, then
- Q.7**  $K_a$  of the acid is -  
 (A)  $1.1 \times 10^{-5}$  (B)  $10^{-5}$  (C)  $1.1 \times 10^{-4}$  (D)  $10^{-4}$
- Q.8** Concentration of  $H^+$  ion is -  
 (A)  $10^{-2}$  M (B)  $10^{-5}$  M (C)  $10^{-4}$  M (D)  $10^{-3}$  M
- III.** A weak acid having  $K_a = 2.5 \times 10^{-5}$  gives  $[H^+] = 1.3 \times 10^{-4}$  M.
- Q.9** On the basis of above information, degree of dissociation of acid is  
 (A) 0.25 (B) 0.161 (C) 0.05 (D) 0.025
- Q.10** Concentration of acid would be  
 (A)  $8.06 \times 10^{-2}$  M (B)  $4.03 \times 10^{-4}$  M (C)  $8.06 \times 10^{-4}$  M (D)  $4.03 \times 10^{-2}$  M
- IV.** In a  $10^{-2}$  M solution of acid HA having  $K_a = 10^{-4}$ ,
- Q.11** What will be the  $[H^+]$  -  
 (A)  $9.5 \times 10^{-4}$  M (B)  $1 \times 10^{-3}$  M (C)  $9.5 \times 10^{-2}$  M (D)  $1.1 \times 10^{-4}$  M
- V.** For an acid HA having  $K_a = 2.1 \times 10^{-4}$  & molecular weight = 90.

- Q.12** The amount of acid which should be dissolved in  $10^{2/21}$  of solution having  $\alpha = 8\%$  is  
 (A) 34.67 gm                      (B) 29.53 gm                      (C) 13.63 gm                      (D) 27.17 gm
- VI** In a 10% dissociated solution of a weak acid HA, concentration of  $H^+$  ion is  $3.5 \times 10^{-3}$  M, then
- Q.13**  $K_a$  for the acid is  
 (A)  $7.0 \times 10^{-6}$                       (B)  $3.5 \times 10^{-5}$                       (C)  $3.9 \times 10^{-4}$                       (D)  $4.9 \times 10^{-6}$

## 2. Daily Practice Problem Sheet

### Q-1 to Q-9)

Generally all organic acids are weak acids. Acetic acid ( $CH_3COOH$ ) & formic acid ( $HCOOH$ ) both are organic acids, hence both are weak acids & most commonly used in ionic equilibrium  $CH_3COOH$  is weaker than  $HCOOH$  due to +I effect of  $-CH_3$  group. Stronger acid has higher value of  $K_a$  & weaker acid has smaller value of  $K_a$ . Thus for



What will be the degree of dissociation and  $H^+$  ion concentration :

- Q.1** When concentration of acetic acid is 1 M -  
 (A)  $4.24 \times 10^{-4}$ ,  $4.24 \times 10^{-4}$                       (B)  $1.34 \times 10^{-3}$ ,  $1.34 \times 10^{-3}$   
 (C)  $4.24 \times 10^{-3}$ ,  $4.24 \times 10^{-3}$                       (D)  $1.34 \times 10^{-3}$ ,  $1.34 \times 10^{-4}$
- Q.2** If 1M formic acid is taken -  
 (A)  $4.24 \times 10^{-4}$ ,  $1.34 \times 10^{-2}$                       (B)  $1.34 \times 10^{-2}$ ,  $1.34 \times 10^{-2}$   
 (C)  $4.24 \times 10^{-4}$ ,  $4.24 \times 10^{-4}$                       (D)  $3.4 \times 10^{-5}$ ,  $1.34 \times 10^{-5}$
- Q.3** When concentration of acetic acid is reduced to 0.1 M  
 (A)  $4.24 \times 10^{-4}$ ,  $1.34 \times 10^{-2}$                       (B)  $1.34 \times 10^{-2}$ ,  $1.34 \times 10^{-3}$   
 (C)  $4.24 \times 10^{-2}$ ,  $1.34 \times 10^{-3}$                       (D)  $1.34 \times 10^{-2}$ ,  $1.34 \times 10^{-2}$
- Q.4** When 0.1 M  $HCOOH$  is considered -  
 (A)  $4.24 \times 10^{-2}$ ,  $4.24 \times 10^{-3}$                       (B)  $1.34 \times 10^{-2}$ ,  $1.34 \times 10^{-3}$   
 (C)  $4.24 \times 10^{-3}$ ,  $4.24 \times 10^{-2}$                       (D)  $3.4 \times 10^{-5}$ ,  $3.4 \times 10^{-6}$
- Q.5** When the concentration of acetic acid is further reduced to  $10^{-2}$  M  
 (A)  $3.4 \times 10^{-5}$ ,  $3.4 \times 10^{-6}$                       (B)  $2.36 \times 10^{-3}$ ,  $2.36 \times 10^{-4}$   
 (C)  $1.34 \times 10^{-2}$ ,  $1.34 \times 10^{-4}$                       (D)  $4.24 \times 10^{-2}$ ,  $4.24 \times 10^{-4}$
- Q.6** Now  $10^{-2}$  M  $HCOOH$  is taken, then  
 (A) 1.34,  $1.34 \times 10^{-3}$                       (B) 0.125,  $1.25 \times 10^{-3}$   
 (C) 1.25,  $1.25 \times 10^{-3}$                       (D) 0.25,  $2.5 \times 10^{-3}$
- Q.7** When concentration of acetic acid is  $10^{-4}$  M  
 (A) 0.34,  $3.4 \times 10^{-5}$                       (B) 1.34,  $1.34 \times 10^{-5}$   
 (C) 0.71,  $7.1 \times 10^{-6}$                       (D) 0.25,  $2.5 \times 10^{-3}$
- Q.8** Similarly, now  $10^{-4}$  M  $HCOOH$  is considered  
 (A) 0.715,  $7.15 \times 10^{-5}$                       (B) 1.34,  $1.34 \times 10^{-5}$   
 (C) 0.61,  $6.1 \times 10^{-6}$                       (D) 0.34,  $3.4 \times 10^{-5}$
- Q.9** Finally concentration of acetic acid is reduced to  $10^{-5}$  M  
 (A) 0.34,  $3.4 \times 10^{-6}$                       (B) 0.236,  $2.36 \times 10^{-5}$   
 (C) 0.71,  $7.1 \times 10^{-6}$                       (D) 0.25,  $2.5 \times 10^{-5}$



### IONIC EQUILIBRIUM

- Q.10** In a  $5 \times 10^{-2}$  M solution of acetic acid, having  $\alpha = 1\%$  and  $K_a = 1.8 \times 10^{-5}$ . The amount of acetic acid present in the solution is -  
(A) 54 gm (B) 27 gm (C) 60 gm (D) 30 gm
- Q.11**  $\alpha$  of 0.1 M acetic acid is -  
(A)  $1.34 \times 10^{-3}$  (B)  $4.24 \times 10^{-2}$  (C)  $1.34 \times 10^{-2}$  (D)  $4.24 \times 10^{-3}$
- Q.12** How much water must be added in 900 ml of 0.1 M  $\text{CH}_3\text{COOH}$  solution to triple its degree of dissociation (Assume  $\alpha < 5\%$  is negligible) -  
(A)  $7.2 \times 10^2$  (B)  $3.6 \times 10^2$  (C)  $5.8 \times 10^2$  (D)  $2.4 \times 10^2$
- Q.13** When 35 gm of  $\text{NH}_4\text{OH}$  is dissolved in  $10^2$  of water, then its degree of dissociation will be -  
(A)  $1.34 \times 10^{-3}$  (B)  $1.34 \times 10^{-2}$  (C)  $4.24 \times 10^{-2}$  (D)  $4.24 \times 10^{-3}$
- Q.14** In the above question concentration of  $\text{OH}^-$  ion is -  
(A)  $0.134 \times 10^{-3}$  (B)  $1.34 \times 10^{-3}$  (C)  $4.24 \times 10^{-3}$  (D)  $0.424 \times 10^{-3}$
- Q.15** The amount of  $\text{CH}_3\text{NH}_2$  dissolve in  $2 \times 10^2$  of water so that it produces concentration  $\text{OH}^-$  is equal to  $5 \times 10^{-4}$  M, is - [Given  $K_b$  of  $\text{CH}_3\text{NH}_2 = 2 \times 10^{-6}$ ]  
(A) 5.6 gm (B) 3.88 gm (C) 7.75 gm (D) 8.3 gm

## 3. Daily Practice Problem Sheet

### Common ion effect

Whenever any electrolyte (strong/acid) producing common ion is dissolved in the solution of weak acid & weak base, concentration of common ion increases but degree of dissociation of weak acid or weak base decreases hence concentration of other ion also decreases. In terms of concentration, more is the concentration of common ion, more will be the increase in the degree of dissociation. In terms of nature of electrolyte, more strong electrolyte changes degree of dissociation more.

#### Case I : Mixture of strong electrolyte + weak electrolyte

- Q.1** In presence of 2M HCl solution degree of dissociation of 0.1 M  $\text{CH}_3\text{COOH}$  is -  
(A)  $9 \times 10^{-6}$  (B)  $3 \times 10^{-6}$  (C)  $9.5 \times 10^{-5}$  (D)  $3.5 \times 10^{-5}$
- Q.2** In the above question concentration of  $\text{H}^+$  ion will be -  
(A) 1 M (B) 0.1 M (C) 2 M (D) 0.2 M
- Q.3** The pH of the solution containing 0.1 M  $\text{HNO}_3$  & 0.1 M  $\text{HCOOH}$  - [ $K_a$  of  $\text{HCOOH}$  is  $1.8 \times 10^{-4}$ ]  
(A) 0.1 (B) 1 (C) 2 (D) 0.2
- Q.4** Degree of dissociation of 1 M  $\text{CH}_3\text{COOH}$  in presence of 1 M  $(\text{CH}_3\text{COO})_2\text{Pb}$  having degree of dissociation 80% and 3 M  $(\text{CH}_3\text{COO})_2\text{Ca}$ , is -  
(A)  $2.36 \times 10^{-6}$  (B)  $1.36 \times 10^{-6}$  (C)  $1.34 \times 10^{-3}$  (D)  $4.24 \times 10^{-3}$
- Q.5** In the above question  $[\text{H}^+]$  &  $[\text{CH}_3\text{COO}^-]$  is -  
(A)  $[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 7.6$  (B)  $[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 2.36 \times 10^{-6}$   
(C)  $[\text{CH}_3\text{COO}^-] = 7.6$ ;  $[\text{H}^+] = 2.36 \times 10^{-6}$  (D)  $[\text{CH}_3\text{COO}^-] = 1.34 \times 10^{-2}$ ;  $[\text{H}^+] = 7.6$
- Q.6** Degree of dissociation of 1 M  $\text{CH}_3\text{COOH}$  in presence of 2 M  $\text{HClO}_4$  + 0.1 M HCl having  $\alpha = 95\%$ , is -  
(A)  $2.36 \times 10^{-6}$  (B)  $8.6 \times 10^{-6}$  (C)  $3.34 \times 10^{-5}$  (D)  $1.86 \times 10^{-5}$
- Q.7** In the above Q.  $[\text{H}^+]$  &  $[\text{CH}_3\text{COO}^-]$  is -  
(A)  $[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 8.6 \times 10^{-6}$  (B)  $[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 2.095$   
(C)  $[\text{CH}_3\text{COO}^-] = 7.6$ ;  $[\text{H}^+] = 2.36 \times 10^{-6}$  (D)  $[\text{CH}_3\text{COO}^-] = 8.6 \times 10^{-6}$ ;  $[\text{H}^+] = 2.095$

**(Q.8 to Q. 11) Degree of dissociation and  $[\text{OH}^-]$  in 0.1 M  $\text{NH}_4\text{OH}$**

- Q.8** In presence of 1.2 M  $(\text{NH}_4)_3\text{PO}_4$  having  $\alpha = 50\%$  -  
 (A)  $10^{-6}$ ,  $10^{-5}$  (B)  $10^{-5}$ ,  $10^{-6}$   
 (C)  $1.34 \times 10^{-2}$ ,  $1.34 \times 10^{-3}$  (D)  $2.36 \times 10^{-5}$ ,  $2.36 \times 10^{-6}$
- Q.9** In presence of 2 M  $\text{Ca}(\text{OH})_2$  having  $\alpha = 90\%$  -  
 (A)  $5 \times 10^{-5}$ ,  $5 \times 10^{-6}$  (B)  $2.36 \times 10^{-5}$ ,  $2.36 \times 10^{-6}$   
 (C)  $1.34 \times 10^{-2}$ , 3.6 (D)  $5 \times 10^{-6}$ , 3.6
- Q.10** In presence of 0.1 M  $(\text{NH}_4)_2\text{SO}_4$  -  
 (A)  $1.34 \times 10^{-2}$ , 3.6 (B)  $10^{-5}$ ,  $10^{-6}$   
 (C)  $9 \times 10^{-5}$ ,  $9 \times 10^{-6}$  (D)  $5 \times 10^{-6}$ , 3.6
- Q.11** In presence of 1.8 M  $\text{Al}(\text{OH})_3$  having  $\alpha = 10\%$  -  
 (A)  $3.34 \times 10^{-5}$ , 0.54 (B)  $5 \times 10^{-5}$ , 0.54  
 (C)  $9 \times 10^{-5}$ ,  $9 \times 10^{-6}$  (D)  $5 \times 10^{-6}$ , 0.65
- Q.12** The amount of  $(\text{NH}_4)_2\text{SO}_4$  having degree of dissociation 75% which should be dissolved in 1500 ml of 1 M  $\text{NH}_4\text{OH}$  to decrease its degree of dissociation by 200 times, is -  
 (A) 112.1 gm (B) 224.2 gm (C) 56.0 gm (D) 65.4 gm
- Q.13** 500 ml of 0.2 M  $\text{H}_2\text{SO}_4$  is mixed with 1500 ml of 0.1 M  $\text{HCOOH}$  solution. If  $K_a$  for formic acid is  $1.8 \times 10^{-4}$ , then pH of the final solution is -  
 (A) 1 (B) 0.1 (C) 0.02 (D) 2
- Q.14** 0.1 M  $\text{CH}_3\text{COONa}$  is mixed with 0.05 M  $\text{HCl}$ , then the final pH of the solution is -  
 (A) 4.74 (B) 3.74 (C) 7.34 (D) 3.6

## 4. Daily Practice Problem Sheet

### Common ion effect

#### Case-II : Mixture of two weak electrolytes

- Q.1** A solution contains 0.09 M  $\text{HCl}$ , 0.09 M  $\text{CCl}_2\text{HCOOH}$ , and 0.1 M  $\text{CH}_3\text{COOH}$ . If total  $[\text{H}^+] = 0.1$  and  $K_a$  for  $\text{CH}_3\text{COOH} = 10^{-5}$ ,  $K_a$  for  $\text{CCl}_2\text{HCOOH}$  is  
 (A)  $1.35 \times 10^{-4}$  (B)  $0.18 \times 10^{-2}$  (C)  $0.18 \times 10^{-5}$  (D)  $1.25 \times 10^{-2}$
- Q.2** If 0.1 M  $\text{CH}_3\text{COOH}$  is mixed with 0.1 M  $\text{CH}_2\text{ClCOOH}$ ,  
 [Given :  $K_a$   $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ ,  $K_a$   $\text{CH}_2\text{ClCOOH} = 1.8 \times 10^{-4}$ ]  
 Find out total  $[\text{H}^+]$  -  
 (A)  $0.404 \times 10^{-2}$  (B)  $1.44 \times 10^{-3}$  (C)  $4.44 \times 10^{-3}$  (D)  $8.44 \times 10^{-4}$
- Q.3** In a solution containing 0.1 M  $\text{HCOOH}$  and 0.1 M  $\text{HOCN}$ ,  $[\text{H}^+]$  will be -  
 Given :  $K_a$  for  $\text{HCOOH}$  and  $\text{HOCN}$  are  $1.8 \times 10^{-4}$  and  $3.3 \times 10^{-4}$   
 (A)  $7.13 \times 10^{-3}$  M (B)  $3.56 \times 10^{-3}$  M (C)  $1.35 \times 10^{-4}$  M (D)  $7.97 \times 10^{-4}$  M
- Q.4** On addition of ammonium chloride to a solution of  $\text{NH}_4\text{OH}$   
 (A) dissociation of  $\text{NH}_4\text{OH}$  increases (B) concentration of  $\text{OH}^-$  decreases  
 (C) concentration of  $\text{OH}^-$  increases (D) concentration of  $\text{NH}_4^+$  and  $\text{OH}^-$  decreases

**(Q.5-Q.6)**

Considering a 0.1 M  $\text{H}_3\text{PO}_4$  solution, answer the questions given below :

[Given :  $K_1 = 7.5 \times 10^{-3}$ ,  $K_2 = 6.2 \times 10^{-8}$ ,  $K_3 = 3.6 \times 10^{-13}$ ]

- Q.5** In the given solution  $[\text{H}^+]$  &  $[\text{H}_2\text{PO}_4^-]$  is  
 (A)  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.024$  M (B)  $[\text{H}^+] = 0.024$  M ;  $[\text{H}_2\text{PO}_4^-] = 0.012$  M

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(C)  $[H^+] = 0.076 \text{ M}$  ;  $[H_2PO_4^-] = 0.024 \text{ M}$       (D)  $[H^+] = [H_2PO_4^-] = 0.076 \text{ M}$

**Q.6** concentration of  $[H_3PO_4]$  at equilibrium is

(A) 0.076 M                      (B) 0.024 M                      (C) 0.012 M                      (D) 0.76 M

**Q.7** The degree of dissociation of a weak electrolyte increases -

(A) on increasing pressure                      (B) on decreasing dilution  
(C) on increasing dilution                      (D) on increasing concentration

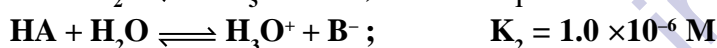
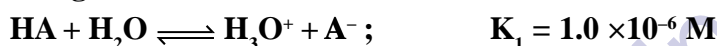
**Q.8** The amount of  $H_2SO_4$  solution, which should be mixed with 500 ml of 0.1 M  $H_2S$  solution to obtain concentration of sulphide ion equal to  $10^{-20}$  moles/litre, is -

[Given :  $K_a$  for  $H_2S$  is  $1.3 \times 10^{-21}$  ]

(A) 5.38 gm                      (B) 12.79 gm                      (C) 1.27gm                      (D) 2.79 gm

**(Q.9–Q.11)**

**A solution is prepared by mixing one mole of HA with one mole of HB, diluting to a total volume of 1 dm<sup>3</sup> with water. Both HA and HB are weak acids which dissociate according to the following reversible reactions.**



**Q.9** Equilibrium concentrations of  $H_3O^+$  is

(A)  $2 \times 10^{-6} \text{ M}$                       (B)  $1.414 \times 10^{-3} \text{ M}$                       (C)  $0.707 \times 10^{-3} \text{ M}$                       (D)  $1 \times 10^{-3} \text{ M}$

**Q.10** Equilibrium concentrations of  $A^-$  and  $B^-$  are

(A)  $[A^-] = [B^-] = 0.707 \times 10^{-3} \text{ M}$   
(B)  $[A^-] = 1.414 \times 10^{-3} \text{ M}$  ;  $[B^-] = 0.707 \times 10^{-3} \text{ M}$   
(C)  $[A^-] = 2 \times 10^{-3} \text{ M}$   $[B^-] = 0.707 \times 10^{-3} \text{ M}$   
(D)  $[A^-] = 0.707 \times 10^{-3} \text{ M}$   $[B^-] = 1 \times 10^{-3} \text{ M}$

**Q.11** How does the presence of HB affect the dissociation of HA ?

(A) no effect on concentration of  $H_3O^+$                       (B) no effect on dissociation of HA  
(C) increases the concentration of  $H_3O^+$                       (D) suppresses the dissociation of HA

**(Q.12–Q.13)**

**The dissociation constant of HF and  $HNO_2$  are  $6.71 \times 10^{-4} \text{ M}$  and  $4.5 \times 10^{-4} \text{ M}$ , respectively. Concentration is 0.5 M in HF and 0.5 M in  $HNO_2$ , then -**

**Q.12** pH of the solution is

(A) 0.65                      (B) 2.36                      (C) 1.63                      (D) 1.49

**Q.13** The ratio of  $[F^-]$  to  $[NO_2^-]$  in a solution is -

(A) 1.49                      (B) 9.52                      (C) 1.63                      (D) 7.24

## 5. Daily Practice Problem Sheet

### *Dissociation of water*

**Q.1** The ionization constant and degree of dissociation of water at 25°C, is -

(A)  $1.8 \times 10^{-9}$ ,  $1.8 \times 10^{-16}$                       (B)  $1.8 \times 10^{-16}$ ,  $1.8 \times 10^{-9}$

(C)  $1.8 \times 10^{-12}$ ,  $1.8 \times 10^{-14}$

(D)  $1.8 \times 10^{-14}$ ,  $1.8 \times 10^{-12}$

**(Q.2–Q.3)**

**The degree of ionization of water was found to be  $1.28 \times 10^{-8}$ .**

**Q.2** The ionization constant of water at  $90^\circ\text{C}$  is -

(A)  $1.28 \times 10^{-14}$  M (B)  $12.81 \times 10^{-15}$  M (C)  $9.07 \times 10^{-15}$  M (A)  $7.52 \times 10^{-12}$  M

**Q.3** The ionic product of water at this temperature is -

(A)  $5.04 \times 10^{-13}$  M<sup>2</sup> (B)  $4.02 \times 10^{-11}$  M<sup>2</sup> (C)  $6.34 \times 10^{-14}$  M<sup>2</sup> (D)  $5.98 \times 10^{-14}$  M<sup>2</sup>

**Q.4** The ionic product of water is  $1 \times 10^{-14}$  (mol/l)<sup>2</sup>. The number of H<sup>+</sup> ions that present in one millionth part of 1 ml of pure water is -

(A) 66.9 million (B) 52.2 million (C) 48.3 million (D) 60.3 million

**Q.5** The pH of pure water at  $25^\circ$  and  $35^\circ\text{C}$  are 7 and 6 respectively. The heat of formation of water from H<sup>+</sup> and OH<sup>-</sup> will be-

(A) -77.11 kcal/mole (B) -84.55 kcal/mole (C) -92.36 kcal/mole (D) -66.25 kcal/mole

**Q.6**  $K_w$  for  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$  changes from  $10^{-14}$  at  $25^\circ\text{C}$  to  $9.62 \times 10^{-14}$  at  $60^\circ\text{C}$ . The pH of water at this temperature is -

(A) 6.51 (B) 7.02 (C) 8.17 (D) 6.99

**Q.7** If  $K_w$  of water at  $50^\circ\text{C}$  is  $5 \times 10^{-14}$ , then the nature of solutions having pH = 7, pH = 6 & pH = 8.2 is respectively -

(A) neutral, basic, acidic (B) neutral, acidic, basic  
(C) basic, acidic, basic (D) basic, acidic, neutral

**Q.8** The value of ionic product of water at various temperature are given below

$\theta/^\circ\text{C}$	0	25	40
$K_w \times 10^{-14}/\text{M}^2$	0.114	1.008	2.919

The pH value of the pure water at  $0^\circ\text{C}$ ,  $25^\circ\text{C}$  &  $40^\circ\text{C}$  is respectively -

(A) 7.47, 7.26, 6.76 (B) 7.26, 7.00, 6.76 (C) 7.47, 7.00, 6.76 (D) 7.26, 6.76, 6.63

**Q.9** The ionic product of water at  $100^\circ\text{C}$  is 55 times than that at  $25^\circ\text{C}$ . The value of pH of water at  $100^\circ\text{C}$  is -

(A) 6.13 (B) 7.02 (C) 6.63 (D) 7.12

**Q.10** The pH of a solution at  $25^\circ\text{C}$  which is twice as alkaline as pure water will be -

(A) 7.0 (B) 7.3 (C) 6.8 (D) 8.1

## 6. Daily Practice Problem Sheet

### *Concentration of H<sup>+</sup> and OH<sup>-</sup> in aq. solution of acid and base*

**Q.1** [H<sup>+</sup>] and [OH<sup>-</sup>] in a solution obtained by dissolving 0.365 g of HCl in 5<sup>2</sup>/<sub>21</sub> of water is -

(A) [H<sup>+</sup>] =  $2 \times 10^{-3}$ , [OH<sup>-</sup>] =  $5 \times 10^{-12}$  (B) [H<sup>+</sup>] =  $3 \times 10^{-4}$ , [OH<sup>-</sup>] =  $5 \times 10^{-10}$   
(C) [H<sup>+</sup>] =  $2 \times 10^{-5}$ , [OH<sup>-</sup>] =  $4 \times 10^{-13}$  (D) [H<sup>+</sup>] =  $3 \times 10^{-4}$ , [OH<sup>-</sup>] =  $4 \times 10^{-13}$

**Q.2** On dissolving w gm of H<sub>2</sub>SO<sub>4</sub> in 10<sup>2</sup>/<sub>21</sub> of pure water, concentration of H<sup>+</sup> ion changed by 10,000 times as compared to H<sup>+</sup> ion in pure water at  $25^\circ\text{C}$ . The value of w is -

(A) 1.8 gm (B) 1.2 gm (C) 0.98 gm (D) 0.49 g

**Q.3** Concentration of H<sup>+</sup> ion in  $10^{-5}$  M H<sub>2</sub>SO<sub>4</sub> &  $3.1 \times 10^{-3}$  M HClO<sub>4</sub> is respectively -

(A)  $10^{-5}$  M,  $3.1 \times 10^{-3}$  M (B)  $2 \times 10^{-5}$  M,  $3.1 \times 10^{-3}$  M  
(C)  $2 \times 10^{-5}$  M,  $6.2 \times 10^{-3}$  M (D)  $2 \times 10^{-10}$  M,  $3.1 \times 10^{-6}$  M

## IONIC EQUILIBRIUM

### (Q.4–Q.6)

**When 36.5 ~ gm of HCl is dissolved in 1 litre of water, the solution will be acidic in nature due to increase in concentration of  $H^+$  ion, then find out-**

- Q.4** Concentration of  $H^+$  ion in the above solution if we neglect  $H^+$  due to water is -  
(A)  $10^{-5}$  (B)  $10^{-7}$  (C)  $10^{-6}$  (D)  $10^{-8}$
- Q.5** Concentration of  $H^+$  ion in the above solution if we consider  $H^+$  due to water is -  
(A)  $1.0099 \times 10^{-6}$  (B)  $10.099 \times 10^{-6}$  (C)  $1 \times 10^{-5}$  (D)  $1.02 \times 10^{-7}$
- Q.6** % error in the above two questions will be -  
(A) 0.99 % (B) 9.9% (C) 99% (D) no error

### (Q.7–Q.9)

A small amount of acid brings large difference in  $H^+$  ion concentration. If  $10^{-7}$  moles of HCl are dissolved in 1 litre of water then find out -

- Q.7** Concentration of  $H^+$  ion in the above solution if we neglect  $H^+$  due to water is -  
(A)  $10^{-5}$  (B)  $10^{-7}$  (C)  $10^{-6}$  (D)  $10^{-8}$
- Q.8** Concentration of  $H^+$  ion in the above solution if we consider  $H^+$  due to water is -  
(A)  $1.0099 \times 10^{-6}$  (B)  $1.099 \times 10^{-7}$  (C)  $1 \times 10^{-5}$  (D)  $1.615 \times 10^{-7}$
- Q.9** % error in the above two questions will be -  
(A) 99 % (B) 9.9% (C) 61.5 % (D) no error
- Q.10**  $[H^+]$  &  $[OH^-]$  ion in  $10^{-6}$  M  $H_2SO_4$  solution is -  
(A)  $[H^+] = 2 \times 10^{-6}$   $[OH^-] = 5 \times 10^{-9}$  (B)  $[H^+] = 2 \times 10^{-6}$   $[OH^-] = 2 \times 10^{-6}$   
(C)  $[H^+] = 1 \times 10^{-6}$   $[OH^-] = 1 \times 10^{-8}$  (D)  $[H^+] = 1 \times 10^{-6}$   $[OH^-] = 5 \times 10^{-9}$
- Q.11** Concentration of  $H^+$  ion and  $OH^-$  ion in a solution obtained by mixing 600 ml of  $10^{-2}$  M  $H_2SO_4$ , 800 ml of  $10^{-3}$  M  $HNO_3$  and 1100 ml of  $10^{-7}$  M HCl, is -  
(A)  $5.12 \times 10^{-3}$ ,  $5.19 \times 10^{-11}$  (B)  $5.12 \times 10^{-3}$ ,  $1.99 \times 10^{-11}$   
(C)  $3.21 \times 10^{-5}$ ,  $2.19 \times 10^{-9}$  (D)  $5.12 \times 10^{-3}$ ,  $0.19 \times 10^{-11}$
- Q.12** Concentration of  $H^+$  ion in 0.1 M HA solution having  $K_a = 10^{-14}$ , is  
(A)  $1.045 \times 10^{-7}$  (B)  $1 \times 10^{-7}$  (C)  $0.1 \times 10^{-7}$  (D)  $1.45 \times 10^{-7}$
- Q.13**  $[H^+]$  and  $[OH^-]$  ion in a 8 litre solution containing 9.25 gm/l of  $Ca(OH)_2$  at  $25^\circ C$ , is  
(A)  $[OH^-] = 0.25 \times 10^{-7}$ ,  $[H^+] = 4 \times 10^{-7}$  (B)  $[OH^-] = 0.25$ ,  $[H^+] = 4 \times 10^{-14}$   
(C)  $[OH^-] = 1.25 \times 10^{-7}$ ,  $[H^+] = 4 \times 10^{-7}$  (D)  $[OH^-] = 2.5$ ,  $[H^+] = 4 \times 10^{-14}$
- Q.14** Concentration of  $H^+$  and  $OH^-$  ion in  $10^{-8}$  M NaOH, is respectively  
(A)  $1 \times 10^{-6}$ ,  $1 \times 10^{-8}$  (B)  $0.95 \times 10^{-6}$ ,  $1.05 \times 10^{-8}$   
(C)  $0.95 \times 10^{-7}$ ,  $1.05 \times 10^{-7}$  (D)  $1.05 \times 10^{-7}$ ,  $0.95 \times 10^{-7}$

## 7. Daily Practice Problem Sheet

### Ph and POH

### (Q.1–Q.5)

In the question given below, find out the pH of the following solutions

- Q.1** 0.1 M  $CH_3COOH$   
(A) 2.87 (B) 2.37 (C) 1.34 (D) 4.74
- Q.2** 0.1 M  $NH_4OH$   
(A) 2.87 (B) 11.13 (C) 8.17 (D) 12.31

- Q.3** 0.1 M HCOOH  
(A) 1.37 (B) 4.74 (C) 2.37 (D) 3.18
- Q.4** 1M CH<sub>3</sub>COOH  
(A) 1.34 (B) 3.18 (C) 4.74 (D) 2.37
- Q.5** 0.1M HA ( $K_a = 10^{-2}$ )  
(A) 1.57 (B) 2.72 (C) 3.14 (D) 2.33
- Q.6** The pH of  $10^{-6}$  M HCl,  $10^{-7}$  M HCl &  $10^{-8}$  M HCl respectively is -  
(A) 6, 7, 8 (B) 6, 6.79, 6.98 (C) 6, 6.79, 7.02 (D) 6, 6.98, 8
- Q.7** Find out pH of 0.1 M CH<sub>3</sub>COOH in presence of 0.1 M CH<sub>3</sub>COONa -  
(A) 4.74 (B) 1.37 (C) 2.33 (D) 1.57
- Q.8** The pH of a solution obtained by mixing 200 ml of HCl solution having pH = 1 with 300 ml of NaOH having pH = 13 will be -  
(A) 10.33 (B) 13 (C) 11.13 (D) 12.3
- Q.9** If 1 ml of  $10^{-6}$  M HCl is diluted to 100 ml, the change in pH will be -  
(A) 1.98 (B) 1.54 (C) 0.98 (D) 0.49
- Q.10** When 200 ml of solution of pH = 2 is mixed with 300 ml of solution of pH = 3, the final pH of the solution will be -  
(A) 2.33 (B) 2.13 (C) 1.57 (D) 5
- Q.11** What volume of NaOH solution having pH = 11 should be added in 1 litre of 0.1 M HCl solution to increase its pH by 2 units.  
(A) 54 litres (B) 49.5 litre (C) 62.7 litres (D) 98 litres
- Q.12** The pH of a solution is 5.0. To this solution sufficient acid is added to decrease the pH to 2.0. The increase in hydrogen ion concentration is -  
(A) 100 times (B) 10 times (C) 1000 times (D) 2.5 times
- Q.13** The pH of a solution is 2. Its pH is to be changed to 4. Then the H<sup>+</sup> ion concentration of original solution has to be -  
(A) halved (B) doubled  
(C) increased 100 times (D) decreased 100 times
- Q.14** An acid solution of pH 6 is diluted hundred times. The pH of the solution becomes -  
(A) 6 (B) 6.98 (C) 4 (D) 8
- Q.15** The pH value of 0.1 mol/litre HCl is approximately 1. The approximate pH value of 0.05 mol/litre H<sub>2</sub>SO<sub>4</sub> is most likely to be -  
(A) 0.05 (B) 0.5 (C) 1 (D) 2
- Q.16** How much water must be evaporated from 5 litre of  $10^{-3}$  M HCl to change its pH by 2 units -  
(A) 1.5 litre (B) 0.5 litre (C) 2.54 litre (D) 4.95 litre
- Q.17** How much water must be added in 1 litre of  $10^{-2}$  M H<sub>2</sub>SO<sub>4</sub> to change its pH by 3 units -  
(A) 850 litre (B) 999 litre (C) 99.9 litre (D) 1000 litre
- Q.18** The pH of the solution obtained by mixing 300 ml of 0.1 M NH<sub>4</sub>OH with 700 ml of 0.1 M NaOH solution will be -  
(A) 12.85 (B) 12.7 (C) 11.13 (D) 13.78
- Q.19** How much Ca(OH)<sub>2</sub> must be added in 5 litre of water to change its pH by 3 units -  
(A) 1.37 gm (B) 0.0185 gm (C) 0.037 gm (D) 1.85 gm
- Q.20** Correct order of the following equimolar (0.1 M) solution in increasing order of pH is -  
(A) CH<sub>3</sub>COOH < NH<sub>4</sub>OH < Ca(OH)<sub>2</sub> < H<sub>2</sub>S < H<sub>2</sub>O  
(B) CH<sub>3</sub>COOH < H<sub>2</sub>S < H<sub>2</sub>O < Ca(OH)<sub>2</sub> < NH<sub>4</sub>OH