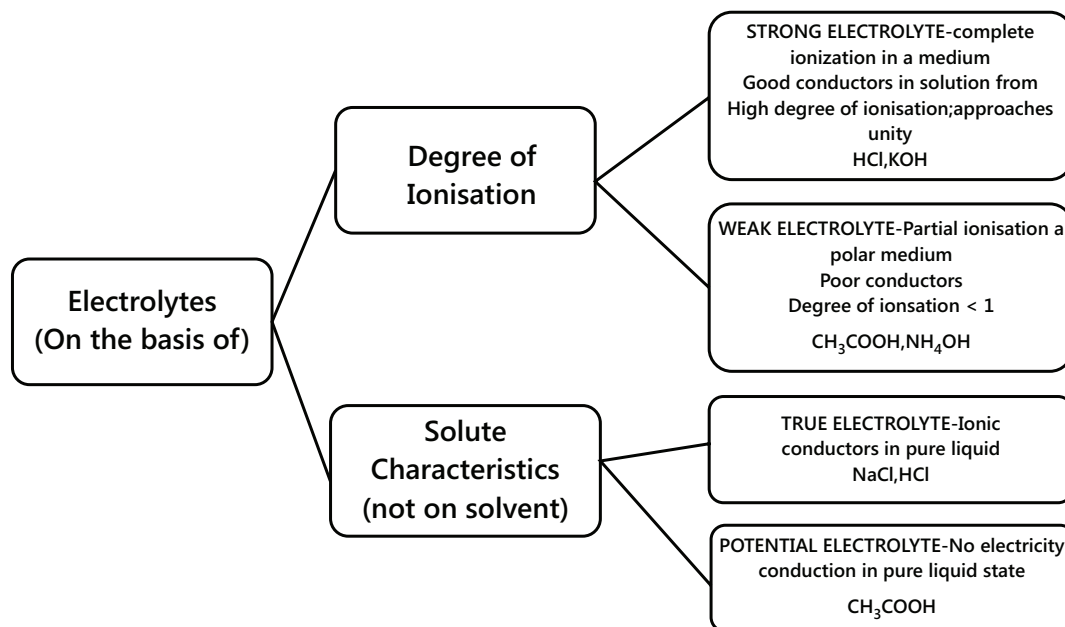


# 6. IONIC EQUILIBRIUM

## 1. INTRODUCTION

### 1.1 What is an Electrolyte?

Compounds which supply ions, either in the molten state or in a solution are called electrolytes. In the solid state, they are bad conductors of electricity, which, become good conductors either in the molten state or in a solution.



Flowchart 6.1: Classification of electrolyte

\* Substances which on dissolution in water form non- conducting liquids are called non-electrolytes, urea, glucose, etc.

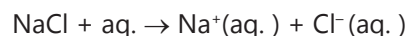
### 1.2 Dissociation and Ionization

#### Dissociation

(a) A reversible decomposition is called dissociation, e.g.,  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$

(b) Formation of ions by a weak electrolyte is also called dissociation. e.g.  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

**Ionization:** Separation of ions either on fusion or dissolution is called ionization



## PLANCESS CONCEPTS

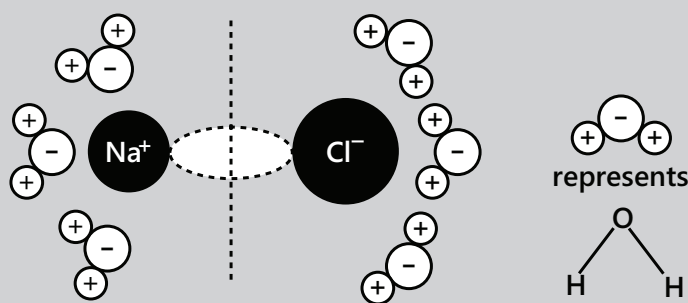
- **Misconception:** The two terms ionisation and dissociation often appears confusing.

When an ionic compound is dissolved in water, the ions which are already present in the solid compound separate out this process is known as dissociation. Whereas, when a neutral molecule like HCl (i. e. a polar covalent compound) which does not contain ions is dissolved in water, splits to produce ions in the solution, the process is called ionization. However, generally the two terms are used without any difference.

Also, note that the general term used for weak electrolyte is dissociation and strong electrolyte is ionization.

- **How does dissociation occur?**

An ionic compound is a cluster of positively and negatively charged ions held together by electrostatic forces of attraction. When such an ionic compound is put into water, the high dielectric constant of water (i. e., 80) reduces the electrostatic forces of attraction (to 1/80th). Thus, ions become free to move in the solution. For NaCl solid, the situation may be represented as shown in the Figure.



**Figure 6.1** :Dissociation of NaCl in water

- **Key Note:** In the case of weak electrolytes, the extent of ionization depends on the strength of the bond and the extent of solvation of ions produced.

**Vaibhav Krishnan (JEE 2009, AIR 22)**

### 1.3 Factors Influencing Degree of Dissociation

The extent of dissociation of a substance is expressed in terms of degree of dissociation. The degree of dissociation of an electrolyte in a solution is given by:

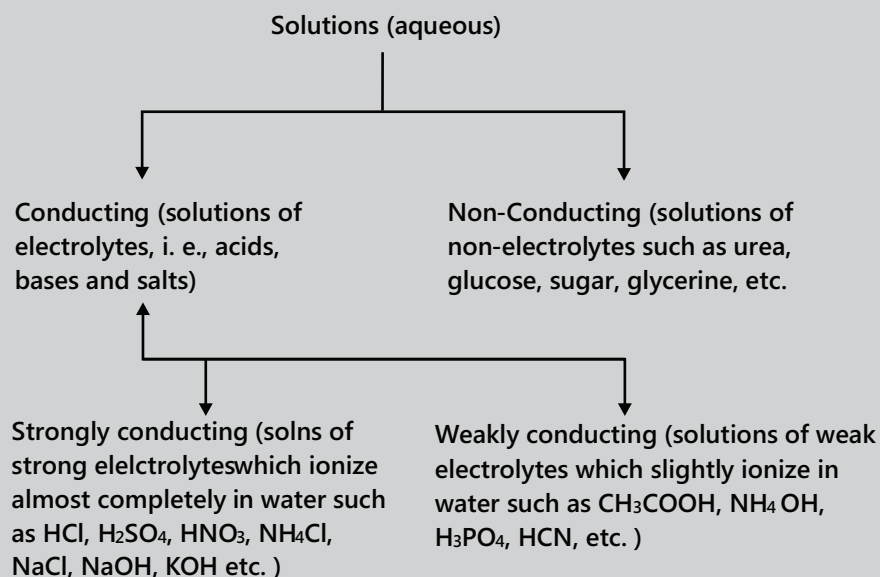
$$\alpha = \frac{\text{Moles dissociated at any time}}{\text{Total moles present or dissolved initially}}$$

The variation of ' $\alpha$ ' of an electrolyte is governed by:

- Nature of solute:** All ionic compounds, i.e. strong electrolytes have  $\alpha \approx 1$  at normal dilution. Most of the polar covalent compounds, i.e. weak electrolytes have  $\alpha \ll 1$ .
- Nature of solvent:** Solvents having a high dielectric constant are themselves feebly ionized, but an electrolyte in a solvent with a high dielectric constant, for instance water shows a higher degree of dissociation than in a solvent of low dielectric constant (say methanol).
- Dilution:** The extent of dissociation of a weak electrolyte increases with the dilution of solution.

- (d) **Temperature:** The extent of dissociation of a weak electrolyte also increases with an increase in temperature.
- (e) **Addition of other species:** The addition of another solute having an ion common to that of a weak electrolyte shows a decrease in the degree of dissociation of a weak electrolyte (see common ion effect).

### PLANCESS CONCEPTS



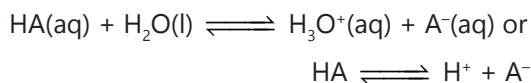
**Flowchart 6.2:** Types of solution

The degree of dissociation of an electrolyte is assumed to be unity at infinite dilution, i. e.,  $\alpha = 1$  at infinite dilution

**Vaibhav Krishnan (JEE 2009, AIR 22)**

## 2. OSTWALD'S DILUTION LAW

This is an application of the law of mass action for a weak electrolyte dissociation equilibria. Consider ionization of a weak electrolyte say a monoprotic acid, HA



Moles before dissociation    1            0        0

Moles after dissociation     $1 - \alpha$              $\alpha$          $\alpha$

Where,  $\alpha$  is degree of dissociation of a weak acid HA. Let ' $c$ ' mol litre<sup>-1</sup> be the concentration of the acid, HA, then,  $[\text{HA}] = c(1 - \alpha)$ ;  $[\text{H}^+] = c\alpha$ ;  $[\text{A}^-] = c\alpha$

According to equilibrium constant expression,

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

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

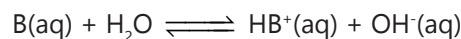
.... (i)

Where,  $K_a$  is the dissociation constant of a weak acid, Since,  $\alpha$  is small for weak electrolytes, thus,  $1 - \alpha \approx 1$

$$\therefore K_a = c\alpha^2 \text{ or } \alpha = \sqrt{\left(\frac{K_a}{c}\right)} = \sqrt{K_a V} \quad \dots (ii)$$

Where,  $V$  is the volume in litre, containing 1 mole of electrolyte. Thus, it may be concluded that the degree of dissociation of a weak electrolyte is inversely proportional to the square root of its concentration.

Similar expression can also be made for a weak base  $B$  or  $BOH$  as



$$\text{Or } BOH \rightleftharpoons B^+ + OH^-; K_b = \frac{c\alpha^2}{(1-\alpha)}$$

$$\text{If } 1 - \alpha \approx 1 \text{ and } K_b = c\alpha^2 \quad \dots (iii)$$

$$\text{or } \alpha = \sqrt{\left(\frac{K_b}{c}\right)} \quad \dots (iv)$$

Where,  $K_b$  is the dissociation constant of a weak base.

Eqs. (i) and (iii) also reveals that when  $c \rightarrow 0$ ,  $(1 - \alpha) \rightarrow 0$ , i. e.  $\alpha$  approaches unity, i. e. at infinite dilution, the whole of the weak electrolyte gets dissociated. This is the Ostwald's dilution law.

### PLANCESS CONCEPTS

Smaller the value of  $K_a$  or  $K_b$ , weaker will be the electrolyte. This can be used to solve objective questions easily & directly. The approximation  $1 - \alpha \approx 1$  can be applied only if  $\alpha < 5\%$ . If on solving a problem by applying approximate formula,  $\alpha$  comes out to be  $\geq 5\%$ , the problem may be solved again by applying exact formula and  $\alpha$  may be calculated by applying solution of a quadratic equation, i. e.  $A =$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{Equation (ii) implies } c\alpha^2 + K\alpha - K = 0)$$

**Misconception:** Generally, it is assumed that Ostwald's Dilution law can be used for any electrolyte. But electrolytes having,  $\alpha \approx 1$ , i. e.,  $K_a \rightarrow \infty$  (from equation (ii)) can be studied.

**Rohit Kumar (JEE 2012, AIR 79)**

## 2.1 Limitations of Ostwald's Dilution Law

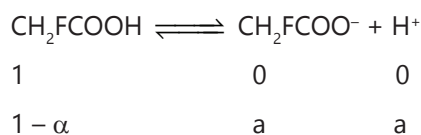
The law is applicable only for weak electrolytes and fails completely in the case of strong electrolytes. The value of ' $\alpha$ ' is determined by conductivity measurements by applying the formula  $\wedge / \wedge_\infty$ .

(i) The law is based on the notion that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilution and  $\wedge / \wedge_\infty$  does not give an accurate value of ' $\alpha$ '

(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, the law of mass action in its simple form cannot be strictly applied in the case of strong electrolytes.

**Illustration 1:** Calculate the conc. of fluoroacetic acid when  $[H^+] = 1.50 \times 10^{-3}$  M.  $K_a$  of acid =  $2.6 \times 10^{-3}$  (**JEE MAIN**)

**Sol:** This problem can be solved using Ostwald's Dilution law. From the given value of hydrogen ion concentration and equilibrium constant calculate degree of dissociation. By using the value of  $\alpha$  determine the concentration of fluoroacetic acid.



Given,  $[H^+] = c\alpha = 1.5 \times 10^{-3}$ ;  $K_a = 2.6 \times 10^{-3}$

Also,  $\therefore K_a = \frac{c\alpha^2}{(1-\alpha)}$

$\therefore 2.6 \times 10^{-3} = \frac{1.5 \times 10^{-3} \cdot \alpha}{(1-\alpha)}$  [See  $\alpha$  is not small]

$\therefore \alpha = 0.634$

$\therefore c\alpha = 1.5 \times 10^{-3}$

$\therefore c = \frac{1.5 \times 10^{-3}}{0.634} = 2.37 \times 10^{-3}$  M

**Illustration 2:** At  $30^\circ\text{C}$ , the degree of dissociation of 0.006 M HA is 0.0145. What would be the degree of dissociation of 0.02 M solution of the acid at the same temperature? (**JEE MAIN**)

**Sol:** Solve the problem using Ostwald dilution law. Use the expression relating degree of dissociation and concentration.

Let the ionization constant of the acid be  $K_a$ . Degree of dissociation of 0.066 M concentration = 0.0145.

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

$0.0145 = \sqrt{\frac{K_a}{0.066}}$  .... (i)

Let the degree of dissociation of the acid at 0.02 M concentration be  $\alpha_1$ .

$\alpha_1 = \sqrt{\frac{K_a}{0.02}}$  .... (ii)

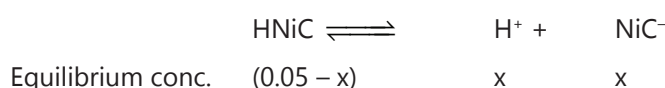
$\therefore (0.0145)^2 \times 0.066 = \alpha_1^2 \times 0.02$

$\therefore \alpha_1 = 0.0145 \times \sqrt{\frac{0.066}{0.02}}$

$\alpha_1 = 0.0263$

**Illustration 3:** Nicotinic acid ( $K_a = 1.4 \times 10^{-5}$ ) is represented by the formula  $\text{HNiC}$ . Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2 litre of solution. (**IIT 1993**)

**Sol:** Initial concentration of the nicotinic acid =  $\frac{0.10}{2} = 0.05 \text{ mol L}^{-1}$



As  $x$  is very small,  $(0.05 - x)$  can be taken as 0.05

$$K_a = \frac{[H^+][NiC^-]}{[HNiC]} = \frac{x \times x}{0.05}$$

$$\text{or } x^2 = (0.05) \times (1.4 \times 10^{-5}) \text{ or } x = 0.83 \times 10^{-3} \text{ mol L}^{-1}$$

$$\% \text{ dissociation} = \frac{0.83 \times 10^{-3}}{0.05} \times 100 = 1.66\%$$

**Alternative method:** Let  $\alpha$  be the degree of dissociation



$$\text{At equilibrium} \quad 0.05(1 - \alpha) \quad 0.05\alpha \quad 0.05\alpha$$

$$K_a = \frac{0.05\alpha \times 0.05\alpha}{0.05(1 - \alpha)}$$

As  $\alpha$  is very small,  $(1 - \alpha) \rightarrow 1$

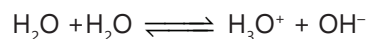
$$\text{So, } 1.4 \times 10^{-5} = 0.05\alpha^2$$

$$\text{Or } \alpha = \sqrt{\frac{1.4 \times 10^{-5}}{0.05}} = 1.67 \times 10^{-2}$$

$$\text{Percent dissociation} = 100 \times \alpha = 100 \times 1.67 \times 10^{-2} = 1.67\%$$

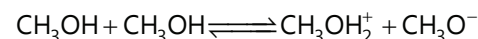
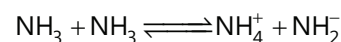
## 2.2 Phenomenon of Autoprotolysis

Water shows autoprotolysis as:

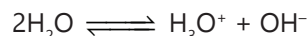
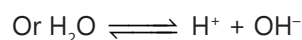


The phenomenon of self-ionisation is called autoprotolysis.

Many liquids are likely to undergo autoprotolysis like  $H_2O$ , e.g.,



The autoprotolysis is confirmed by the conducting nature of solvents in a pure state, although its molecular formula does not indicate the presence of ions in its molecule. Pure water is a weak electrolyte and dissociates as



$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_w = [H^+][OH^-] \quad \dots (7)$$

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

$$\therefore \text{By eq. (7), } [H^+]^2 = K_w = 10^{-14} \text{ } ([H^+] = [OH^-] = 10^{-7} \text{ M at } 25^\circ\text{C})$$

$$\therefore [H^+] = 10^{-7} \text{ or } \alpha = 10^{-7}$$

Since, concentration or molarity of  $H_2O = 55.6$

$$\therefore \alpha = \frac{10^{-7}}{55.6} = \frac{1}{(55.6 \times 10^6)} = 1.8 \times 10^{-9}$$

$$\text{Thus, } K_{eq} = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.6} = 1.79 \times 10^{-16}$$

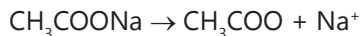
### 3. COMMON ION EFFECT

The phenomenon in which the degree of dissociation of a weak electrolyte is suppressed by the addition of a strong electrolyte having an ion common to weak electrolyte is known as common ion effect. Consider dissociation of a weak electrolyte, say, acetic acid.

$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$  The equilibrium constant,  $K_a$  is given by:

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

Now, suppose sodium acetate is added to this solution.



The concentration of  $\text{CH}_3\text{COO}^-$  in the solution increases and thus, in order to have  $K_a$  constant,  $[\text{H}^+]$  must decrease or the concentration of undissociated acetic acid must increase. In other words, the dissociation of acetic acid is suppressed on addition of  $\text{CH}_3\text{COONa}$  to its solution. Similar results are obtained on addition of HCl to acetic acid solution, this time  $\text{H}^+$  provided by HCl acts as common ion.

**Illustration 4:** Liquid ammonia ionises to a slight extent. At  $-50^\circ\text{C}$ , its ionisation constant,  $K_b = K_{\text{NH}_3} = [\text{NH}_4^+][\text{NH}_2^-] = 10^{-30}$ . How many amide ions, are present per  $\text{cm}^3$  of pure liquid ammonia? Assume  $N = 6.0 \times 10^{23}$ .

(JEE MAIN)

**Sol:**  $2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$  (self-ionisation)

and  $K_{\text{NH}_3} = [\text{NH}_4^+][\text{NH}_2^-]$

$$\therefore [\text{NH}_4^+] = [\text{NH}_2^-]$$

$$\therefore [\text{NH}_2^-] = \sqrt{K_{\text{NH}_3}} = \sqrt{10^{-30}} = 10^{-15}\text{M}$$

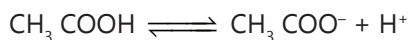
Number of amide ions in  $10^3\text{cm}^3 = 10^{-15} \times 6 \times 10^{23}$

$$\therefore \text{Number of amide ions in } 1\text{ cm}^3 = \frac{10^{-15} \times 6 \times 10^{23}}{10^3} = 6 \times 10^5 \text{ ions}$$

**Illustration 5:** What is the  $\text{H}^+$  ion concentration of a solution known to contain 0.1 g mole of  $\text{CH}_3\text{COONH}_4$  in one litre of 0.1 M  $\text{CH}_3\text{COOH}$ ? Assume effective ionisation of ammonium acetate is 80%.  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .

(JEE MAIN)

**Sol:** Write down the complete reaction for dissociation of acetic acid and expression for equilibrium constant. By using Ostwald's dilution law determine the hydrogen ion concentration.



(0.1 - x)                      x                      x

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

The solution also contains  $\text{CH}_3\text{COONH}_4$  which is 80% dissociated i. e.  $\alpha = 0.8$ . Thus, the acetate concentration provided by 0.1 M  $\text{CH}_3\text{COONH}_4 = 0.1 \times 0.8 = 0.08\text{ M}$

Total  $[\text{CH}_3\text{COO}^-] = (0.08 + x)\text{ M}$

$$\text{So, } K_a = \frac{(0.08 + x)x}{(0.1 - x)}$$

As  $x$  is very small,  $(0.1 - x) \rightarrow 0.1$  and neglecting  $x^2$ ,

$$K_a = \frac{0.08x}{0.1} \text{ or } 1.8 \times 10^{-5} \times 0.1 = 0.08x$$

$$\text{or } x = [\text{H}^+] = \frac{1.8 \times 10^{-5} \times 0.1}{0.08} = 2.25 \times 10^{-5} \text{ mol L}^{-1}$$

**Illustration 6:** The ionisation constant for pure formic acid,  $K = [\text{HCOOH}_2^+][\text{HCOO}^-]$  has been estimated as  $10^{-6}$  at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is  $1.22 \text{ g/cm}^3$ . **(JEE ADVANCED)**

**Sol:** We are asked to find out the % dissociation of formic acid. The density of acetic acid is provided so from density determine the weight of acetic acid in 1 litre solution. By using weight and molecular weight relation find out the initial molarity of the solution.

According to definition,  $\alpha = \frac{\text{Moles dissociated at any time}}{\text{Total moles present or dissolved initially}}$

Given density of formic acid =  $1.22 \text{ g/cm}^3$

$\therefore$  Weight of formic acid in 1 litre solution =  $1.22 \times 10^3 \text{ g}$

$$\text{Thus, } [\text{HCOOH}] = \frac{1.22 \times 10^3}{46} = 26.5 \text{ M}$$

Since, in case of auto ionization,

$$[\text{HCOOH}_2^+] = [\text{HCOO}^-]$$

$$\text{and } [\text{HCOO}^-][\text{HCOOH}_2^+] = 10^{-6}$$

$$\therefore [\text{HCOO}^-] = 10^{-3}$$

$$\text{Now, \% dissociation of HCOOH} = \frac{[\text{HCOO}^-] \times 100}{[\text{HCOOH}]} = \frac{10^{-3}}{26.5} \times 100 = 0.004\%$$

**Illustration 7:** A solution contains  $0.1 \text{ M H}_2\text{S}$  and  $0.3 \text{ M HCl}$ . Calculate the concentration of  $\text{S}^{2-}$  and  $\text{HS}^-$  ions in solution. Given,  $K_{a1}$  and  $K_{a2}$  for  $\text{H}_2\text{S}$  are  $10^{-7}$  and  $1.3 \times 10^{-13}$  respectively. **(JEE ADVANCED)**

**Sol:**  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$

$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \dots (i)$$

Further  $\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$

$$K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \quad \dots (ii)$$

Multiplying both the equations

$$K_{a1} \times K_{a2} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

Due to common ion, the ionization of  $\text{H}_2\text{S}$  is suppressed and the  $[\text{H}^+]$  in solution is due to the presence of  $0.3 \text{ M HCl}$ .

$$[\text{S}^{2-}] = \frac{K_{a1} \times K_{a2} [\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{1.0 \times 10^{-7} \times 1.3 \times 10^{-13} \times (0.1)}{(0.3)^2} = 1.44 \times 10^{-20} \text{ M}$$



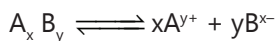
Putting the value of  $[S^{2-}]$  in eq. (ii)

$$1.3 \times 10^{-13} = \frac{0.3 \times 1.44 \times 10^{-20}}{[HS^-]} \text{ or } [HS^-] = \frac{0.3 \times 1.44 \times 10^{-20}}{1.3 \times 10^{-13}} = 3.3 \times 10^{-8} \text{ M}$$

## 4. SOLUBILITY PRODUCT

When a solute is added gradually to an amount of solvent, at a particular temperature, there comes a point when no more solute can be dissolved. This point gives a saturated solution. A solution which remains in contact with undissolved solute is said to be saturated. At the saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

Consider in general, the electrolyte of the type  $A_x B_y$  which is dissociated as:



Applying law of mass action,  $\frac{[A^{y+}]^x [B^{x-}]^y}{[A_x B_y]} = K$

When the solution is saturated,

$$[A_x B_y] = K' \text{ (constant)}$$

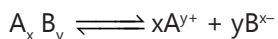
$$\text{Or } [A^{y+}]^x [B^{x-}]^y = K[A_x B_y] = KK' = K_{sp} \text{ (constant)}$$

Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times, the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

### 4.1 Relationship between Solubility and Solubility Product

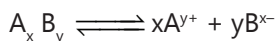
Salts like AgI,  $BaSO_4$ ,  $PbSO_4$ ,  $PbI_2$ , etc.. are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolytes contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, i. e., it is completely dissociated.

The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:



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

Let 'S' mol litre<sup>-1</sup> be the solubility of the salt; then



$xS.yS$

$$\text{So, } K_{sp} = [xS]^x [yS]^y = x^x \cdot y^y (S)^{x+y}$$

#### Special Cases:

(i) 1: 1 type salts: Examples: AgCl, AgI,  $BaSO_4$ ,  $PbSO_4$ , etc.

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

(ii) 1: 2 or 2: 1 type salts: Examples:  $Ag_2CO_3$ ,  $Ag_2CrO_4$ ,  $PbCl_2$ ,  $CaF_2$ , etc.

$$S = \sqrt[3]{K_{sp} / 4}$$

(iii) 1: 3 type salts: Examples:  $\text{AlI}_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ , etc.

$$S = \sqrt[4]{K_{sp} / 27}$$

### PLANCESS CONCEPTS

The presence of a common ion affects the solubility of a salt. Let AB be a sparingly soluble salt in solution and A'B be added to it. Let S and S' be the solubilities of the salt AB before and after addition of the electrolyte A'B. Let c be the concentration of A'B.

Before addition of A'B,  $K_{sp} = S^2$  ..... (i)

After addition of A'B, the concentration of  $\text{A}^+$  and  $\text{B}^-$  ions become S' and  $(S' + c)$ , respectively.

So,  $K_{sp} = S'(S' + c)$  ..... (ii)

Equating (i) and (ii),

$$S^2 = S'(S' + c)$$

**T P Varun (JEE 2012, AIR 64)**

## 4.2 Simultaneous Solubility

The solubility of two electrolytes having a common ion; when they are dissolved in the same solution, is called simultaneous solubility, e.g.

(i) Solubility of AgBr and AgSCN, when dissolved together.

(ii) Solubility of  $\text{CaF}_2$  and  $\text{SrF}_2$ , when dissolved together.

(iii) Solubility of  $\text{MgF}_2$  and  $\text{CaF}_2$ , when dissolved together.

Calculation of simultaneous solubility is divided into two cases:

**Case I:** When the two electrolytes are almost equally strong (having close solubility product), e.g.,

AgBr ( $K_{sp} = 5 \times 10^{-13}$ ); AgSCN ( $K_{sp} = 10^{-12}$ )

**Case II:** When solubility products of two electrolytes are not close, i. e., they are not equally strong, e.g.

$\text{CaF}_2$  ( $K_{sp} = 3.4 \times 10^{-11}$ );  $\text{SrF}_2$  ( $K_{sp} = 2.9 \times 10^{-9}$ )

Most of fluoride ions come from stronger electrolyte.

### PLANCESS CONCEPTS

- It must be noted that hydration of molecule doesn't influence  $K_{sp}$
- $K_{sp}$  of a hydrated molecule say  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  can be given by  $K_{sp} = [\text{Na}^+]^2[\text{CO}_3^{2-}]$

**Aishwarya Karnawat (JEE 2012, AIR 839)**

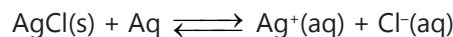
**Illustration 8:**  $K_{sp}$  of AgCl is  $2.8 \times 10^{-10}$  at  $25^\circ\text{C}$ . Calculate solubility of AgCl in

(i) Pure water (ii) 0.1 M  $\text{AgNO}_3$ . (iii) 0.1 M NaCl.

**Sol:** Solubility and Solubility product are related by the expression,  $S = \sqrt{K_{sp}}$

second and third example contains common ion, hence for these example we can use the expression,  $K_{sp} = S'(S' + c)$

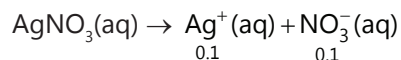
**(i) In pure water:** Let solubility of AgCl be  $S$  mol litre<sup>-1</sup>



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

$$\text{Or } S = \sqrt{K_{sp}} = \sqrt{(2.8 \times 10^{-10})} = 1.673 \times 10^{-5} \text{ mol litre}^{-1}$$

**(ii) In 0.1 M AgNO<sub>3</sub>:**  $\text{AgCl(s)} + \text{Aq} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$



$$\therefore K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (0.1 + S)(S)$$

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

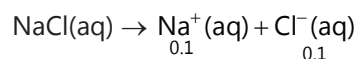
$$\therefore S \lll 0.1, [\text{Ag}^+] = 0.1 \text{ M}$$

$\therefore S \lll 0.1$  since solubility decreases in presence of common ion

$$\therefore S \times 0.1 = 2.8 \times 10^{-10}$$

$$\text{or } S = 2.8 \times 10^{-9} \text{ mol litre}^{-1}$$

**(iii) In 0.1 M NaCl:**  $\text{AgCl(s)} + \underset{S}{\text{Aq}} \rightleftharpoons \underset{S}{\text{Ag}^+} + \text{Cl}^-$



$$\therefore K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (0.1 + S)(S)$$

$$\text{Here, } [\text{Cl}^-] = 0.1 + s \text{ but } s \lll 0.1$$

$$\therefore [\text{Cl}^-] = 0.1 \text{ M}$$

$$\therefore S \lll 0.1$$

$$\therefore S \times 0.1 = 2.8 \times 10^{-10}$$

$$\therefore S = 2.8 \times 10^{-9} \text{ mol litre}^{-1}$$

**Illustration 9:** Equal volumes of 0.02 M CaCl<sub>2</sub> and 0.0004 M Na<sub>2</sub>SO<sub>4</sub> are mixed. Will a precipitate be formed?  $K_{sp}$  for CaSO<sub>4</sub> =  $2.4 \times 10^{-5}$  **(JEE MAIN)**

**Sol:** Assuming volume of 0.02 M CaCl<sub>2</sub> soln = volume of 0.0004 M Na<sub>2</sub>SO<sub>4</sub> = VL.

$$\therefore \text{no. of moles of Ca}^{2+} = 0.02 V \text{ and}$$

$$\text{No. of moles of SO}_4^{2-} = 0.0004 V$$

$$\therefore [\text{Ca}^{2+}] = \frac{0.02V}{2V} = 0.01 \text{ mol litre}^{-1}$$

$$[\text{SO}_4^{2-}] = \frac{0.0004V}{2V} = 0.0002 \text{ mol litre}^{-1}$$

$$\therefore [\text{Ca}^{2+}][\text{SO}_4^{2-}] = [0.01][0.0002] = 2 \times 10^{-6}$$

Thus,  $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$  in solution  $< K_{sp}$  [Here Ionic product  $< K_{sp}$ ]

$$(\because 2 \times 10^{-6} < 2.4 \times 10^{-5})$$

$\therefore \text{CaSO}_4$  will not precipitate.

**Illustration 10:** What  $[\text{H}_3\text{O}^+]$  must be maintained in a saturated  $\text{H}_2\text{S}$  solution to precipitate  $\text{Pb}^{2+}$ , but not  $\text{Zn}^{2+}$  from a solution in which each ion is present at a concentration of 0.1 M?

( $K_{\text{sp}}$  for  $\text{H}_2\text{S} = 1.1 \times 10^{-22}$ ,  $K_{\text{sp}}$  for  $\text{ZnS} = 1.0 \times 10^{-21}$ ).

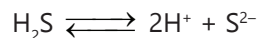
**(JEE ADVANCED)**

**Sol:** For  $\text{ZnS}$  not to be precipitated from a solution of  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$

$$[\text{Zn}^{2+}][\text{S}^{2-}] < K_{\text{sp}} \text{ of } \text{ZnS}$$

$$[10^{-2}][\text{S}^{2-}] < 1.0 \times 10^{-21}$$

Or the maximum  $[\text{S}^{2-}] = 10^{-19}$  at which  $\text{ZnS}$  will begin to precipitate or upto this concentration, no precipitation will occur.



$$\therefore [\text{H}^+]^2 [\text{S}^{2-}] = 1.1 \times 10^{-22} \therefore [\text{H}^+]^2 [10^{-19}] = 1.1 \times 10^{-22}$$

$$\therefore [\text{H}^+]^2 = 11 \times 10^{-4} \therefore [\text{H}^+] = 3.3 \times 10^{-2} \text{ M}$$

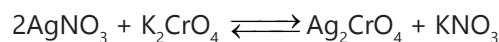
Thus, if  $[\text{H}^+] = 3.3 \times 10^{-2}$  or slightly higher, the precipitation of  $\text{ZnS}$  will not take place and only  $\text{PbS}$  will precipitate.

**Illustration 11:** 25 mL of 0.10 M  $\text{AgNO}_3$  are mixed with 35 mL of 0.05 M  $\text{K}_2\text{CrO}_4$  solution. Calculate (a) The concentration of each ionic species at equilibrium (b) Is the precipitation of silver quantitative ( $> 99.9\%$ )?  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4 = 1.1 \times 10^{-12}$ .

**(JEE ADVANCED)**

**Sol:** First calculate the  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4$  in solution in order to check whether precipitation will occur or not on mixing.

As concentration of solution and volume term is given concentration of each ionic species at equilibrium can be determined easily.



Millimoles at equilibrium =  $25 \times 0.1$  &  $35 \times 0.5$  respectively.

= 2.5 & 1.75

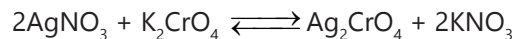
Let us first see whether precipitation occurs or not on mixing.

$$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = K_{\text{sp}} = 1.1 \times 10^{-12}$$

Also after mixing

$$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = \left[ \frac{2.5}{60} \right]^2 \left[ \frac{1.75}{60} \right] = 5.06 \times 10^{-5} > K_{\text{sp}}$$

Thus, precipitation will take place



Millimoles before mixing = 2.5 & 1.75 respectively

Millimoles after mixing =  $(1.75 - 1.25) = 0.50$  & 2.25 respectively.

$$\text{Now, } [\text{K}^+] = \frac{1.25}{60} = 0.0208$$

$$[\text{NO}_3^-] = \frac{2.5}{60} = 0.0417 \text{ M}$$

$$[\text{CrO}_4^{2-}] = \frac{0.5}{60} = 0.0083 \text{ M}$$

Let solubility of  $\text{Ag}_2\text{CrO}_4$  be  $S$  mol litre $^{-1}$ , then

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

$$1.1 \times 10^{-12} = (2s)^2 \times (0.0083)$$

$$\therefore s = 5.8 \times 10^{-6}$$

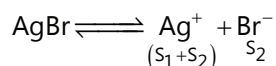
$$\text{Or } [\text{Ag}^+] = 2 \times 5.8 \times 10^{-6} = 1.16 \times 10^{-5} \text{ M}$$

$$\text{The \% of Ag precipitated} = \frac{2.5 - (60 \times 1.16 \times 10^{-5})}{2.5} \times 100 = 99.97\%$$

i.e. precipitation is quantitative.

**Illustration 12:**  $K_{sp}$  of AgCl and AgBr are  $1.0 \times 10^{-10}$  and  $5.0 \times 10^{-13}$ . Calculate the simultaneous solubility of AgCl and AgBr in water. **(JEE ADVANCED)**

**Sol:**  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$  Let solubility of AgCl and AgBr be  $S_1, S_2$  mol litre<sup>-1</sup>  
 $(S_1 + S_2) \quad S_1$



$$\therefore \frac{K_{sp} \text{ AgCl}}{K_{sp} \text{ AgBr}} = \frac{S_1(S_1 + S_2)}{S_2(S_1 + S_2)}$$

$$\therefore \frac{S_1}{S_2} = \frac{1.0 \times 10^{-10}}{5.0 \times 10^{-13}} = 200$$

$$\text{Now, } K_{sp}(\text{AgCl}) = S_1(S_1 + S_2)$$

$$\frac{S_1}{S_2} = 200 \quad S_2 = \frac{S_1}{200}$$

$$\frac{S_1}{S_2} = 200, \quad S_2 = \frac{S_1}{200}$$

$$\text{Or } 1 \times 10^{-10} = S_1 \left( S_1 + \frac{S_1}{200} \right)$$

$$\therefore \frac{201}{200} S_1^2 = 1 \times 10^{-10}$$

$$\therefore S_1 = 9.98 \times 10^{-6} \text{ M}$$

$$\text{And } S_2 = \frac{9.98 \times 10^{-6}}{200} = 4.99 \times 10^{-8} \text{ M}$$

### 4.3 Selective Precipitation

The phenomenon involving the precipitation of sparingly soluble species one by one on the addition of a precipitating reagent in a solution of two or more soluble compounds is known as selective precipitation. The principle of a selective precipitation is of much importance in the qualitative and quantitative aspects of chemistry.

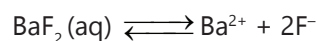
For example, a solution contains  $\text{CaCl}_2$  and  $\text{BaCl}_2$ . If we add  $\text{Na}_2\text{SO}_4$  to this solution slowly and slowly, we can first precipitate the sulphate of Ba (on the basis of  $K_{sp}$  values of  $\text{CaSO}_4$  and  $\text{BaSO}_4$  which are  $2 \times 10^{-4}$  and  $1.5 \times 10^{-9}$  respectively).

This is due to the fact that as we go on adding  $\text{Na}_2\text{SO}_4$ , the concentration of  $\text{SO}_4^{2-}$  ion increases and since  $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{sp}$ , the lower value is attained first.

## 4.4 Solubility of Salts in the Presence of an Acid or Base

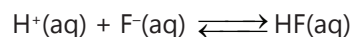
The solubility of salts is greatly influenced by the presence of acids or bases.

For example,  $\text{BaF}_2(\text{aq})$



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

In an acidic medium, the higher  $[\text{H}^+]$  shifts the equilibrium from left to right:



As  $[\text{F}^-]$  decreases,  $[\text{Ba}^{2+}]$  increases to maintain the equilibrium.

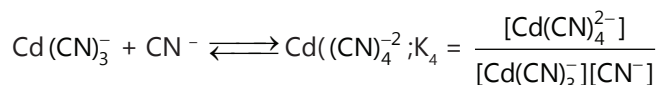
## 4.5 Stability Constant

Let us consider dissociation of the ion,  $\text{FeBr}^+$ ,  $\text{FeBr}^+ \rightleftharpoons \text{Fe}^{2+} + \text{Br}^-$

Dissociation constant for above the equilibria may be given as:  $K_d = \frac{[\text{Fe}^{2+}][\text{Br}^-]}{[\text{FeBr}^+]}$

Reciprocal of dissociation constant is called stability constant.  $K_s = \frac{[\text{FeBr}^+]}{[\text{Fe}^{2+}][\text{Br}^-]}$

Let us consider the formation of a complex  $\text{K}_2\text{Cd}(\text{CN})_4$ . Complex ion is  $\text{Cd}(\text{CN})_4^{2-}$  where the oxidation state of a central metal  $\text{Cd}^{2+}$  is (+2). The complexing process proceeds in four steps as:



Overall reaction may be given as:  $\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cd}(\text{CN})_4^{2-}]; K_5 = \frac{[\text{Cd}(\text{CN})_4^{2-}]}{[\text{Cd}^{2+}][\text{CN}^-]^4}$

Here,  $K_5 = K_1 K_2 K_3 K_4$

### PLANCESS CONCEPTS

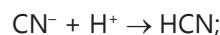
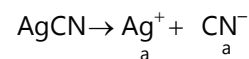
- (a) Greater the stability constant, more stable is the compound.
- (b) (i) If on the addition of a common ion in a bait solution (sparingly soluble), formation of a complex ion takes place, then ionization increases, i. e.. Equilibrium shifts towards the right hand direction to maintain the value of  $K_{\text{sp}}$  constant. It means, addition of a common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the CONCEPTS of the common ion effect.
- (ii) When we add an electrolyte to another electrolyte solution having no common ion, then the ionisation of the latter increases.
- (iii) For a given electrolyte, solubility product is always constant at a particular temperature

## 4.6 Application of Solubility Product

- (a) **In the purification of common salt:** A saturated solution of NaCl leads to precipitation of NaCl on passing HCl gas through it. An increase in  $[Cl^-]$ , shifts the equilibrium,  $NaCl(s) \rightleftharpoons Na^+ + Cl^-$  to backward direction because of higher ionic product concentration, i. e.,  $[Na^+][Cl^-] > K_{sp}$ .
- (b) **In the preparation of  $NaHCO_3$ :** The precipitation of  $NaHCO_3$  from its saturated solution in Solvay's ammonia soda process from its saturated solution is made by the addition of  $NH_4HCO_3$ .
- (c) **Predicting precipitation in ionic reactions:** During an ionic reaction, the product's precipitation can be predicted when the product of ionic concentration of solute exceeds its  $K_{sp}$ .
- (d) **Salting out action of soap:** A saturated solution of soap ( $RCOONa$ ), the sodium salt of higher fatty acids show precipitation of soap on the addition of sodium chloride. This is because of the fact that an increase in  $Na^+$  ion concentration helps in crossing over  $[Na^+][RCOO^-]$  to their  $K_{sp}$  value.
- (e) **In Qualitative Analysis:** The Qualitative analysis of a mixture is based on the principle of solubility product.

**Illustration 13:** Calculate the solubility of  $AgCN$  in 1 M  $HNO_3$  if  $K_{sp AgCN} = 1.2 \times 10^{-16}$  and  $K_a(HCN) = 6.2 \times 10^{-10}$  **(JEE MAIN)**

**Sol:** Let solubility of  $AgCN$  be 'a' mol/lit



$$K_{aHCN} = \frac{[H^+][CN^-]}{[HCN]}$$

$$\therefore [CN^-] = \frac{K_{aHCN} \times [HCN]}{[H^+]}$$

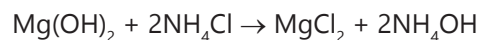
$$\therefore K_{sp AgCN} = [Ag^+][CN^-] = \frac{a \times K_{aHCN} \times [HCN]}{[H^+]}$$

$$1.2 \times 10^{-16} = \frac{a \times 6.2 \times 10^{-10} \times a}{(1-a)} \quad (1-a \approx 1)$$

$$\therefore a = \sqrt{\frac{1.2 \times 10^{-16}}{6.2 \times 10^{-10}}} = 4.39 \times 10^{-4}$$

**Illustration 14:**  $Mg(OH)_2$  is soluble in  $NH_4Cl$  and not in  $NaCl$ . Why? **(JEE MAIN)**

**Sol:** Addition of  $NH_4Cl$  to  $Mg(OH)_2$  brings in interaction:



The  $NH_4OH$  being a weak base reduces the  $OH^-$  in solution and thus product of  $[Mg^{2+}]$  and  $[OH^-]^2$  remains lower than  $K_{sp}$  of  $Mg(OH)_2$  to give no precipitation of  $Mg(OH)_2$ . On the other hand, interaction of  $NaCl$  with  $Mg(OH)_2$  gives strong alkali  $NaOH$  and the product of  $[Mg^{2+}]$  and  $[OH^-]^2$  exceeds their  $K_{sp}$  to show precipitation.

**Illustration 15:** 0.01 mole of  $AgNO_3$  is added to 1 litre of a solution which is 0.1 M in  $Na_2CrO_4$  and 0.005 M in  $NaIO_3$ . Calculate the mole of precipitate formed at equilibrium and the concentrations of  $Ag^+$ ,  $IO_3^-$  and  $CrO_4^{2-}$  ( $K_{sp}$  values of  $Ag_2CrO_4$  and  $AgIO_3$  are  $10^{-8}$  and  $10^{-13}$  respectively) **(JEE ADVANCED)**

**Sol:** From the given values of  $K_{sp}$  of  $[Ag^+][IO_3^-]$  and  $[Ag^+][CrO_4^{2-}]$  in solution first determine the  $[Ag^+]_{needed}$  and  $[CrO_4^{2-}]$  left in solution.

Remaining concentration  $[Ag^+]_{\text{left}} [IO_3^-]_{\text{left}}$  can be determined as,  $[A^+]_{\text{left}} = \frac{K_{sp}[AB]}{[B^-]}$

The  $K_{sp}$  values of  $Ag_2CrO_4$  and  $AgIO_3$  reveals that  $CrO_4^{2-}$  and  $IO_3^-$  will be precipitated on addition of  $AgNO_3$  as:

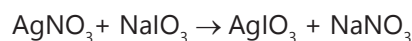
$$[Ag^+][IO_3^-] = 10^{-13}$$

$$[Ag^+]_{\text{needed}} = \frac{10^{-13}}{[0.005]} = 2 \times 10^{-11}$$

$$[Ag^{+2}][CrO_4^{2-}] = 10^{-8}$$

$$[Ag^+]_{\text{needed}} = \sqrt{\frac{10^{-8}}{0.1}} = 3.16 \times 10^{-4}$$

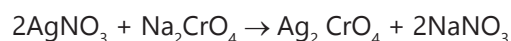
Thus,  $AgIO_3$  will be precipitated first. Now, in order to precipitate  $AgIO_3$ , one can show:



$$0.01 \quad 0.005 \quad 0 \quad 0$$

$$0.005 \quad 0 \quad 0.005 \quad 0.005$$

The left mole of  $AgNO_3$  are now used to precipitate  $Ag_2CrO_4$



$$0.005 \quad 0.01 \quad 0 \quad 0$$

$$0 \quad 0.0975 \quad 0.0025 \quad 0.005$$

Thus,  $[CrO_4^{2-}]$  left in solution = 0.0975

Now, solution has  $AgIO_3(s) + Ag_2CrO_4(s) + CrO_4^{2-}$  ions

$$0.005 \quad 0.0025 \quad 0.0975$$

$$\therefore [Ag^+]_{\text{left}} = \frac{K_{sp Ag_2CrO_4}}{[CrO_4^{2-}]} = \sqrt{\frac{10^{-8}}{0.0975}} = 3.2 \times 10^{-4} \text{ M}$$

$$\therefore [IO_3^-]_{\text{left}} = \frac{K_{sp AgIO_3}}{[Ag^+]} = \frac{10^{-13}}{3.2 \times 10^{-4}} = 3.1 \times 10^{-10} \text{ M}$$

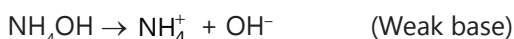
## 5. ACIDS AND BASES

### 5.1 Arrhenius Concept

(a) An Arrhenius acid is a substance which furnishes the hydrogen ion ( $H^+$  ions) in an aqueous solution, e.g.



(b) An Arrhenius base is a substance which furnishes the hydroxyl ( $OH^-$ ) ions in an aqueous solution, e.g.

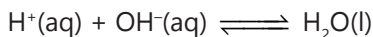


(c) The strength of an acid or a base depends upon its tendency to furnish  $H^+$  or  $OH^-$  ions in the solution respectively.

(d) Water is amphoteric because it furnishes both  $H^+$  and  $OH^-$  ions in the solution  $H_2O \rightleftharpoons H^+ + OH^-$



- (e) The neutralization of an acid and base is basically a neutralization reaction between  $\text{H}^+$  and  $\text{OH}^-$  ions.

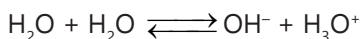


#### Limitations of Arrhenius Concept:

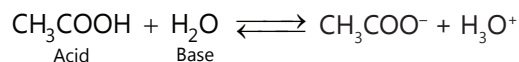
- (a) It fails to explain the behaviour of acids and bases in non-aqueous solvents.
- (b) It fails to explain the neutralisation reactions giving rise to salt formation in the absence of a solvent  
e.g.  $\text{CO}_2 + \text{CaO} \rightarrow \text{CaCO}_3$ ;  $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{g})$  or (s)
- (c) It fails to explain the acidic character of certain salts, e.g.,  $\text{AlCl}_3$ ,  $\text{BF}_3$ , etc., and the basic character of  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{Na}_2\text{CO}_3$ , etc. Neither  $\text{AlCl}_3$  nor  $\text{BF}_3$  on dissolution in water directly produces a proton. Similarly, when  $\text{Na}_2\text{CO}_3$  is dissolved in water, it neutralises an acid but  $\text{Na}_2\text{CO}_3$  cannot dissociate itself directly to produce hydroxyl ions.
- (d) It fails to explain the fact that the  $\text{H}^+$  ion exists in water as  $\text{H}_3\text{O}^+$ , i. e., hydronium ion. Since  $\text{H}^+$  is the simplest and smallest ion and thus, possesses strong tendency of hydration (hydration energy of  $\text{H}^+$  is  $-256 \text{ kcal mol}^{-1}$ ).

## 5.2 Bronsted Lowry Concept

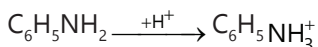
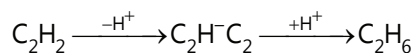
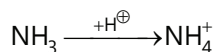
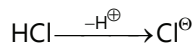
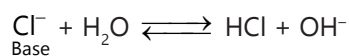
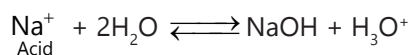
- (a) A Bronsted acid is proton donor whereas, a Bronsted base is proton acceptor.
- (b) The strength of acids and bases depends upon their tendency to donate or accept protons respectively.
- (c) Water is amphoteric because it donates as well as accepts proton.



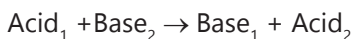
- (d) The proton donated by an acid is not capable of a separate existence and is always solvated.



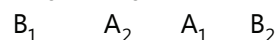
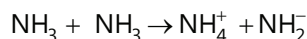
- (e) Each cation behaves as an acid and each anion behaves as base. However, some of them behave as amphoteric by nature.



According to Bronsted-Lowry, all acid-base reactions involve two conjugate acid-base pairs



$\text{Acid}_1$  has its conjugate base<sub>1</sub> in product and base<sub>2</sub> has its conjugate acid<sub>2</sub>

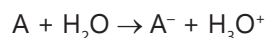


**Limitations of Bronsted-Lowry Concept:** This classification also fails to explain the behaviour of acids and bases in non-aqueous solvents, as well as acid-base neutralisation in the absence of solvents; e.g.,  $\text{BF}_3$ , an electron deficient molecule reacts directly with  $\text{NH}_3$  to show the formation of  $[\text{F}_3\text{B} \rightarrow \text{NH}_3]$  molecule.

**Retain In Memory:** All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases. This is because an Arrhenius acid is a substance which can give a  $\text{H}^+$  ion whereas a Bronsted acid is a substance which can donate a proton which is also a  $\text{H}^+$  ion. On the other hand, an Arrhenius base is a substance which gives the  $\text{OH}^-$  ion in the solution but Bronsted base is a substance which accepts a proton. It may not contain  $\text{OH}^-$  ion. For example,  $\text{NaOH}$  is an Arrhenius base because it gives  $\text{OH}^-$  ion in aqueous solutions but not a Bronsted base because it cannot accept a proton.

### 5.3 Levelling Effect

The levelling effect, or solvent levelling, is an effect that places an upper-limit on the strength of an acid (or base) in a given solvent when the solvent is Lewis acidic or Lewis basic. The strength of a strong acid is limited ("levelled") by the basicity of the solvent. Similarly, the strength of a strong base is levelled by the acidity of the solvent. When a strong acid is dissolved in water, it reacts with it to form the hydronium ion ( $\text{H}_3\text{O}^+$ ) in the following reaction:



Any acid that is stronger than  $\text{H}_3\text{O}^+$  reacts with  $\text{H}_2\text{O}$  to form  $\text{H}_3\text{O}^+$ . Therefore, no acid stronger than  $\text{H}_3\text{O}^+$  exists in  $\text{H}_2\text{O}$ . Similarly, when ammonia is the solvent, the strongest acid is ammonium ( $\text{NH}_4^+$ ), thus  $\text{HCl}$  and a super acid (one with a low  $\text{pK}_a$ ) exert the same acidifying effect in water.

The same argument applies to bases. In water,  $\text{OH}^-$  is the strongest base. Thus, even though sodium amide ( $\text{NaNH}_2$ ) is an exceptional base ( $\text{pK}_a$  of  $\text{NH}_3 \sim 33$ ), in water it is only as good as sodium hydroxide. On the other hand,  $\text{NaNH}_2$  is a far more basic reagent in ammonia than is  $\text{NaOH}$ .

**Levelling Versus Differentiating Solvents:** In a differentiating solvent, various acids dissociate to different degrees and thus, have different strengths. In a levelling solvent, several acids are completely dissociated and are thus of the same strength. A weakly basic solvent has fewer tendencies than a strongly basic one to accept a proton. Similarly, a weak acid has fewer tendencies to donate protons than a strong acid. As a result, a strong acid (such as perchloric acid) exhibits more strongly acidic properties than a weak acid (such as acetic acid) when dissolved in a weakly basic solvent. On the other hand, all acids tend to become indistinguishable in strength when dissolved in strongly basic solvents owing to the greater affinity of strong bases for protons. This is called the levelling effect. Strong bases are levelling solvents for acids; weak bases are differentiating solvents for acids. Because of the levelling effect of common solvents, studies on super acids are conducted in solvents that are very weakly basic such as sulphur dioxide (liquefied) and  $\text{SO}_2\text{ClF}$  (these solvents would be considered differentiating solvents).

#### PLANCESS CONCEPTS

- If a strong acid is added to a solvent that it can protonate, such as water, then the acid will protonate the water to produce the hydronium ion, now the strongest acid in the solution. Because of this, acid stronger than the  $\text{pK}_a$  of the conjugate acid of the solvent are all "levelled" to the same strength.
- A similar phenomenon is observed with bases, for example, in water, where any base stronger than hydroxide will simply deprotonate water to produce hydroxide, again providing an upper limit of  $\text{pK}_b$  beyond which all bases behave the same in that solvent.
- Discriminating solvents are those that do not have a significant levelling effect, because they are themselves not acidic or basic to an appreciable extent. The study of particularly strong acid and bases is often conducted in a levelling solvent.

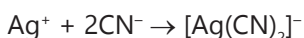
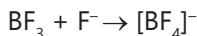
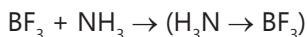
**Mredul Sharda (JEE Advanced 2013)**

## 5.4 Lewis Concepts (1923)

Bronsted concept was extended to give a new theory by Lewis. According to Lewis:

- (a) A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.
- (b) An acid base reaction takes place when a base shares an electron pair with an acid. The process is called neutralization or simply, co-ordination. The product is a co-ordinated compound, co-ordinated complex or adduct, made up of an acid portion and a base portion, e.g.,

Acid + Base  $\rightarrow$  Co-ordinate complex



### (c) Lewis acids

(i) **Simple cations:**  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ , etc., are all Lewis acids.

Acid strength of simple cations increases with

- An increase in +ve charge on the ion, i. e.,  $\text{Fe}^{2+} < \text{Fe}^{3+}$
- A decrease in ionic radius, i. e.,  $\text{K}^+ < \text{Na}^+ < \text{Li}^+$
- An increase in the effective nuclear charge for atoms, i. e.,  $\text{Li}^+ < \text{Be}^{2+} < \text{B}^{3+}$

(ii) **Compounds whose central atom has an incomplete octet:** All compounds having a central atom with a lack of electrons are Lewis acids, e.g.,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{RMgX}$ ,  $\text{MgCl}_2$ , etc.

Strength of these Lewis acids increases with

- An increase in the nuclear charge of the central atom.
- An increase in the no. and the relative electronegativity of atoms attached on central atoms  $\text{SO}_2 < \text{SO}_3$ .
- A decrease in the atomic radius of the central atom. However, these rules show some anomalies, e.g., acidic strength of boron trihalides is  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ .

This anomaly to rule (b) has been explained in terms of back bonding.

(iii) **Compounds whose central atom can show expansion of octet:**  $\text{SiF}_4$  and  $\text{SiCl}_4$  act as Lewis acids because Si can expand its octet using vacant d-orbitals.

**Note:** The strength of cations as acids can be alternatively expressed in terms of effective nuclear charge. More the effective nuclear charge, greater is the tendency to attract a lone pair of electrons and thus, more is the acidic nature, i. e.,

Acidic nature order:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$

(d) **Lewis Base:** Compounds having electron pair available for co-ordination show Lewis base nature

e.g.,  $\text{:NH}_3$ ,  $\text{:PH}_3$ ,  $\text{:PCl}_3$ ,  $(\text{CH}_3)_2\text{O}$ , ligands, i. e.,  $\text{CN}^-$ ,  $\text{CNS}^-$ ,  $\text{OH}^-$ ,  $\text{SH}^-$  etc.

**Note:** The strength of anions as a base can alternatively be expressed in terms of the electronegativity of the atom. More the electronegativity of the atom carrying negative charge, greater will be its basic nature, i. e.,

Basic nature order:  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

$\text{NH}_2^- > \text{OH}^- > \text{SH}^-$

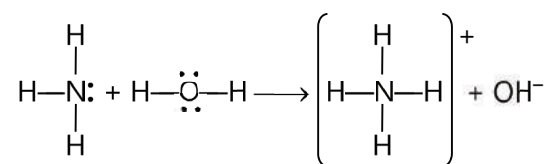
The Lewis base nature of nitrogen trihalides follows the order:  $\text{NF}_3 < \text{NCl}_3 < \text{NBr}_3 < \text{NI}_3$ .

This may be explained in terms of the electronegativity of halogens. Greater the electronegative difference in N—X bond, more is the partial +ve charge on N-atom and thus, tendency to donate electron pair by N-atom becomes lesser.

### Limitations of Lewis Concepts

- (a) It does not explain the behaviour of protonic acids such as  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , etc., which do not accept electron pair, i. e., do not undergo co-ordination bonding with bases.
- (b) It does not predict the magnitude of the relative strength of acids and bases.
- (c) It is specially a general approach for the co-ordination compound formation and co-ordination reaction.
- (d) Usually, co-ordination reactions are slow. It means that neutralization of acid-base should occur slowly, but these are extremely fast.

**Retain In Memory:** All Lewis bases are also Bronsted bases but all Bronsted acids may not be Lewis acids. This is because a substance that is capable of giving an electron pair has the tendency to accept a proton. For example, consider the reaction:



Here,  $\text{NH}_3$  is Lewis base as well as Bronsted base. However, in the above case,  $\text{H}_2\text{O}$  is a Bronsted acid because it is giving a proton but is not a Lewis acid because it is electronically satisfied. Similarly,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  etc. are Bronsted acids but not Lewis acids as they cannot accept pairs of electrons.

### Some Conceptual Questions

**Q.1** Sulphuric acid is a very strong acid yet it can also act as a base in some reactions. Explain how?

**Ans.** Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) is a weaker acid with respect to perchloric acid ( $\text{HClO}_4$ ).  $\text{H}_2\text{SO}_4$  can take up a proton from  $\text{HClO}_4$  to form  $\text{H}_3\text{SO}_4^+$ . Hence, it acts as a base in this reaction.

**Q.2** Metal ions like  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , etc. can also act as acids. Explain how?

**Ans.** Metal ions (cations) can accept lone pairs of electrons. Hence, they act as Lewis acids.

## 5.5 Classification of Solvents

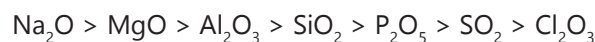
**Table 6.1:** Classification of solvents

Name		Characteristic	Example
(i)	Protophilic	Tendency to accept protons	$\text{H}_2\text{O}$ , liq. $\text{NH}_3$ , $\text{CH}_3\text{OH}$ etc
(ii)	Protogenic	Tendency to give protons	$\text{H}_2\text{O}$ , $\text{CH}_3\text{COOH}$ , $\text{HCl}$ etc.
(iii)	Amphiprotic	Act as both (i) & (ii)	$\text{H}_2\text{O}$ , $\text{NH}_3$ , $\text{CH}_3\text{OH}$ etc.
(iv)	Aprotic	Neither donate nor accept protons	Benzene

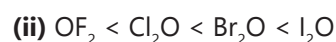
### Nature of Oxides

(a) Basic character of oxides decreases along the period and increases down the group, e.g.,

Basic character decreases along the period:



Basic character increases down the group:

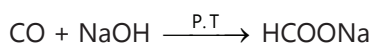


- (b) Oxides of metals are normally basic (few exceptions are amphoteric), oxides of non-metals are normally acidic. CO, N<sub>2</sub>O and NO are neutral. \_

Table 6.2: Classifications of oxides

Basic oxides	Acidic oxides	Amphoteric
K <sub>2</sub> O, CaO, MgO CuO, Fe <sub>2</sub> O <sub>3</sub> , etc. All are metal ox-ides	CO <sub>2</sub> CO(Neutral) <u>N<sub>2</sub>O, NO</u> , N <sub>2</sub> O <sub>3</sub> , N <sub>2</sub> O <sub>4</sub> , N <sub>2</sub> O <sub>5</sub> , Neutral F <sub>2</sub> O, SiO <sub>2</sub> , P <sub>2</sub> O <sub>3</sub> , P <sub>2</sub> O <sub>5</sub> , SO <sub>2</sub> , etc. (All are non-metal oxides)	ZnO, Al <sub>2</sub> O <sub>3</sub> , BeO, SnO <sub>2</sub> , (All are metal oxides) As <sub>2</sub> O <sub>3</sub> (metalloid oxide)

**Note:** 1. CO acts as an acid, if allowed to react with NaOH at high P and T.



- (c) CO acts as Lewis base (ligand) in complex formation.

- (i) Oxides of non-metals having same oxidation no. of non-metal in their respective oxo-acids are known as acid anhydrides. The acid anhydrides on dissolution in water give their respective oxo-acids.

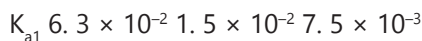
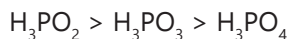
Table 6.3: Oxo-acids of non-metals

Acid anhydride	Oxo-acids
<b>Non-metal oxides</b>	
P <sub>2</sub> O <sub>5</sub>	HPO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub>
P <sub>2</sub> O <sub>3</sub>	HPO <sub>2</sub> , H <sub>3</sub> PO <sub>3</sub>
SO <sub>2</sub>	H <sub>2</sub> SO <sub>3</sub>
SO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
CO <sub>2</sub>	H <sub>2</sub> CO <sub>3</sub>
N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>
N <sub>2</sub> O <sub>3</sub>	HNO <sub>2</sub>
<b>Metal Oxides</b>	
CrO <sub>3</sub>	H <sub>2</sub> CrO <sub>4</sub>
Mn <sub>2</sub> O <sub>7</sub>	HMnO <sub>4</sub>

- (ii) Greater the number of oxygen atoms and more is the electronegative nature of the atom of oxo-acid, stronger is the acid.



**Note:** However, this rule is not obeyed in oxo-acids of phosphorus.

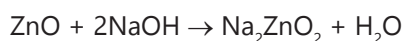
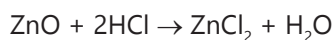


This is due to overall inductive effect of the added O-atom on the central atom which decreases from H<sub>3</sub>PO<sub>2</sub> to H<sub>3</sub>PO<sub>4</sub> on account of increasing number of unprotonated O-atoms from H<sub>3</sub>PO<sub>2</sub> to H<sub>3</sub>PO<sub>4</sub>.

(iii) On the other hand, basic anhydrides are the oxides of metals which form an alkali in water, e.g.,  $\text{Na}_2\text{O}$  is basic anhydride of  $\text{NaOH}$ .

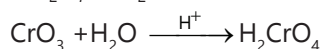
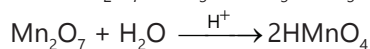
(iv) Some oxides of metals are amphoteric as they react with both acid and base,

e.g.  $\text{ZnO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , etc.



(v) Oxides of some metals in higher oxidation state, acidic in nature.

e.g.,  $\text{Mn}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ , etc.



## 5.6 Relative Strength of Acids and Bases

The ratio of strengths of acids is known as relative strength, i. e.

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

**For weak acids:** Relative strength for weak acids can be derived as follows:

Say acid  $\text{HA}_1$  and  $\text{HA}_2$  are taken, then for,  $\text{HA}_1 \rightleftharpoons \text{H}^+ + \text{A}_1^-$ ;  $K_{a1} = c_1 \alpha_1^2$

For,  $\text{HA}_2 \rightleftharpoons \text{H}^+ + \text{A}_2^-$ ;  $K_{a2} = c_2 \alpha_2^2$

$$\text{Now, relative strength} = \frac{[\text{H}^+] \text{ furnished by acid } \text{HA}_1}{[\text{H}^+] \text{ furnished by acid } \text{HA}_2} = \frac{c_1 \alpha_1}{c_2 \alpha_2} = \frac{c_1 \sqrt{\left(\frac{K_{a1}}{c_1}\right)}}{c_2 \sqrt{\left(\frac{K_{a2}}{c_2}\right)}} = \sqrt{\frac{(K_{a1} \cdot c_1)}{(K_{a2} \cdot c_2)}} \left[ \because \alpha = \sqrt{\frac{K_a}{c}} \right]$$

If concentrations are same, then

$$\text{Relative strength} = \sqrt{\frac{K_{a1}}{K_{a2}}} \quad \dots(5)$$

**For strong acids:** Relative strength for strong acids can be derived by studying the rate constant (see chemical kinetics) of ester hydrolysis or inversion of cane sugar in the presence of different acids.

$$\text{Relative strength} = \frac{\text{Rate constant for the reaction catalysed by I acid}}{\text{Rate constant for the reaction catalysed by II acid}} \quad \dots(6)$$

Some definitions which will be important

**Retain in memory:** Just as we have  $\text{pH} = -\log[\text{H}^+]$ , similarly, we have

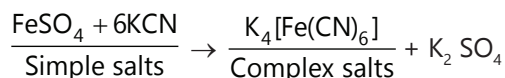
$\text{pOH} = -\log[\text{OH}^-]$ ,  $\text{p}K_a = -\log K_a$ ,  $\text{p}K_b = -\log K_b$ ,  $\text{p}K_w = -\log K_w$  where  $K_a$  and  $K_b$  represent ionization constants of the acid and the base respectively and  $K_w$  is ionic product of water.

This can be effectively used as a problem solving trick.

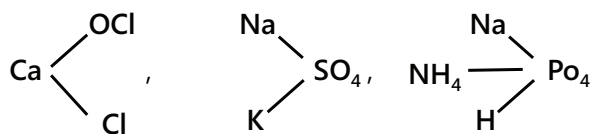
## 5.7 Acid-Base Neutralization: Salt

(a) **Simple Salts:** The salts formed by the neutralization process, i. e., the interaction between acid and base, are termed as simple salts. These are of three types:

- (i) **Normal salts:** The salts formed by the loss of all possible protons of an acid (replaceable hydrogen atoms as  $H^+$ ) are called normal salts. Such a salt does not contain either a replaceable hydrogen or a hydroxyl group, e.g.,  $NaCl$ ,  $NaNO_3$ ,  $K_2SO_4$ ,  $Ca_3(PO_4)_2$ ,  $Na_3BO_3$ ,  $Na_2HPO_3$  (one H-atom is not replaceable as  $H_3PO_3$  is a dibasic acid),  $NaH_2PO_2$  (both H-atoms are not replaceable as  $H_3PO_2$  is a monobasic acid), etc.
- (ii) **Acid Salts:** Salts formed by the incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen atoms. These salts when neutralized by bases form normal salts. This is because  $NaHCO_3 + NaOH$  cannot exist together in a mixture, e.g.,  $NaHCO_3$ ,  $NaHSO_4$ ,  $NaH_2PO_4$ ,  $Na_2HPO_4$ , etc.
- (iii) **Basic Salts:** Salts formed by the incomplete neutralisation of poly acidic bases are called basic salts. Such salts still contain one or more hydroxyl groups. These salts when neutralized by acids form normal salts, e.g.,  $Zn(OH)Cl$ ,  $Mg(OH)Cl$ ,  $Fe(OH)_2Cl$ ,  $Bi(OH)_2Cl$ , etc.
- (b) **Double Salts:** The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only and lose their identity in the solution state.
- (c) **Complex Salts:** Complex salts are formed by the combination of simple salts or molecular compounds. These are stable in the solid state as well as retain their identity in solutions.



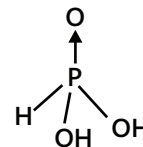
- (d) **Mixed Salts:** The salt which furnishes more than one cation (excluding  $H^+$ ) or more than one anion (excluding  $OH^-$ ) when dissolved in water is called in mixed salt.



**Illustration 16:** What type of salts are  $Na_2HPO_3$  and  $NaHS$ ?

(JEE MAIN)

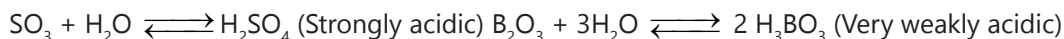
**Sol:**  $Na_2HPO_3$  is obtained through a reaction between  $NaOH$  and  $H_3PO_3$  (a dibasic acid), i. e. Both displaceable hydrogens are replaced by  $Na$ . No acidic hydrogen is left. Hence,  $Na_2HPO_3$  is a normal salt.  $NaHS$  is obtained by the replacement of one acidic hydrogen of  $H_2S$  by  $Na$  (on reaction with  $NaOH$ ). Hence,  $NaHS$  is an acidic salt.



**Illustration 17:** Arrange the given compounds in the decreasing order of basicity on the basis of the Bronsted-Lowry concept:  $BaO$ ,  $CO_2$ ,  $SO_3$ ,  $B_2O_3$ ,  $Cl_2O_7$

(JEE MAIN)

**Sol:** According to the Bronsted-Lowry theory, base is a substance which can accept a proton.



Hence, in the decreasing order of basicity, we have  $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$ .

**Illustration 18:** Why is the  $PO_4^{3-}$  ion is not amphoteric?

(JEE MAIN)

**Sol:** An amphoteric ion is one which can donate protons as well as accept protons.  $PO_4^{3-}$  ion can accept proton(s) but cannot donate any proton. Hence,  $PO_4^{3-}$  is not amphoteric.

**Illustration 19:** Classify the following as an acid or base according to Bronsted-Lowry theory and name their corresponding conjugate base or acid **(JEE MAIN)**

- (i)  $\text{NH}_3$     (ii)  $\text{CH}_3\text{COO}^-$     (iii)  $\text{H}_3\text{O}^+$     (iv)  $\text{H}^+$     (v)  $\text{HOO}^-$     (vi)  $\text{S}_2\text{O}_8^{2-}$ .

**Sol:** According to the Bronsted-Lowry theory, an acid is a substance which can donate a proton while a base is a substance which can accept a proton.

(i)  $\text{NH}_3$  is a Bronsted base because it can accept a proton. Its conjugate acid is  $\text{NH}_4^+$ .

$\text{NH}_3$  is also a Bronsted acid because it can donate a proton.

Its conjugate base  $\text{NH}_2^-$ .

(ii)  $\text{CH}_3\text{COO}^-$  is a Bronsted base ( $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$ ).

Its conjugate acid is  $\text{CH}_3\text{COOH}$ .

(iii)  $\text{H}_3\text{O}^+$  is a Bronsted acid ( $\text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{H}^+$ ). Its conjugate base is  $\text{H}_2\text{O}$ .

(iv)  $\text{H}^+$  is a Bronsted base ( $\text{H}^- + \text{H}^+ \rightarrow \text{H}_2$  in the reaction  $\text{H}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{OH}^-$ ). Its conjugate acid is  $\text{H}_2$ .

(v)  $\text{HOO}^-$  is a Bronsted acid ( $\text{HOO}^- \rightarrow \text{O}_2^{2-} + \text{H}^+$  in the reaction  $\text{HOO}^- + \text{H}_2\text{O} \rightarrow \text{O}_2^{2-} + \text{H}_3\text{O}^+$ ).

Its conjugate acid is  $\text{O}_2^{2-}$  (peroxide ion).

(vi)  $\text{S}_2\text{O}_8^{2-}$  is a Bronsted base ( $\text{S}_2\text{O}_8^{2-} + 2\text{H}^+ \rightarrow 2\text{HSO}_4^-$  in the reaction  $\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + 2\text{OH}^-$ ).

Its conjugate acid is  $\text{HSO}_4^-$ .

**Illustration 20:** Classify each of the following substances into an acid or base or both and mention the concept/concepts on the basis of which you can do so. **(JEE ADVANCED)**

- (i)  $\text{HCl}$  (aq)    (ii)  $\text{NH}_3$  (g)    (iii)  $\text{Na}_2\text{CO}_3$  (aq)    (iv)  $\text{CH}_3\text{COOH}$  (aq)    (v)  $\text{CO}_2$  (g)    (vi)  $\text{BF}_3$     (vii)  $\text{Ag}^+$   
 (viii)  $\text{CN}^-$     (ix)  $\text{H}_2\text{O}$     (x)  $\text{H}_2\text{SO}_4$     (xi)  $\text{HCO}_3^-$     (xii)  $\text{SiF}_4$

**Sol:** (i)  $\text{HCl}$  (aq) — Acid (Arrhenius concepts and Bronsted - Lowry concept)

(ii)  $\text{NH}_3$  (g) — Base (Bronsted concepts and Lewis concept)

(iii)  $\text{Na}_2\text{CO}_3$  (aq) — Base (Bronsted concept)

(iv)  $\text{CH}_3\text{COOH}$  (aq) — Acid (Arrhenius concepts and Bronsted concept)

(v)  $\text{CO}_2$  (g) — Acid (Bronsted concepts and Lewis concept)

(vi)  $\text{BF}_3$  — Acid (Lewis concept)

(vii)  $\text{Ag}^+$  — Acid (Lewis concept)

(viii)  $\text{CN}^-$  — Base (Lewis concept)

(ix)  $\text{H}_2\text{O}$  — Both an acid and base, i. e., amphoteric (Bronsted concept)

(x)  $\text{H}_2\text{SO}_4$  — Both an acid and base, i. e., amphoteric (Bronsted concept)

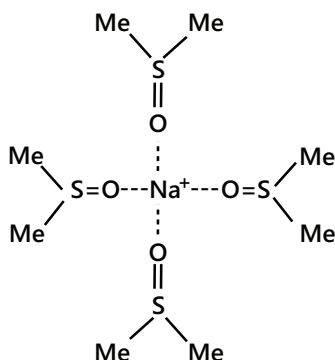
(xi)  $\text{HCO}_3^-$  — Both an acid and base, i. e., amphoteric (Bronsted concept)

(xii)  $\text{SiF}_4$  — Acid (Lewis concept), as silicon can expand its octet.

**Illustration 21:** How a polar aprotic solvent acts to dissolve an ionic solute? Also report one polar aprotic solvent which can dissolve  $\text{NaCl}$ . **(JEE ADVANCED)**

**Sol:** A polar aprotic solvent strongly solvates the cation by ion-dipole attraction using the negative end of its dipole which is exposed (aprotic solvent solvate anion and cations both by forming H-bonds and thus, stabilise them to exist freely in the solution state). Thus, the anion is left free because it is only very weakly solvated by the positive end of the dipole which is deeply buried within the molecules. A polar aprotic solvent is DMSO, i. e., dimethyl sulphoxide.





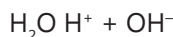
$\text{Cl}^-$  (free; since bulky methyl groups prevent  $\text{Cl}^-$  to approach +ve end i. e., S-atom of solvent).

## 6. pH VALUE

As  $[\text{H}^+]$  increases, the effective concentration of  $\text{H}^+$  ions becomes progressively less than might be expected, because of the increased inter ionic attractions at higher concentrations. A more precise definition of pH is  $\text{pH} = -\log a_{\text{H}^+}$  where,  $a_{\text{H}^+}$  is the hydrogen ion activity (or the effective  $\text{H}^+$  concentration). The  $\text{H}^+$  activity is obtained by multiplying  $[\text{H}^+]$  by a suitable activity coefficient based on thermodynamic measurements. They approach 1.0 for very dilute solutions but get smaller as concentration increases.

### The pH Scale

It is clear from the dissociation of water at  $25^\circ\text{C}$ .



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

For pure water,  $[\text{H}^+] = [\text{OH}^-]$

$$\therefore [\text{H}^+]^2 = 10^{-14} \text{ and } [\text{H}^+] = 10^{-7}$$

Thus, if  $[\text{H}^+] > 10^{-7}$  solution is acidic, i. e.,  $\text{pH} < 7$

$< 10^{-7}$  solution is alkaline, i. e.,  $\text{pH} > 7$

$= 10^{-7}$  solution is neutral, i. e.,  $\text{pH} = 7$

pH of a solution decreases as  $[\text{H}^+]$  in the solution increases. For all practical purposes, the pH scale extends from 0 to 14 (at  $25^\circ\text{C}$ ). A solution of  $\text{pH} = 0$  is acidic and  $\text{pH} = 14$  is alkaline.

The mid-point of the scale at  $\text{pH} = 7$  represents neutrality, pH below 7 being increasingly acidic and those above 7 increasingly basic.

Theoretically, pH values greater than 14 are possible for concentrated strong bases and negative pH values are possible for concentrated strong acids, but it is for dilute solutions that the pH scale is most useful. The pH for concentrated solution should be derived by

$\text{pH} = -\log a_{\text{H}^+}$  where  $a_{\text{H}^+}$  represents active mass of  $\text{H}^+$  ions.

For any aqueous solution at  $25^\circ\text{C}$  it must be true that

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

No matter how acidic or basic a solution might be. It must contain  $\text{H}^+$  and  $\text{OH}^-$  ions and the product of effective molar concentration equal to  $10^{-14}$  'OR  $K_w$ .

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

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

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

**Note:**

(1) The relationship between pH and acidic nature is an inverse one. Thus, as the pH goes up, the acidic nature goes down.

(2) The pH of a mixture of two weak acids can be obtained as:

$$\text{pH} = \sqrt{K_{a1} \times c_1 + K_{a2} \times c_2}$$

However, if both acids are too weak ( $\text{pK}_a$  ranging in  $10^{-10}$  to  $10^{-14}$ ) or the solutions are too dilute the alternate formula from charge-balance method is given as

$$[\text{H}^+] = \sqrt{K_{a1} c_1 + K_{a2} c_2 + K_w}$$

(3) The pH of a dipolar ion molecule say glycine ( $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$ ) at isoelectric point can be represented as  $^+\text{NH}_3 - \text{CH}_2 - \text{COO}^-$ . The pH at isoelectric point can be calculated or evaluated by the formula:  $\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2}$

(4) Same is the case with Amphiprotic Salts

A weak acid in water

$$(a) \text{ if } c_0 \geq 2500 K_a, [\text{H}^+] \approx \sqrt{K_a c_0 + K_w}$$

Mostly,  $K_w$  is insignificant and is neglected so  $[\text{H}^+] \approx \sqrt{K_a c_0}$

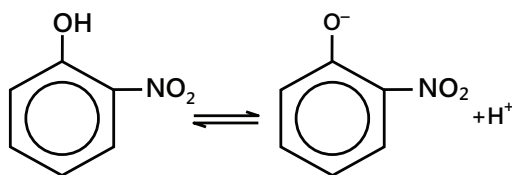
(5) This is sometimes called Ostwald's Dilution Law.

$$\text{Total concentration of } [\text{H}^+] \text{ or } [\text{H}_3\text{O}^+] \text{ in a mixture of weak acid and a strong acid} = \frac{C_2 + \sqrt{C_2^2 + 4K_a C_1}}{2}$$

Where,  $C_1$  is the concentration of weak acid (in mol litre<sup>-1</sup>) having a dissociation constant of  $K_a$  and  $C_2$  is the concentration of a strong acid.

**Illustration 22:** A saturated solution of o-nitrophenol has a pH equal to 4.53. What is the solubility of o-nitrophenol in water?  $\text{pK}_a$  for o-nitrophenol is 7.23 **(JEE ADVANCED)**

**Sol:** According to Ostwald's dilution law  $[\text{H}^+] = c\alpha$ , where  $\alpha = \sqrt{\frac{K_a}{c}}$  using the log term of this expression, concentration can be determine as  $\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log C$



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

$$\text{Or } \text{pH} = -\log[\text{H}^+] = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log C$$

$$\text{Or } 4.53 = \frac{1}{2} \times 7.23 - \frac{1}{2} \log C$$

$$C = 0.015 \text{ M}$$

$$\therefore \text{Solubility in g/litre} = 0.015 \times \text{mol. Wt. of compound}$$

$$= 0.015 \times 139 = 2.085 \text{ g/litre}$$

## 7. BUFFER SOLUTIONS

A solution which has reserve acidic nature or alkaline nature or a solution with reserve pH is buffer solution. A solution whose pH does not change significantly on addition of a small amount of acid or alkali.

### (a) General Characteristics of a Buffer Solution

- (i) It has a definite pH, i. e., it has reserve acidity or alkalinity.
- (ii) Its pH does not change on standing for long.
- (iii) Its pH does not change on dilution.
- (iv) Its pH is slightly changed by the addition of a small quantity of an acid or a base.

### (b) Buffer solutions can be obtained by:

- (i) By mixing a weak acid with its salt with a strong base,
  - $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
  - Boric acid + Borax
  - Phthalic acid + Potassium acid phthalate
- (ii) By mixing a weak base with its salt with a strong acid,
  - $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
  - Glycine + Glycine hydrochloride
- (iii) By a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.
- (iv) By a mixture of an acid salt and a normal salt of a polybasic acid, e.g.,  $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$  or a salt of a weak acid and a weak base, such as  $\text{CH}_3\text{COONH}_4$ .

**(c) Basic buffer:** Consider the case of the solution containing  $\text{NH}_4\text{OH}$  and its salt  $\text{NH}_4\text{Cl}$ . The solution will have  $\text{NH}_4\text{OH}$  molecule.  $\text{NH}_4^+$  ions,  $\text{Cl}^-$  ions.  $\text{OH}^-$  ions and  $\text{H}^+$  ions.

$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  (Feebly ionised)

$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$  (Completely ionised)

$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  (Very feebly ionised)

When a drop of NaOH is added, the added  $\text{OH}^-$  ions combine with  $\text{NH}_4^+$  ions to form feebly ionised  $\text{NH}_4\text{OH}$  whose ionization is further suppressed due to the common ion effect. Thus, pH is not disturbed considerably.

$\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_4\text{OH}$

↑

(From strong base)

When a drop of HCl is added, the added  $\text{H}^+$  ions combine with  $\text{NH}_4\text{OH}$  to form undissociated water molecules.

$\text{NH}_4\text{OH} + \text{H}^+ \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$

↑

(From strong acid)

Thus, pH of the buffer is practically unaffected.

A similar thing will also happen in an Acidic Buffer. The overall picture is represented in the following diagram.

**Acid Buffer** ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ )

**Basic Buffer** ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ )

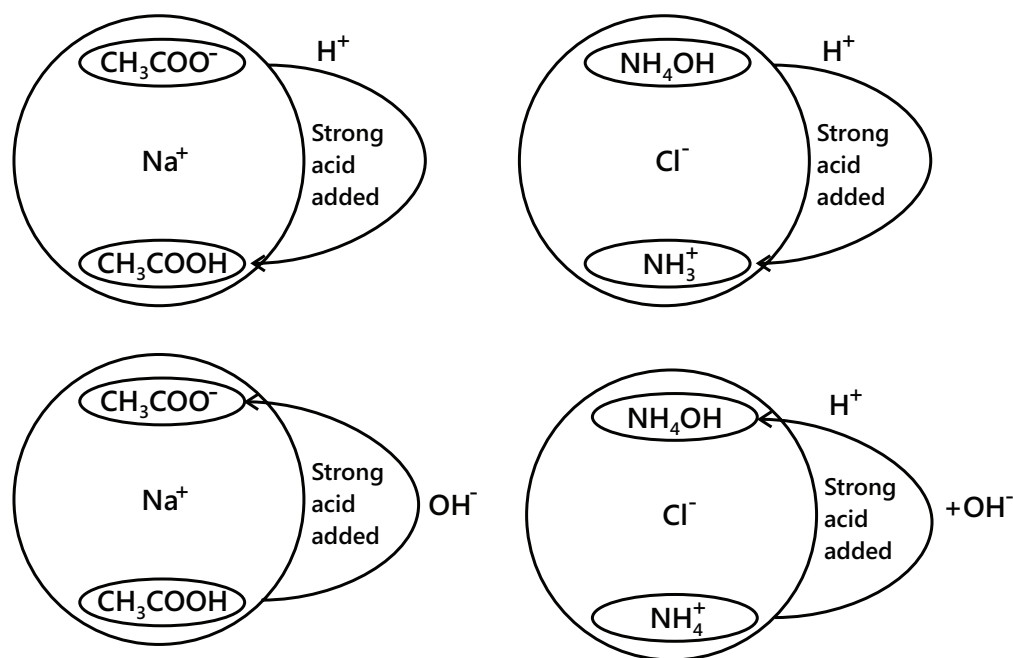


Figure 6.2: Mechanism of buffer solution

## 7.1 Henderson's Equation

### pH of a Buffer-Mixtures

Consider a buffer mixture say an acidic buffer, e.g., HA + NaA

HA  $\rightleftharpoons$  H<sup>+</sup> + A<sup>-</sup> and NaA  $\rightarrow$  Na<sup>+</sup> + A<sup>-</sup>

Applying law of mass action to dissociation equilibrium of HA.

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

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

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

$$\text{Or } \text{pH} = -\log K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{Or } \text{pH} = \text{p}K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} \quad \dots (11)$$

Where, [A<sup>-</sup>] = [conjugate base] or [conjugate base of HA] obtained from concentration of the salt which is 100% ionised. All the [A<sup>-</sup>] come from the salt since the dissociation of HA in the presence of NaA is appreciably suppressed.

[HA] = [Acid] = Initial concentration of acid since it is almost unionised in presence of NaA

Similarly for basic buffer mixture, one can write

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Conjugate base}]}{[\text{Base}]} \quad \dots (12)$$

**Key concept:** When  $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$ , then  $\text{pH} = 1 + \text{pK}_a$

And when  $\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{10}$ , then  $\text{pH} = \text{pK}_a - 1$

So, weak acid may be used for preparing buffer solutions having pH values lying within the ranges  $\text{pK}_a + 1$  and  $\text{pK}_a - 1$ . The acetic acid has a  $\text{pK}_a$  of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3.8 to 5.8.

## 7.2 Buffer Capacity

**Buffer capacity:** The property of a buffer solution to resist an alteration in its pH value is known as its buffer capacity. It has been found that if the ratio  $\frac{[\text{Salt}]}{[\text{Acid}]}$  or  $\frac{[\text{Salt}]}{[\text{Base}]}$  is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as number of moles of acid or base added in one litre of solution as to change the pH by unity, i. e.

$$\text{Buffer capacity } (\phi) = \frac{\text{No. of moles of acid or base added to 1 litre}}{\text{Change in pH}} \quad \text{or } (\phi) = \frac{\partial b}{\partial(\text{pH})}$$

where,  $\partial b \rightarrow$  number of moles of acid or base added to 1 litre solution and

$\partial(\text{pH}) \rightarrow$  change in pH.

Buffer capacity is maximum:

(i) When  $[\text{Salt}] = [\text{Acid}]$ , i. e.,  $\text{pH} = \text{pK}_a$  for acid buffer

(ii) When  $[\text{Salt}] = [\text{Base}]$ , i. e.,  $\text{pOH} = \text{pK}_b$  for base buffer

Under the above conditions, the buffer is called efficient.

### Uses

#### (a) Buffer Solutions in Analytical Chemistry

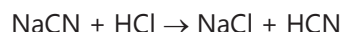
- (i) To determine the pH with the help of indicators.
  - (ii) For the removal of the phosphate ion in the qualitative inorganic analysis after the second group using  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  buffer.
  - (iii) For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer,  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ , is used.
  - (iv) For precipitation of hydroxides of the third group of qualitative analysis, a buffer,  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ , is used.
  - (v) A buffer solution of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  is used for the precipitation of carbonates of fifth group in qualitative inorganic analysis.
  - (vi) The pH of intracellular fluid, blood is naturally maintained. This maintenance of pH is essential to sustain life because, enzyme catalysis is pH sensitive process. The normal pH of blood plasma is 7.4. Following two buffers in the blood help to maintain pH (7.4):
    - Buffer of carbonic acid ( $\text{H}_2\text{CO}_3$  and  $\text{NaHCO}_3$ )
    - Buffer of phosphoric acid ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ )
- (b) Buffers are used in industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc. Buffers are also employed in agriculture, dairy products and in the preservation of various types of foods and fruits.

**Illustration 23:** How many moles of HCl will be required to prepare one litre of buffer solution (containing NaCN + HCl) of pH 8.5 using 0.01 g formula weight of NaCN.  $K_{\text{HCN}} = 4.1 \times 10^{-10}$  **(JEE MAIN)**

**Sol:** We are provided with concentration of hydrogen ion and equilibrium constant, so we can find out the concentration by using following expression,

$$\text{pH} = -\log K_a + \log c$$

Addition of HCl to NaCN results in a buffer solution, when HCl is added in lesser amount than NaCN, i. e.



Moles added      0.01      a      0      0

Moles after reaction (0.01 - a) 0      a      a

Thus, buffer solution contains a moles of HCN and (0.01 - a) moles of NaCN

$$\therefore \text{pH} = -\log K_a + \log \frac{0.01 - a}{a}$$

$$\text{Or } 8.5 = -\log[4.1 \times 10^{-10}] + \log \frac{0.01 - a}{a}$$

$$\therefore a = 8.85 \times 10^{-3} \text{ moles of HCl}$$

**Illustration 24:** Calculate  $[\text{H}^+]$  and  $[\text{CHCl}_2\text{COO}^-]$  in a solution that is 0.01 M HCl and 0.01 M in  $\text{CHCl}_2\text{COOH}$ .  $K_a$  for  $\text{CHCl}_2\text{COOH}$  is  $5 \times 10^{-2}$  **(JEE MAIN)**

**Sol:**  $\text{CHCl}_2\text{COOH} \rightleftharpoons \text{CHCl}_2\text{COO}^- + \text{H}^+$

c                      0                      0.01

$c(1 - \alpha)$                $c\alpha$                $c\alpha + 0.01$

$$\therefore K_a = \frac{c\alpha \times (c\alpha + 0.01)}{c(1 - \alpha)} = \frac{\alpha(0.01\alpha + 0.01)}{(1 - \alpha)} = 5 \times 10^{-2}$$

$$\text{Or } \frac{0.01\alpha(1 + \alpha)}{(1 - \alpha)} = 5 \times 10^{-2}$$

$$\text{Or } \alpha^2 + 6\alpha - 5 = 0$$

$$\therefore \alpha = 0.7416$$

$$\therefore [\text{CHCl}_2\text{COO}^-] = 0.01 \times 0.7416 = 7.416 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = 7.416 \times 10^{-3} + 0.01 = 0.0174 \text{ M}$$

**Illustration 25:** 20 ml of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of solution 4.74. The ionization constant of acetic acid is  $1.8 \times 10^{-5}$  **(JEE ADVANCED)**

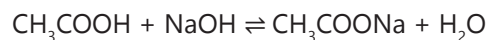
**Sol:** First find out the no of moles NaOH present in 20 ml and Acetic acid present in 50 ml and remaining problem can be solved using Henderson's equation.

No. of moles of NaOH in

$$20 \text{ mL} = \frac{0.2}{1000} \times 20 = 0.004$$

$$\text{No. of moles of acetic acid in 50 mL} = \frac{0.2}{1000} \times 50 = 0.01$$

When NaOH is added,  $\text{CH}_3\text{COONa}$  is formed.



1 mole      1 mole      1 mole      1 mole

No. of moles of  $\text{CH}_3\text{COONa}$  in 70 mL solution = 0.004

No. of moles of  $\text{CH}_3\text{COOH}$  in 70 mL solution =  $(0.01 - 0.004) = 0.006$

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log k_a = \log \frac{0.004}{0.006} - \log 1.8 \times 10^{-5} = 4.5687$$

On further addition of NaOH, the pH becomes 4.74.

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log k_a = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log 1.8 \times 10^{-5}$$

$$\text{or } \log = \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pH} + \log 1.8 \times 10^{-5} = (4.74 - 4.7448) = -0.0048$$

$$\text{So, } \log = \bar{1}.9952$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = 0.9891$$

Let 'x' moles of NaOH be Added

$$[\text{Salt}] = (0.004 + x) \text{ mole}$$

$$[\text{Acid}] = (0.006 - x) \text{ mole}$$

$$\frac{0.004 + x}{0.006 - x} = 0.9891$$

$$x = 0.00097 \text{ moles}$$

**Illustration 26:** What volume of 0.10 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH 4.0?  $\text{p}K_a$  for formic acid is 3.80. **(JEE ADVANCED)**

**Sol:** Let x mL of 0.10 M sodium formate be added.

$$\text{No. of moles in x mL of 0.10 M sodium formate} = \frac{0.10}{1000} \times x$$

$$\text{No. of moles in 50 mL of 0.05 M formic acid} = \frac{0.05}{1000} \times 50$$

$$\frac{[\text{Sod. formate}]}{[\text{Formic acid}]} = \frac{\frac{0.10 \times x}{1000}}{\frac{0.05 \times 50}{1000}} = \frac{0.10x}{2.5} = 0.04x$$

Applying the equation,

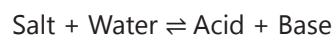
$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} + \text{p}K_a$$

$$4.0 = \log 0.04x + 3.8 = \log 0.04x = 2.0, 0.04x = \text{Antilog } 2.0$$

$$x = 39.6 \text{ mL}$$

## 8. SALT HYDROLYSIS

Salt hydrolysis is the phenomenon of interaction of cations and anions of a salt with  $\text{H}_2\text{O}$  in order to produce an acidic nature or an alkaline nature.

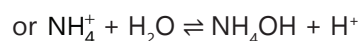
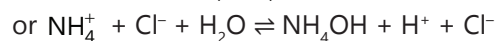
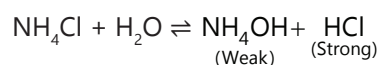


The process of salt hydrolysis is actually reverse the process of neutralization.

**Note:** The net effect of dissolving a salt (which undergoes hydrolysis) is to break up the water molecules (hydrolysis) to produce a weak acid or weak base or both and thus, phenomenon is always endothermic.

### Case I: Salts made up from a Strong Acid and Weak Base

- Such salts include  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CuSO}_4$ ,  $\text{FeCl}_3$ , etc.
- The solution of such salts show acidic character on hydrolysis which may be explained as follows; hydrolysis which may be explained as follows; consider a salt  $\text{NH}_4\text{Cl}$  of this category

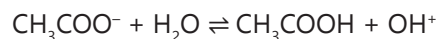


The reaction equilibrium suggests that  $\text{NH}_4\text{Cl}$  on dissolution in water shows the interaction of  $\text{NH}_4^+$  to react with  $\text{H}_2\text{O}$  to produce  $\text{NH}_4\text{OH}$ , a weak base having a low degree of dissociation. Furthermore, the dissociation of  $\text{NH}_4\text{OH}$  is also suppressed due to the unhydrolysed  $\text{NH}_4^+$  ions and thus, after interaction the  $(\text{H}^+)$  in the solution increases and the solution acquires an acidic nature.

- In this category of salt, it is the cation that undergoes hydrolysis.
- The pH of category of salt is always lesser than 7.

### Case II: Salts made up from a Strong Base and Weak Acids

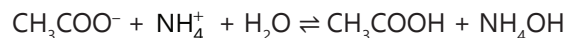
- This category includes salts such as  $\text{KCN}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{Na}_2\text{S}$ ,  $\text{HCOOK}$ , etc.
- The solutions of such salts in water show alkaline character on hydrolysis, eg.,  $\text{CH}_3\text{COONa}$ .



- In this category of salt, it is the anion that undergoes hydrolysis.
- The pH of this category of salt is always greater than 7.

### Case III: Salts of Weak Acids and Weak Base

- This category includes salts such as  $\text{CH}_3\text{COONH}_4$ ,  $(\text{CH}_3\text{COO})_2\text{Be}$ ,  $\text{BeCO}_3$ ,  $(\text{NH}_4)_3\text{PO}_4$ ,  $\text{BeC}_2\text{O}_4$ , etc.
- The solutions of such salts in water shows an almost neutral character on hydrolysis, e.g.,  $\text{CH}_3\text{COONH}_4$ .



If  $K_{\text{CH}_3\text{COOH}} > K_{\text{NH}_4\text{OH}}$  solution is acidic,

$K_{\text{CH}_3\text{COOH}} < K_{\text{NH}_4\text{OH}}$  solution is alkaline

- Both the cation and anion of the salt undergo hydrolysis.
- The pH of this category of salt is nearly equal to 7, this however, depends upon the respective values of the dissociation constants of the acids and bases by which a salt is formed.

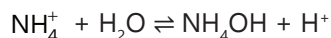


**Case IV: Salts of Strong Acids and Strong Bases**

1. This category includes salts such as  $\text{KNO}_3$ ,  $\text{NaCl}$ ,  $\text{K}_2\text{SO}_4$ , etc.
2. The solution of such salts in water is neutral and this category of salts does not undergo salt hydrolysis.
3. Neither the cation nor anion undergo hydrolysis.
4. The pH of solution is equal to 7.

**The Hydrolysis Constant and Degree of Hydrolysis**

Consider a salt say  $\text{NH}_4\text{Cl}$  (Case I) in water. Let  $c$  mol/litre is concentration of salt and  $h$  is its degree of hydrolysis then,



Before hydrolysis            1            0            0

After hydrolysis             $(1 - h)$      $h$              $h$

$\therefore$  At equilibrium  $[\text{NH}_4^+] = (1 - h)c$ ,  $[\text{NH}_4\text{OH}] = c \cdot h$ ,  $[\text{H}^+] = c \cdot h$

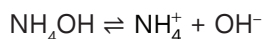
$[\text{H}^+] = c \cdot h$

Therefore, according to law of mass action

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

$$\text{Or } K_H = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{.....(16)}$$

Where  $K_H$  is hydrolysis constant of salt  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4^+$  ion. Also we have for weak base  $\text{NH}_4\text{OH}$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{..... (17)}$$

There, by Eqs. (16) and (17)

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

$$\text{Or } K_H = \frac{K_w}{K_b} \quad \text{..... (18)}$$

Also, by Eq. (16)

$$K_H = \frac{ch \cdot ch}{c(1-h)} = \frac{c^2 h^2}{c(1-h)} = \frac{ch^2}{(1-h)}$$

Since  $h$  is small and thus,  $1 - h = 1$

$$\therefore K_H = ch^2 \text{ or } h = \sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot c}\right)} \quad \text{..... (19)}$$

Similar equations can be obtained for other case

Now, if we discuss all the cases again;

**Case I: Strong acid vs weak base**

$$K_H = \frac{K_w}{K_b} \text{ and } h = \sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot c}\right)} \quad \text{.....(20)}$$

$$[H^+] = ch = c \sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w \cdot c}{K_b}\right)} \quad \dots (23)$$

Since pH is decided by free  $H^+$  given by strong acid

$$\therefore pH = \frac{1}{2} [\log K_b - \log K_w - \log c] \quad \dots (24)$$

$$= \frac{1}{2} [pK_w - \log c - pK_b] \quad \dots (25)$$

**Case II:** Weak acid Vs Weak Base

$$K_H = \frac{K_w}{K_a} \text{ and } h = c \sqrt{\left(\frac{K_H}{c}\right)} = \sqrt{\left(\frac{K_w \cdot c}{K_a}\right)} \quad \dots (21)$$

$$[OH^-] = ch = NH_3 + HCl \rightarrow NH_4Cl \quad \dots (26)$$

Since pH is decided by free  $OH^-$  given by strong alkali

$$\therefore pOH = \frac{1}{2} [\log K_a - \log K_w - \log c] \quad \dots (27)$$

$$= \frac{1}{2} [pK_w - \log c - pK_a] \quad \dots (28)$$

$$\text{Also, } [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{K_w}{\sqrt{\left(\frac{K_w \cdot c}{K_a}\right)}} = \sqrt{\left(\frac{K_w \times K_a}{c}\right)}$$

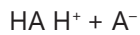
$$\therefore pH = \frac{1}{2} [\log c - \log K_w - \log K_a] \quad \dots (29)$$

$$pH = \frac{1}{2} [pK_w + pK_a + \log c] \quad \dots (30)$$

**Case III:** Weak acid Vs weak Base

$$K_H = \frac{K_w}{K_a \cdot K_b} \text{ and } h = \sqrt{K_H} = \sqrt{\left(\frac{K_w}{K_a \cdot K_b}\right)} \quad \dots (22)$$

In this case both the acid and alkali formed are weak. Consider the weak acid dissociation.



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

$$\text{Or } [H^+] = \frac{K_a[HA]}{[A^-]} = \frac{K_a ch}{c(1-h)} = K_a \cdot h$$

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

$$\therefore pH = \frac{1}{2} [\log K_b - \log K_w - \log K_a] \quad \dots (31)$$

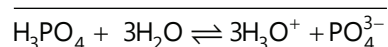
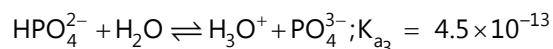
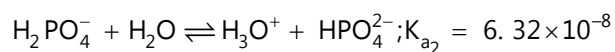
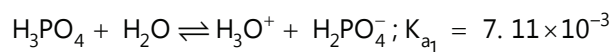
$$pH = \frac{1}{2} [pK_w + pK_a - pK_b] \quad \dots (32)$$

**Key Note:**

It must be noted here that pH of such salt is independent of their concentration.

**Case IV:** Hydrolysis of amphichroic anion:

Polyprotic acids and  $K_a$  values:



$K_{a_1} K_{a_2} K_{a_3}$

$$K_{a_1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.11 \times 10^{-3}$$

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.32 \times 10^{-8}$$

$$K_{a_3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13}$$

$$\text{pH of } \text{H}_2\text{PO}_4^{2-} \text{ in aq. medium} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$$

$$\text{pH of } \text{HPO}_4^{2-} \text{ in aq medium} = \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2}$$

**Table 6.4:** Hydrolysis at a Glance

Salt	Nature	Degree	Hydrolysis Constant	pH
1. NaCl (Strong acid + Strong base)	Neutral	No hydrolysis		
2. $\text{CH}_3\text{COONa}$ (Weak acid + Strong base)	Basic	$h = \sqrt{\frac{K_w}{CK_a}}$	$K_h = \frac{K_w}{K_a}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$
3. $\text{NH}_4\text{Cl}$ (Strong acid + Weak base)	Acidic	$h = \sqrt{\frac{K_w}{CK_b}}$	$K_h = \frac{K_w}{K_b}$	$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$
4. $\text{CH}_3\text{COONH}_4$ (Weak acid + Weak base)		$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$K_h = \frac{K_w}{K_a \times K_b}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$

In the case of the salt of the weak acid and weak base, the nature of the medium after hydrolysis is decided in the following manner:

- (i) If  $K_a = K_b$ , the medium will be neutral.
- (ii) If  $K_a > K_b$ , the medium will be acidic,
- (iii) If  $K_a < K_b$ , the medium will be basic.

The degree of hydrolysis of salts of weak acids and weak bases is unaffected by the dilution because there is no concentration term in the expression of degree of hydrolysis.

**[Note:** Degree of hydrolysis always increases with the increase in temperature because at an elevated temperature, the increase in  $K_w$  is greater as compared to  $K_a$  and  $K_b$ .]

**Illustration 27:** A student prepared solutions of NaCl,  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{Cl}$ . He put them separately. In three test tubes. He forgot to label them. All solutions were colourless. How should he proceed to know the solutions present in the three test tubes?

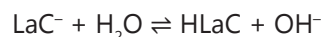
**Sol:** He can test the solutions with blue and red litmus solutions. NaCl solution is neutral. It will neither turn blue litmus red nor red litmus blue.  $\text{NH}_4\text{Cl}$  solution is acidic. It will turn blue litmus red but will have no effect on red litmus.  $\text{Na}_2\text{CO}_3$  solution is basic, it will turn red litmus blue but will have no effect on blue litmus.

**Illustration 28:** Calcium lactate is a salt of weak acid and represented as  $\text{Ca}(\text{LaC})_2$ . A saturated solution of  $\text{Ca}(\text{LaC})_2$  contains 0.13 mole of salt in 0.50 litre solution. The pOH of this is 5.60 Assuming complete dissociation of salt, calculate  $K_b$  of lactic acid. **(JEE MAIN)**

**Sol:**  $[\text{Ca}(\text{LaC})_2] = \frac{0.13}{0.5} = 0.26 \text{ M}$

$\therefore$  1 Mole  $\text{Ca}(\text{LaC})_2$  gives 2 mole  $(\text{LaC})$

$\therefore [\text{LaC}] = 0.26 \times 2 = 0.52 \text{ M}$



$$\therefore [\text{OH}^-] = c \cdot h = c \sqrt{\frac{K_H}{c}} = \sqrt{(K_H \cdot c)} = \sqrt{\frac{K_w \cdot c}{K_a}}$$

where,  $c$  is the conc. of anion which undergoes hydrolysis

$$\text{or } 10^{-5.60} = \sqrt{\frac{10^{-14} \times 0.52}{K_a}} \therefore K_a = 8.25 \times 10^{-4}$$

**Illustration 29:** Calculate the pH at the equilibrium point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH.  $K_a$  for acid =  $1.9 \times 10^{-5}$ . **(JEE MAIN)**

**Sol:** Calculate the concentration of sodium acetate formed during the reaction between acetic acid and NaOH.

Hydroxide ion concentration can be calculated using Ostwald's dilution law as  $[\text{OH}^-] = c \sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \times c}{K_a}}$

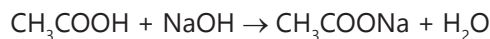
Now from  $[\text{OH}^-]$  we can determine pOH as,

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

pH can be calculated by using following expression,

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

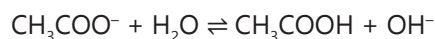
Suppose V mL of 0.1 N acid and 0.1 N NaOH are used at equivalence point



mm before reaction      0.1 × V      1 × V      0      0

$$\therefore [\text{CH}_3\text{COONa}] = \frac{0.1 \times V}{2V} = \frac{0.1}{2} = 0.05 \text{ M}$$

For hydrolysis of  $\text{CH}_3\text{COO}^-$



1                      0                      0  
(1 - h)              h                      h

$$[\text{OH}^-] = c \cdot h = c \sqrt{\frac{K_b}{c}} = \sqrt{\frac{K_w \times c}{K_a}} = \sqrt{\frac{10^{-14} \times 0.05}{1.9 \times 10^{-5}}} = 5.12 \times 10^{-6}$$

$$\therefore \text{pOH} = 5.29 \quad \therefore \text{pH} = 8.71$$

**Illustration 30:** Calculate change in pH upon ten-fold dilution of the following solutions:

(a) 0.1 HCl      (b) 0.1 M acetic acid      (c) 0.1  $\text{MNH}_4\text{Cl}$

$$K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}, K_b \text{ NH}_3 = 1.8 \times 10^{-5}$$

**(JEE ADVANCED)**

**Sol:** (a) HCl is a strong acid. It is completely ionised in solution.



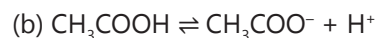
$$[\text{H}^+] = 0.1 = 10^{-1}$$

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

After dilution,  $[\text{H}^+] = 0.01 = 10^{-2} \text{ M}$

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

pH change from 1 to 2.



(0.1 - x)              x                      x

( $\text{CH}_3\text{COOH}$  is a weak acid)

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5} \text{ or } x^2 = 1.8 \times 10^{-6} \text{ or } x = 1.34 \times 10^{-3}$$

$$\text{pH} = -\log x = -\log (1.34 \times 10^{-3}) = 2.87$$

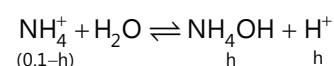
After dilution,

$$\frac{x_1^2}{0.01} = 1.8 \times 10^{-5} \text{ or } x_1^2 = 1.8 \times 10^{-8} \text{ or } x_1 = 4.24 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log x = -\log 4.24 \times 10^{-4} = 3.37$$

pH change from 2.87 to 3.37.

(c)  $\text{NH}_4\text{Cl}$  is a salt of weak base and strong acid



$$\frac{h^2}{0.1} = K_h \text{ or } h^2 = 0.1 \times K_h$$

$$\left[ K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10} \right] = 0.1 \times 5.55 \times 10^{-10}$$

$$h = 7.45 \times 10^{-6} = [H^+]$$

$$pH = -\log(7.45 \times 10^{-6}) = 5.128$$

$$\text{After dilution, } h^2 = 0.01 \times K_h = 0.01 \times 5.55 \times 10^{-10}$$

$$h = 2.35 \times 10^{-6}$$

$$pH = -\log 2.35 \times 10^{-6} = 5.627$$

pH change from 5.128 to 5.627.

**Illustration 31:** How much must a 0.2 M solution of sodium acetate be diluted at 25 °C in order to double the degree of hydrolysis? **(JEE ADVANCED)**

**Sol:** Let  $h$  be the initial degree of hydrolysis

$$K_h = Ch^2 = 0.2 \times h^2 \quad \dots (i)$$

Let the concentration be  $C_1$  when degree of hydrolysis is  $2h$ .

$$K_h = C_1(2h)^2 \quad \dots (ii)$$

$$\text{Dividing both the equations, } 1 = \frac{0.2 \times (h^2)}{4C_1 \times (h)^2}$$

$$C_1 = \frac{0.2}{4} = 0.05 \text{ M}$$

$$\text{Applying, } M_1V_1 = M_2V_2$$

$$0.2V_1 = 0.05 \times V_2$$

$$V_2 = \frac{0.2}{0.05} V_1 = 4V_1$$

The solution be diluted four times.

## 9. THEORY OF INDICATORS

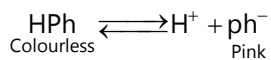
**Theory of acid-base Indicators:** Following theories have been given to explain working of acid-base indicators.

### 1. Ostwald theory

According to this theory

- (i) Indicators are either weak acids or weak bases.
- (ii) Their unionised molecules possess different colours from those of the ions which are part of the solution.
- (iii) An indicator having acidic nature yields a coloured anion while an indicator having basic nature yields a coloured cation in the solution.
- (iv) Since the indicators are weak electrolytes, they are not sufficiently ionised in the solution. But in presence of strong acid or alkali, their degree of ionisation is considerably increased and they produce a large number of coloured ions.
- (v) An indicator changes colour when the concentration of hydrogen ion (in mol per litre) in the solution is equal to the dissociation constant of the indicator, i. e., indicator is 50% dissociated, e.g. Some of the common acid base indicators are:

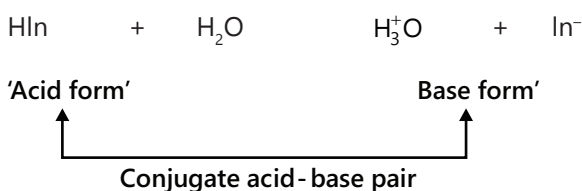
**Phenolphthalein:** It can be represented as HPh. It ionises in solution to a small extent as:



Applying law of mass action,  $K = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]}$

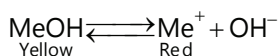
The undissociated molecules of phenolphthalein are colourless while  $\text{Ph}^-$  ions are pink in colour. In presence of an acid, the ionisation of HPh is practically negligible as the equilibrium shifts to the left hand side due to a high concentration of  $\text{H}^+$  ions. Thus, the solution would 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 the right hand side. Thus, the concentration of  $\text{Ph}^-$  ions increases in solution and they impart a pink colour to the solution.

Let us derive Henderson's equation for an indicator



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

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



Applying law of mass action,

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

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

### PLANCESS CONCEPTS

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.

- Phenolphthalein and thymolphthalein are suitable indicators for weak acids and strong base titrations.
- Methyl orange, bromocresol green and methyl red are suitable indicators for strong acid and weak base titrations.
- Bromothymol blue, phenolphthalein and methyl orange are suitable indicators for strong acid and strong base titrations.

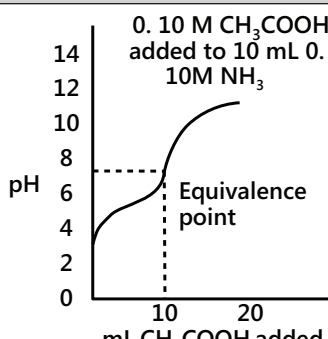
**Vaibhav Krishnan (JEE 2009, AIR 22)**

## 10. TITRATIONS

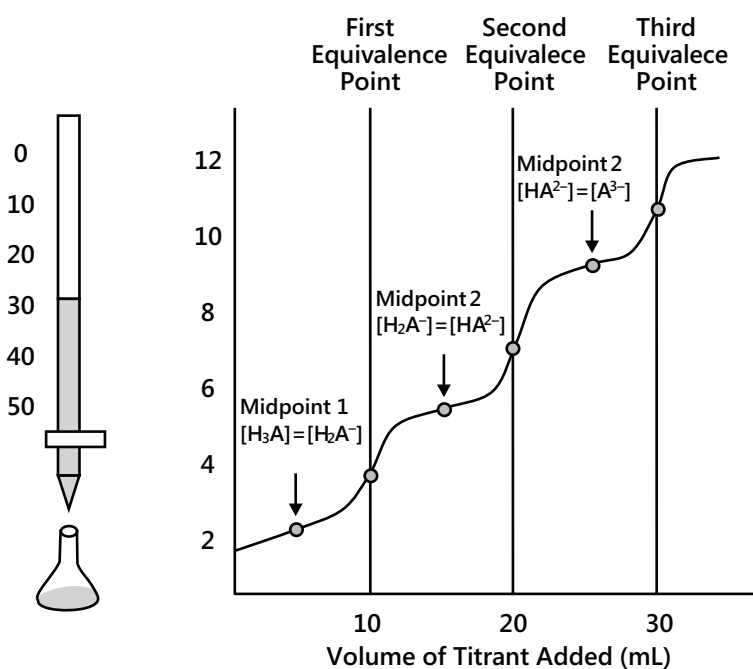
**Table 6.5:** Typical titration curves for different types of solutions

General Type	Typical Titration Curve	Features of Curve
Strong Acid and Strong Base $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$		Curve begins at high pH typical of strong base and ends at low pH typical of strong acid.  There is a large rapid change in pH near the equivalence point ( $\text{pH} = 7$ )
Strong Base and Strong acid $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$		Curve begins at low pH typical of strong acid, and ends at high pH typical of strong base.  There is a large rapid change in pH near the equivalence point ( $\text{pH} = 7$ )
Weak Acid and Strong Base $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$		Curve begins at a higher acidic pH and ends at high basic pH.  The pH change at the equivalence point ( $\text{pH} > 7$ ) is not so great.
Weak Base and Strong Acid $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$		Curve begins at low pH and ends at a less high basic pH.  The pH change at the equivalence point ( $\text{pH} > 7$ ) is similar to that for a strong Base and Weak Acid.



General Type	Typical Titration Curve	Features of Curve
Weak Acid and Weak Base $\text{CH}_3\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{COONH}_4$		Curve begins at a higher acidic pH and ends at low basic pH.  There is no great pH change at the equivalence point (pH~7) making this a very difficult titration to perform.

### Titrations of a weak polyprotic acid



**Figure 6.3** Titration of a Weak Polyprotic Acid.

The final equivalence point is attained by adding another 10 ml, or a total of 30 ml, of the titrant to the weak polyprotic acid. Image created by Heather Yee.

- The curve starts at a higher pH than a titration curve of a strong base
- There is a steep climb in pH before the first midpoint
- Gradual increase of pH until past the midpoint.
- Right before the equivalence point there is a sharp increase in pH
- pH steadies itself around the midpoint because the solutions at this point in the curve are buffer solutions, which means that adding small increments of a strong base will only barely change the pH
- Increase in pH near the equivalence point

## PROBLEM-SOLVING TACTICS

### Calculation of Degree of Ionization, pH of Weak Acid/Base and Equilibrium Concentrations of All Species

Knowing the ionization constant of the weak acid/base and its initial concentration, the degree of ionization and equilibrium concentrations are calculated as follows:

**Step 1.** Write the balanced equation for dissociation in the solution.

**Step 2.** Assume  $\alpha$  as the degree of dissociation (or  $x$  as the amount dissociated) and calculate the equilibrium concentrations.

**Step 3.** Substitute the equilibrium concentrations in the expression for  $K_a$  or  $K_b$ , and calculate  $\alpha$  (or calculate the amount dissociated  $x$  and then  $\alpha = x/c$  where  $c$  is the initial concentration).

As already discussed in Art. 7. 18, if  $\alpha$  is very small, we can calculate  $\alpha$  directly using the expression  $\alpha = \sqrt{k_a / c}$

**Step 4.** Knowing  $[H^+]$ , calculate pH or knowing  $[OH^-]$ , calculate pOH. Then  $pH = 14 - pOH$ .

#### (a) Criteria for Precipitation

**Case I:** When  $K_{ip} < K_{sp}$ , then solution is unsaturated in which more solute can be dissolved.

**Case II:** When  $K_{ip} = K_{sp}$ , then solution is saturated in which no more solute can be dissolved.

**Case III:** When  $K_{ip} > K_{sp}$ , then solution is supersaturated and precipitation takes place. When the ionic product exceeds the solubility product, the equilibrium shifts towards left hand side, i. e., increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

**(b)** Calculation of the remaining concentration after precipitation: Sometimes, an ion remains after precipitation, if it is in excess. Remaining concentration can be determined, e.g. .

$$(i) [A^+]_{left} = \frac{K_{sp}[AB]}{[B^-]}$$

$$(ii) [Ca^{2+}]_{left} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}$$

$$(iii) [A^{n+}]_{left}^m = \frac{K_{sp}[A_m B_n]}{[B^{m-}]^n}$$

$$\text{Percentage precipitation of an ion} = \left[ \frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}} \right] \times 100$$

## POINTS TO REMEMBER

Ostwalds dilution law for weak electrolyte	$K_a = \left( \frac{\alpha^2}{1-\alpha} \right) \left( \frac{1}{V} \right)$
Acid & Bases : Arrhenius theory	(i) An Arrhenius acid is a substance which furnishes the hydrogen ion ( $H^+$ ions) in an aqueous solution (ii) An Arrhenius base is a substance which furnishes the hydroxyl ( $OH^-$ ) ions in an aqueous solution
Bronsted Lowry theory	(i) A Bronsted acid is proton donor (ii) Bronsted base is proton acceptor.
Lewis concept	(i) A Lewis acid is an electron pair acceptor (ii) A Lewis base is an electron pair donor.
Some basic concept	pH scale: $pH = -\log [H^+]$ Autoionization of water: $K_w = [H^+][OH^-]$ . $K_a[H_2O] = K_w/[H_2O]$
Homogenous Ionic equilibria Acid base equilibrium	(a) Strong acid/base $[H]^+ = \frac{c}{2} + \sqrt{\frac{c^2}{4} + K_w} ; c = \text{conc. of (acid)}$ (b) pH due to polyprotic weak acids (c) Weak monobasic acid/base $[H]^+ = \sqrt{K_a \cdot c}$ (if $\alpha < 0.1$ ) (d) Mixture of S. A. /W. A. (e) Mixture of W. A. /W. A. $H^+ = \sqrt{K_1 c_1 + K_2 c_2}$ (f) Buffer solutions: $pH = pK_a + \log \left( \frac{\text{salt}}{\text{acid}} \right)$ $pOH = pK_b + \log \left( \frac{\text{salt}}{\text{base}} \right)$ (g) Salt hydrolysis – (W. A. /S. B. ) $pH = \frac{1}{2} (pK_w + pK_a + \log c)$ (W. B. /S. A. ) $pH = \frac{1}{2} (pK_w - pK_b - \log c)$ (W. A. /W. B. ) $pH = \frac{1}{2} (pK_w + pK_a - pK_b)$ (h) pH due to hydrolysis of polyprotic acid. Complexation equilibrium $\{M^{n+} + m\text{Lig} \rightleftharpoons [M(\text{Lig})m]^{n+1}\}$ $\left\{ K_{sb} = \frac{[M(\text{Lig})m]^{n+1}}{[M^n(\text{Lig})m]} \right\}$
Heterogeneous equilibrium	Solubility of sparingly soluble salt' $(AB, AB_2, A_x B_y) K_{sp} = (S^{x+y}) X^x Y^y$

Solubility Product	$K_{sp} = [xS]^x [yS]^y = x^x \cdot y^y (S)^{x+y}$ <p><b>Special Cases:</b></p> <p>(i) 1: 1 type salts: Examples: AgCl, AgI, BaSO<sub>4</sub>, PbSO<sub>4</sub>, etc. <math>S = \sqrt{K_{sp}}</math></p> <p>(ii) 1: 2 or 2: 1 type salts: Examples: Ag<sub>2</sub>CO<sub>3</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, PbCl<sub>2</sub>, CaF<sub>2</sub>, etc.  <math display="block">S = \sqrt[3]{K_{sp} / 4}</math></p> <p>(iii) 1: 3 type salts: Examples: AlI<sub>3</sub>, Fe(OH)<sub>3</sub>, Cr(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, etc.  <math display="block">S = \sqrt[4]{K_{sp} / 27}</math></p> <p>In presence of common ion effect –</p> $K_{sp} = S'(S' + c)$ <p>(i) <math>[A^+]_{left} = \frac{K_{sp}[AB]}{[B^-]}</math></p> <p>(ii) <math>[Ca^{2+}]_{left} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}</math></p> <p>(iii) <math>[A^{n+}]_{left}^m = \frac{K_{sp}[A_m B_n]}{[B^{m-}]^n}</math></p> <p>Percentage precipitation of an ion = <math>\left[ \frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}} \right] \times 100</math></p>
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## Solved Examples

### JEE Main/Boards

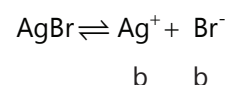
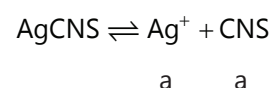
**Example 1:** Calculate simultaneous solubility of AgCNS and AgBr in a solution of water  $K_{sp}$  of AgCNS =  $1 \times 10^{-12}$ ,  $K_{sp}$  of AgBr =  $5 \times 10^{-13}$ .

**Sol:** For solution containing common ion, solubility and solubility product are related by following expression.

$$K_{sp} = S(S+c)$$

By taking the ratios of solubility product of two solutions, solubility can be determined.

Let the solubility of AgCNS and AgBr in water be  $a$  and  $b$  respectively.



$$[\text{Ag}^+] = a + b, [\text{CNS}^-] = a \text{ and}$$

$$[\text{Br}^-] = b$$

$$K_{sp} \text{AgCNS} = [\text{Ag}^+][\text{CNS}^-] = a(a + b)$$

$$1 \times 10^{-12} = a(a + b) \quad \dots (i)$$

$$K_{sp} \text{AgBr} = [\text{Ag}^+][\text{Br}^-] = b(a + b)$$

$$5 \times 10^{-13} = b(a + b) \quad \dots (ii)$$

Dividing eq. (i) by (ii),

$$\frac{1 \times 10^{-12}}{5 \times 10^{-13}} = \frac{a}{b}$$

$$2 = \frac{a}{b} \text{ or } a = 2b$$

Putting the value of  $a$  in eq. (i).

$$6b^2 = 1 \times 10^{-12}$$

$$b^2 = \frac{1}{6} \times 10^{-12}$$

$$b = 4.08 \times 10^{-7} \text{ mol L}^{-2}$$

$$a = 2 \times 4.08 \times 10^{-7} = 8.16 \times 10^{-7} \text{ mol L}^{-1}$$

**Example 2:**  $\text{MgSO}_4$  gives a precipitate with  $\text{NH}_4\text{OH}$  but not with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . Why?

**Sol:** No doubt  $\text{NH}_4\text{OH}$  is weak base but it provides appreciable  $\text{OH}^-$  ion to exceed the product of ionic concentration of  $\text{Mg}^{2+}$  and  $\text{OH}^-$  than their  $K_{sp}$  and thus  $\text{MgSO}_4$  is precipitated out as  $\text{Mg}(\text{OH})_2$ . On the other hand the dissociation of  $\text{NH}_4\text{OH}$  is suppressed in presence of  $\text{NH}_4\text{Cl}$  and thus  $[\text{OH}^-]$  diminishes to the extent that  $[\text{Mg}^{2+}][\text{OH}^-]^2 < K_{sp}$ . Thus,  $\text{MgSO}_4$  is not precipitated.

**Example 3:** An aqueous solution contains 0.1 M of  $\text{Ba}^{2+}$  and 0.1 M  $\text{Ca}^{2+}$ . Calculate the maximum concentration of  $\text{Na}_2\text{SO}_4$  at which one of them is completely precipitated almost completely. What % of that ion is precipitated?

$$K_{sp} \text{ of } \text{BaSO}_4 = 1.5 \times 10^{-9};$$

$$K_{sp} \text{ of } \text{CaSO}_4 = 2 \times 10^{-4}.$$

**Sol:**  $[\text{SO}_4^{2-}]$  needed for precipitation of  $[\text{Ba}^{2+}]$  as  $\text{BaSO}_4$

$$= \frac{K_{sp}}{[\text{Ba}^{2+}]} = \frac{1.5 \times 10^{-9}}{0.1} = 1.5 \times 10^{-8}$$

$[\text{SO}_4^{2-}]$  needed for precipitation of  $[\text{Ca}^{2+}]$  as  $\text{CaSO}_4$

$$= \frac{2 \times 10^{-4}}{0.1} = 2 \times 10^{-3}.$$

Thus,  $[\text{SO}_4^{2-}]$  required for precipitation of  $\text{BaSO}_4$  is less and thus  $\text{BaSO}_4$  will precipitate first. The precipitation of  $\text{BaSO}_4$  will start when  $[\text{Na}_2\text{SO}_4]$  is  $1.5 \times 10^{-8}$  and will be maximum when  $[\text{Na}_2\text{SO}_4]$  is  $2 \times 10^{-3}$ .

Thus, maximum  $[\text{Na}_2\text{SO}_4]$  required for precipitation of  $\text{Ba}^{2+} = 2 \times 10^{-3}$  M. At this conc, of  $\text{SO}_4^{2-}$ ,  $[\text{Ba}^{2+}]$  left in solution is

$$[\text{Ba}^{2+}]_{\text{left}} = \frac{K_{sp}}{[\text{SO}_4^{2-}]} = \frac{1.5 \times 10^{-9}}{2 \times 10^{-3}} = 7.5 \times 10^{-7}$$

$$\therefore \% \text{ of } \text{Ba}^{2+} \text{ left} = \frac{7.5 \times 10^{-7} \times 100}{0.1} = 7.5 \times 10^{-4}\%$$

$$\therefore \% \text{ of } \text{Ba}^{2+} \text{ precipitated}$$

$$= 100 - 7.5 \times 10^{-4} = 99.9992\%$$

**Example 4:** Will a precipitate of  $\text{Mg}(\text{OH})_2$  be formed in a 0.001 M solution of  $\text{Mg}(\text{NO}_3)_2$ , if the pH of solution is adjusted to 9?

$$K_{sp} \text{ of } \text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}.$$

**Sol:** If  $K_{sp}$  of  $\text{Mg}(\text{OH})_2 > K_{sp}$  of  $\text{Mg}(\text{OH})_2$  in solution, precipitation will not occur.

If  $K_{sp}$  of  $\text{Mg}(\text{OH})_2 < K_{sp}$  of  $\text{Mg}(\text{OH})_2$  in solution, precipitation will occur.

$$\text{Given. pH} = 9; \therefore [\text{H}^+] = 10^{-9}$$

$$\text{or } [\text{OH}^-] = 10^{-5}$$

$$0.001 \text{ M } \text{Mg}(\text{NO}_3)_2 \text{ is present in a solution of } [\text{OH}^-] = 10^{-5}$$

Then product of ionic concentration for  $\text{Mg}(\text{OH})_2$

$$= [\text{Mg}^{2+}][\text{OH}^-]^2$$

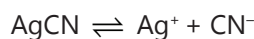
$$= [0.001][10^{-5}]^2$$

$$= 10^{-3} < K_{sp}, \text{ i. e., } 8.9 \times 10^{-12}$$

Therefore,  $\text{Mg}(\text{OH})_2$  will not precipitate out.

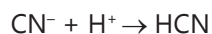
**Example 5:** Calculate the solubility of  $\text{AgCN}$  in a buffer solution of pH = 3. Given  $K_{sp}$  of  $\text{AgCN} = 1.2 \times 10^{-16}$  and  $K_a$  for  $\text{HCN} = 4.8 \times 10^{-10}$ .

**Sol:** Solution Let solubility of  $\text{AgCN}$  be a mol litre<sup>-1</sup>



$$a \quad a \quad (\text{After reaction})$$

However, the  $\text{CN}^-$  formed will react with  $\text{H}^+$  to form  $\text{HCN}$



$$a \quad 10^{-3} \quad (\text{Before reaction})$$

$$0 \quad 10^{-3} \quad a \quad (\text{After reaction})$$

(buffer)

$$\therefore [\text{Ag}^+] = a \text{ and } [\text{HCN}] = a$$

Since  $\text{HCN}$  is weak acid and has low degree of dissociation. Also its dissociation is suppressed in presence of  $[\text{H}^+]$ . Thus



$$\therefore \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = K_a$$

$$\text{or } [\text{CN}^-] = \frac{K_a[\text{HCN}]}{[\text{H}^+]} = \frac{a \times (4.8 \times 10^{-10})}{10^{-3}}$$

Now for  $\text{AgCN(s)} = \text{aq.} \rightleftharpoons \text{Ag}^+ + \text{CN}^-$

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

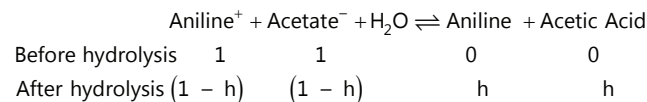
$$1.2 \times 10^{-16} = \frac{a \times a \times 4.8 \times 10^{-10}}{10^{-3}}$$

$$\therefore a^2 = \frac{1.2 \times 10^{-16} \times 10^{-3}}{4.8 \times 10^{-10}}$$

$$\therefore a = 1.58 \times 10^{-5} \text{ mol litre}^{-1}$$

**Example 6:** The dissociation constant 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 its pH.

**Sol:**



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

$$\therefore K_H = \frac{[\text{Aniline}][\text{Acetic acid}]}{[\text{Aniline}^+][\text{Acetate}^{-1}]} = \frac{ch \cdot ch}{c(1-h)c(1-h)}$$

$$K_H = \frac{h^2}{(1-h)^2} \quad \text{or} \quad \frac{h}{1-h} = \sqrt{K_H} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$= \sqrt{\frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}}}$$

$$\therefore h = 54.95\%$$

$$\text{Also, } \text{pH} = \frac{1}{2} [\log K_b - \log K_w - \log K_a]$$

$$= \frac{1}{2} \log [3.83 \times 10^{-10}] - \log [1.008 \times 10^{-14}]$$

$$[-\log [1.75 \times 10^{-5}]] = 4.6683$$

If  $K_H = h^2$  is assumed (assuming  $1 - h \approx 1$ ), the value of  $h$  comes greater than 1 which is not possible and thus  $1 - h$  should not be neglected.

**Example 7:** A solution has 0.05M Mg<sup>2+</sup> and 0.05M NH<sub>3</sub>. Calculate the concentration of NH<sub>4</sub>Cl required to prevent the formation of Mg(OH)<sub>2</sub> in solution.

$$K_{sp} \text{ of } \text{Mg(OH)}_2 = 9.0 \times 10^{-12} \text{ and}$$

$$K_b \text{ of } \text{NH}_3 = 1.8 \times 10^{-5}$$

**Sol:** Suppose  $V$  mL of solution containing 0.1 M Mg<sup>2+</sup> and 0.8 M NH<sub>4</sub>Cl. Now  $V$  mL of NH<sub>3</sub> of a M is added to it in order to have just precipitation of Mg(OH)<sub>2</sub>, then

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = K_{sp} \text{Mg(OH)}_2$$

$$\text{or} \left[ \frac{0.1 \times V}{2V} \right] [\text{OH}^-]^2 = 1.4 \times 10^{-5}$$

$$\left[ \therefore [\text{Mg}^{2+}] = \frac{\text{Milli moles}}{\text{Total Volume}} \right]$$

$$\therefore [\text{OH}^-] = 1.67 \times 10^{-5} \text{M}$$

The solution must therefore, contain [OH<sup>-</sup>] equal to  $1.67 \times 10^{-5} \text{M}$ . Which are obtained by buffer solution of NH<sub>3</sub> and NH<sub>4</sub>Cl

$$\therefore -\log \text{OH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

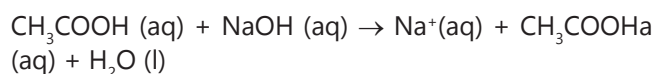
$$\text{or } -\log [1.67 \times 10^{-5}]$$

$$= -\log [1.8 \times 10^{-5}] + \log \frac{(0.8 \times V) / 2V}{(a \times V) / 2V}$$

$$\therefore a = 0.7421 \text{ M}$$

$$\therefore [\text{NH}_3] \text{ in solution} = \frac{0.7421 \times V}{2V} = 0.3710 \text{ M.}$$

**Example 8:** Calculate the molarity of an acetic acid solution if 34.57 mL of this solution are needed to neutralize 25.19 mL of 0.1025 M sodium hydroxide



**Sol: Strategy:**

1. Figure out how many moles of the titrant (in this case, the base) were needed.

$$25.19 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.02519 \text{ L}$$

$$0.02519 \text{ L} \times \frac{0.1025 \text{ mol}}{1 \text{ L}} = 0.002582 \text{ mol NaOH}$$

2. Use the balanced chemical equation to calculate the moles of analyte (in this case, the acid) present. 0.002582 mol

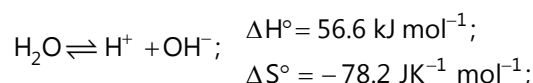
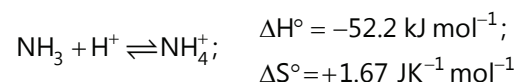
$$\text{NaOH} \times \frac{1 \text{ mol CH}_3\text{COOH}}{1 \text{ mol NaOH}} = 0.002582 \text{ mol CH}_3\text{COOH}$$

3. Use the volume of analyte to find the concentration of the analyte.

$$34.57 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.03457 \text{ L}$$

$$\frac{0.002582 \text{ mol CH}_3\text{COOH}}{0.03457 \text{ L}} = 0.07469 \text{ M CH}_3\text{COOH}$$

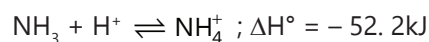
**Example 9:** Calculate the dissociation constant of NH<sub>4</sub>OH at 25°C, if  $\Delta H^\circ$  and  $\Delta S^\circ$  for the given changes are as follows:



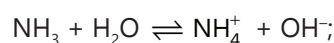
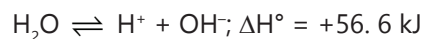
**Sol:** First calculate free energy from the given value of enthalpy and entropy by using the following expression,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Value of free energy change can be used to estimate the value of equilibrium constant can be calculated as  $\Delta G^\circ = -2.303 RT \log K_b$

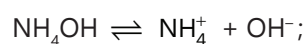


Adding,



$$\Delta H^\circ = +4.4 \text{ kJ mol}^{-1}$$

Similarly,  $\Delta S^\circ$  for the change =  $-76.53 \text{ J K}^{-1} \text{ mol}^{-1}$  or for the change



$$\Delta H^\circ = 4.4 \text{ kJ mol}^{-1} \text{ and } \Delta S^\circ = -76.53 \text{ J K}^{-1} \text{ mol}^{-1}$$

Now, we have  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\therefore \Delta G^\circ = 4.4 - (-76.53 \times 10^{-3}) \times 298 = 27.21 \text{ kJ mol}^{-1}$$

$$\text{Also, } \Delta G^\circ = -2.303 RT \log K_b$$

$$27.21 = -2.303 \times 8.314 \times 10^{-3} \times 298 \times \log K_b$$

$$\therefore K_b = 1.7 \times 10^{-5}$$

## JEE Advanced/Boards

**Example 1:** Prove that the degree of dissociation of a weak monoprotic acid is given by  $\alpha = \frac{1}{1 + 10^{(\text{p}K_a - \text{pH})}}$

where  $K_a$  is the dissociation constant of the acid.

**Sol:** Suppose we start with  $C \text{ mol L}^{-1}$  of the monoprotic acid HA. Then



Initial molar conc.  $C$

Molar conc.  $C - C\alpha \quad C\alpha \quad C\alpha$

After dissociation =  $C(1 - \alpha)$

$$\text{Thus, } K_a = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

$$\text{Or } C = \frac{K_a(1 - \alpha)}{\alpha^2} \quad \dots (i)$$

$$\text{Also, } [\text{H}^+] = C\alpha \quad \dots (ii)$$

Substituting the value of  $C$  from eqs. (i), we get

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

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

$$\text{Or } \text{pH} = \text{p}K_a - \log(1 - \alpha) - \log \alpha$$

$$\text{Or } \log \frac{1 - \alpha}{\alpha} = \text{p}K_a - \text{pH}$$

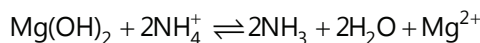
$$\text{Or } \frac{1 - \alpha}{\alpha} = 10^{\text{p}K_a - \text{pH}}$$

$$\text{Or } \frac{1}{\alpha} - 1 = 10^{\text{p}K_a - \text{pH}}$$

$$\text{Or } \frac{1}{\alpha} = 1 + 10^{\text{p}K_a - \text{pH}}$$

$$\text{Or } \alpha = \frac{1}{1 + 10^{\text{p}K_a - \text{pH}}}$$

**Example 2:** The solubility of  $\text{Mg}(\text{OH})_2$  is increases by the addition of  $\text{NH}_4^+$  ion. Calculate  $K_c$  for,



$$K_{\text{spMg}(\text{OH})_2} = 6 \times 10^{-12}, K_{\text{bNH}_3} = 1.8 \times 10^{-5}.$$

**Sol:** The given reaction is:



$$\begin{aligned} \therefore K_c &= \frac{[\text{NH}_3]^2 [\text{Mg}^{2+}]}{[\text{NH}_4^+]^2} \\ &= \frac{[\text{NH}_4\text{OH}]^2 [\text{Mg}^{2+}]}{[\text{NH}_4^+]^2} \quad \dots (i) \end{aligned}$$

For  $\text{NH}_4\text{OH}$ , a weak base

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

By Eqs. (i) and (ii)

$$K_c \times (K_b)^2 = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$= K_{\text{spMg}(\text{OH})_2}$$

$$\therefore K_c = \frac{K_{\text{sp}}}{(K_b)^2} = \frac{6 \times 10^{-12}}{(1.8 \times 10^{-5})^2} = 1.85 \times 10^{-2}$$

**Example 3:** 0.1 M  $\text{CH}_3\text{COOH}$  solution is titrated against 0.05 M  $\text{NaOH}$  solution. Calculate pH at  $\frac{1}{4}$  th and th stages of neutralization of acid. The pH for 0.1 M  $\text{CH}_3\text{COOH}$  is 3.

**Sol:** Given pH for 0.1 M  $\text{CH}_3\text{COOH} = 3$

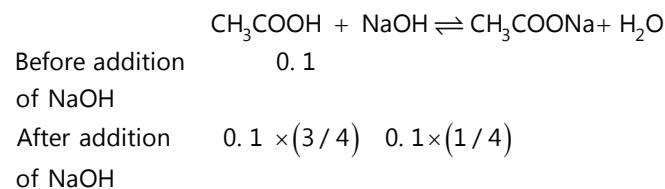
$$\therefore [\text{H}^+] = 10^{-3}$$

$$\text{Or } \alpha = 10^{-3}$$

$$\text{Or } \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$$

$$K_a = c\alpha^2 = (0.1) \times (10^{-2})^2 = 10^{-5}$$

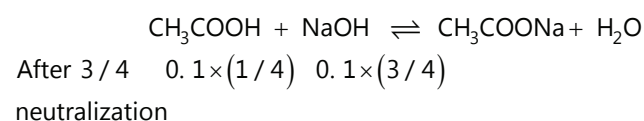
**Case I:** At 1/4th neutralization of acid



$$\therefore \text{pH} = -\log K_a + \log \frac{[\text{conjugate base}]}{[\text{Acid}]}$$

$$\text{Or pH} = -\log 10^{-5} + \log \frac{(0.1/4)}{(0.3/4)} \Rightarrow \text{pH} = 4.5228$$

**Case II:**



$$\therefore \text{pH} = -\log[10^{-5}] + \log \frac{0.3/4}{0.1/4} \Rightarrow \text{pH} = 5.4771$$

**Example 4:** 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH.

[Assume there is no change in volume in mixing;  $K_a$  of acetic acid is  $1.75 \times 10^{-5} \text{ mol L}^{-1}$ ]

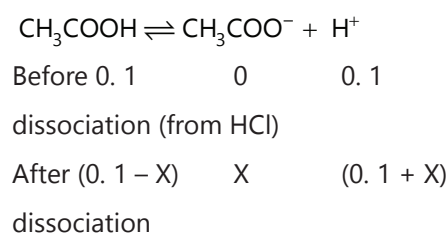
**Sol:** (i) Meq. of  $\text{CH}_3\text{COOH} = 500 \times 0.2 = 100$

Meq. of HCl =  $500 \times 0.2 = 100$

$$\therefore [\text{HCl}] = \frac{100}{1000} = 0.1;$$

$$[\text{CH}_3\text{COOH}] = \frac{100}{1000} = 0.1$$

**For  $\text{CH}_3\text{COOH}$ :**



$$\therefore K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{X(0.1 + X)}{(0.1 - X)}$$

Due to common ion effect dissociation of  $\text{CH}_3\text{COOH}$  is very small in presence of HCl.

Therefore,  $(0.1 + X) = 0.1$  and  $(0.1 - X) = 0.1$

$$\therefore K_a = \frac{X \cdot 0.1}{0.1}$$

$$\therefore X = K_a = 1.75 \times 10^{-5}$$

Thus, degree of dissociation

$$\alpha = \frac{X}{0.1} = \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

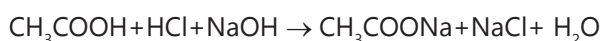
$$= 0.000175 = 0.0175\%$$

Also,  $[\text{H}^+] = 0.1 + X = 0.1 (X \ll 0.1)$

$$\therefore \text{pH} = -\log[\text{H}^+] = -\log[0.1] = 1$$

(ii) Eq. of NaOH or mole of NaOH added =  $6/40 = 0.15$

Therefore, new equilibrium will have,



$$\begin{array}{cccccc} 0.1 & 0.1 & 0.15 & 0 & 0 & 0 \\ 0.05 & 0 & 0 & 0.05 & 0 & 0 \end{array}$$

Thus, the solution will act as acidic buffer having

$$[\text{CH}_3\text{COOH}] = \frac{0.05}{1000}$$

$$\text{and } [\text{CH}_3\text{COONa}] = \frac{0.05}{1000}$$

$$\text{Thus, pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log [1.75 \times 10^{-5}] + \log \frac{[0.05/1000]}{[0.05/1000]} = 4.757$$

**Example 5:** The average concentration of  $\text{SO}_2$  in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of  $\text{SO}_2$  in water at 298 K is  $1.3653 \text{ mol litre}^{-1}$  and the  $\text{p}K_a$  of  $\text{H}_2\text{SO}_4$  is 1.92. Estimate the pH of rain on that day.

**Sol:** Use Henry's law to find out  $[\text{SO}_2]$  dissolved in water. Concentration of  $\text{SO}_2$  in air is 10 ppm or 10 mole in  $10^6$  mole air or  $10^{-5}$  mole  $\text{SO}_2$  per mol of air. The concentration of  $\text{SO}_2$  in air being substantial and since, rain water is falling from enormously great height so, each drop of rain water will get saturated with  $\text{SO}_2$  before it reaches earth.

Now the given concentration or solubility of  $\text{SO}_2$  at 298 K is 1.3653 M.



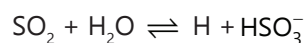
This value of solubility corresponds when  $P_{\text{SO}_2} = 1 \text{ atm}$

Thus, according to Henry's law

$[\text{SO}_2]$  dissolved in water  $\propto P_{\text{SO}_2}$  in gas phase

$[\text{SO}_2]$  dissolved in water  $\propto P_{\text{SO}_2}$  in air

$\therefore [\text{SO}_2]$  dissolved in water =  $1.3653 \times 10^{-5} \text{ M}$



$$1 \quad \quad \quad 0 \quad \quad 0$$

$$(1 - \alpha) \quad \quad \quad a \quad \quad a$$

$$\therefore K_a = 10^{-1.92} = \frac{c\alpha \cdot c\alpha}{c(1 - \alpha)} = \frac{c\alpha^2}{1 - \alpha} \quad (\alpha \text{ is small})$$

$$\text{or } 0.012 = \frac{1.3653 \times 10^{-5} \times \alpha^2}{1 - \alpha}$$

$$(\because pK_b = 1.92, \therefore K_b = 0.012)$$

$$\therefore 1.3653 \times 10^{-5} \alpha^2 + 0.012 \alpha - 0.012 = 0$$

$$\therefore \alpha = 1$$

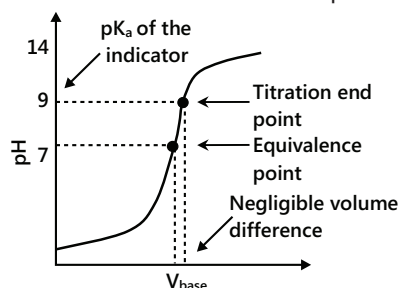
(Solving quadratic equation)

$$\therefore [\text{H}^+] = c\alpha = 1.3653 \times 1 = 1.3653$$

$$\therefore \text{pH} = 4.8648$$

**Example 6:** Why is it acceptable to use an indicator whose  $pK_a$  is not exactly the pH at the equivalence point?

**Sol:** As we can see in the following titration curve, even if the  $pK_a$  of the indicator is several units away from the pH at the equivalence point, there is only a negligible change in volume of titrant added due to the steep slope of the titration curve near the equivalence point.

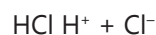


**Example 7:** What is the pH of the following solutions?

(a)  $10^{-3} \text{ M HCl}$       (b)  $0.0001 \text{ M NaOH}$

(c)  $0.0001 \text{ M H}_2\text{SO}_4$

**Sol:** (a) HCl is a strong electrolyte and is completely ionised.



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

$$\text{pH} = -\log[\text{H}^+] = -\log(10^{-3}) = 3$$

(b) NaOH is a strong electrolyte and is completely ionized.



$$\text{So, } [\text{H}^+] = 0.0001 \text{ M} = 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(10^{-4}) = 4$$

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

$$\text{So, } \text{pH} + 4 = 14$$

$$\text{or } \text{pH} = 10$$

**Alternative method:**

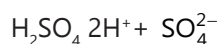
$$[\text{OH}^-] = 10^{-4} \text{ M}$$

$$\text{We know that, } [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$\text{So, } [\text{H}^+] = \frac{1.0 \times 10^{-14}}{10^{-4}} = 10^{-10} \text{ M}$$

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

(c)  $\text{H}_2\text{SO}_4$  is a strong electrolyte and is ionized completely.



One molecule of  $\text{H}_2\text{SO}_4$  furnishes  $2\text{H}^+$  ions.

$$\text{So, } [\text{H}^+] = 2 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2 \times 10^{-4}) = 3.70$$

**Example 8:** If very small amount of phenolphthalein is added to  $0.15 \text{ mol litre}^{-1}$  solution of sodium benzoate what fraction of the indicator will exist in the coloured form? State any assumption that you make.

$$K_a (\text{Benzoic acid}) = 6.2 \times 10^{-5},$$

$$K_w (\text{H}_2\text{O}) = 1 \times 10^{-14},$$

$$K_{\text{In}} (\text{Phenolphthalein}) = 3.16 \times 10^{-10}$$

**Sol:** Use the following expression to find out pH of salt hydrolysis and pH of indicator.

Formula for pH of salt hydrolysis:

$$\text{pH} = \frac{1}{2} [pK_w + pK_a + \log C]$$

Formula for pH of indicator:

$$\text{pH} = pK_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

Substitute the values in the above equation,

For pH of salt hydrolysis:

$$= \frac{1}{2} [14 - \log_{10} 6.2 \times 10^{-5} + \log 0.15] = 8.6918$$

For pH of indicator:

$$8.6918 = -\log_{10} (3.16 \times 10^{-10}) + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$0.16 = [\text{In}^-]/[\text{HIn}] = \text{Fraction of indicator in coloured form}$$

## JEE Main/Boards

## Exercise 1

**Q.1** The degree of dissociation of acetic acid in a 0.1 N solution is  $1.32 \times 10^{-2}$ . At what concentration of nitrous acid, its degree of dissociation will be same as that of acetic acid?

$$K_a(\text{HNO}_2) = 4 \times 10^{-4}$$

**Q.2** How many times is the  $\text{H}^+$  concentration in the blood ( $\text{pH} = 7.36$ ) greater than in the spinal fluid ( $\text{pH} = 7.53$ )?

**Q.3** A 0.400 M formic acid solution freezes at  $-0.758^\circ\text{C}$ . Calculate the  $K_a$  of the acid at that temperature. (Assume molarity equal to molality).  $K_f(\text{H}_2\text{O}) = 1.86^\circ\text{mol}^{-1}\text{kg}$ .

**Q.4** A sample of AgCl was treated with 5 mL of 1.5 M  $\text{Na}_2\text{CO}_3$  solution to give  $\text{Ag}_2\text{CO}_3$  the remaining solution contained 0.0026 g/litre  $\text{Cl}^-$  ion. Calculate the solubility of AgCl.

**Q.5** 100 mL of solution  $S_1$  contains 0.17 mg of  $\text{AgNO}_3$ . Another 200 mL solution  $S_2$  contains 0.117 mg of NaCl. On mixing these two solutions predict whether the precipitate of AgCl will appear or not  $K_{sp} \text{ AgCl} = 10^{-10} \text{ M}^2$

**Q.6** An indicator is a weak acid and the 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 given pH range, calculate the ionization constant of the indicator.

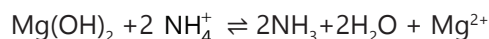
**Q.7** Calculate the hydrolysis constant of  $\text{NH}_4\text{Cl}$ ; determine the degree of hydrolysis of this salt in 0.01 M solution and the pH of the solution.  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$

**Q.8** Calculate the pH of 0.1 M acetic acid solution if its dissociation constant is  $1.8 \times 10^{-5}$ . If 1 litre of this solution is mixed with 0.05 mole of HCl, what will be the pH of the mixture

**Q.9** It is found that 0.1 M solution of three sodium salts NaX, NaY and NaZ have pHs 7.0, 9.0 and 11.0, respectively. Arrange the acids HX, HY and HZ in order of increasing strength. Where possible, calculate the ionisation constants of the acids.

**Q.10** Given a solution that is 0.5 M  $\text{CH}_3\text{COOH}$ . To what volume at  $25^\circ\text{C}$  must one  $\text{dm}^3$  of this solution be diluted in order to (a) double the pH; (b) double the hydroxide-ion concentration. Given that  $K_a = 1.8 \times 10^{-5} \text{ M}$ .

**Q.11** The solubility of  $\text{Mg}(\text{OH})_2$  is increased by addition of  $\text{NH}_4^+$  ion.



If  $K_{sp}$  of  $\text{Mg}(\text{OH})_2 = 1 \times 10^{-11}$ ,  $K_b$  for  $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$  then calculate  $K_c$  for the reaction.

**Q.12** An unknown volume and unknown concentration of weak acid HX is titrated with NaOH of unknown concentration. After addition of 10.0  $\text{cm}^3$  of NaOH solution, pH of solution is 5.8 and after the addition of 20.0  $\text{cm}^3$  of NaOH solution, the pH is 6.4. Calculate the pH of aqueous solution of 0.1 M NaX.

**Q.13** A solution containing zinc and manganese ions each at a concentration of 0.01  $\text{mol dm}^3$  is saturated with  $\text{H}_2\text{S}$ . Calculate

- pH at which the  $\text{MnS}$  will form a precipitate
- Conc. of  $\text{Zn}^{+2}$  ions remaining.

Given:  $[\text{H}_2\text{S}] = 0.1 \text{ mol/lit}$ ,

$$K_{sp}(\text{ZnS}) = 1 \times 10^{-22} \text{ mol}^2 \text{ lit}^{-2},$$

$$K_{sp}(\text{MnS}) = 5.6 \times 10^{-16} \text{ mol}^2 \text{ lit}^{-2}.$$

$K_1$  and  $K_2$  for  $\text{H}_2\text{S}$  are  $1 \times 10^{-7}$  and  $1.1 \times 10^{-14}$

**Q.14** For the indicator thymol blue, the value of pH is 2.0, when half of the indicator is present in an unionized form. Calculate the percentage of the indicator in the unionized form in a solution of  $4.0 \times 10^{-3} \text{ mol/dm}^3$  hydrogen ion concentration.

**Q.15** The first ionization constant of  $\text{H}_2\text{S}$  is  $9.1 \times 10^{-8}$ . Calculate the concentration of  $\text{HS}^-$  ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ . Calculate the concentration of  $\text{S}^{2-}$  under both conditions.

**Q.16** The ionization constant of acetic acid is  $1.74 \times 10^{-5}$ . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

**Q.17** It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its  $pK_a$

**Q.18** Assuming complete dissociation, calculate the pH of the following solutions:

- (i) 0.003 M HCl                      (ii) 0.005 M NaOH  
(iii) 0.002 M HBr                    (iv) 0.002 M KOH

**Q.19** Calculate the pH of the following solutions:

- (i) 2 g of TIOH dissolved in water to give 500 ml of solution.  
(ii) 0.3 g of  $\text{Ca}(\text{OH})_2$  dissolved in water to give 2 litre of solution  
(iii) 0.3 g of NaOH dissolved in water to give 200 mL of solution.  
(iv) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution

**Q.20** If the solubility product of silver oxalate is  $1 \times 10^{-11}$ , what will be the weight of  $\text{Ag}_2\text{C}_2\text{O}_4$  in 2.5 litres of a saturated solution?

**Q.21** Determine hydrolysis constant, degree of hydrolysis and the pH of 0.01 M solution of ammonium cyanide.  $K_a(\text{HCN}) = 7.2 \times 10^{-10}$ .  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

**Q.22** Assuming that the buffer in blood is  $\text{CO}_3^{2-} - \text{HCO}_3^-$ , calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH, 7.4.  $K_1(\text{H}_2\text{CO}_3) = 4.5 \times 10^{-7}$ .

**Q.23** How many moles of sodium hydroxide can be added to 1.0 L of a solution 0.10 M in  $\text{NH}_3$  and 0.10 M in  $\text{NH}_4\text{Cl}$  without changing the pOH by more than 1 unit. Assume no change in volume.  $K_b = 1.8 \times 10^{-5}$

## Exercise 2

### Single Correct Choice Type

**Q.1** The conjugate acid of  $\text{NH}_2^-$  is

- (A)  $\text{NH}_3$                       (B)  $\text{NH}_2\text{OH}$                       (C)  $\text{NH}_4^+$                       (D)  $\text{N}_2\text{H}_4$

**Q.2** Out of the following, amphoteric species are

- I.  $\text{HPO}_3^{2-}$                       II.  $\text{OH}^-$                       III.  $\text{H}_2\text{PO}_4^-$                       IV.  $\text{HCO}_3^-$   
(A) I, III, IV                      (B) I and III                      (C) III and IV                      (D) All

**Q.3** pH of an aqueous solution of NaCl at  $85^\circ\text{C}$  should be

- (A) 7                      (B)  $> 7$                       (C)  $< 7$                       (D) 0

**Q.4** 1 cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be

- (A) 7                      (B) 3                      (C) 4                      (D) 1

**Q.5** 10 ml of  $\frac{M}{200}$   $\text{H}_2\text{SO}_4$  is mixed with 40 ml of  $\frac{M}{200}$   $\text{H}_2\text{SO}_4$ . The pH of the resulting solution is

- (A) 1                      (B) 2  
(C) 2.3                      (D) None of these

**Q.6** If  $pK_b$  for fluoride ion at  $25^\circ\text{C}$  is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is:

- (A)  $1.74 \times 10^{-5}$                       (B)  $3.52 \times 10^{-3}$   
(C)  $6.75 \times 10^{-4}$                       (D)  $5.38 \times 10^{-2}$

**Q.7** The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is

- (A) 1                      (B) 2                      (C) 3                      (D) 11

**Q.8** If  $K_1$  and  $K_2$  be first and second ionization constant of  $\text{H}_3\text{PO}_4$  and  $K_1 > K_2$  which is incorrect.

- (A)  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$                       (B)  $[\text{H}^+] = K_1[\text{H}_3\text{PO}_4]$   
(C)  $K_2 = [\text{HPO}_4^{2-}]$                       (D)  $[\text{H}^+] = 3[\text{PO}_4^{3-}]$

**Q.9** Which of the following solution will have pH close to 1.0?

- (A) 100 ml of M/100 HCl + 100 ml of M/10  
(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
(C) 10 ml of M/10 HCl + 90 ml of m/10 NaOH  
(D) 75ml of M/5 HCl + 25ml of M/5 NaOH

**Q.10** What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is  $1.3 \times 10^{-9}$  and  $K_w = 1.0 \times 10^{-14}$

- (A) 2.48                      (B) 5.26                      (C) 8.2                      (D) 9.6

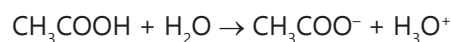
**Q.11** The compound whose 0.1 M solution is basic is

- (A) Ammonium acetate                      (B) Ammonium chloride  
(C) Ammonium sulphate                      (D) Sodium acetate

**Q.12** The  $\approx$  pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

- (A) 1 (B) 6 (C) 7 (D) 9

**Q.13** If equilibrium constant of



Is  $1.8 \times 10^{-5}$ , equilibrium constant for



- (A)  $1.8 \times 10^{-9}$  (B)  $1.8 \times 10^{-9}$   
(C)  $5.55 \times 10^{-9}$  (D)  $5.55 \times 10^{10}$

**Q.14** The  $\text{pK}_a$  of a weak acid, HA, is 4.80. The  $\text{pK}_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

- (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22

**Q.15** The range of most suitable indicator which should be used for titration of  $\text{X}^- \text{Na}^+$  (0.1 M, 10 ml) with 0.1 M HCl should be (Given:  $K_{b(\text{X}^-)} = 10^{-6}$ )

- (A) 2-3 (B) 3-5 (C) 6-8 (D) 8-10

**Q.16** The solubility of  $\text{A}_2\text{X}_3$  is  $y \text{ mol dm}^{-3}$ . Its solubility product is

- (A)  $6y^2$  (B)  $64y^4$  (C)  $36y^5$  (D)  $108y^5$

**Q.17** If  $K_{sp}$  for  $\text{HgSO}_4$  is  $6.4 \times 10^{-5}$ , then solubility of this substance in mole per  $\text{m}^3$  is

- (A)  $8 \times 10^{-3}$  (B)  $6.4 \times 10^{-5}$   
(C)  $8 \times 10^{-6}$  (D) None of these

**Q.18** The solubility of a sparingly soluble salt  $\text{AB}_2$  in water is  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ . Its solubility product is:

- (A)  $10^{-15}$  (B)  $10^{-10}$  (C)  $4 \times 10^{-15}$  (D)  $4 \times 10^{-10}$

**Q.19** Which of the following is most soluble in water?

- (A)  $\text{MnS}$  ( $K_{sp} = 8 \times 10^{-37}$ ) (B)  $\text{ZnS}$  ( $K_{sp} = 7 \times 10^{-16}$ )  
(C)  $\text{Bi}_2\text{S}_3$  ( $K_{sp} = 1 \times 10^{-72}$ ) (D)  $\text{Ag}_3(\text{PO}_4)$  ( $K_{sp} = 1.8 \times 10^{-18}$ )

**Q.20** When equal volumes of the following solutions are mixed, precipitation of  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) will occur only with:

- (A)  $10^{-4} \text{M}$  ( $\text{Ag}^+$ ) and  $10^{-4} \text{M}$  ( $\text{Cl}^-$ )  
(B)  $10^{-5} \text{M}$  ( $\text{Ag}^+$ ) and  $10^{-5} \text{M}$  ( $\text{Cl}^-$ )  
(C)  $10^{-6} \text{M}$  ( $\text{Ag}^+$ ) and  $10^{-6} \text{M}$  ( $\text{Cl}^-$ )  
(D)  $10^{-10} \text{M}$  ( $\text{Ag}^+$ ) and  $10^{-10} \text{M}$  ( $\text{Cl}^-$ )

**Q.21** The precipitate of  $\text{CaF}_2$  ( $K_{sp} = 1.7 \times 10^{-10}$ ) is obtained when equal volumes of the following are mixed

- (A)  $10^{-4} \text{M}$   $\text{Ca}^{3+}$  +  $10^{-4} \text{M}$   $\text{F}^-$   
(B)  $10^{-2} \text{M}$   $\text{Ca}^{2+}$  +  $10^{-3} \text{M}$   $\text{F}^-$   
(C)  $10^{-5} \text{M}$   $\text{Ca}^{2+}$  +  $10^{-3} \text{M}$   $\text{F}^-$   
(D)  $10^{-3} \text{M}$   $\text{Ca}^{2+}$  +  $10^{-5} \text{M}$   $\text{F}^-$

**Q.22** 50 litre of a solution containing  $10^{-5}$  mole of  $\text{Ag}^+$  is mixed with 50 litre of a  $2 \times 10^{-7} \text{M}$  HBr solution.  $[\text{Ag}^+]$  in resultant solution is: [Given:  $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$ ]

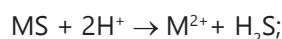
- (A)  $10^{-5} \text{M}$  (B)  $10^{-6} \text{M}$   
(C)  $10^{-7} \text{M}$  (D) None of these

**Q.23** pH of a saturated solution of silver salt of monobasic acid HA is found to be 9.

Find the  $K_{sp}$  of sparingly soluble salt  $\text{AgA(s)}$ . Given:  $K_a(\text{HA}) = 10^{-10}$

- (A)  $1.1 \times 10^{-11}$  (B)  $1.1 \times 10^{-10}$   
(C)  $10^{-12}$  (D) None of these

**Q.24** The solubility of metal sulphides in saturated solution of  $\text{H}_2\text{S}$  ( $[\text{H}_2\text{S}] = 0.1 \text{M}$ ) can be represented by



$$K_{eq} = \frac{[\text{M}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

The value of  $k_{eq}$  is given for few metal sulphide. If conc. of each metal ion in solution is 0.01 M, which metal sulphides are selectively ppt at total  $[\text{H}^+] = 1 \text{M}$  in saturated  $\text{H}_2\text{S}$  solution.

$$K_{eq} = \frac{[\text{M}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

Mns	ZnS	CoS	PbS
$3 \times 10^{10}$	$3 \times 10^{-2}$	3	$3 \times 10^{-7}$

- (A)  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{CoS}$  (B)  $\text{PbS}$ ,  $\text{ZnS}$ ,  $\text{CoS}$   
(C)  $\text{PbS}$ ,  $\text{ZnS}$  (D)  $\text{PbS}$

**Q.25** Solid  $\text{Ba}(\text{NO}_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4} \text{M}$   $\text{Na}_2\text{CO}_3$  solution. At what concentration of  $\text{Ba}^{2+}$  will a precipitate begin to form? ( $K_{sp}$  for  $\text{BaCO}_3 = 5.1 \times 10^{-9}$ )

- (A)  $4.1 \times 10^{-5} \text{M}$  (B)  $5.1 \times 10^{-5} \text{M}$   
(C)  $8.1 \times 10^{-8} \text{M}$  (D)  $8.1 \times 10^{-7} \text{M}$

**Q.26**  $K_{sp}$  of  $MX_4$  and solubility of  $MX_4$  is  $S$  mol/litre is related by:

- (A)  $S = [K_{sp}/256]^{1/5}$  (B)  $S = [128/K_{sp}]^{1/4}$   
 (C)  $S = [256K_{sp}]^{1/5}$  (D)  $S = [K_{sp}/128]^{1/4}$

## Previous Years' Questions

**Q.1** A 0.004 M solution of  $Na_2SO_4$  is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of association of  $Na_2SO_4$  is **(2004)**

- (A) 25% (B) 50% (C) 75% (D) 85%

**Q.2**  $K_{sp}$  for  $Cr(OH)_3$  is  $2.7 \times 10^{-31}$ . What is its solubility in moles/litre. **(2004)**

- (A)  $1 \times 10^{-8}$  (B)  $8 \times 10^{-8}$   
 (C)  $1.1 \times 10^{-8}$  (D)  $0.18 \times 10^{-8}$

**Q.3**  $pK_a$  of acetic acid is 4.74. The concentration of  $CH_3COONa$  is 0.01 M. The pH of  $CH_3COONa$  is **(2004)**

- (A) 8.37 (B) 4.37 (C) 4.74 (D) 0.474

**Q.4** A weak acid HX has the dissociation constant  $1 \times 10^{-5}$  M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is **(2004)**

- (A) 0.0001% (B) 0.01% (C) 0.1% (D) 0.15%

**Q.5** In the given reaction, the oxide of sodium is



- (A) Acidic (B) Basic (C) Amphoteric (D) Neutral

**Q.6** The dissociation of water at  $25^\circ C$  is  $1.9 \times 10^{-7}\%$  and the density of water is  $1.0 \text{ g/cm}^3$ . The ionisation constant of water is **(1995)**

- (A)  $3.42 \times 10^{-6}$  (B)  $3.42 \times 10^{-8}$   
 (C)  $1.00 \times 10^{-14}$  (D)  $2.00 \times 10^{-16}$

**Q.7** Which of the following statement (s) is (are) correct **(1998)**

- (A) The pH of  $1.0 \times 10^{-8} \text{ M}$  solution of HCl is 8  
 (B) The conjugate base of  $H_2PO_4^-$  is  $HPO_4^{2-}$   
 (C) Autoprotolysis constant of water increases with temperature

(D) When a solution of a weak monoprotic acid is treated against a strong base, at half-neutralization point  $pH = \left(\frac{1}{2}\right)pK_a$

**Q.8** A buffer solution can be prepared from a mixture of **(1999)**

- (A) Sodium acetate and acetic acid in water  
 (B) Sodium acetate and hydrochloric acid in water  
 (C) Ammonia and ammonium chloride in water  
 (D) Ammonia and sodium hydroxide in water

Each of the questions given below consists of two statements, an assertion (Assertion) and reason (Reason). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and reason is the correct explanation of assertion.

(B) If both assertion and reason are true and reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If assertion is false but reason is true.

**Q.9 Assertion:**  $BaCO_3$  is more soluble in  $HNO_3$  than in plain water. **(2006)**

**Reason:** Carbonate is a weak base and reacts with the  $H^+$  from the strong acid, causing the barium salt to dissociate.

**Q.10 Assertion:**  $CHCl_3$  is more acidic than  $CHF_3$  **(2003)**

**Reason:** The conjugate base of  $CHCl_3$  is more stable than  $CHF_3$ .

**Q.11** The  $pK_a$  of a weak acid HA is 4.80. The  $pK_a$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA will be **(2008)**

- (A) 9.58 (B) 4.79 (C) 7.01 (D) 9.22

**Q.12** The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reaction  $X \rightleftharpoons 2Y$  and  $Z \rightleftharpoons P + Q$ , respectively are in the ratio of 1:9 the degree of dissociation of X and Z be equal then ration of total pressure at these equilibria is **(2008)**

- (A) 3 : 36 (B) 1 : 1 (C) 1 : 3 (D) 1 : 9

**Q.13** Solubility product of silver bromide is  $5.0 \times 10^{-13}$ . The quantity of potassium bromide (molar mass taken as 120 g of  $\text{mol}^{-1}$ ) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **(2010)**

- (A)  $1.2 \times 10^{-10}$  g (B)  $1.2 \times 10^{-9}$  g  
(C)  $6.2 \times 10^{-5}$  g (D)  $5.0 \times 10^{-8}$  g

**Q.14** In aqueous solution the ionization constants for carbonic acid are  $K_1 = 4.2 \times 10^{-7}$  and  $K_2 = 4.8 \times 10^{-11}$ . Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **(2010)**

- (A) The concentration of  $\text{CO}_3^{2-}$  is 0.034 M.  
(B) The concentration of  $\text{CO}_3^{2-}$  is greater than that of  $\text{HCO}_3^-$   
(C) The concentration of  $\text{H}^+$  and  $\text{HCO}_3^-$  are approximately equal.  
(D) The concentration of  $\text{H}^+$  is double that of  $\text{HCO}_3^-$

**Q.15** At  $25^\circ\text{C}$ , the solubility product of  $\text{Mg}(\text{OH})_2$  is  $1.0 \times 10^{-11}$ . At which precipitating in the form of  $\text{Mg}(\text{OH})_2$  from a solution 0.001 M  $\text{Mg}^{2+}$  **(2010)**

- (A) 9 (B) 10 (C) 11 (D) 8

**Q.16** The strongest acid amongst the following compounds is: **(2011)**

- (A)  $\text{HCOOH}$  (B)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$   
(C)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$  (D)  $\text{CH}_3\text{COOH}$

**Q.17** A vessel at 1000 K contains  $\text{CO}_2$  with a Pressure of 0.5 atm. Some of the  $\text{CO}_2$  is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm the value of K is **(2011)**

- (A) 3 atm (B) 0.3 atm (C) 0.18 atm (D) 1.8 atm

**Q.18** The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant,  $K_a$  of this acid is: **(2012)**

- (A)  $3 \times 10^{-1}$  (B)  $1 \times 10^{-3}$  (C)  $1 \times 10^{-5}$  (D)  $1 \times 10^{-7}$

**Q.19** How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **(2013)**

- (A) 0.1 L (B) 0.9 L (C) 2.0 L (D) 9.0 L

**Q.20** The equilibrium constant at 298 K for the reaction  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in  $\text{mol L}^{-1}$ ) will be: **(2016)**

- (A) 0.818 (B) 1.818 (C) 1.182 (D) 0.182

## JEE Advanced/Boards

### Exercise 1

**Q.1** Calculate the number of  $\text{H}^+$  present in one ml of solution whose pH is 13.

**Q.2** Calculate change in concentration of  $\text{H}^+$  ion in one litre of water, when temperature changes from 298 K to 310 K.

Given  $K_w(298) = 11^{-14}$  (310) =  $2.56 \times 10^{-14}$ .

**Q.3** (i)  $K_w$  for  $\text{H}_2\text{O}$  is  $9.62 \times 10^{-14}$  at  $60^\circ\text{C}$ .

What is pH of water at  $60^\circ\text{C}$ .

(ii) What is the nature of solution at  $60^\circ\text{C}$  whose

- (a) pH = 6.7 (b) pH = 6.35

**Q.4** The value of  $K_w$  at the physiological temperature ( $37^\circ\text{C}$ ) is  $2.56 \times 10^{-14}$ . What is the pH at the neutral point of water at this temperature?

**Q.5** Calculate pH of following solutions:

(a) 0.1 M  $\text{H}_2\text{SO}_4$  (50 ml) + 0.4 M HCl 50 (ml)

(b) 0.1 M HA + 0.1 M HB

$[K_a(\text{HA}) = 2 \times 10^{-5}; K_a(\text{HB}) = 4 \times 10^{-5}]$

**Q.6** What are the concentration of  $\text{H}^+$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  in a 0.1 M solution of oxalic acid?

$[K_1 = 10^{-2} \text{ M and } K_2 = 10^{-5} \text{ M}]$

**Q.7** What are the concentrations of  $\text{H}^+$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{SO}_4$  in a 0.20 M solution of sulphuric acid?

Given:  $\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-$ ; strong  $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$ ;  $K_2 = 1.3 \times 10^{-2} \text{ M}$



**Q.8** Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M  $\text{NH}_3$ .

$[\text{p}K_a(\text{NH}_4^+)] = 9.26$

**Q.9** Calculate the pH of a solution made by mixing 50.0 ml of 0.2 M  $\text{NH}_4\text{Cl}$  & 75.0 ml of 0.1 M NaOH.

$[\text{p}K_a(\text{NaOH})] = 0.2$

**Q.10** What indicator should be used for the titration of 0.10 M  $\text{KH}_2\text{BO}_3$  with 0.10 M HCl?  $K_a(\text{H}_3\text{BO}_3) = 7.2 \times 10^{-10}$

**Q.11** An acid indicator has a  $K_a$  of  $3 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue. By how much must the pH change in order to change the indicator from 75% red to 75% blue?

**Q.12** What is the  $\text{OH}^-$  concentration of a 0.08 M solution of  $\text{CH}_3\text{COONa}$ .  $[\text{K}_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$

**Q.13** Calculate the pH of a 2.0 M solution of  $\text{NH}_4\text{Cl}$ .

$[\text{K}_b(\text{NH}_3)] = 1.8 \times 10^{-5}$

**Q.14** Calculate  $\text{OH}^-$  concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH.  $[\text{K}_a \text{ for the acid} = 1.9 \times 10^{-5}]$

**Q.15** Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10 M acetic acid,  $\text{CH}_3\text{COOH}$ , with 22.0 mL of 0.10 M NaOH.  $[\text{K}_a = 1.8 \times 10^{-5}]$

**Q.16** The values of  $K_{sp}$  for the slightly soluble salts MX and  $\text{QX}_2$  are each equal to  $4.0 \times 10^{-18}$ . Which salt is more soluble? Explain your answer.

**Q.17** Calculate the Simultaneous solubility of AgSCN and AgBr.  $K_{sp}(\text{AgSCN}) = 1.1 \times 10^{-12}$   $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$ .

**Q.18** A solution contains HCl,  $\text{Cl}_2\text{HCCOOH}$  &  $\text{CH}_3\text{COOH}$  at concentrations 0.09 M in HCl, 0.09 M in  $\text{Cl}_2\text{HCCOOH}$  & 0.1 M in  $\text{CH}_3\text{COOH}$ . pH for the solution is 1. Ionization constant of  $\text{CH}_3\text{COOH} = 10^{-5}$ . What is the magnitude of K for dichloroacetic acid?

**Q.19** Determine the  $[\text{S}^{2-}]$  in a saturated (0.1 M)  $\text{H}_2\text{S}$  solution to which enough HCl has been added to produce a  $[\text{H}^+]$  of  $2 \times 10^{-4}$ .  $K_1 = 10^{-7}$ ,  $K_2 = 10^{-14}$ .

**Q.20** What is the pH of a 1.0 M solution of acetic acid? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given  $K_a = 1.8 \times 10^{-5}$ .

**Q.21** It is desired to prepare 100 ml of a buffer of pH 5.00. Acetic, benzoic and formic acids and their salts are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used?  $\text{p}K_a$  values of these acids are: acetic 4.74; benzoic 4.18 and formic 3.68.

**Q.22** When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

**Q.23** A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution.  $K_a$  for formic acid is  $1.80 \times 10^{-4}$ .

(a) Calculate the pH of the solution.

(b) If this solution were diluted to 10 times its volume, what would be the pH?

(c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?

## Exercise 2

### Single Correct Choice Type

**Q.1** A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:

- (A) 3      (B) 4      (C) 3000      (D) 10000

**Q.2** The first and second dissociation constants of an acid  $\text{H}_2\text{A}$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be:

- (A)  $5.0 \times 10^{-5}$       (B)  $5.0 \times 10^{15}$   
(C)  $5.0 \times 10^{-15}$       (D)  $0.2 \times 10^5$

**Q.3** An aqueous solution contains 0.01 M  $\text{RNH}_2$

$(K_b = 2 \times 10^{-6})$  &  $10^{-4}$  M NaOH.

The concentration of  $\text{OH}^-$  is nearly:

- (A)  $2.414 \times 10^{-4}$       (B)  $10^{-4}$  M  
(C)  $1.414 \times 10^{-4}$       (D)  $2 \times 10^{-4}$

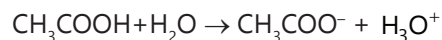
**Q.4** The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

- (A) 100% (B) 50% (C) 25% (D) None of these

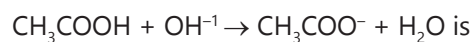
**Q.5** The pH of the neutralisation point of 0.1N ammonium hydroxide with 0.1N HCl is

- (A) 1 (B) 6 (C) 7 (D) 9

**Q.6** If equilibrium constant of



Is  $1.8 \times 10^{-5}$ , equilibrium constant for



- (A)  $1.8 \times 10^{-9}$  (B)  $1.8 \times 10^9$   
(C)  $5.55 \times 10^{-9}$  (D)  $5.55 \times 10^{10}$

**Q.7** The  $\text{pK}_a$  of a weak acid, HA, is 4.80. The  $\text{pK}_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

- (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22

**Q.8** How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each w.r.t. Acid HA and salt  $\text{Na}^+ \text{A}^-$  to make the pH of solution 5.5. Given  $\text{pK}_a(\text{HA}) = 5$ . (Use  $\text{antilog}(0.5) = 3.16$ )

- (A)  $2.08 \times 10^{-1}$  (B)  $3.05 \times 10^{-3}$   
(C)  $2.01 \times 10^{-2}$  (D) None of these

**Q.9** If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [ $\text{K}_a = 2 \times 10^{-4}$ ], the pOH of the resulting solution is

- (A) 3.4 (B) 3.7 (C) 7 (D) 10.3

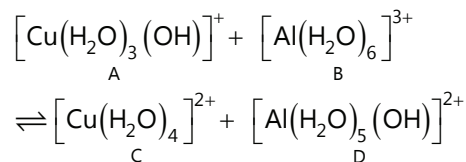
**Q.10** 1 M NaCl and 1M HCl are present in an aqueous solution. The solution is

- (A) Not a buffer solution and with  $\text{pH} < 7$   
(B) Not a buffer solution with  $\text{pH} > 7$   
(C) A buffer solution with  $\text{pH} < 7$   
(D) A buffer solution with  $\text{pH} > 7$

**Q.11** The  $\text{pK}_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is:

- (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0

**Q.12** In the following reaction:



(A) C is the conjugate base of A, and D is the conjugate acid of B

(B) A is a base and B the acid

(C) C is the conjugate acid of A, and D is the conjugate base of B

(D) None of the above

**Q.13** Which does not react with NaOH or which is not acid salt?

- (A)  $\text{NaH}_2\text{PO}_2$  (B)  $\text{Na}_2\text{HPO}_3$  (C)  $\text{Na}_2\text{HPO}_4$  (D)  $\text{NaHCO}_3$

**Q.14** pH of the following solution is affected by dilution:

- (A) 0.01 M  $\text{CH}_3\text{COONa}$   
(B) 0.01 M  $\text{NaHCO}_3$   
(C) Buffer of 0.01 M  $\text{CH}_3\text{COONa}$  and 0.01 M  $\text{CH}_3\text{COOH}$   
(D) 0.01 M  $\text{CH}_3\text{COONH}_4$

**Q.15** Which of the following mixtures does not constitute a buffer?

- (A)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  (B)  $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$   
(C)  $\text{NaCl} + \text{HCl}$  (D)  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4$

**Q.16** Which of the following mixtures constitute a buffer?

- (A)  $\text{Na}_2\text{CO}_3 + \text{HCl}$  (B)  $\text{NaOH} + \text{CH}_3\text{COOH}$   
(C)  $\text{NH}_3 + \text{CH}_3\text{COONH}_4$  (D)  $\text{NaOH} + \text{BaCl}_2$

### Multiple Correct Choice Type

**Q.17** In which of the following pairs of solutions is there no effect on the pH upon dilution?

- (A) 0.1 M  $\text{NH}_3$  and 0.1 M  $(\text{NH}_4)_2\text{SO}_4$   
(B) 0.1 M  $\text{NaH}_2\text{PO}_4$  and 0.1 M  $\text{Na}_2\text{HPO}_4$   
(C) 0.1 M HCl and 0.01 M NaOH  
(D) 0.1 M KCl and 0.1 M HCl



**Q.18** Which of the following statement(s) is/are correct?

- (A) The pH of  $1.0 \times 10^{-8}$  M solution of HCl is 8  
 (B) The conjugate base of  $\text{H}_2\text{PO}_4^-$  is  $\text{HPO}_4^{2-}$   
 (C) Autoprotolysis constant of water increases with temperature  
 (D) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point  $\text{pH} = (1/2) \text{pK}_a$ .

**Q.19** A 2.5 gm impure sample containing weak monoacidic base (Mol. wt. = 45) is dissolved in 100 ml water and titrated with 0.5 M HCl when  $\left(\frac{1}{5}\right)^{\text{th}}$  of the base was neutralised the pH was found to be 9 and at equivalent point pH of solution is 4.5. Given: All data at  $25^\circ\text{C}$  &  $\log 2 = 0.3$ .

Select correct statement(s).

- (A)  $K_b$  of base is less than  $10^{-6}$   
 (B) Concentration of salt (C) at equivalent point is 0.25 M  
 (C) Volume of HCl is used at equivalent point is 100 ml  
 (D) Weight percentage of base in given sample is 80%.

**Q.20** Select incorrect statement(s).

- (A) Phenolphthalein is suitable indicator for the titration of HCl (aq) with  $\text{NH}_4\text{OH}$  (aq).  
 (B) An acid-base indicator in a buffer solution of  $\text{pH} = \text{pK}_{\text{in}} + 1$  is ionized to the extent of 90%.  
 (C) In the titration of a monoacidic weak base with a strong acid, the pH at the equivalent point is always calculated by

$$\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$$

- (D) When  $\text{Na}_3\text{PO}_4$  (aq) is titrated with HCl (aq), the pH of solution at second equivalent point is calculated by  $\frac{1}{2} [\text{pK}_{a1} + \text{pK}_{a2}]$

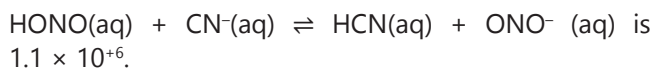
**Q.21** Which of the following is true for alkaline aqueous solution?

- (A)  $\text{pH} > \frac{\text{pK}_w}{2}$  (B)  $\text{pH} > \text{pOH}$   
 (C)  $\text{pOH} < \frac{\text{pK}_w}{2}$  (D)  $\text{pH} < \text{pOH}$

**Q.22** An acid-base indicator has a  $K_a$  of  $3.0 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue, then:

- (A) pH is 4.05 when indicator is 75% red  
 (B) pH is 5.00 when indicator is 75% blue.  
 (C) pH is 5.00 when indicator is 75% red  
 (D) pH is 4.05 when indicator is 75% blue.

**Q.23** The equilibrium constant for the reaction



From the magnitude of this  $K_{\text{eq}}$  one can conclude that

- (A)  $\text{CN}^-$  is stronger base than  $\text{ONO}^-$   
 (B) HCN is a stronger acid than HONO  
 (C) The conjugate base of HONO is  $\text{ONO}^-$   
 (D) The conjugate acid of  $\text{CN}^-$  is HCN

**Q.24** Which of the following are acid-base conjugate pairs:

- (A)  $\text{HF}, \text{F}^-$  (B)  $\text{H}_3\text{O}^+, \text{OH}^-$   
 (C)  $\text{CH}_3\text{NH}_3^+, \text{CH}_3\text{NH}_2$  (D)  $\text{HS}^-, \text{S}_2^-$

**Q.25** Which of the following will suppress the ionization of phthalic acid in an aqueous solution.

- (A) KCl (B)  $\text{H}_2\text{SO}_4$  (C)  $\text{HNO}_3$  (D) NaOH

### Match the Columns

**Q.26** Match the following

List I	List II weak
(A) $\text{CH}_3\text{COOH}$	(p) Base
(B) $\text{H}_2\text{SO}_4$	(q) Weak acid
(C) NaOH	(r) Strong acid
(D) $\text{NH}_3$	(s) Strong base

## Q.27

Column I (pH of resultant solution)	Column II (Exist between Colour transition range of an indicator)
(A) 200 ml of $\text{H}_2\text{SO}_4$ solution (specific gravity 1.225 containing 25% $\text{H}_2\text{SO}_4$ by weight) + 800 ml of 0.525 M strong triacidic base $\text{X}(\text{OH})_3$	(p) Phenol Red (6.8 to 8.4)
(B) 50 ml of 0.1 M $\text{HCO}_3^-$ + 50 ml of 0.8 M $\text{CO}_3^{2-}$ ( $\text{H}_2\text{CO}_3$ : $K_{a1} = 4 \times 10^{-7}$ , $K_{a2} = 2 \times 10^{-11}$ )	(q) Propyl red (4.6 to 6.4)
(C) 50 ml of 0.2 M $\text{HA}(\text{aq})$ ( $K_a = 10^{-5}$ ) + 50 ml of 0.1 M $\text{HCl}(\text{aq})$ + 100 ml of 0.13M $\text{NaOH}(\text{aq})$	(r) Phenolphthalein (8.3 to 10.1)
	(s) Malachite green (11.4 to 13)

## Previous Years' Questions

**Q.1** Pure ammonia is placed in a vessel at a temperature where its dissociation constant ( $\alpha$ ) is appreciable. At equilibrium  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons \text{NH}_3$  (1984)

- (A)  $K_p$  does not change significantly with pressure  
 (B)  $\alpha$  does not change with pressure  
 (C) Concentration of  $\text{NH}_3$  does not change with pressure  
 (D) Concentration of hydrogen is less than that of nitrogen

**Q.2** A certain buffer solution contains equal concentration of  $\text{X}^-$  and  $\text{HX}$ . The  $K_b$  for  $\text{X}^-$  is  $10^{-10}$ . The pH of the buffer is (1984)

- (A) 4 (B) 7 (C) 10 (D) 14

**Q.3** A certain weak acid has a dissociation constant of  $1.0 \times 10^{-4}$ . The equilibrium constant for its reaction with a strong base is (1984)

- (A)  $1.0 \times 10^{-4}$  (B)  $1.0 \times 10^{-10}$   
 (C)  $1.0 \times 10^{10}$  (D)  $1.0 \times 10^{14}$

**Q.4** Solubility product constant ( $K_{sp}$ ) of salts of types  $\text{MX}$ ,  $\text{MX}_2$  and  $\text{M}_3\text{X}$  at temperature 'T' are  $4.0 \times 10^{-8}$ ,  $3.2 \times 10^{-14}$  and  $2.7 \times 10^{-15}$ , respectively. Solubilities ( $\text{mol. dm}^{-3}$ ) of the salts at temperature 'T' are in the order (2008)

- (A)  $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$  (B)  $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$   
 (C)  $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$  (D)  $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

**Q.5** 2.5 mL of  $\frac{2}{5}$  M weak monoacidic base

( $K_b = 1 \times 10^{-12}$  at  $25^\circ\text{C}$ ) is titrated with  $\frac{2}{15}$  M

$\text{HCl}$  in water at  $25^\circ\text{C}$ . The concentration of  $\text{H}^+$  at equivalence point is ( $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ ) (2008)

- (A)  $3.7 \times 10^{-13}$  M (B)  $3.2 \times 10^{-7}$  M  
 (C)  $3.2 \times 10^{-2}$  M (D)  $2.7 \times 10^{-2}$  M

**Q.6** Aqueous solutions of  $\text{HNO}_3$ ,  $\text{KOH}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COONa}$  of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) (2010)

- (A)  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$   
 (B)  $\text{KOH}$  and  $\text{CH}_3\text{COONa}$   
 (C)  $\text{HNO}_3$  and  $\text{CH}_3\text{COONa}$   
 (D)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$

**Q.7** The equilibrium  $2\text{Cu}^+ \rightleftharpoons \text{Cu}^0 + \text{Cu}^{2+}$  in aqueous medium at  $25^\circ\text{C}$  shifts towards the left in the presence of. (2011)

- (A)  $\text{NO}_3^-$  (B)  $\text{Cl}^-$  (C)  $\text{SCN}^-$  (D)  $\text{CN}^-$

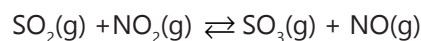
**Q.8** The solubility of  $\text{Mg}(\text{OH})_2$  in pure water is  $9.57 \times 10^{-3}$  g/L. Calculate its solubility (in g/L) in 0.02M  $\text{Mg}(\text{NO}_3)_2$  solution. (1986)

**Q.9** What is the pH of the solution when 0.20 moles of  $\text{HCl}$  is added to one litre of a solution containing:

- (i) 1 M each of acetic acid and acetate ion  
 (ii) 0.1 M each of acetic acid and acetate ion

Assume the total volume is one litre.  $K_a$  for acetic acid =  $1.8 \times 10^{-5}$  (1987)

**Q.10** At a certain temperature, equilibrium constant ( $K_c$ ) is 16 for the reaction;



If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and  $\text{NO}_2$ ? **(1987)**

**Q.11 Statement-I:** In water, orthoboric acid behaves as a weak monobasic acid.

**Statement-II:** In water, orthoboric acid acts as a proton donor. **(2007)**

(A) Statement-I is True, statement-II is True; statement-II is a correct explanation for statement-I.

(B) Statement-I is True, statement-II is True; statement-II is NOT a correct explanation for statement-I.

(C) Statement-I is True, statement-II is False.

(D) Statement-I is False, statement-II is True.

**Q.12** The INCORRECT statement among the following, for this reaction, is **(2016)**

(A) Decrease in the total pressure will result in formation of more moles of gaseous X.

(B) At the start of the reaction, dissociation of gaseous  $\text{X}_2$ , takes place spontaneously.

(C)  $\beta_{\text{equilibrium}} = 0.7$

(D)  $K_c < 1$

**Q.13** In 1 L saturated solution of AgCl [ $K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$ ], 0.1 mol of CuCl [ $K_{sp}(\text{CuCl}) = 1.0 \times 10^{-6}$ ] is added. The resultant concentration of  $\text{Ag}^+$  in the solution is  $1.6 \times 10^{-x}$ . The value of "x" is **(2011)**

**Q.14** The solubility product ( $K_{sp}$ ;  $\text{mol}^3\text{dm}^{-9}$ ) of  $\text{MX}_2$  at 298 based on the information available the given concentration cell is (take  $2.303 \times \frac{298}{F} = 0.059 \text{ V}$ ) **(2012)**

(A)  $1 \times 10^{-15}$

(B)  $4 \times 10^{-15}$

(C)  $1 \times 10^{-12}$

(D)  $4 \times 10^{-12}$

**Q.15** The compound that does NOT liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution, is **(2013)**

(A) Benzoic acid

(B) Benzenesulphonic acid

(C) Salicylic acid

(D) Carboic acid (phenol)

**Q.16** The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at  $25^\circ \text{C}$ . The  $K_a$  of HA is **(2013)**

(A)  $1 \times 10^{-4}$

(B)  $1 \times 10^{-5}$

(C)  $1 \times 10^{-6}$

(D)  $1 \times 10^{-3}$

**Q.17** The  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at 298K. The solubility (in mol/L) of  $\text{Ag}_2\text{CrO}_4$  in a 0.1M  $\text{AgNO}_3$  solution is **(2013)**

(A)  $1.1 \times 10^{-11}$

(B)  $1.1 \times 10^{-10}$

(C)  $1.1 \times 10^{-12}$

(D)  $1.1 \times 10^{-9}$

**Paragraph 1:** Thermal decomposition of gaseous  $\text{X}_2$  to gaseous X at 298 K takes place according to the following equation:  $\text{X}_2(\text{g}) \rightleftharpoons 2\text{X}(\text{g})$

The standard reaction Gibbs energy,  $\Delta_r G^\circ$  of this reaction is positive. At the start of the reaction, there is one mole of  $\text{X}_2$  and no X. As the reaction proceeds, the number of moles of X formed is given by b. Thus,  $b_{\text{equilibrium}}$  is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given:  $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$ )

**Q.18** The equilibrium constant  $K_p$  for this reaction at 298 K, in terms of  $b_{\text{equilibrium}}$ , is **(2016)**

(A)  $\frac{8\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$

(B)  $\frac{8\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

(C)  $\frac{4\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}^2}$

(D)  $\frac{4\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

# PlancEssential Questions

## JEE Main/Boards

### Exercise 1

Q.1      Q.4      Q.6      Q.8  
Q.13      Q.17      Q.19      Q.28  
Q.29

### Exercise 2

Q.5      Q.8      Q.9      Q.13  
Q.17      Q.22      Q.24

### Previous Years' Questions

Q.4      Q.7      Q.11

## JEE Advanced/Boards

### Exercise 1

Q.2      Q.6      Q.9      Q.11  
Q.16      Q.21      Q.24      Q.25  
Q.29      Q.30

### Exercise 2

Q.1      Q.4      Q.7      Q.8  
Q.9      Q.13      Q.16      Q.19  
Q.21      Q.22

### Previous Years' Questions

Q.3      Q.5      Q.8      Q.10

## Answer Key

## JEE Main/Boards

### Exercise 1

**Q.1** 2.3 mol/lit  
**Q.2.** 1.5 times  
**Q.3**  $1.44 \times 10^{-4}$   
**Q.4**  $2 \times 10^{-8}$   
**Q.5** No  
**Q.6**  $4.11 \times 10^{-4}$  M  
**Q.7**  $5.6 \times 10^{-10}$ ,  $2.4 \times 10^{-4}$ , 5.63  
**Q.8** 1.3  
**Q.9**  $\text{HZ} < \text{HY} < \text{HX}$ ,  $K_a(\text{HY}) = 10^{-5}$  M,  $K_a(\text{HZ}) = 10^{-9}$  M  
**Q.10** (a)  $3.72 \times 10^4 \text{ dm}^3$  (b)  $4 \text{ dm}^3$   
**Q.11**  $K_c = 3.02 \times 10^{-2}$ ,  $S = 0.123$  M

**Q.12** 6.1

**Q.13** (i) pH = 4.35 (ii)  $1.79 \times 10^{-9}$  mol/lit

**Q.14** (i) 28.6%

**Q.15**  $[\text{HS}^-] = 9.54 \times 10^{-5}$ , in 0.1 M HCl  $[\text{HS}^-] = 9.1 \times 10^{-8}$  M,  
 $[\text{S}^{2-}] = 1.2 \times 10^{-13}$  M, in 0.1 M HCl  $[\text{S}^{2-}] = 1.09 \times 10^{-19}$  M

**Q.16**  $[\text{Ac}^-] = 0.00093$ , pH = 3.03

**Q.17**  $[\text{A}^-] = 7.08 \times 10^{-5}$  M,  $K_a = 5.08 \times 10^{-7}$ ,  $\text{p}K_a = 6.29$

**Q.18** (i) 2.52 (ii) 2.30 (iii) 2.7 (iv) 2.70

**Q.19** (i) 11.65 (ii) 12.21 (iii) 12.57 (iv) 1.87

**Q.20** 0.103g

**Q.21** pH = 9.20,  $k_H = 0.772$ ,  $h = 0.467$

**Q.22** 11

**Q.23** 0.082 mol of NaOH can be added

## Exercise 2

### Single Correct Choice Type

Q.1 A	Q.2 C	Q.3 C	Q.4 C	Q.5 B	Q.6 C
Q.7 C	Q.8 D	Q.9 D	Q.10 A	Q.11 D	Q.12 B
Q.13 B	Q.14 C	Q.15 B	Q.16 D	Q.17 A	Q.18 C
Q.19 A	Q.20 B	Q.21 B	Q.22 C	Q.23 A	Q.24 D
Q.25 B	Q.26 A				

### Previous Years Questions

Q.1 C	Q.2 A	Q.3 A	Q.4 B	Q.5 B	Q.6 D
Q.7 B,C	Q.8 A,C	Q.9 A	Q.10 A	Q.11 C	Q.12 A
Q.13 B	Q.14 C	Q.15 B	Q.16 B	Q.17 D	Q.18 C
Q.19 D	Q.20 B				

## JEE Advanced/Boards

### Exercise 1

Q.1 $6.022 \times 10^7$	Q.2 $1.6 \times 10^{-7}$
Q.3 (i) 6.50 ; (ii) (a) Basic, (b) Acidic	Q.4 6.79
Q.5 (a) 0.522, (b) 2.61	Q.6 0.027 M, 0.073 M, 0.027 M, $10^{-5}$ M
Q.7 0.2116 M, 0.1884 M, 0.0116 M, 0	Q.8 8.7782
Q.9 12.8	
Q.10 (Methyl red), one with pH = 5.22 as midpoint of colour range	
Q.11 $\Delta\text{pH} = 0.95$	Q.12 $[\text{OH}^-] = 6.664 \times 10^{-6}$
Q.13 pH = 4.477	Q.14 $5.12 \times 10^{-6}$ M
Q.15 8.86	Q.16 $\text{QX}_2$ is more soluble
Q.17 $4 \times 10^{-7}$ mol/L AgBr, $9 \times 10^{-7}$ mol/L AgSCN	Q.18 $K_a = 1.25 \times 10^{-2}$
Q.19 $[\text{S}^{2-}] = 2.5 \times 10^{-15}$	Q.20 $V = 2.77 \times 10^4$ litre
Q.21 Acetic acid, salt-acid molar ratio 1.8: 1	Q.22 9.168
Q.23 (a) pH = 3.83 (b) pH = 3.85, (c) = 3.99	

### Exercise 2

#### Single Correct Choice Type

Q.1 A	Q.2 C	Q.3 D	Q.4 B	Q.5 B	Q.6 D
Q.7 C	Q.8 B	Q.9 A	Q.10 D	Q.11 A	Q.12 A
Q.13 A	Q.14 B	Q.15 C	Q.16 C		

**Multiple Correct Choice Type**

- Q.17 A, B      Q.18 B, C      Q.19 B, C      Q.20 A, B, C      Q.21 A, B, C      Q.22 A, B  
 Q.23 A, C, D      Q.24 A, D      Q.25 B, C, D

**Match the Columns**

Q.26 A → q; B → r; C → s; D → p

Q.27 A → s; B → s; C → q

**Previous Years Questions**

- Q.1 A      Q.2 A      Q.3 C      Q.4 D      Q.5 D      Q.6 C, D  
 Q.7 B, C, D      Q.8  $8.7 \times 10^{-4} \text{ g L}^{-1}$       Q.9 (i) 4.56 (ii) 1      Q.10  $[\text{NO}] = 0.80 \text{ M}$ ;  $[\text{NO}_2] = 0.20 \text{ M}$       Q.11 C  
 Q.12 C      Q.13 7      Q.14 B      Q.15 D      Q.16 A      Q.17 B  
 Q.18 B

**Solutions****JEE Main/Boards****Exercise 1**

**Sol 1:**  $\alpha = \sqrt{\frac{K_a}{C}}$

∴  $\alpha$  will be equal, equate the terms on R.H.S. for both the acids.

$\text{CH}_3\text{COOH}$	$\text{HNO}_2$
$\frac{K_a}{C}$	$\frac{K_a}{C}$

**Sol 2:**

Blood	Spinal fluid
$[\text{H}^+] = 10^{-7.36}$ $= 4.36 \times 10^{-8}$	$[\text{H}^+] = 10^{-7.53}$ $= 2.95 \times 10^{-8}$

**Sol 3:** The freezing point depression is given by  $\Delta T = K_f \times m$

$1.86 \text{ K mol}^{-1} \text{ kg} \times m = 0.758 \text{ K}$  so,  $m = 0.40752 \text{ mol kg}^{-1}$ . If this can be taken to be  $0.40752 \text{ mol L}^{-1}$  for this question.

The van't Hoff factor  $i = \frac{0.40752}{0.400} = 1.0188$

Ans: van't Hoff factor  $i = 1.02$

(ii) Formic acid ionizes in water according to:  
 $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$

If the initial concentration before ionization is  $0.400 \text{ mol L}^{-1}$  and  $x \text{ mol L}^{-1}$  ionizes then the final number of particles in the solution is

$$(0.400 \text{ mol L}^{-1} - x \text{ mol L}^{-1}) + 2x \text{ mol L}^{-1} = 0.400 \text{ mol L}^{-1} + x \text{ mol L}^{-1}$$

$$\text{Now, } 0.400 \text{ mol L}^{-1} + x \text{ mol L}^{-1} = 0.40752 \text{ mol L}^{-1}$$

$$x \text{ mol L}^{-1} = 7.52 \times 10^{-3} \text{ mol L}^{-1} = [\text{H}^+] = [\text{HCOO}^-]$$

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{[7.52 \times 10^{-3} \text{ mol L}^{-1}]}{[0.400 - 7.52 \times 10^{-3}] \text{ mol L}^{-1}} = 1.44 \times 10^{-4}$$

**Sol 4:**  $2\text{AgCl}(s) + \text{CO}_3^{2-} \rightleftharpoons \text{Ag}_2\text{CO}_3(s) + 2\text{Cl}^-$

$$K = \frac{[\text{Cl}^-]}{[\text{CO}_3^{2-}]} = \frac{[\text{Cl}^-]^2}{[\text{CO}_3^{2-}]} \times \frac{[\text{Ag}^+]^2}{[\text{Ag}^+]^2} = \frac{[K_{sp}(\text{AgCl})]^2}{K_{sp}(\text{Ag}_2\text{CO}_3)}$$

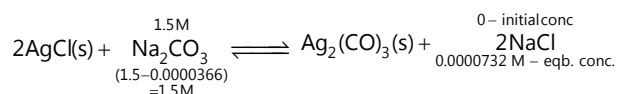
$$[\text{Cl}^-] = \frac{0.0026}{35.5} \text{ M} = 7.5 \times 10^{-5} \text{ M}$$

The above concentration of  $\text{Cl}^-$  indicates that  $[\text{CO}_3^{2-}]$  remains almost unchanged.

$$\Rightarrow \frac{7.3 \times 10^{-5}}{1.5} = \frac{[K_{sp}(\text{AgCl})]^2}{8.2 \times 10^{-12}} \Rightarrow K_{sp}(\text{AgCl}) = 2 \times 10^{-8}$$

**Sol 5:** Initial  $[\text{Na}_2\text{CO}_3] = [\text{CO}_3^{2-}] = 1.5 \text{ M}$

$$\text{Equilibrium } [\text{Cl}^-] = [\text{NaCl}] = \frac{0.0026}{35.5} = 0.0000732 \text{ M}$$



$$[\text{Ag}^+] = \sqrt{\frac{K_{sp}(\text{Ag}_2\text{CO}_3)}{[\text{CO}_3^{2-}]}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}}$$

$$= 2.338 \times 10^{-6} \text{ M}$$

$$\therefore K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (2.338 \times 10^{-6})(0.0000732)$$

$$= 1.71 \times 10^{-10}$$

Precipitate of AgCl will not be formed.

**Sol 6:** The hydrogen ion concentrations of the given pH range are

$$\text{pH} = 3.1 = -\log \left\{ \frac{[\text{H}^+]}{\text{M}} \right\}$$

$$\text{i.e. } \log \left\{ \frac{[\text{H}^+]}{\text{M}} \right\} = -3.1 = \bar{4}.9$$

$$\text{Hence, } [\text{H}^+] = 7.9 \times 10^{-4} \text{ M}$$

$$\text{pH} = 4.5 \text{ i.e. } \log \left\{ \frac{[\text{H}^+]}{\text{M}} \right\} = -4.5 = \bar{5}.5$$

$$\text{Hence, } [\text{H}^+] = 3.2 \times 10^{-5} \text{ M}$$

The average of these two hydrogen ion concentration is

$$\frac{7.9 \times 10^{-4} \text{ M} + 3.2 \times 10^{-5} \text{ M}}{2} = 4.11 \times 10^{-4} \text{ M}$$

At this  $\text{H}^+$  concentration,

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

Therefore,  $\text{pH} = \text{p}K_{\text{HIn}}$

$$\text{Or } [\text{H}^+] = K_{\text{HIn}} = 4.11 \times 10^{-4} \text{ M}$$

**Sol 7:**  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ;  $C = 0.01 \text{ M}$

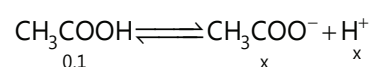
$$\frac{K_w}{K_b} = cx^2 \quad (x = \text{degree of hydrolysis})$$

$$K_h = cx^2 \quad (K_h = \text{hydrolysis constant})$$

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

**Sol 8:**  $C = 0.1 \text{ M}$

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



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} ; 1.8 \times 10^{-5} = \frac{x^2}{0.1}$$

$$(i) [\text{H}^+] = x \therefore \text{pH} = -\log[\text{H}^+]$$

$$(ii) \text{Vol. of } \text{CH}_3\text{COOH} = 1 \text{ L}$$

Addition of 0.05 mole of HCl increases the concentration of  $\text{CH}_3\text{COOH}$  by 0.05 and reduces the conc. of  $\text{CH}_3\text{COO}^-$  by 0.05 mol / L.

$$\therefore [\text{CH}_3\text{COOH}] = 0.1 + 0.05 = 0.15 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 1.34 \times 10^{-3} - 0.05 = 0.05134 \text{ M}$$

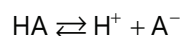
$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log 1.8 \times 10^{-5} + \log \frac{0.05134}{0.15}$$

$$\text{pH} = 1.3$$

**Sol 9:** The pH of NaX is 7, thus the acid HX must be a strong acid. The ions  $\text{Y}^-$  and  $\text{Z}^-$  undergo hydrolysis  $\text{Y}^- + \text{H}_2\text{O} \rightleftharpoons \text{HY} + \text{OH}^-$  and  $\text{Z}^- + \text{H}_2\text{O} \rightleftharpoons \text{HZ} + \text{OH}^-$ .

The stronger the base, larger the  $\text{OH}^-$  concentration and thus larger the pH of the solution. Thus  $\text{Z}^-$  is stronger base than  $\text{Y}^-$  and thus conjugate acid HZ will be weaker than HY. Hence, the correct order is  $\text{HX} > \text{HY} > \text{HZ}$

**Sol 10:** We have



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]^2}{[\text{HA}]_0 - [\text{H}^+]} \approx \frac{[\text{H}^+]^2}{[\text{HA}]_0}$$

$$\text{Or } [\text{H}^+] = \sqrt{K_a[\text{HA}]_0} = \left[ (1.8 \times 10^{-5} \text{ M})(0.5 \text{ M}) \right]^{1/2} \\ = 3.0 \times 10^{-3} \text{ M}$$

(a) Now to double the pH, we will have

$$[\text{H}^+] = \text{antilog}(-2 \times 2.523) = 9.0 \times 10^{-6} \text{ M}$$

Now from the expression

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]_0 - [\text{H}^+]}$$
 we get

$$1.8 \times 10^{-5} \text{ M} = \frac{(9.0 \times 10^{-6} \text{ M})^2}{[\text{HA}]_0 - (9.0 \times 10^{-6} \text{ M})}$$

$$[\text{HA}]_0 = \frac{(9.0 \times 10^{-6} \text{M})^2 (1.8 \times 10^{-5} \text{M})}{(1.8 \times 10^{-5} \text{M})}$$

$$\text{This given} = \frac{8.0 \times 10^{-11} \text{M}^2 + 1.62 \times 10^{-10} \text{M}^2}{1.8 \times 10^{-5} \text{M}}$$

$$= \frac{2.42 \times 10^{-10} \text{M}^2}{1.8 \times 10^{-5} \text{M}} = 1.344 \times 10^{-5} \text{M}$$

$$\text{Dilution factor} = \frac{0.5 \text{M}}{1.344 \times 10^{-5} \text{M}} = 3.72 \times 10^4$$

(b) To double the  $[\text{OH}^-]$ , we have

$$[\text{H}^+] = \frac{1}{2} \times 3.0 \times 10^{-3} \text{M}$$

$$\text{Hence, } [\text{HA}]_0 = \frac{[\text{H}^+]^2}{K_a} = \frac{(1.5 \times 10^{-3} \text{M})^2}{(1.8 \times 10^{-5} \text{M})} = 0.125 \text{M}$$

$$\text{Dilution factor} = \frac{0.5 \text{M}}{0.125 \text{M}} = 4$$

$$\text{Sol 11: } K_c = \frac{K_{sp}}{K_b^2} = \frac{10^{-11}}{(1.8 \times 10^{-5})^2} = 3.02 \times 10^{-2}$$

$$\text{Sol 12: } \text{pH} = \text{p}K_a^0 + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{We get } 5.8 = \text{p}K_a^0 + \log \left[ \frac{(10 \text{mL})M_2}{VM_1 - (10 \text{mL})M_2} \right]$$

$$6.402 = \text{p}K_a^0 + \log \left[ \frac{(20 \text{mL})M_2}{VM_1 - (20 \text{mL})M_2} \right]$$

Subtracting Eq. (i) from Eq. (ii), we get

$$6.402 = \left[ \frac{(20 \text{mL})M_2}{VM_1 - (20 \text{mL})M_2} - \frac{VM_1 - (10 \text{mL})M_2}{(10 \text{mL})M_2} \right]$$

$$\text{Or } \frac{2[VM_1 - (10 \text{mL})M_2]}{VM_1 - (20 \text{mL})M_2} = 4$$

$$\text{or } \frac{VM_1}{M_2} = \frac{60 \text{mL}}{2} = 30 \text{mL}$$

Substituting this in either Eq. (i) or Eq. (ii) we get

$$\text{p}K_a^0 = 5.8 - \log \left( \frac{10}{30 - 10} \right) = 5.8 + 0.30 = 6.1$$

**Sol 13:** The minimum of concentration  $\text{S}^{2-}$  ion to start of the precipitation is obtained from the  $K_{tp}$  with  $[\text{Mn}^{2+}] = 0.01 \text{M}$ . Therefore, we have

$$[\text{S}^{2-}] = \frac{K_{sp}(\text{MnS})}{[\text{Mn}^{2+}]} = \frac{5.6 \times 10^{-16} \text{M}^2}{(0.01 \text{M})} = 5.6 \times 10^{-14} \text{M}$$

The  $\text{H}^+$  concentration of the solution having the above  $[\text{S}^{2-}]$  can be computed from the expression of  $\text{H}_2\text{S}$  equilibrium:

$$\frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{[\text{H}^+]^2 (5.6 \times 10^{-14} \text{M})}{(0.10 \text{M})} = 1.1 \times 10^{-21} \text{M}^2$$

This gives

$$[\text{H}^+] = 4.43 \times 10^{-5} \text{M} \text{ or } \text{pH} = 4.35$$

If the  $[\text{H}^+] > 4.43 \times 10^{-5} \text{M}$ , then the  $[\text{S}^{2-}]$  will be less than  $5.6 \times 10^{-14} \text{M}$  and  $\text{MnS}$  will no longer precipitate from the solution.

The concentration of  $\text{Zn}^{2+}$  ion remaining in the solution can be calculated from the solubility product of  $\text{ZnS}$ :

$$[\text{Zn}^{2+}] = \frac{K_{sp}(\text{ZnS})}{[\text{S}^{2-}]} = \frac{1.0 \times 10^{-22} \text{M}^2}{(5.6 \times 10^{-14} \text{M})} = 1.79 \times 10^{-9} \text{M}$$

Thus, by properly adjusting the  $[\text{H}^+]$  in the solution, it is possible to precipitate effectively all of zinc ions from the solution without precipitating any  $\text{Mn}^{2+}$  ion.

**Sol 14:** Since at  $\text{pH} = 2.0$ , half of the indicator is present in the unionized form, therefore

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

$$\text{Using } \text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\text{p}K_{\text{In}} = \text{pH} = 2.0$$

$\text{pH}$  of the solution containing  $4.0 \times 10^{-3} \text{M}$  of  $\text{H}^+$  is

$$\text{pH} = -\log(4.0 \times 10^{-3}) = 2.4$$

$$\text{Thus, } \log \left( \frac{[\text{In}^-]}{[\text{HIn}]} \right) = \text{pH} - \text{p}K_{\text{In}} = 2.4 - 2.0 = 0.4$$

$$\text{Or } \frac{[\text{In}^-]}{[\text{HIn}]} = 2.5$$



Adding 1 on both sides, we get

$$\frac{[\text{In}^-] + [\text{HIn}]}{[\text{HIn}]} = 3.5$$

$$\text{or } \frac{[\text{HIn}]}{[\text{In}^-] + [\text{HIn}]} = \frac{1}{3.5} = 0.286$$

Thus, the percentage of indicator in the unionized form = 28.6

**Sol 15:** dissociation constant of  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ , calculate the concentration of  $\text{S}^{2-}$  under both conditions.

Ans. To calculate  $[\text{HS}^-]$

	$\text{H}_2\text{S}$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{HS}^-$
Initial	0.1M		x		x
After disso.	0.1-x				
	$\approx 0.1$				

$$K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8} \quad \text{or } x^2 = 9.1 \times 10^{-9}$$

$$\text{or } x = 9.54 \times 10^{-5}$$

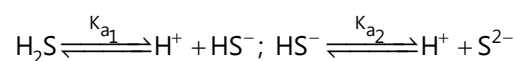
In presence of 0.1 M HCl, suppose  $\text{H}_2\text{S}$  dissociated is y. Then at equilibrium,

$$[\text{H}_2\text{S}] = 0.1 - y \approx 0.1, [\text{H}^+] = 0.1 + y \approx 0.1$$

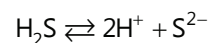
$$[\text{HS}^-] = y \text{ M}$$

$$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8} \text{ (Given) or } y = 9.1 \times 10^{-8} \text{ M}$$

To calculate  $[\text{S}^{2-}]$



For the overall reaction,



$$K_a = K_{a1} \times K_{a2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13}$$

$$= 1.092 \times 10^{-20}$$

$$K_a = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$\text{In the absence of 0.1 M HCl, } [\text{H}^+] = 2[\text{S}^{2-}]$$

$$\text{Hence, if } [\text{S}^{2-}] = x, [\text{H}^+] = 2x$$

$$\therefore \frac{(2x)^2 x}{0.1} = 1.092 \times 10^{-20} \quad \text{or } 4x^3$$

$$= 1.092 \times 10^{-21} = 273 \times 10^{-24}$$

$$3 \log x = \log 273 - 24 = 2.4362 - 24$$

$$\log x = 0.8127 - 8 = \bar{8}.8127,$$

$$\text{Or } x = \text{Antilog } \bar{8}.8127 = 273 \times 10^{-24}$$

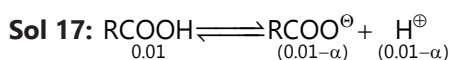
$$= 6.497 \times 10 = 6.5 \times 10^{-8} \text{ M}$$

In presence of 0.1 M HCl, suppose  $[\text{S}^{2-}] = y$ , then

$$[\text{H}_2\text{S}] = 0.1 - y \approx 0.1 \text{ M}, [\text{H}^+] = 0.1 + y \approx 0.1 \text{ M}$$

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20} \quad \text{or } y = 1.09 \times 10^{-19} \text{ M}$$

$$\text{Sol 16: } K_a = 1.74 \times 10^{-5} \quad \sqrt{\frac{K_a}{C}} = \alpha$$



$$\text{pH} = 4.15$$

$$\text{conc.} = 0.01 \text{ M}$$

Get conc. of  $\text{H}^\oplus$  from pH. Calculate  $\alpha$  and  $K_a$ .

**Sol 18:** (i) pH of 0.003 M HCl

$$[\text{H}^+] = 0.003 \text{ M}; \text{pH} = -\log(0.003) = 2.52$$

(ii) pH of 0.005 M NaOH

$$[\text{OH}^-] = 0.005 \text{ M}; \text{pOH} = -\log(0.005) = 2.30$$

(iii) pH of 0.002 M HBr

$$[\text{H}^+] = 0.002 \text{ M}; \text{pH} = -\log(0.002) = 2.70$$

(iv) pH of 0.002 M KOH

$$[\text{OH}^-] = 0.002 \text{ M}; \text{pOH} = -\log(0.002) = 2.70$$

**Sol 19:** Calculate  $\text{H}^\oplus$  /  $\text{OH}^\ominus$  conc. using the volume and weight. Thus, calculate pH.

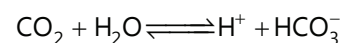
**Sol 20:** Calculate solubility and then calculate it using volume of 2.5 L.

**Sol 21:**

$$K_h = \frac{K_w}{K_a \times K_b} = \frac{10^{-14}}{7.2 \times 10^{-10} \times 1.8 \times 10^{-5}} = 0.772$$

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}} = \frac{\sqrt{0.772}}{1 + \sqrt{0.772}} = \frac{0.878}{1.878} = 0.467$$

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b = 7.0 + \frac{9.14}{2} - \frac{4.74}{2} = 9.20$$

**Sol 22:**  $\text{CO}_2$  with  $\text{H}_2\text{O}$  forms  $\text{H}_2\text{CO}_3$ .

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 4.5 \times 10^{-7}$$

$$\text{Now, pH} = -\log[\text{H}^+] = 7.4; [\text{H}^+] = 4 \times 10^{-8}$$

$$\text{Thus, } \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{4.5 \times 10^{-7}}{4 \times 10^{-8}} = 11$$

**Sol 23:** The original  $\text{pOH} = 4.75$ . The  $\text{pOH}$  after addition of  $\text{NaOH}$  cannot be less than 3.75.

$$\text{pOH} = 3.75 = 4.75 + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$\log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = -1.00 \quad \text{so} \quad \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 0.10$$

Hence  $\text{NaOH}$  can be added until the ratio of  $[\text{NH}_4^+]$  to  $[\text{NH}_3]$  is 0.10. Initially  $[\text{NH}_4^+] + [\text{NH}_3] = 0.200$

Although the reaction with  $\text{OH}^-$  converts  $\text{NH}_4^+$  into  $\text{NH}_3$ , the sum of these two concentrations remains 0.200.

$$[\text{NH}_4^+] + [\text{NH}_3] = 0.200$$

$$[\text{NH}_4^+] = 0.10[\text{NH}_3] \quad (\text{From above})$$

$$0.10[\text{NH}_3] + [\text{NH}_3] = 0.200$$

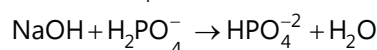
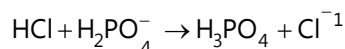
$$\text{so } 1.10[\text{NH}_3] = 0.200 \quad \text{and} \quad [\text{NH}_3] = 0.182\text{M}$$

Hence  $[\text{NH}_4^+] = 0.018\text{M}$  Assuming no change in volume,  $0.100 - 0.018 = 0.082\text{ mol}$  of  $\text{NaOH}$  can be added without changing the  $\text{pOH}$  by more than 1.00  $\text{pOH}$  unit.

**Exercise 2****Single Correct Choice Type**

**Sol 1: (A)** The conjugate acid has one proton ( $\text{H}^+$ ) more. Hence, for  $\text{NH}_2^-$  the conjugate acid would be  $\text{NH}_3$  (the positive charge of  $\text{H}^+$  and the negative charge of  $\text{NH}_2^-$  cancel each other out).

**Sol 2: (C)**  $\text{H}_2\text{PO}_4^-$  And  $\text{HCO}_3^-$  are amphoteric in nature.



**Sol 3: (C)** Halides and alkaline metals dissociate and do not affect the  $\text{H}^+$  as the cation does not alter the  $\text{H}^+$  and the anion does not attract the  $\text{H}^+$  from water. This is why  $\text{NaCl}$  is a neutral salt. But  $\text{pH}$  of water **decreases** as the temperature **increases**. So option C is correct

$$\text{Sol 4: (C)} \quad \text{No' moles HCl} = \frac{(1 \times 0.1)}{1000} = 10^{-4}$$

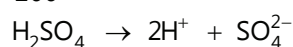
$$\text{Volume} = 1\text{dm}^3 \quad \text{Concentration} = \text{moles/volume}$$

$$= \frac{10^{-4}}{1} = 10^{-4} \quad \text{This gives a pH of 4 so option (C) is correct.}$$

**Sol 5: (B)**

$$\text{We have } 50\text{mL of } \frac{M}{200} \text{ H}_2\text{SO}_4$$

$$\frac{M}{200} = 0.005\text{M solution}$$



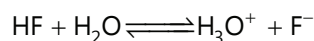
$$\text{Then } [\text{H}^+] = 2 \times 0.005\text{M} = 0.01\text{M}$$

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

$$\text{pH} = -\log 0.01\text{M}$$

$$\text{pH} = 2.00$$

**Sol 6: (C)** The equation for the dissociation of  $\text{HF}$  is as follow:



$$\text{Here } \text{p}K_b = 10.83$$

$$\Rightarrow -\log K_b = 10.83$$

$$\text{Hence, } K_b = 1.48 \times 10^{-11}$$

Thus Ionization constant of acid  $K_a = K_w / K_b$

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

$$K_a = 10^{-14} / 1.48 \times 10^{-11}$$

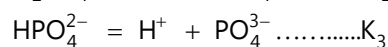
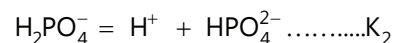
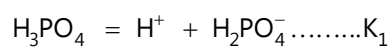
$$K_a = 6.76 \times 10^{-4}$$

Thus Ionization constant of HF is  $6.76 \times 10^{-4}$

**Sol 7: (C)**  $[H_3O^+] = C\alpha = 0.1 \times \frac{1}{100} = 1 \times 10^{-3}$

$$pH = -\log[H_3O^+] = -\log 10^{-3} = 3$$

**Sol 8: (D)**



$$K_3 = [HPO_4^{2-}]$$

$$H^+ = [PO_4^{3-}]$$

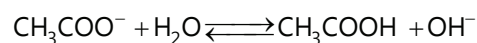
**Sol 9: (D)** Molarity of both acid and base is same. Amount of acid used is thrice the amount of base. Thus the pH of the solution will be highly acidic,

**Sol 10: (A)** Since NaCN is the salt of a weak acid (HCN) and strong base (NaOH), the degree of hydrolysis,

$$\begin{aligned} \alpha &= \sqrt{\frac{K_w}{K_a \times C}} \\ &= \frac{1.0 \times 10^{-14} \times 80}{1.3 \times 10^{-9}} \\ &= \sqrt{6.16 \times 10^{-4}} \\ &= 2.48 \times 10^{-2} \end{aligned}$$

$\therefore$  Percentage hydrolysis of NaCN in N/80 Solution is 2.48

**Sol 11: (D)** Sodium acetate undergoes anionic hydrolysis



**Sol 12: (B)**  $NH_4OH + HCl \rightleftharpoons NH_4Cl$

$NH_4Cl$  Is a salt of weak base and strong acid .so it give s acidic solution with  $pH > 7$

**Sol 13: (B)** The pH of the solution at the equivalence point will be greater than 7 due to salt hydrolysis. So an indicator giving colour on the basic side will be suitable.

**Sol 14: (C)** It is a salt of weak acid and weak base.

$$[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

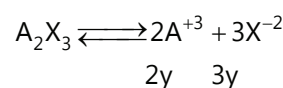
On solving we get

$$pH = 7.01$$

**Sol 15: (B)**  $CH_3COONa + HCl \rightleftharpoons CH_3COOH + NaCl$

It is an example of titration of weak base with strong acid. Observed pH range for the end point is 3.00 to 6.00.

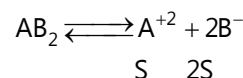
**Sol 16: (D)**



$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3 = (2y)^2 (3y)^3 = 108y^5$$

**Sol 17: (A)** Solubility  $= \sqrt{K_{sp}} = \sqrt{6.4 \times 10^{-5}} = 8 \times 10^{-3}$

**Sol 18: (C)**



$$K_{sp} = [A^{+2}]^2 [B^{-}]^2 = (S)(2S)^2 = 4(1 \times 10^{-5})^3 = 4 \times 10^{-15}$$

**Sol 19: (A)**  $(AB, AB_2, A_xB_y) K_{sp} = (S^{x+y})X^xY^y$

**Sol 20: (B)** Precipitation takes place when the ionic product of a salt is greater than the solubility product. Solubility product of AgCl is  $1.8 \times 10^{-10}$ . So, the ionic product of AgCl should be greater than this value. On using the values given in option (B), the ionic product comes out to be  $1 \times 10^{-10}$ . Hence the correct answer is option (B)

**Sol 21: (B)** Precipitation takes place when the ionic product of a salt is greater than the solubility product. We are given that the solubility product of  $CaF_2$  is  $1.7 \times 10^{-10}$ . So, the ionic product of  $CaF_2$  should be greater than this value. The ionic product of  $CaF_2$  can be calculated as follows:

$$= [Ca^{2+}] \times [F^-]^2$$

On using the values given option (A), the ionic product of  $CaF_2$  comes out to be  $1 \times 10^{12}$ , while using the values given in option (C), we get  $1 \times 10^{11}$  as the answer. However, on using the values given in option (B), the ionic product comes out to be

$$= [10^2] \times [10^3]^2$$

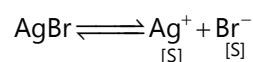
$$= 10^2 \times 10^6$$

$$= 10^8$$

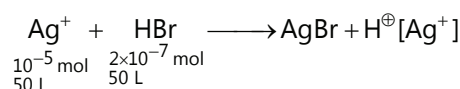
Thus, in this case, the ionic product of  $\text{CaF}_2$  is greater than solubility product. Hence the correct answer is option (b)  $10^2 \text{ M Ca}^{2+}$  and  $10^3 \text{ MF}$ .

**Sol 22: (C)**

$$K_{\text{sp}}(\text{AgBr}) = 5 \times 10^{-13}$$



$$K_{\text{sp}} = S^2 ; S = \sqrt{K_{\text{sp}}} \dots (1)$$



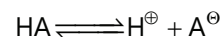
M = mole / V

The obtained  $[\text{Ag}^+]$  should be subtracted from the available 50 L  $\text{Ag}^+$  solution.

$$\text{Sol 23: (A)} \quad \text{pH}(\text{HA}) = 9 \Rightarrow [\text{H}^+] = 10^{-9}$$

$$K_{\text{sp}}(\text{AgA}) = [\text{Ag}^+][\text{A}^-]$$

$$K_{\text{a}}(\text{HA}) = 10^{-10}$$



$$K_{\text{a}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{ . Get conc. of } [\text{A}^-]$$

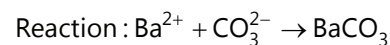
Thus, calculate  $K_{\text{sp}}$ .

**Sol 24: (D)**  $\text{Na}_2\text{CO}_3$  is salt of weak acid  $\text{H}_2\text{CO}_3$  and strong base  $\text{NaOH}$  therefore, it has a pH more than 7. Also, it dissociates to give two moles of  $\text{NaOH}$ .

**Sol 25: (B)**

$$\text{Concentration of } \text{Na}_2\text{CO}_3 = [\text{CO}_3^{2-}] = 1.0 \times 10^{-4} \text{ M}$$

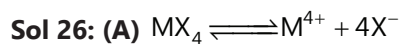
$$K_{\text{sp}} \text{ of } \text{BaCO}_3 = 5.1 \times 10^{-9}$$



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

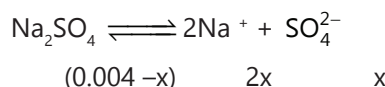
$$[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{CO}_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}}$$

$$= 5.1 \times 10^{-5}$$



$$\therefore K_{\text{sp}} = [\text{S}][4\text{S}]^4 = 256$$

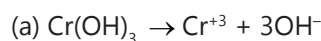
$$S = \left( \frac{K_{\text{sp}}}{256} \right)^{1/4}$$

**Previous Years' Questions****Sol 1: (C)**

Since both the solution are isotonic  $0.004 + 2x = 0.01$

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

$$\text{Percent dissociation} = \frac{3 \times 10^{-3}}{0.004} \times 100 = 75\%$$

**Sol 2: (A)**

$$x \qquad 3x$$

$$K_{\text{sp}} = x.(3x)^3 = 27x^4$$

$$x = \sqrt[4]{\frac{K_{\text{sp}}}{27}} ; x = \sqrt[4]{\frac{2.7 \times 10^{-31}}{27}}$$

$$x = 1 \times 10^{-8} \text{ mole/litre.}$$

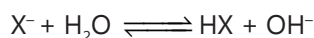
**Sol 3: (A)**

$$(a) \text{pH} = 7 + \frac{1}{2} [\text{p}K_{\text{a}} + \log C]$$

$$= 7 + \frac{1}{2} [4.74 + \log 10^{-2}]$$

$$= 7 + \frac{1}{2} [4.74 - 2]$$

$$= 7 + \frac{2.74}{2} = 8.37$$

**Sol 4: (B)**

$$K_{\text{h}} = \frac{10^{-14}}{10^{-5}} \text{ so } h = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$$

$$100 \times 10^{-4} = 10^{-2}$$

$$\text{So\% of hydrolysis} = 0.01\%.$$

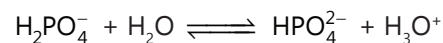
**Sol 5: (B)**  $\text{Na}_2\text{O}$  from  $\text{NaOH}$ . So that it is basic oxide.

**Sol 6: (D)**  $\alpha = 1.9 \times 10^{-9}$ ;  $C = \frac{1000}{18}$

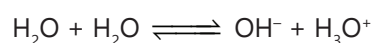
$$K = \frac{[\text{H}^+][\text{OH}^-]}{(\text{H}_2\text{O})} = c\alpha^2$$

$$= 1.9 \times 10^{-9} \times 1.9 \times 10^{-9} \times \frac{1000}{18} = 2.0 \times 10^{-16}$$

**Sol 7: (B, C)** pH of  $1 \times 10^{-8} \text{ M}$  is below to 7



Conjugate base of  $\text{H}_2\text{PO}_4^-$  acid



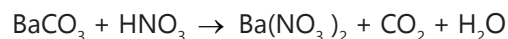
$K$  (Auto protolysis constant of water i.e., with ionic product of water) increases with temperature. For half neutralization of a weak acid by a weak base

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$[\text{Salt}] = [\text{Acid}] \therefore \text{pH} = \text{pK}_a.$$

**Sol 8: (A, C)** A buffer solution can be prepared by mixing weak acid/base with salt of its Conjugate base/acid.

**Sol 9: (A)** (a) Barium carbonate is more soluble in  $\text{HNO}_3$  than in water because carbonate is a weak base and reacts with the  $\text{H}^+$  ion of  $\text{HNO}_3$  causing the barium salt to dissociate.



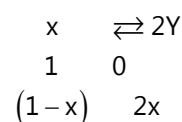
**Sol 10: (A)** (a) The conjugate base of  $\text{CHCl}_3$  is more stable than conjugate base of  $\text{CHF}_3(\text{CF}_3)$ .  $\text{CCl}_3$  stabilized by  $-\text{I}$  effect of chlorine atoms as well as by the electrons. But conjugate base of  $\text{CH}_3(\text{CH}_3)$  is stabilized only by  $-\text{I}$  effect of fluorine atoms. Here both assertion and reason are true and reason is correct explanation of assertion.

**Sol 11: (C)** It is a salt of weak acid and weak base

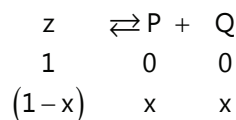
$$[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$\text{pH} = 7.01$$

**Sol 12: (A)**  $\text{X} \rightleftharpoons 2\text{Y}$



$$K_{p1} = \frac{(2x)^2}{(1-x)} \left( \frac{P_1}{1+x} \right)^1$$



$$K_{p2} = \frac{x^2}{(1-x)} \left( \frac{P_2}{1+x} \right)^1$$

$$\frac{4 \times P_1}{P_2} = \frac{1}{9} \Rightarrow \frac{P_1}{P_2} = \frac{1}{36}$$

**Sol 13: (B)**  $\text{Ag}^+ + \text{Br}^- \rightleftharpoons \text{AgBr}$

Precipitation starts when ionic product just exceeds solubility product

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

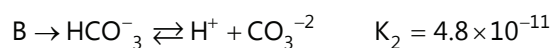
$$[\text{Br}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when  $10^{-11}$  moles of  $\text{KBr}$  is added to 1 L  $\text{AgNO}_3$  solution. No. of moles of  $\text{KBr}$  to be added  $= 10^{-11}$

$$= 10^{-11} \times 120$$

$$= 1.2 \times 10^{-9} \text{ g}$$

**Sol 14: (C)**



As  $K_2 \ll 1$

$$\text{All major } [\text{H}^+]_{\text{total}} \approx [\text{H}^+]_{\text{A}}$$

**Sol 15: (B)**  $\text{Mg}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Mg}(\text{OH})_2$

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

$$[\text{OH}^-] = \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} = 10^{-4}$$

$$\therefore \text{pOH} = 4 \quad \text{and} \quad \text{pH} = 10$$

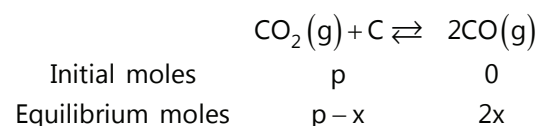
**Sol 16: (B)** Electron releasing groups (Alkyl groups) de stabilizes conjugate base.

The + I effect of  $C_3H_7$  is less than - I effect of Cl

$K_a$  of  $HCOOH$  is  $17.9 \times 10^{-5}$

$K_a$  of  $CH_3CH_2\underset{\text{Cl}}{\underset{|}{CH}}-COOH$  is  $139 \times 10^{-5}$

**Sol 17: (D)**



Total pressure at equilibrium = 0.8 atm; Total no. of moles = p + x.

Therefore,  $p \propto n$ ;  $\frac{0.5}{0.8} = \frac{p}{p+x} \Rightarrow x = 0.3$

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8 \text{ atm}$$

**Sol 18: (C)**  $[H^+] = \sqrt{K_a \cdot C} \Rightarrow 10^{-3} = \sqrt{K_a \cdot 10^{-1}}$   
 $\Rightarrow K_a = 10^{-5}$

**Sol 19: (D)**  $pH = 1$   $[H^+] = 10^{-1} = 0.1 \text{ M}$

$$pH = 2$$
  $[H^+] = 10^{-2} = 0.01 \text{ M}$

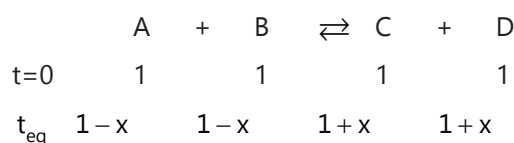
for dilution of HCl  $M_1V_1 = M_2V_2$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10 \text{ lt}$$

Volume of water added = 10 - 1 = 9 litre.

**Sol 20: (B)**



$$\Rightarrow \frac{(1+x)^2}{(1-x)^2} = 100 \quad \Rightarrow \frac{1+x}{1-x} = 10$$

$$\Rightarrow 1+x = 10-10x \quad \Rightarrow 11x = 9$$

$$\Rightarrow x = \frac{9}{11}$$

$$\Rightarrow [D] = 1 + \frac{9}{11}; \Rightarrow [D] = 1.818$$

## JEE Advanced/Boards

### Exercise 1

**Sol 1:**  $pH = 13$

$$\therefore C = [H^+] = 10^{-13}$$

$$n = \frac{C}{V} = \frac{10^{-13}}{10^3} = 10^{-16}$$

$$\text{No. of } H^+ \text{ ions} = n \times N_A = 10^{-16} \times 6.023 \times 10^{23} = 6.022 \times 10^7$$

**Sol 2:**  $K_w = [H^+][OH^-]$

Substitute in the value for  $K_w$  at 298 K:

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

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

$$10^{-14} = [H^+]^2$$

Take the root of both sides of the equation to find

$$[H^+]:$$

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

$$[H^+] = 10^{-7} \text{ M at } 298 \text{ K}$$

Similarly At 310 K,

$$2.56 \times 10^{-14} = [H^+]^2$$

$$[H^+] = \sqrt{2.56 \times 10^{-14}} = 1.6 \times 10^{-7} \text{ M at } 310 \text{ K}$$

**Sol 3:**  $K_w = 9.62 \times 10^{-14}$

$$pK_w = -\log(9.62 \times 10^{-14}) = 13.01$$

$$pH = \frac{1}{2}(pK_w) = \frac{13.01}{2} = 6.50$$

(ii) (a) Basic, (b) Acidic

**Sol 4:**  $K_w = 2.56 \times 10^{-14} \longrightarrow 60^\circ\text{C}$

$$pK_w = -\log(2.56 \times 10^{-14}) = 13.58$$

$$\text{Apply } pH = \frac{1}{2}(pK_w) = \frac{13.58}{2} = 6.79$$

**Sol 5:**

(a) Since  $\text{H}_2\text{SO}_4$  dissociates as  $\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$

$$[\text{H}_3\text{O}^+] = \frac{(50 \times 0.2) + (50 \times 0.4)}{50 + 50} = \frac{30}{100} = 0.3$$

$$\text{pH} = -\log(0.3) = 0.522$$

(b) 0.1 M HA + 0.1 M HB

$$K_a = 2 \times 10^{-5} \quad K_a = 4 \times 10^{-5}$$

$$[\text{H}^+] = \sqrt{K_{a(\text{HA})} \times C_1 + K_{a(\text{HB})} \times C_2}$$

$$= \sqrt{2 \times 10^{-5} \times 0.1 + 4 \times 10^{-5} \times 0.1}$$

$$= 0.00244$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.00244) = 2.61$$

**Sol 6:** Since the solution is fairly concentrated and  $K_2 / K_1 \approx 10^{-3}$  ( $K_2 \ll K_1$ ), we can use the expression:

$$K_1 = \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{A}]_0 - [\text{H}_3\text{O}^+]} \quad (\text{Eq.1.10.10})$$

Which gives

$$[\text{H}_3\text{O}^+] = \frac{-K_1 \sqrt{K_1^2 + 4[\text{H}_2\text{A}]_0 K_1}}{2}$$

Substituting the given values of  $K_1$  and  $[\text{H}_2\text{A}]_0$  in the above expression, we get

$$[\text{H}_3\text{O}^+] = \frac{-(5.9 \times 10^{-2} \text{M}) + \sqrt{(5.9 \times 10^{-2} \text{M})^2 + 4(0.1 \text{M})(5.9 \times 10^{-2} \text{M})}}{2}$$

$$= \frac{-(5.9 \times 10^{-2} \text{M}) + (1.645 \times 10^{-1} \text{M})}{2}$$

$$= 0.0528 \text{M}$$

We can obtain the concentrations of  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  in 0.1 M solution of oxalic acid from the following relations:

$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}_2\text{A}]_0}{1 + \frac{K_1}{[\text{H}_3\text{O}^+]}} = \frac{0.1 \text{M}}{1 + \left( \frac{5.9 \times 10^{-2} \text{M}}{5.28 \times 10^{-2} \text{M}} \right)}$$

$$= \frac{0.1 \text{M}}{1 + 1.118} = 0.0472 \text{M}$$

$$[\text{HC}_2\text{O}_4^-] = \frac{[\text{H}_2\text{A}]_0}{\frac{K_1}{[\text{H}_3\text{O}^+]} + 1} = \frac{0.1 \text{M}}{\left( \frac{5.28 \times 10^{-2} \text{M}}{5.90 \times 10^{-2} \text{M}} \right) + 1}$$

$$= \frac{0.1 \text{M}}{0.8949 + 1} = 0.0528 \text{M}$$

$$[\text{C}_2\text{O}_4^{2-}] = \frac{[\text{H}_2\text{A}]_0}{\frac{K_1 K_2}{[\text{H}_3\text{O}^+]^2} + \frac{K_2}{[\text{H}_3\text{O}^+]}}$$

$$= \frac{0.1 \text{M}}{\frac{(5.28 \times 10^{-2} \text{M})^2}{(5.9 \times 10^{-2} \text{M})(6.4 \times 10^{-5} \text{M})} + \frac{5.28 \times 10^{-2} \text{M}}{6.4 \times 10^{-5} \text{M}}}$$

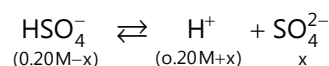
$$= \frac{0.1 \text{M}}{738.3 + 825.0} = 0.000064 \text{M}$$

**Sol 7:** Since the dissociation is strong, therefore, the  $[\text{H}^+]$  due to this dissociation is 0.20 M.

Let  $x$  be the amount of  $\text{H}^+$  due to this dissociation  
Hence,

$$[\text{H}^+]_{\text{total}} = 0.20 \text{M} + x$$

This in equilibrium gives



$$K = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.20 \text{M} + x)(x)}{(0.20 \text{M} - x)} = 1.3 \times 10^{-2} \text{M}$$

$$\text{Or } (0.20 \text{M} + x)(x) = (1.3 \times 10^{-2} \text{M})(0.20 \text{M} - x)$$

$$x^2 + (0.20 \text{M} + 1.3 \times 10^{-2} \text{M})$$

$$x - (1.3 \times 10^{-2} \text{M})(0.20 \text{M}) = 0$$

This is quadratic equation in  $x$ , which gives

$$x = \frac{-0.213 \text{M} + \sqrt{0.213^2 + 4(1.3 \times 10^{-2} \text{M})(0.20 \text{M})}}{2}$$

$$= \frac{-0.213 \text{M} + 0.2362 \text{M}}{2} = 0.0116 \text{M}$$

$$\text{Thus, } [\text{H}^+]_{\text{total}} = (0.2 \text{M} + x) = 0.2116 \text{M}$$

$$[\text{HSO}_4^-] = 0.2\text{M} - x = 0.1884\text{M}$$

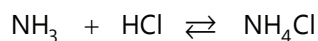
$$[\text{SO}_4^{2-}] = x = 0.0116\text{M}$$

$$[\text{H}_2\text{SO}_4] = 0$$

**Sol 8:**

$$\text{pK}_a(\text{NH}_4^+) = 9.26$$

$$\therefore \text{pK}_b(\text{NH}_3) = 14 - 9.26 = 4.74$$



Initial	20	15	0
---------	----	----	---

After	5	0	15
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Mixture is a buffer containing 5 millimol of  $\text{NH}_3$  (base)And 15 millimol of  $\text{NH}_4^+$  (conjugate acid)

$$\begin{aligned} \therefore \text{pOH} &= \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} \\ &= 4.74 + \log 3 \end{aligned}$$

$$\begin{aligned} \therefore \text{pH} &= 14 - \text{pOH} \\ &= 9.26 - \log 3 \\ &= 9.26 - 0.48 = 8.78 \end{aligned}$$

$$\text{Sol 9: } \text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Final Volume of NaOH after reaction = 50 + 75 = 125 ml

$$M_1V_1 = M_2V_2$$

$$M_2 = \frac{0.1 \times 50}{125} = 0.04\text{M}$$

Final Volume of  $\text{NH}_4\text{Cl}$  = 25 ml

$$M_1V_1 = M_2V_2$$

$$M_2 = \frac{0.2 \times 50}{25} = 0.4\text{M}$$

$$\text{pOH} = 0.2 + \log \frac{[0.4]}{[0.04]} = 0.2 + 1 = 1.2$$

$$\text{pH} = 14 - 1.2 = 12.8$$

**Sol 10:** Methyl red, one with pH = 5.22 as midpoint of colour range.

$$\text{Sol 11: } \text{pH} = \text{pK}_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\text{Initial concentration of } [\text{HIn}] = 75\%$$

$$\text{Initial concentration of } [\text{In}^-] = 25\%$$

$$\text{Final concentration of } [\text{HIn}] = 25\%$$

$$\text{Initial concentration of } [\text{In}^-] = 75\%$$

Thus,

$$\text{pH}_1 = -\log(3 \times 10^{-5}) + \log 75 / 25$$

$$\text{pH}_1 = 5$$

$$[\text{H}^+]_1 = 10^{-5}\text{M}$$

$$\text{pH}_2 = -\log(3 \times 10^{-5}) + \log 25 / 75 = -4.045$$

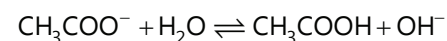
$$[\text{H}^+]_2 = 8.91 \times 10^{-5}\text{M}$$

$$[\text{H}^+]_2 = 8.91 \times 10^{-5}\text{M}$$

$$[\text{H}^+]_2 - [\text{H}^+]_1 = 7.91 \times 10^{-5}\text{M}$$

$$\text{Sol 12: } K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

$$\text{CH}_3\text{COONa}(0.08\text{M})$$



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

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

$$\frac{1}{K_a} = \frac{[\text{HA}]}{[\text{H}^+][\text{A}^-]}$$

$$K_b = K_w \times K_a$$

$$K_w = 1 \times 10^{-14}$$

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

$$K_b = 5.6 \times 10^{-20} = \frac{x^2}{(0.08 - x)} = \frac{x^2}{(0.08)}$$

$$x = [\text{OH}^-] = 0.669 \times 10^{-5}\text{M}$$



**Sol 13:**  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

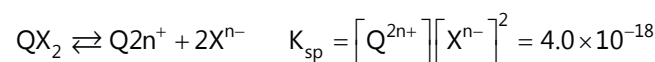
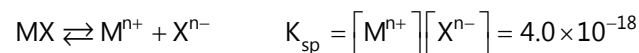
2M  $\text{NH}_4\text{Cl}$  solution of strong acid and weak base.

$$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C] = 4.477$$

**Sol 14:**  $\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C]$

**Sol 15:**  $\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C] = 8.86$

**Sol 16:**



$$\text{Solving yield } [\text{M}^{n+}] = 2.0 \times 10^{-9} \quad [\text{Q}^{2n+}] = 1.0 \times 10^{-6}$$

Soluble.

**Sol 17:** Let the simultaneous solubilities of  $\text{AgSCN}$  and  $\text{AgBr}$  be  $s_1$  and  $s_2$  mole per litre

$$[\text{Ag}^+] = s_1 + s_2, [\text{SCN}^-] = s_1 \text{ and } [\text{Br}^-] = s_2$$

$$K_{sp}(\text{AgSCN}) = [\text{Ag}^+][\text{SCN}^-]$$

$$1.0 \times 10^{-12} = (s_1 + s_2) \times s_1 \quad \dots (i)$$

$$5.0 \times 10^{-13} = (s_1 + s_2) s_2 \quad \dots (ii)$$

Dividing Equation (i) by Equation (ii), we get

$$\frac{s_1}{s_2} = 2$$

$$\text{Or } s_1 = 2s_2$$

Substituting this value in Equation (ii)

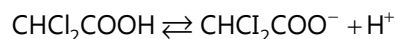
$$5.0 \times 10^{-13} = 3s_2^2$$

$$s_2 = 4.08 \times 10^{-7}$$

$$\therefore s_1 = 8.16 \times 10^{-7}$$

This simultaneous solubilities of  $\text{AgSCN}$  and  $\text{AgBr}$  are  $8.16 \times 10^{-7}$  mole per litre and  $4.08 \times 10^{-7}$  mole per litre respectively.

**Sol 18:** pH will be decided by  $[\text{H}^+]$  furnished by  $\text{HCl}$  and  $\text{CHCl}_2\text{COOH}$ .  $\text{CH}_3\text{COOH}$  being weak does not dissociate due to common ion effect.



Initial conc.	0.09	0	0.09 (from $\text{HCl}$ )
Final conc.	$(0.09 - x)$	$x$	$(0.09 = x)$

$$\therefore [\text{H}^+] = 0.09 + x;$$

But  $\text{pH} = 1$

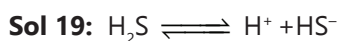
$$\therefore [\text{H}^+] = 10^{-1} = 0.1$$

$$\therefore 0.09 + x = 0.1$$

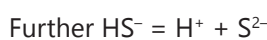
$$\therefore x = 0.01$$

$K_a$  for  $\text{CHCl}_2\text{COOH}$  can be given as:

$$K_a = \frac{[\text{H}^+][\text{CHCl}_2\text{COO}^-]}{[\text{CHCl}_2\text{COOH}]} = \frac{0.1 \times 0.01}{(0.09 - 0.01)} = 1.25 \times 10^{-2}$$



$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \dots (i)$$



$$K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \quad \dots (ii)$$

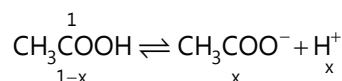
Multiplying both the equations

$$K_{a1} \times K_{a2} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

Due to common ion, the ionization of  $\text{H}_2\text{S}$  is suppressed and the  $[\text{H}^+]$  in solution is due to the presence of 0.3 M  $\text{HCl}$ .

$$[\text{S}^{2-}] \frac{K_{a1} \times K_{a2} [\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{10^{-7} \times 10^{-14} \times (0.1)}{(2 \times 10^{-4})^2} = 2.5 \times 10^{-15}$$

**Sol 20:** Use  $\text{pH} = -\log [\text{H}^+]$  for 1 M.



$$K_a = \frac{x^2}{1-x} = x^2 = 1.8 \times 10^{-5}; x = 4.2 \times 10^{-3} = [\text{H}^+]$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log(4.2 \times 10^{-3}) = 2.37$$

Now, let 1 litre of 1 M  $\text{CH}_3\text{COOH}$  be diluted to  $V$  litres so that the pH of the solution doubles. Let the concentration of the diluted solution be  $c$  moles / litre.

Thus,  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$K_a = \frac{x' \cdot x'}{(c - x')} = 1.8 \times 10^{-5} \quad \dots(i);$$

Further  $\text{pH} = -\log x' = 2 \times 2.37 = 4.74$  (pH doubles on dilution)

$$\text{Or } \log x' = -4.74 = \bar{5}.26; x' = 1.8 \times 10^{-5}.$$

Sub.  $x'$  in (1) we get,  $c = 3.6 \times 10^{-5}$

As the number of moles of  $\text{CH}_3\text{COOH}$  before and after dilution will be the same.

$\therefore$  Moles of  $\text{CH}_3\text{COOH}$  = Molarity  $\times$  Volume in litres.

$$\therefore 3.6 \times 10^{-5} \times V = 1 \times 1 \left( \begin{array}{l} \text{Initial molarity} = 1 \\ \text{Initial volume} = 1 \end{array} \right)$$

$$V = 2.78 \times 10^4 \text{ litres}$$

**Sol 21:** Acetic acid has to use as salt-acid molar ratio is 1.8: 1

**Sol 22:** At the end point, m.e. (on millimoles) of the salt produced

$$= \text{m.e. of NaOH} = 0.1 \times 36.12 = 3.612$$

(Since salt formed will be univalent and so for such salts m.m. = m.e.)

$$\text{m.e. (millimole) of HCl added} = 0.1 \times 18.06 = 1.806$$

The addition of 1.806 m.e. of HCl will produce the same number of m.e. of the unknown acid and reduce the amount of the salt by 1.806 m.e.

$$\therefore \text{m.e. (millimole) of the unknown acid} = 1.806$$

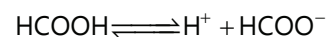
$$\text{And m.e. (or millimole) of the salt} = 3.612 - 1.806 = 1.806.$$

Using,

$$\text{pH} = \text{p}K_a + \log \frac{\text{millimole of salt}}{\text{millimole of acid}}$$

**Sol 23:** Let us find  $[\text{H}^+]$  of  $\text{HCOOH}$  before adding  $\text{HCOONa}$ .

For the equilibrium,



$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$$

$$(\because [\text{H}^+] = [\text{HCOO}^-])$$

$$\therefore [\text{H}^+] = \sqrt{K_a \cdot [\text{HCOOH}]} = \sqrt{1.8 \times 10^{-4} \times 0.2} = 6 \times 10^{-3}$$

Now, on the addition of sodium formate in the acid, we have,

$$[\text{H}^+] = \frac{[\text{acid}]}{[\text{salt}]} = 1.8 \times 10^{-4} \times \frac{0.2}{0.1} = 3.6 \times 10^{-4}$$

Calculate pH.

## Exercise 2

### Single Correct Choice Type

$$\text{Sol 1: (A)} \quad \text{pH} = -\log [4^+] = \frac{1}{\log_{10}[4^+]} \text{ or}$$

$$[4^+] = 10^{-\text{pH}}$$

$$\therefore [4^+] = 10^{-2} \text{ and } [\text{H}^+] = 10^{-6}$$

$$10^{-2} = 10^{-6}$$

$$\therefore \text{Factor} = 10^4$$

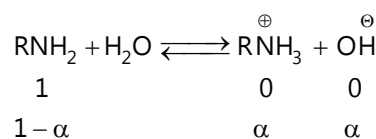
**Sol 2: (C)** Overall dissociation

$$\text{Constant} = 1.0 \times 10^{-5} \times 5.0 \times 10^{-10}$$

$$\text{Acid } (\text{H}_2\text{A}) = 5.0 \times 10^{-15}$$

**Sol 3: (D)**  $k_b = 2 \times 10^{-6}$ ; 0.01 M  $\text{RNH}_2$

$10^{-4}$  M NaOH



Common ion effect due to NaOH

$$k_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

$$\text{pOH} = -\log k_b + \log \frac{[\text{C.A.}]}{[\text{Base}]}$$

$$= -\log (2 \times 10^{-6}) + \log \frac{(0.01)}{10^{-4}}$$

$$= -\log 2 + 6 + \log 0.01 + 4$$

$$= 10 - 2 - 0.3010 = 7.699$$

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

$$[\text{OH}^-] = 10^{-7.699}$$

**Sol 4: (B)** Salt of WB & WA

Degree of hydrolysis = 50 %; M = 0.1 M

$$M_2 = 0.2 \text{ M}$$

% hydrolysis of salt = ?

$$h_1 = \sqrt{\frac{K_h}{C_1}} \quad h_2 = \sqrt{\frac{K_h}{C_2}}$$

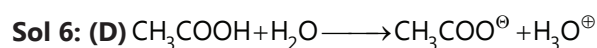
$$h_1^2 C_1 = K_h \quad h_2^2 C_2 = K_h$$

$$h_1^2 C_1 = h_2^2 C_2$$

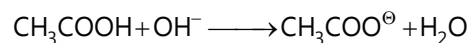


$$K = \frac{x^2}{(0.1-x)^2}; \quad \sqrt{K} = \frac{x}{0.1-x}$$

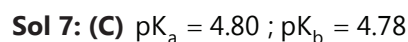
$$\frac{12}{12} = 1$$



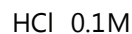
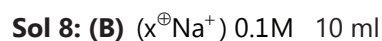
$$K_a = 1.8 \times 10^{-5}$$



$$k_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$



$$\text{pH} = \frac{1}{2} (pR_w + pK_a - pK_b)$$



$$k_b(x^\oplus) = 10^{-6}$$

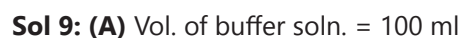
$$K_a \times K_b = K_w$$

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$$K_{\text{In}} = K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{H}_{\text{In}}]} = \frac{[\text{H}^+][\text{base}]}{[\text{acid}]}$$

$$[\text{H}^+] = K_a = \frac{[\text{acid}]}{[\text{base}]} = 10^{-9} \frac{[0.1]}{[0.1]}$$

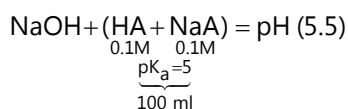
$$\text{pH} = \frac{1}{2} (pK_w - pK_b - \underbrace{\log a}_{pK_a})$$



$$M_{\text{buffer}} = 0.1\text{M}$$

$$\text{pH} = 5.5$$

$$pK_a(\text{HA}) = 5$$



$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 5 + \log \frac{[0.1]}{[0.1]} = 5$$

Contributing pH = 0.5 by NaOH

$$0.5 = -\log [\text{H}^+]$$

$$A \log (-0.5) = [\text{H}^+]$$

$$[\text{H}^+] = 3.16$$

$$[\text{OH}^-] = 10.84 = \frac{\text{no. of moles}}{\text{vol.}}$$



$$K_a = 2 \times 10^{-4}$$

$$\text{No. of Millimoles} = M \times \text{Vol}$$

$$\therefore \text{Milimoles of KOH} = 0.2 \times 40 = 8$$

$$\text{Milimoles of HCOOH} = 0.1 \times 160 = 16$$

$$\text{Milimoles of HCOOK produced} = 8$$

$$\text{Milimoles of HCOOH remained} = 16 - 8 = 8$$

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

$$= -\log(2 \times 10^{-4}) + \log \frac{8}{8} = 4 - 0.3010 = 3.699$$

$$\text{pOH} = 14 - 3.699 = 10.3$$



$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 4.5 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{As H A is 50\% ionized, } [\text{Salt}] = [\text{Acid}]$$

This is because of the total 100% only %50 is ionized which is equivalent to the concentration of the remaining buffer solution.

If it was 75% then we would consider  $(100 - 75)\%$ , but in this case  $[\text{Salt}] \neq [\text{Acid}]$ .

$$\text{pH} = 4.5$$

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

$$\text{or } \text{pOH} = 14 - 4.5 = 9.5$$

**Sol 12: (A)** C is the conjugate acid of A, and D is the conjugate base of B

**Sol 13: (A)**  $\text{NaH}_2\text{PO}_2$  is not an acid salt.

**Sol 14: (B)** pH of buffer solution is not affected by dilution.

**Sol 15: (C)** Buffer solution constitute of weak acid and its conjugate base or vice versa.

**Sol 16: (C)** Buffer solution constitute of weak acid and its conjugate base or vice versa.

### Multiple Correct Choice Type

**Sol 17: (A, B)** Buffer solution constitute of weak acid and its conjugate base or vice versa.

**Sol 18: (B, C)** (B)  $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$   
Acid Conjugate Base

(C) Conceptual fact

**Sol 19: (B, C)** Concentration of salt (C) at equivalent point is 0.25 M

Volume of HCl is used at equivalent point is 100 ml

**Sol 20: (A, B, C)** Phenolphthalein is suitable indicator for the titration of weak acid vs strong base and strong acid vs strong base.

**Sol 21: (A, B, C)** All the three relation are correct for alkaline solution.

(A)  $\text{pH} > \frac{\text{pK}_w}{2}$

(B)  $\text{pH} > \text{pOH}$

(C)  $\text{pOH} < \frac{\text{pK}_w}{2}$

**Sol 22: (A, B)**  $\text{pH} = \text{pK}_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$

Initial concentration of  $[\text{HIn}] = 75\%$

Initial concentration of  $[\text{In}^-] = 25\%$

Final concentration of  $[\text{HIn}] = 25\%$

Final concentration of  $[\text{In}^-] = 75\%$

$$\text{pH}_1 = -\log(3 \times 10^{-5}) + \log \frac{75}{25} = 5$$

$$[\text{H}_1^+] = 10^{-5} \text{ M}$$

$$\text{pH}_2 = -\log(3 \times 10^{-5}) + \log \frac{25}{75} = 4.05$$

**Sol 23: (A, C, D)** A very high value of equilibrium constant indicates that the forward is almost complete. Thus  $\text{CN}^-$  is stronger base than  $\text{ONO}^-$ . (C) and (D) are factual.

**Sol 24: (A, D)**



**Sol 25: (B, C, D)**  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{NaOH}$  all of them will suppress the ionization of phthalic acid in an aqueous solution.

### Match the Columns

**Sol 26:**  $\text{A} \rightarrow \text{q}$ ;  $\text{B} \rightarrow \text{r}$ ;  $\text{C} \rightarrow \text{s}$ ;  $\text{D} \rightarrow \text{p}$

(A)  $\text{CH}_3\text{COOH}$  - Weak acid

(B)  $\text{H}_2\text{SO}_4$  - Strong acid

(C)  $\text{NaOH}$  - Strong base

(D)  $\text{NH}_3$  - Weak base

**Sol 27:**  $\text{A} \rightarrow \text{s}$ ;  $\text{B} \rightarrow \text{s}$ ;  $\text{C} \rightarrow \text{q}$

Propyl red and malachite green are suitable indicators for strong acid and strong base titrations.

### Previous Years' Questions

**Sol 1: (A)**  $K_p$  for a given reversible reaction depends only on temperature.

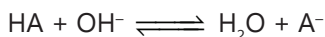
**Sol 2: (A)**  $K_a(\text{HX}) = \frac{K_w}{K_b} = 10^{-4}$

$$\Rightarrow \text{pH} = \text{pK}_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

$$= \text{pK}_a$$

$$[\therefore [\text{X}^-] = [\text{HX}]] = 4$$

**Sol 3: (C)** The reaction of HA with strong base is :



$$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} \times \frac{[\text{H}^+]}{[\text{H}^+]} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

**Sol 4: (D)** MX:  $K_{sp} = S^2 = 4 \times 10^{-8} \Rightarrow S = 2 \times 10^{-4}$

$$\text{MX}_2 : K_{sp} = 4S^3 = 3.2 \times 10^{-4} \Rightarrow S = 2 \times 10^{-5}$$

$$\begin{aligned} \text{M}_3\text{X} : K_{sp} &= 27S^4 \\ &= 2.7 \times 10^{-15} \\ &\Rightarrow S = 10^{-4} \end{aligned}$$

Order of solubility is:



**Sol 5: (D)**  $\text{BOH} + \text{Ha} \rightarrow \text{Ba} + \text{H}_2\text{O} \cdot \text{B}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH}_{\text{ch}} + \text{H}^+_{\text{ch}}$

For titration  $N_{\text{acid}_1} V_{\text{acid}_1} = N_{\text{acid}_2} V_{\text{acid}_2}$

$$\begin{aligned} \frac{2}{15} \times v &= 2.5 \times \frac{2}{5} \\ v &= \text{vol g HCl} 7.5\text{mL} \end{aligned}$$

In resulting solution, conc. of salt

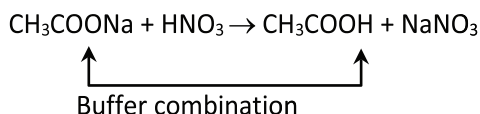
$$[\text{BCl}] = \frac{\frac{2}{5} \times 2.5}{10} = 0.1$$

$$\therefore \frac{ch^2}{1-h} = \frac{k_w}{k_b} \text{ or } h = \sqrt{\frac{k_w}{k_b \times c}} = \sqrt{\frac{10^{-19}}{16^{-12} \times 0.1}}$$

$$h = \sqrt{\frac{1}{10}} \text{ how}$$

$$[\text{H}^+] = ch = 0.1 \times \sqrt{\frac{1}{0.1}} = 3.16 \times 10^{-2} \text{M} = 3.2 \times 10^{-2} \text{M}$$

**Sol 6: (C, D)** In  $\text{HNO}_3$  and  $\text{CH}_3\text{COONa}$  combination, if  $\text{HNO}_3$  is present in limiting amount, it will be neutralised completely, leaving behind some excess of  $\text{CH}_3\text{COONa}$ :



**Sol 7: (B, C, D)**  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{SCN}^-$  forms precipitate with Cu (I), remove Cu (I) ion from equilibrium and reaction shift in backward direction according to Le-Chatelier's principle.

**Sol 8:** In pure water, solubility =  $\frac{9.57}{58} \times 10^{-3}$   
 $= 1.65 \times 10^{-4} \text{M}$

$$K_{sp} = 4S^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$$

In 0.02 M  $\text{Mg}(\text{NO}_3)_2$ ;

$$\begin{aligned} \text{solubility of } \text{Mg}(\text{OH})_2 &= \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} \times \frac{1}{2} \\ &= 1.5 \times 10^{-5} \text{ mol L}^{-1} \\ &= 1.5 \times 10^{-5} \times 58 \text{g L}^{-1} \\ &= 8.7 \times 10^{-4} \text{ g L}^{-1} \end{aligned}$$

**Sol 9:** (i) 0.20 mole HCl will neutralise 0.20 mole  $\text{CH}_3\text{COONa}$ , producing 0.20 mol  $\text{CH}_3\text{COOH}$ . Therefore, in the solution

moles of  $\text{CH}_3\text{COOH} = 1.20$

moles of  $\text{CH}_3\text{COONa} = 0.80$

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

$$= -\log (1.8 \times 10^{-5}) + \log \frac{(0.80)}{1.20} = 4.56$$

(ii)  $\text{CH}_3\text{COONa} + \text{HCl} \rightarrow \text{CH}_3\text{COOH} + \text{NaCl}$

Initial	0.10	0.20	0	0
Final	0	0.10	0.10	0.10

Now the solution has 0.2 mol acetic acid and 0.1 mole HCl. Due to presence of HCl, ionisation of  $\text{CH}_3\text{COOH}$  can be ignored (common mainly due to HCl).

$$\Rightarrow [\text{H}^+] = 0.10$$

$$\Rightarrow \text{pH} = -\log (0.10) = 1.0$$

**Sol 10:**  $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$

$$1-x \quad 1-x \quad x \quad x$$

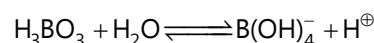
$Q_c = I < K_c$ , ie, reaction proceed in forward direction to attain equilibrium.

$$\Rightarrow 16 = \left( \frac{x}{1-x} \right)^2$$

$$\Rightarrow x = 0.80$$

$$\Rightarrow [\text{NO}] = 0.80 \text{ M}, [\text{NO}_2] = 0.20 \text{ M}$$

**Sol 11: (C)**  $\text{H}_3\text{BO}_3$  (orthoboric acid) is a weak lewis acid.



It does not donate proton rather it acceptors  $\text{OH}^-$  form water.

Hence, (C) is correct.

**Sol 12: (C)** If  $\beta_{eq} = 0.7$ 

$$K_p = \frac{8 \times (0.7)^2}{4 - (0.7)^2} = \frac{3.92}{3.51} > 1$$

Which can't be possible as  $\Delta G^\circ > 0 \Rightarrow K_p < 1$ . $\therefore$  Therefore, option (C) is incorrect.**Sol 13:**Let the solubility of AgCl is x mol/litre  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ Let the solubility of AgCl is x mol/litre  $\text{CuCl} \rightleftharpoons \text{Cu}^+ + \text{Cl}^-$ 

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

$$1.6 \times 10^{-10} = x(x + y) \quad \dots (i)$$

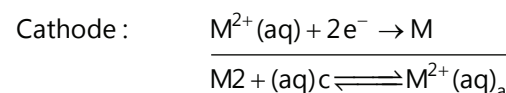
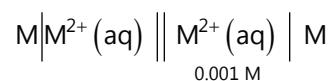
Similarly  $K_{sp}$  of CuCl =  $[\text{Cu}^+][\text{Cl}^-]$ 

$$1.6 \times 10^{-6} = y(x + y) \quad \dots (ii)$$

On solving (i) and (ii)

$$[\text{Ag}^+] = 1.6 \times 10^{-7}$$

$$\therefore x = 7$$

**Sol 14: (B)**

$$E_{\text{cell}} = 0 - \frac{0.059}{2} \log \left\{ \frac{\text{M}^{2+}(\text{aq})_a}{10^{-3}} \right\}$$

$$0.059 = -\frac{0.059}{2} \log \left\{ \frac{\text{M}^{2+}(\text{aq})_a}{10^{-3}} \right\} - 2 = \log \left\{ \frac{\text{M}^{2+}(\text{aq})_a}{10^{-3}} \right\}$$

$$10^{-2} \times 10^{-3} = \text{M}^{2+}(\text{aq})_a = \text{solubility} = s$$

$$K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$$

**Sol 15: (D)**  $pK_a$  of PhOH (carboxylic acid) is 9.98 and that of carbonic acid ( $\text{H}_2\text{CO}_3$ ) is 6.63 thus phenol does not give effervescence with  $\text{HCO}_3^-$  ion.**Sol 16: (A)** Rate in weak acid =  $\frac{1}{100}$  (rate in strong

acid)

$$\therefore [\text{H}^+]_{\text{weak acid}} = \frac{1}{100} [\text{H}^+]_{\text{strong acid}}$$

$$\therefore [\text{H}^+]_{\text{weak acid}} = \frac{1}{100} M = 10^{-2} M$$

$$\therefore C\alpha = 10^{-2}$$

$$\therefore K_a = 10^{-4}$$

Option (A) is correct.

**Sol 17: (B)**  $K_{sp} = 1.1 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$ 

$$1.1 \times 10^{-12} = [0.1]^2 [s]$$

$$s = 1.1 \times 10^{-10}$$

**Sol 18: (B)**

	$X_{2(g)} \rightarrow$	$2X_{(g)}$
t = 0 (No. of moles)	1	0
t = t	$1 - \frac{\beta}{2}$	$\beta$
t = $t_{eq}$	$\left(1 - \frac{\beta_{eq}}{2}\right)$	$\beta_{eq}$

$$P_x = 2 \left( \frac{\beta_{eq}}{1 + \frac{\beta_{eq}}{2}} \right) \quad n_{\text{Total}} = 1 - \frac{\beta_{eq}}{2} + \beta_{eq} = \left(1 + \frac{\beta_{eq}}{2}\right)$$

$$P_{X_2} = 2 \left( \frac{1 - \beta_{eq}/2}{1 + \beta_{eq}/2} \right)$$

$$K_p = \frac{(P_x)^2}{P_{X_2}} = \frac{\left[ 2 \left( \frac{\beta_{eq}}{1 + \beta_{eq}/2} \right) \right]^2}{\left[ 2 \left( \frac{1 - \beta_{eq}/2}{1 + \beta_{eq}/2} \right) \right]^2} = \frac{2\beta_{eq}^2}{1 - \frac{\beta_{eq}^2}{4}} = \frac{8\beta_{eq}^2}{4 - \beta_{eq}^2}$$