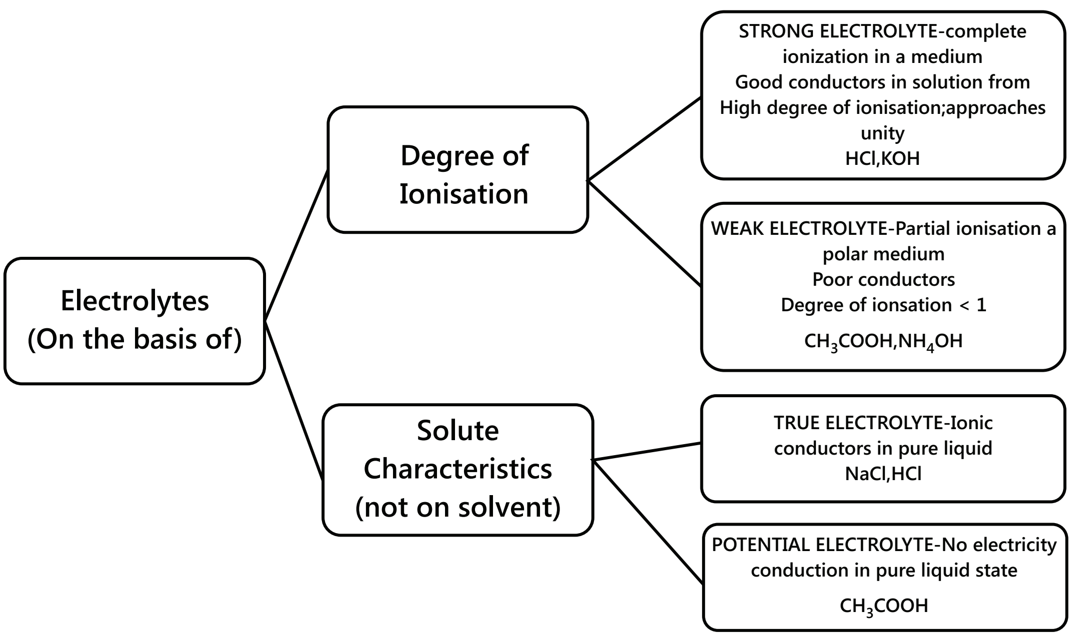
6. IONIC EQUILIBRIUM

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., $CaCO_3 \rightleftharpoons CaO + CO_2$

(b) Formation of ions by a weak electrolyte is also called dissociation. e.g. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

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

$NaCl + aq. \rightarrow Na^+(aq.) + Cl^-(aq.)$

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.

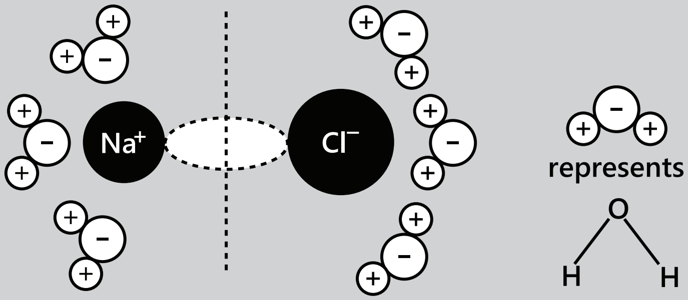


Figure 6.1 :Dissociation of NaCl in water

- **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 'α' of an electrolyte is governed by:

(a) 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 $\alpha << 1$.

(b) 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).

(c) 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).

CONCEPTS

Solutions (aqueous)

Conducting (solutions of electrolytes, i. e., acids, bases and salts)

Non-Conducting (solutions of non-electrolytes such as urea, glucose, sugar, glycerine, etc.

Strongly conducting (solns of strong elelctrolyteswhich ionize almost completely in water such as HCl, H_2SO_4, HNO_3, NH_4Cl, NaCl, NaOH, KOH etc.)

Weakly conducting (solutions of weak electrolytes which slightly ionize in water such as CH_3COOH, NH_4OH, H_3PO_4, HCN, etc.)

Flowchart 6.2: Types of solution

The degree of dissociation of an electrolyte is assumed to be unity at infinite dilution, i. e., α = 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

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$ or

$$HA \rightleftharpoons H^+ + A^-$$

	HA	H^+	A^-
Moles before dissociation	1	0	0
Moles after dissociation	$1 - \alpha$	α	a

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

According to equilibrium constant expression,

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

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \text{.... (i)}$$

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

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

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

$$B(aq) + H_2O \rightleftharpoons HB^+(aq) + OH^-(aq)$$

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

If $1 - \alpha \approx 1$ and $K_b = c\alpha^2$ .... (iii)

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

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

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

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 $1 - \alpha \cong 1$ can be applied only if $\alpha < 5\%$. If on solving a problem by applying Ac approximate formula, α comes out to be $\geq 5\%$, the problem may be solved again by applying exact formula and α may be calculated by applying solution of a quadratic equation, i. e. A = $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ (Equation (ii) implies $Ca^2 + K\alpha - K = 0$)

Misconception: Generally, it is assumed that Ostwald's Dilution law can be used for any electrolyte. But electrolytes having, $\alpha \cong 1$, i. e., $K_a \to \infty$(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 'α' 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 'α'

(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 α determine the concentration of fluoroacetic acid.

$$CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$$

1	0	0
$1-\alpha$	a	a

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

Also, $\because$ $Ka = \dfrac{c\alpha^2}{(1-\alpha)}$

$\therefore$ $2.6 \times 10^{-3} = \dfrac{1.5\times10^{-3}.\alpha}{(1-\alpha)}$ [See α is not small]

$\therefore$ $\alpha = 0.634$

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

$\therefore$ $c = \dfrac{1.5\times10^{-3}}{0.634} = 2.37 \times 10^{-3}$ M

Illustration 2: At 30°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 $\alpha = \sqrt{\dfrac{K_a}{C}}$

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

Let the degree of dissociation of the acid at 0.02 M concentration be α.

$$a_1 = \sqrt{\frac{K_a}{0.02}} \quad \text{.... (ii)}$$

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

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

$\alpha_1 = 0.0263$

Illustration 3: Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula 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 $= \dfrac{0.01}{2} = 0.05$ mol L^{-1}

	HNiC $\rightleftharpoons$	H^+ +	NiC^-
Equilibrium conc.	(0.05 – x)	x	x

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

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

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

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

Alternative method: Let α be the degree of dissociation

	$HNiC \rightleftharpoons$	H^+ +	NiC^-
At equilibrium	$0.05\,(1-\alpha)$	$0.05\,\alpha$	0.05 a

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

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

So, $1.4 \times 10^{-5} = 0.05\underline{a}^2$

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

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

2.2 Phenomenon of Autoprotolysis

Water shows autoprotolysis as:

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

The phenomenon of self-ionisation is called autoprotolysis.

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

$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

$CH_3OH + CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$

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

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

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

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

$K_w = [H^+][OH^-]$ .... (7)

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

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

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

Since, concentration or molarity of H_2O = 55.6

$$\therefore \alpha = \frac{10^{-7}}{55.6} = \frac{1}{(556 \times 10^{6})} = 1.8 \times 10^{-9}$$

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

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.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ The equilibrium constant, K_a is given by:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Now, suppose sodium acetate is added to this solution.

$CH_3COONa \rightarrow CH_3COO + Na^+$

The concentration of CH_3COO^- in the solution increases and thus, in order to have K_a constant, $[H^+]$ must decrease or the concentration of undissociated acetic acid must increase. In other words, the dissociation of acetic acid is suppressed on addition of CH_3COONa to its solution. Similar results are obtained on addition of HCl to acetic acid solution, this time H^+ provided by HCl acts as common ion.

Illustration 4: Liquid ammonia ionises to a slight extent. At -50°C, its ionisation constant, $K_b = K_{NH_3} = [NH_4^+].[NH_2^-] = 10^{-30}$. How many amide ions, are present per cm^3 of pure liquid ammonia? Assume $N = 6.0 \times 10^{23}$.

(JEE MAIN)

Sol: $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (self-ionisation)

and $K_{NH_3} = [NH_4^+].[NH_2^-]$

$\therefore [NH_4^+] = [NH_2^-]$

$\therefore [NH_2^-] = \sqrt{K_{NH_3}} = \sqrt{10^{-30}} = 10^{-15}M$

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

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

Illustration 5: What is the H^+ ion concentration of a solution known to contain 0.1 g mole of CH_3COONH_4 in one litre of 0. 1 M CH_3COOH? Assume effective ionisation of ammonium acetate is 80%. K_a for acetic acid is 1.8×10^{-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.

$$\begin{array}{lcll} CH_3\,COOH & \rightleftharpoons & CH_3\,COO^- & +\ H^+ \\ (0.1 - x) & & x & \quad x \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

The solution also contains CH_3COONH_4 which is 80% dissociated i. e. $\alpha = 0.8$. Thus, the acetate concentration provided by 0. 1 M $CH_3COONH_4 = 0.1 \times 0.8 = 0.08$ M

Total$[CH_3COO^-] = (0.08 + x)$ M

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

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

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

or $x = [H^+] = \frac{1.8\times10^{-5}\times0.1}{0.08} = 2.25 \times 10^{-5}$ mol L^{-1}

Illustration 6: The ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOD^-]$ 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 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, $\alpha = \frac{\text{Moles dissociated at any time}}{\text{Totalmoles present or dissolved initially}}$

Given density of formic acid = 1. 22 g/cm^3

$\therefore$ Weight of formic acid in 1 litre solution = 1.22×10^3g

Thus, $[HCOOH] = \frac{1.22\times10^3}{46} = 26.5$ M

Since, in case of auto ionization,

$[HCOOH_2^+] = [HCOO^-]$

and $[HCOO^-][HCOOH_2^+] = 10^{-6}$

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

Now, % dissociation of HCOOH = $\frac{[HCOO^-]\times100}{[HCOOH]} = \frac{10^{-3}}{26.5} \times 100 = 0.004\%$

Illustration 7: A solution contains 0. 1 M H_2S and 0. 3 M HCl. Calculate the concentration of S^{2-} and HS^- ions in solution. Given, K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively. **(JEE ADVANCED)**

Sol: $H_2S \rightleftharpoons H^+ + HS^-$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \quad \text{.... (i)}$$

Further $HS^- = H^+ + S^{2-}$

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \quad \text{.... (ii)}$$

Multiplying both the equations

$$K_{a_1} \times K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Due to common ion, the ionization of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of 0. 3 M HCl.

$$[S^{2-}] = \frac{K_{a_1}\times K_{a_2}[H_2S]}{[H^+]^2} = \frac{1.0\times10^{-7}\times1.3\times10^{-13}\times(0.1)}{(0.3)^2} = 1.44 \times 10^{-20} \text{ M}$$

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

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

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:

$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$

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

When the solution is saturated,

$[A_x B_y] = K'$ (constant)

Or $[A^{y+}]^x [B^{x-}]^y = K[A_xB_y] = KK' = K_{sp}$ (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:

$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$

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

Let 'S' mol $litre^{-1}$ be the solubility of the salt; then

$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$

xS.yS

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

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: AlI_3, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$,etc.

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

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 A^+ and B^- ions become S′ and (S′ + c)., respectively.

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

Equating (i) and(ii),

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

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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 CaF_2 and SrF_2, when dissolved together.

(iii) Solubility of MgF_2 and 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. CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$); SrF_2 ($K_{sp} = 2.9 \times 10^{-9}$)

Most of fluoride ions come from stronger electrolyte.

CONCEPTS

- It must be noted that hydration of molecule doesn't influence K_{sp}
- K_{sp} of a hydrated molecule say $Na_2CO_3 . 10H_2O$ can be given by $K_{sp} = [Na^+]^2[CO_3^{2-}]$

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Illustration 8: K_{sp} of AgCl is 2.8×10^{-10} at 25°C. Calculate solubility of AgCl in

(i) Pure water (ii) 0. 1 M $AgNO_3$. (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 theses example we can use the expression, $K_{sp} = S'(S' + c)$

(i) In pure water: Let solubility of AgCl be S mol litre^{-1}

$AgCl(s) + Aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

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

Or S = $\sqrt{K_{sp}} = \sqrt{(2.8\times10^{-10})}$ = 1. 673 × 10^{-5} mol litre^{-1}

(ii) In 0. 1 M $AgNO_3$: $AgCl(s) + Aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$AgNO_3(aq) \rightarrow \underset{0.1}{Ag^+}(aq) + \underset{0.1}{NO_3^-}(aq)$

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

Here, $\left[Ag^+\right] = 0.1 + S$

$\because S <<< 0.1, \left[Ag^+\right] = 0.1\text{ M}$

$\because$ S < < < 0. 1 since solubility decreases in presence of common ion

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

or S = 2. 8 × 10^{-9} mol litre^{-1}

(iii) In 0. 1 M NaCl: $AgCl(s) + \underset{S}{Aq} \rightleftharpoons \underset{S}{Ag^+} + Cl^-$

$NaCl(aq) \rightarrow \underset{0.1}{Na^+}(aq) + \underset{0.1}{Cl^-}(aq)$

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

Here, $\left[Cl^-\right] = 0.1 + s$ but $s <<< 0.1$

$\therefore \left[Cl^-\right] = 0.1M$

$\therefore S <<< 0.1$

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

$\therefore$ S = 2. 8 × 10^{-9} mol litre^{-1}

Illustration 9: Equal volumes of 0. 02 M $CaCl_2$ and 0. 0004 M Na_2SO_4 are mixed. Will a precipitate be formed? K_{sp} for $CaSO_4$ = 2. 4 × 10^{-5} **(JEE MAIN)**

Sol: Assuming volume of 0.02 M $CaCl_2$ soln = volume of 0.0004 M Na_2SO_4 = VL.

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

No. of moles of $SO_4^{2-} = 0.0004\,V$

$\therefore [Ca^{2+}] = \dfrac{0.02\,V}{2V}$ = 0. 01 mol litre^{-1}

$[SO_4^{2-}] = \dfrac{0.0004\,V}{2V}$ = 0. 0002 mol litre^{-1}

$\therefore [Ca_4^{2+}][SO_4^{2-}] = [0.01][0.0002] = 2 \times 10^{-6}$

Thus, $[Ca^{2+}]\,[SO_4^{2-}]$ in solution < K_{sp} [Here Ionic product < K_{sp}]

($\because$ 2 × 10^{-6} < 2. 4 × 10^{-5})

$\therefore CaSO_4$ will not precipitate.

Illustration 10: What $[H_3O^+]$ must be maintained in a saturated H_2S solution to precipitate Pb^{2+}, but not Zn^{2+} from a solution in which each ion is present at a concentration of 0. 1 M?

(K_{sp} for H_2S = 1. 1 ×10^{-22}, K_{sp} for ZnS = 1. 0 × 10^{-21}). **(JEE ADVANCED)**

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

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

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

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

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

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

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

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

Illustration 11: 25 mL of 0. 10 M $AgNO_3$ are mixed with 35 mL of 0. 05 M K_2CrO_4 solution. Calculate (a) The concentration of each ionic species at equilibrium (b) Is the precipitation of silver quantitative (> 99. 9%)? K_{sp} of Ag_2CrO_4 = 1. 1 × 10^{-12}. **(JEE ADVANCED)**

Sol: First calculate the K_{sp} of Ag_2CrO_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.

$2AgNO_3 + K_2CrO_4 \rightleftharpoons Ag_2CrO_4 + KNO_3$

Millimoles at equilibrium = 25×0.1 & 35×0.5 respectively.

= 2.5 & 1.75

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

$[Ag^+]^2\ [Cro_4^{2-}] = K_{sp} = 1.1 \times 10^{-12}$

Also after mixing

$[Ag^+]^2\ [Cro_4^{2-}] = \left[\frac{2.5}{60}\right]^2\left[\frac{1.75}{60}\right] = 5.06 \times 10^{-5} > K_{sp}$

Thus, precipitation will take place

$2AgNO_3 + K_2CrO_4 \rightleftharpoons Ag_2CrO_4 + 2KNO_3$

Millimoles before mixing = 2.5 & 1.75 respectively

Millimoles after mixing = (1.75 – 1.25) 21.25=0.50 & 21.25 respectively.

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

$[NO_3^-] = \frac{2.5}{60}$ = 0. 0417 M

$[CrO_4^{2-}] = \frac{0.5}{60}$ = 0. 0083 M

Let solubility of Ag_2CrO_4 be S mol $litre^{-1}$, then

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

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

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

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

The % of Ag precipitated = $\dfrac{2.5-(60\times1.16\times10^{-5})}{2.5}\times 100 = 99.97\%$

i.e. precipitation is quantitative.

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

Sol: $AgCl \rightleftharpoons \underset{(S_1+S_2)}{Ag^+} + \underset{S_1}{Cl^-}$ Let solubility of AgCl and AgBr be S_1, S_2 mol litre^{-1}

$$AgBr \rightleftharpoons \underset{(S_1+S_2)}{Ag^+} + \underset{S_2}{Br^-}$$

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

$$\therefore \frac{S_1}{S_2} = \frac{1.0\times10^{-10}}{5.0\times10^{-13}} = 200$$

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

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

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

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

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

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

And $S_2 = \dfrac{9.98\times10^{-6}}{200} = 4.99 \times 10^{-8}$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 $CaCl_2$ and $BaCl_2$. If we add Na_2SO_4 to this solution slowly and slowly, we can first precipitate the sulphate of Ba (on the basis of K_{sp} values of $CaSO_4$ and $BaSO_4$ which are 2×10^{-4} and 1.5×10^{-9} respectively.

This is due to the fact that as we go on adding Na_2SO_4, the concentration of SO_4^{2-} ion increases and since $[Ba^{2+}][SO_4^{2-}] = K_{sp}$, 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, BaF_2(aq)

$BaF_2\,(aq) \rightleftharpoons Ba^{2+} + 2F^-$

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

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

$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$

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

4.5 Stability Constant

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

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

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

Let us consider the formation of a complex $K_2Cd(CN)_4$. Complex ion is $Cd(CN)_4^{2-}$ where the oxidation state of a central metal Cd^{2+} is (+2). The complexing process proceeds in four steps as:

$Cd^{2+} + CN^- \rightleftharpoons CdCN^+; K_1 = \dfrac{[CdCN^+]}{[Cd^{2+}][CN^-]}$

$CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2; K_2 = \dfrac{[Cd(CN)_2]}{[CdCN^+][CN^-]}$

$Cd(CN)_2 + CN^- \rightleftharpoons Cd\,(CN)_3^-; K_3 = \dfrac{[Cd(CN)_3^-]}{[Cd(CN)_2][CN^-]}$

$Cd\,(CN)_3^- + CN^- \rightleftharpoons Cd((CN)_4^{-2}; K_4 = \dfrac{[Cd(CN)_4^{2-}]}{[Cd(CN)_3^-][CN^-]}$

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

Here, $K_5 = K_1 K_2 K_3 K_4$

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_{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

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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

$$AgCN \rightarrow \underset{a}{Ag^+} + \underset{a}{CN^-}$$

$CN^- + H^+ \rightarrow HCN;$

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

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

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

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

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

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:

$Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$

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

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:

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

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

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

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

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

$AgNO_3 + NaIO_3 \rightarrow AgIO_3 + NaNO_3$

0. 01	0. 005	0	0
0. 005	0	0. 005	0. 005

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

$2AgNO_3 + Na_2CrO_4 \rightarrow Ag_2CrO_4 + 2NaNO_3$

0. 005	0. 01	0	0
0	0. 0975	0. 0025	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 0. 0025 0. 0975

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

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

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.

$HCl \rightarrow H^+ + Cl^-$ (strong acid)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (weak acid)

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

$NaOH \rightarrow Na^+ + OH^-$ (Strong base)

$NH_4OH \rightarrow NH_4^+ + OH^-$ (Weak base)

(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 H^+ and OH^- ions.

$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$

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. $CO_2 + CaO \rightarrow CaCO_3$; $NH_3(g) + HCl(g) \rightarrow NH_4Cl(g)$ or (s)

(c) It fails to explain the acidic character of certain salts, e.g., $AlCl_3$, BF_3, etc., and the basic character of NH_3, PH_3, Na_2CO_3, etc. Neither $AlCl_3$ nor BF_3 on dissolution in water directly produces a proton. Similarly, when Na_2CO_3 is dissolved in water, it neutralises an acid but Na_2CO_3 cannot dissociate itself directly to produce hydroxyl ions.

(d) It fails to explain the fact that the H^+ ion exists in water as H_3O^+, i. e., hydronium ion. Since H^+ is the simplest and smallest ion and thus, possesses strong tendency of hydration (hydration energy of H^+ is – 256 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.

$\underset{Acid_1}{H_2O} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Base_1}{OH^-} + \underset{Acid_2}{H_3O^+}$

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

$\underset{Acid}{CH_3COOH} + \underset{Base}{H_2O} \rightleftharpoons CH_3COO^- + H_3O^+$

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

$\underset{Acid}{Na^+} + 2H_2O \rightleftharpoons NaOH + H_3O^+$

$\underset{Base}{Cl^-} + H_2O \rightleftharpoons HCl + OH^-$

Acid $\xrightarrow{-H^+}$ Conjugate Base Base $\xrightarrow{+H^+}$ Conjugate Acid

$HCl \xrightarrow{-H^{\oplus}} Cl^{\ominus}$

$NH_3 \xrightarrow{+H^{\oplus}} NH_4^+$

$C_2H_2 \xrightarrow{-H^+} C_2H^-C_2 \xrightarrow{+H^+} C_2H_6$

$C_6H_5NH_2 \xrightarrow{+H^+} C_6H_5NH_3^+$

$C_6H_5OH \xrightarrow{-H^+} C_6H_5O^-Al(OH)_3 \xrightarrow{+H^+} Al(aq)$

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

$Acid_1 + Base_2 \rightarrow Base_1 + Acid_2$

$Acid_1$ has its conjugate $base_1$ in product and $base_2$ has its conjugate $acid_2$

$\underset{B_1}{NH_3} + \underset{A_2}{NH_3} \rightarrow \underset{A_1}{NH_4^+} + \underset{B_2}{NH_2^-}$

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., BF_3, an electron deficient molecule reacts directly with NH_3 to show the formation of $[F_3B \neg NH_3]$ 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 H^+ ion whereas a Bronsted acid is a substance which can donate a proton which is also a H^+ ion. On the other hand, an Arrhenius base is a substance which gives the OH^-ion in the solution but Bronsted base is a substance which accepts a proton. It may not contain OH^- ion. For example, NaOH is an Arrhenius base because it gives 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 (H_3O^+) in the following reaction:

$A + H_2O \rightarrow A^- + H_3O^+$

Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+. Therefore, no acid stronger than H_3O^+ exists in H_2O. Similarly, when ammonia is the solvent, the strongest acid is ammonium (NH_4^+), thus HCl and a super acid (one with a low pKa) exert the same acidifying effect in water.

The same argument applies to bases. In water, OH- is the strongest base. Thus, even though sodium amide ($NaNH_2$) is an exceptional base (pKa of NH_3 ~ 33), in water it is only as good as sodium hydroxide. On the other hand, $NaNH_2$ is a far more basic reagent in ammonia than is 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 SO_2ClF (these solvents would be considered differentiating solvents).

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 pKa 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 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.

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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

$BF_3 + NH_3 \rightarrow (H_3N \rightarrow BF_3)$

$BF_3 + F^- \rightarrow [BF_4]^-$

$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$

(c) **Lewis acids**

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

Acid strength of simple cations increases with

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

(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., BF_3, BCl_3, $AlCl_3$, RMgX, $MgCl_2$, 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 $SO_2 < SO_3$.
- A decrease in the atomic radius of the central atom. However, these rules show some anomalies, e.g., acidic strength of boron trihalides is $BF_3 < BCl_3 < BBr_3 < BI_3$.

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

(iii) Compounds whose central atom can show expansion of octet: SiF_4 and $SiCl_4$ 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: $Li^+ > Na^+ > K^+$

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

e.g., $:NH_3$, $:PH_3$, $:PCl_3$, $(CH_3)_2\ddot{O}:$, ligands, i. e., CN^-, CNS^-, OH^-, 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: $F^- > Cl^- > Br^- > I^-$

$NH_2^- > OH^- > SH^-$

The Lewis base nature of nitrogen trihalides follows the order: $NF_3 < NCl_3 < NBr_3 < NI_3$.

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

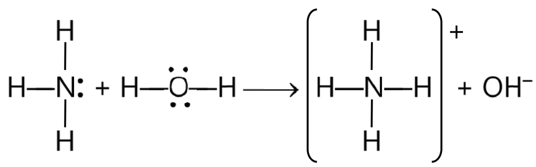
(a) It does not explain the behaviour of protonic acids such as HCl, H_2SO_4, HNO_3, etc., which do not accept electron pair, i. e., do not undergo co-ordination bonding with bases.

(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, NH_3 is Lewis base as well as Bronsted base. However, in the above case, H_2O is a Bronsted acid because it is giving a proton but is not a Lewis acid because it is electronically satisfied. Similarly, HCl, H_2SO_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 (H_2SO_4) is a weaker acid with respect to perchloric acid ($HClO_4$). H_2SO_4 can take up a proton from $HClO_4$ to form $H_3SO_4^+$. Hence, it acts as a base in this reaction.

Q.2 Metal ions like Ag^+, 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	H_2O, liq. NH_3, CH_3OH etc
(ii)	Protogenic	Tendency to give protons	H_2O,CH_3COOH, HCl etc.
(iii)	Amphiprotic	Act as both (i) & (ii)	H_2O, NH_3, CH_3OH 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:

$Na_2O > MgO > Al_2O_3 > SiO_2 > P_2O_5 > SO_2 > Cl_2O_3$

Basic character increases down the group:

(i) $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$

(ii) $OF_2 < Cl_2O < Br_2O < I_2O$

(b) Oxides of metals are normally basic (few exceptions are amphoteric), oxides of non-metals are normally acidic. CO, N_2O and NO are neutral. _

Table 6.2: Classifications of oxides

Basic oxides	Acidic oxides	Amphoteric
K_2O, CaO, MgO CuO, Fe_2O_3, etc. All are metal ox-ides	CO_2 CO(Neutral) $\underbrace{N_2O, NO}_{\text{Neutral}}$, N_2O_3, N_2O_4, N_2O_5, F_2O, SiO_2, P_2O_3, P_2O_5, SO_2, etc. (All are non-metal oxides)	ZnO, Al_2O_3, BeO,SnO_2, (All are metal oxides) As_2O_3 (metalloid oxide)

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

$$CO + NaOH \xrightarrow{P.T} HCOONa$$

(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
Non-metal oxides	HPO_3, H_3PO_4
P_2O_5	HPO_2, H_3PO_3
P_2O_3	H_2SO_3
SO_2	H_2SO_4
SO_3	H_2CO_3
CO_2	HNO_3
N_2O_5	HNO_2
N_2O_3	
Metal Oxides	
CrO_3	H_2CrO_4
Mn_2O_7	$HMnO_4$

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

E.g., $HClO_4 > HClO_3$

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

$H_3PO_2 > H_3PO_3 > H_3PO_4$

K_{a1} 6.3×10^{-2} 1.5×10^{-2} 7.5×10^{-3}

This is due to overall inductive effect of the added O-atom on the central atom which decreases from H_3PO_2 to H_3PO_4 on account of increasing number of unprotonated O-atoms from H_3PO_2 to H_3PO_4.

(iii) On the other hand, basic anhydrides are the oxides of metals which form an alkali in water, e.g., Na_2O is basic anhydride of NaOH.

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

e.g. ZnO, As_2O_3, PbO, Sb_2O_3, Al_2O_3, etc.

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

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

e.g., Mn_2O_7, CrO_3, MoO_3, WO_3, etc.

$Mn_2O_7 + H_2O \xrightarrow{H^+} 2HMnO_4$

$CrO_3 + H_2O \xrightarrow{H^+} H_2CrO_4$

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 HA_1 and HA_2 are taken, then for, $HA_1 \rightleftharpoons H^+ + A_1^-$; $K_{a1} = c_1\alpha_1^2$

For, $HA_2 \rightleftharpoons H^+ + A_2^-$; $K_{a2} = c_2\alpha_2^2$

$$\text{Now, relative strength} = \frac{[H^+] \text{ furnished by acid } HA_1}{[H^+] \text{ furnished by acid } HA_2} = \frac{c_1\alpha_1}{c_2\alpha_2} = \frac{c_1\sqrt{\left(\frac{K_{a1}}{c_1}\right)}}{c_2\sqrt{\left(\frac{K_{a2}}{c_2}\right)}} = \sqrt{\frac{(K_{a1} \cdot c_1)}{(K_{a2} \cdot c_2)}} \quad \left[\because \alpha = \sqrt{\frac{K_a}{c}}\right]$$

If concentrations are same, then

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

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.

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

Some definitions which will be important

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

$pOH = -\log[OH^-]$, $pK_a = -\log K_a$, $pK_b = -k_b$, $pk_w = -\log k_w$ 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.

$$\underset{\text{Simple salts}}{\underline{FeSO_4 + 6KCN}} \rightarrow \underset{\text{Complex salts}}{\underline{K_4[Fe(CN)_6]}} + K_2\,SO_4$$

(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.

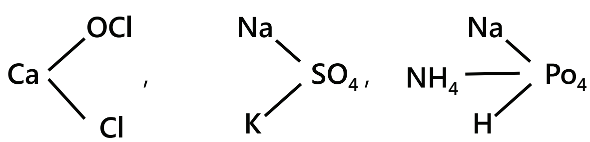


Illustration 16: What type of salts are Na_2HPO_3 and NaHS? **(JEE MAIN)**

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.

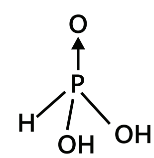


Illustration 17: Arrange the given compounds in the decreasing order of basicity on the basis of the Bronsted-Lowry concept: BaO, CO_2, SO_3, B_2O_3, Cl_2O_7 **(JEE MAIN)**

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

BaO + $H_2O \rightleftharpoons Ba(OH)_2$ (Basic) $CO_2 + H_2O \rightleftharpoons H_2CO_3$ (Weakly acidic)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (Strongly acidic) $B_2O_3 + 3H_2O \rightleftharpoons 2\,H_3BO_3$ (Very weakly acidic)

$Cl_2O_7 + H_2O \rightleftharpoons 2\,HClO_4$ (Very strongly acidic)

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 amphiprotic? **(JEE MAIN)**

Sol: An amphiprotic 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 amphiprotic.

Illustration19: Classify the following as an acid or base according to Bronsted-Lowry theory and name their corresponding conjugate base or acid **(JEE MAIN)**

(i) NH_3 (ii) CH_3COO^- (iii) H_3O^+ (iv) H^+ (v) HOO^- (vi) $S_2O_8^{2-}$.

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) NH_3 is a Bronsted base because it can accept a proton. Its conjugate acid is NH_4^+ .

NH_3 is also a Bronsted acid because it can donate a proton.

Its conjugate base NH_2^-.

(ii) CH_3COO^- is a Bronsted base ($CH_3COO^- + H^+ \rightarrow CH_3COOH$).

Its conjugate acid is CH_3COOH.

(iii) H_3O^+ is a Bronsted acid ($H_3O^+ \rightarrow H_2O + H^+$). Its conjugate base is H_2O.

(iv) H^- is a Bronsted base ($H^- + H^+ \rightarrow H_2$ in the reaction $H^- + H_2O \rightleftharpoons H_2 + OH^-$). Its conjugate acid is H_2.

(v) HOO^- is a Bronsted acid ($HOO^- \rightarrow O_2^{2-} + H^+$ in the reaction $HOO^- + H_2O \rightarrow O_2^{2-} + H_3O^+$).

Its conjugate acid is O_2^{2-} (peroxide ion).

(vi) $S_2O_8^{2-}$ is a Bronsted base ($S_2O_8^{2-} + 2\,H^+ \rightarrow 2\,HSO_4^-$ in the reaction $S_2O_8^{2-} + 2\,H_2O_7\,2HSO_4^- + 2OH^-$).

Its conjugate acid is 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) HCl (aq) (ii) NH_3 (g) (iii) Na_2CO_3 (aq) (iv) CH_3COOH (aq) (v) CO_2 (g) (vi) BF_3 (vii) Ag^+

(viii) CN^- (ix) H_2O (x) H_2SO_4 (xi) HCO_3^- (xii) SiF_4

Sol: (i) HCl (aq) — Acid (Arrhenius concepts and Bronsted - Lowry concept)

(ii) NH_3 (g) — Base (Bronsted concepts and Lewis concept)

(iii) Na_2CO_3 (aq) — Base (Bronsted concept)

(iv) CH_3COOH (aq) — Acid (Arrhenius concepts and Bronsted concept)

(v) CO_2 (g) — Acid (Bronsted concepts and Lewis concept)

(vi) BF_3 — Acid (Lewis concept)

(vii) Ag^+ — Acid (Lewis concept)

(viii) CN^- — Base (Lewis concept)

(ix) H_2O — Both an acid and base, i. e., amphoteric (Bronsted concept)

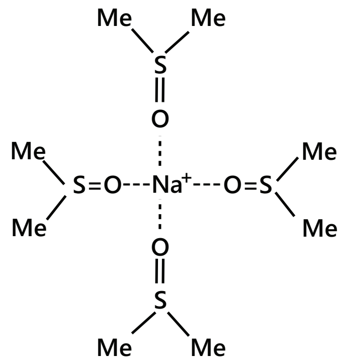
(x) H_2SO_4 — Both an acid and base, i. e., amphoteric (Bronsted concept)

(xi) HCO_3^- — Both an acid and base, Le. t amphoteric (Bronsted concept)

(xii) 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 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.



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

6. pH VALUE

As $[H^+]$ increases, the effective concentration of 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 $pH = -\log a_{H^+}$ where, a_{H^+} is the hydrogen ion activity (or the effective H^+ concentration). The H^+ activity is obtained by multiplying $[H^+]$ 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°C.

$H_2O\ H^+ + OH^-$

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

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

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

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

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

$= 10^{-7}$solution is netural,i. e.,pH = 7

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

The mid-point of the scale at 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

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

For any aqueous solution at 25°C it must be true that

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

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

Also. $\log[H^+] + \log[OH] = -14$

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

Or pH + 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:

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

However, if both acids are too weak (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

$$\left[H^+\right] = \sqrt{K_{a_1} c_1 + K_{a_2} c_2 + K_w}\ .$$

(3) The pH of a dipolar ion molecule say glycine (H_2N — CH_2 — COOH) at isoelectric point can be represented as $\overset{+}{N}H_3$ — CH_2 — $COO^{\ominus}$. The pH at isoelectric point can be calculated or evaluated by the formula: $pH = \dfrac{pK_{a_1} + pK_{a_2}}{2}$

(4) Same is the case with Amphiprotic Salts

A weak acid in water

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

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

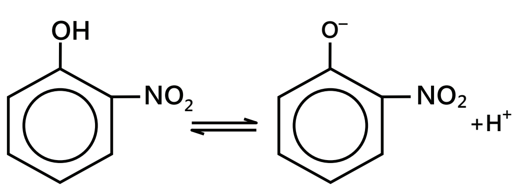
(5) This is sometimes called Ostwald's Dilution Law.

Total concentration of $[H^+]$ or $[H_3O^+]$ in a mixture of weak acid and a strong acid = $\dfrac{C_2 + \sqrt{C_2^2 + 4K_a C_1}}{2}$

Where, C_1 is the concentration of weak acid (in mol $litre^{-1}$) 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? pK_a for o-nitrophenol is 7.23 **(JEE ADVANCED)**

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



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

Or $pH = -\log[H^+] = \dfrac{1}{2} pK_a - \dfrac{1}{2} \log C$

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

C = 0.015 M

∴ Solubility in g/litre = 0.015 × mol. Wt. of compound

= 0.015 × 139 = 2.085 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,

- $CH_3COOH + CH_3COONa$
- Boric acid + Borax
- Phthalic acid + Potassium acid phthalate

(ii) By mixing a weak base with its salt with a strong acid,

- NH_4OH + NH4Cl
- 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.,$Na_2HPO_4 + Na_3PO_4$ or a salt of a weak acid and a weak base, such as CH_3COONH_4.

(c) Basic buffer: Consider the case of the solution containing NH_4OH and its salt NH_4Cl. The solution will have NH_4OH molecule. NH_4^+ ions, Cl^- ions. OH^- ions and H^+ ions.

NH_4OH NH_4^+ + OH^- (Feebly ionised)

NH_4Cl NH_4^+ + Cl^- (Completely ionised)

H_2O H^+ + OH^- (Very feebly ionised)

When a drop of NaOH is added, the added OH^- ions combine with NH_4^+ ions to form feebly ionised NH_4OH whose ionization is further suppressed due to the common ion effect. Thus, pH is not disturbed considerably.

NH_4^+ + $OH^-$$NH_4OH$

↑

(From strong base)

When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.

NH_4OH + H^+ NH_4^+ + H_2O

↑

(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 (CH_3COOH +CH_3COONa)

Basic Buffer (NH_4OH + NH_4 Cl)

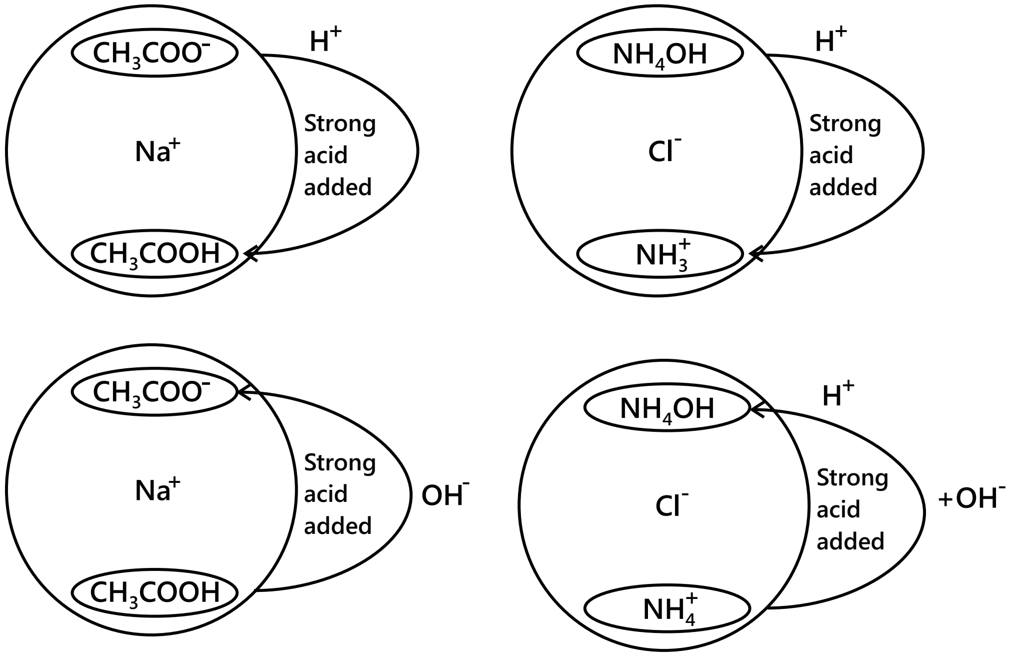


Figure 6.2: Mechanism of buffer solution

7.1 Henderson's Equation

pH of a Buffer-Mixtures

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

HA $H^+ + A^-$ and NaA $\rightarrow Na^+ + A^-$

Applying law of mass action to dissociation equilibrium of HA.

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

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

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

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

$$\text{Or pH} = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} \qquad \text{.... (11)}$$

Where, $[A^-]$ = [conjugate base] or [conjugate base of HA] obtained from concentration of the salt which is 100% ionised. All the $[A^-]$ 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

$$pOH = pK_b + \log \frac{[\text{Conjugate base}]}{[\text{Base}]} \qquad \text{.... (12)}$$

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

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

So, weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid has a pKa 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.

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

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 [Salt] = [Acid], I. e.,pH =pK_a for acid buffer

(ii) When [Salt] = [Base], i. e., pOH =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 $CH_3COOH + CH_3COONa$ buffer.
- **(iii)** For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer, $CH_3COOH + CH_3COONa$, is used.
- **(iv)** For precipitation of hydroxides of the third group of qualitative analysis, a buffer, $NH_4Cl + NH_4OH$, is used.
- **(v)** A buffer solution of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ 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 (H_2CO_3 and $NaHCO_3$)
    - Buffer of phosphoric acid ($H_2PO_4^-$, 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_{HCN} = 4. 1 × $10^{-10?}$ **(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,

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.

	NaCN + HCl → NaCl + HCN			
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

$\because$ pH = – log K_a + log $\frac{0.01-a}{a}$

Or 8. 5 = – log[4. 1 × 10^{-10}] + log $\frac{0.01-a}{a}$

$\therefore$ a = 8. 85 × 10^{-3} moles of HCl

Illustration 24: Calculate [H^+] and [$CHCl_2CO^-$] in a solution that is 0. 01 M HCl and 0. 0. 1 M in $CHCl_2COOH$. K_a for $CHCl_2COOH$ is 5× 10^{-2} **(JEE MAIN)**

Sol: $CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$

c	0	0. 01
c(1– α)	c α	c α + 0. 01

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

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

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

$\therefore$ α = 0. 7416

$\therefore$[$CHCl_2COO^-$] = 0. 01 × 0. 7416 = 7. 416 × 10^{-3}M

[H^+] = 7. 416 × 10^{-3} + 0. 01 = 0. 0174 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 × 10^{-5} **(JEE ADVANCED)**

Sol: Fist 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 mL = $\frac{0.2}{1000}$ × 20 = 0. 004

No. of moles of acetic acid in 50 mL = $\frac{0.2}{1000}$ × 50 = 0. 01

When NaOH is added, CH_3COONa is formed.

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

1 mole 1 mole 1 mole 1 mole

No. of moles of CH_3COONa in 70 mL solution =0. 004

No. of moles of CH_3COOHin 70 mL solution = (0. 01 – 0. 004) = 0. 006

Applying Henderson’s equation,

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

On further addition of NaOH, the pH becomes 4. 74.

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

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

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

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

Let ‘x’ moles of NaOH be Added

[Salt] = (0. 004 + x) mole

[Acid] = (0. 006 – x) mole

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

$x = 0.00097$ 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? pK_a for formic acid is 3. 80. **(JEE ADVANCED)**

Sol: Let x mL of 0. 10 M sodium formate be added.

No. of moles in x mL of 0. 10 M sodium formate = $\frac{0.10}{1000} \times x$

No. of moles in 50 mL of 0. 05 M formic acid = $\frac{0.05}{1000} \times 50$

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

Applying the equation,

$$pH = \log \frac{[Salt]}{[Acid]} + pK_a$$

4. 0= log 0. 04x + 3. 8 $= \log 0.04x = 2.0, 0.04x = \text{Antilog } 2.0$

x = 39. 6 mL

8. SALT HYDROLYSIS

Salt hydrolysis is the phenomenon of interaction of cations and anions of a salt with H_2O in order to produce an acidic nature or an alkaline nature.

Salt + Water $\rightleftharpoons$ Acid + Base

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

1. Such salts include NH_4Cl, NH_4NO_3, $CuSO_4$, $FeCl_3$, etc.

2. 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 NH_4Cl of this category

$NH_4Cl + H_2O \rightleftharpoons \underset{\text{(Weak)}}{NH_4OH} + \underset{\text{(Strong)}}{HCl}$

or $NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$

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

The reaction equilibrium suggests that NH_4Cl on dissolution in water shows the interaction of NH_4 to react with H_2O to produce NH_4OH, a weak base having a low degree of dissociation. Furthermore, the dissociation of NH_4OH is also suppressed due to the unhydrolysed NH_4^+ ions and thus, after interaction the (H^+) in the solution increases and the solution acquires an acidic nature.

3. In this category of salt, it is the cation that undergoes hydrolysis.

4. The pH of category of salt is always lesser than 7.

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

1. This category includes salts such as KCN. CH_3COONa, Na_2S, HCOOK, etc.

2. The solutions of such salts in water show alkaline character on hydrolysis, eg., CH_3COONa.

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

3. In this category of salt, it is the anion that undergoes hydrolysis.

4. The pH of this category of salt is always greater than 7.

Case III: Salts of Weak Acids and Weak Base

1. This category includes salts such as CH_3COONH_4,

$(CH_3COO)_2$ Be, $BeCO_3$, $(NH_4)_3$ PO_4, BeC_2O_4, etc.

2. The solutions of such salts in water shows an almost neutral character on hydrolysis, e.g., CH_3COONH_4.

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

If $K_{CH_3COOH} > K_{NH_4OH}$ solution is acidic,

$K_{CH_3COOH} < K_{NH_4OH}$ solution is alkaline

3. Both the cation and anion of the salt undergo hydrolysis.

4. 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 KNO_3, NaCl, K_2SO_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 to7.

The Hydrolysis Constant and Degree of Hydrolysis

Consider a salt say NH_4 Cl (Case I) in water. Let c mol/litre is concentration of salt and h is its degree of hydrolysis then,

	NH_4^+ + $H_2O \rightleftharpoons$	NH_4OH +	H^+
Before hydrolysis	1	0	0
After hydrolysis	(1 – h)	h	h

$\therefore$ At equilibrium $[NH_4^+] = (1 - h)c$, $[NH_4OH] = c \cdot h$, $[H^+] = c \cdot h$

[H+]=c. h

Therefore, according to law of mass action

$$K = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]} \text{ or } K \times [H_2O] = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$\text{Or } K_H = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad \text{.........(16)}$$

Where K_H is hydrolysis constant of salt NH_4Cl or NH_4^+ ion. Also we have for weak base NH_4OH

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{. . .... . (17)}$$

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

$K_H \times K_b = [H^+][OH^-] = k_w$

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

Also, by Eq. (16)

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

Since h is small and thus. 1 – h = 1

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

Similar equations can be obtained for other case

Now, if we discuss all the cases again;

Case I: Strong acid vs weak base

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

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

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

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

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

Case II: Weak acid Vs West Base

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

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

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

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

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

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

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

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

Case III: Weak acid Vs weak Base

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

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

HA H^+ + A^-

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

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

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

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

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

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:

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-;\ K_{a_1} = 7.11\times10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-};K_{a_2} = 6.32\times10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-};K_{a_3} = 4.5\times10^{-13}$$

$$H_3PO_4 + 3H_2O \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

$Ka_1\ Ka_2\ Ka_3$

$$K_{a_1} = \frac{[H_3O^+]\left[H_2PO_4^-\right]}{[H_3PO_4]} = 7.11\times10^{-3}$$

$$K_{a_2} = \frac{[H_3O^+]\left[HPO_4^{2-}\right]}{[H_2PO_4^-]} = 6.32\times10^{-8}$$

$$K_{a_2} = \frac{[H_3O^+]\left[PO_4^{3-}\right]}{[HPO_4^{2-}]} = 4.5\times10^{-13}$$

pH of $H_2PO^{2-}{}_4$ in aq. medium$=\dfrac{pka_1 + pka_2}{2}$

pH of $HPO^{2-}{}_4$ in aq medium$=\dfrac{pka_2 + pka_3}{2}$

Table 6.4: Hydrolysis at a Glance

Salt	Nature	Degree	Hydrolysis Constant	pH
1. NaCl (Strong acid + Strong base	Neutral	No hydrolysis		
2. CH_3COONa (Weak acid + Strong base)	Basic	$h = \sqrt{\dfrac{K_w}{CK_a}}$	$K_h = \dfrac{K_w}{K_a}$	$pH = \dfrac{1}{2}[pK_w + pK_a + \log C]$
3. NH_4Cl (Strong acid + Weak base)	Acidic	$h = \sqrt{\dfrac{K_w}{CK_b}}$	$K_h = \dfrac{K_w}{K_b}$	$pH = \dfrac{1}{2}[pK_w - pK_b - \log C]$
4. CH_3COONH_4 (Weak acid + Weak base)		$h = \sqrt{\dfrac{K_w}{K_a \times K_b}}$	$K_h = \dfrac{K_w}{K_a \times K_b}$	$pH = \dfrac{1}{2}[pK_w + pK_a - pK_b]$

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, Na_2CO_3 and NH_4Cl. 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. NH_4Cl solution is acidic. It will turn blue litmus red but will have no effect on red litmus. Na_2CO_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 $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ 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: $[Ca\ (LaC)_2] = \dfrac{0.13}{0.5} = 0.\ 26\ M$

$\because$ 1 Mole Ca $(LaC)_2$ gives 2 mole (LaC)

$\therefore$ [LaC] = 0. 26 × 2 = 0. 52 M

$LaC^- + H_2O \rightleftharpoons HLaC + OH^-$

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

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

$$\text{or } 10^{-5.\,60} = \sqrt{\frac{10^{-14}\times 0.52}{K_a}} \quad \therefore K_a = 8.\ 25 \times 10^{-4}$$

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 = 1.9×10^{-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 $[OH^-] = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \times c}{K_a}}$

Now from $[OH^-]$ we can determine pOH as,

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

pH can be calculated by using following expression,

$pH = 14 - pOH$

Suppose V mL of 0. 1 N acid and 0. 1 N NaOH are used at equivalence point

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

mm before reaction 0. 1 × V 0. 1 × V 0 0

$\therefore [CH_3COONa] = \frac{0.1 \times V}{2V} = \frac{0.1}{2} = 0.05$ M

For hydrolysis of CH_3COO^-

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

1 0 0

(1 – h) h h

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

$\therefore$ pOH = 5. 29 $\therefore$ 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 MNH_4Cl

K_a CH_3COOH = 1. 8 × 10^{-5}, K_b NH_3 = 1. 8 × 10^{-5} **(JEE ADVANCED)**

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

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

$[H^+]$ = 0. 1 = 10^{-1}

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

After dilution, $[H^+]$ = 0. 01 = 10^{-2} M

pH = – log$[H^+]$ = – log 10^{-2} = 2

pH change from 1 to 2.

(b) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

(0. 1 – x) x x

(CH_3COOH is a weak acid)

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

pH = – log x = – log (1. 34 × 10^{-3}) = 2. 87

After dilution,

$\frac{x_1^2}{0.01} = 1.8 \times 10^{-5}$ or $x_1^2 = 18 \times 10^{-8}$ or $x_1 = 4.24 \times 10^{-4}$ M

pH = – logx = – log 4. 24 × 10^{-4} = 3. 37

pH change from 2. 87 to 3. 37.

(c) NH_4Cl is a salt of weak base and strong acid

$$\underset{(0.1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$$

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

$$\left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.55\times10^{-10}\right] = 0.1 \times 5.55 \times 10^{-10}$$

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

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

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

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

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

$K_h = C_1(2h)^2$ .... (ii)

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

$C_1 = \dfrac{0.2}{4} = 0.05$ M

Applying, $M_1V_1 = M_2V_2$

$0.2V_1 = 0.05\times V_2$

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

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:

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons H^+ + \underset{\text{Pink}}{ph^-}$$

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

The undissociated molecules of phenolphthalein are colourless while 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 H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to the right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart a pink colour to the solution.

Let as derive Henderson's equation for an indicator

$$HIn \quad + \quad H_2O \qquad H_3^+O \quad + \quad In^-$$

'Acid form' **Base form'**

Conjugate acid-base pair

$K_{In} = \dfrac{[In^-][H_3^+O]}{[HIn]}$; (K_{In} = 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 Me^+ and OH^- ions.

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

Applying law of mass action,

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

In the presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to the right hand side. Thus, sufficient Me^+ ions are produced which imparts red colour to the solution. On the addition of alkali, the concentration of 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.

CONCEPTS

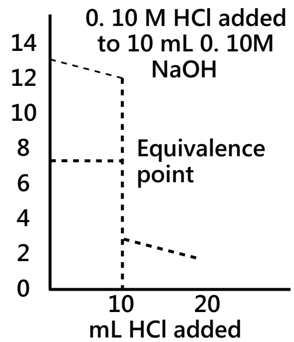
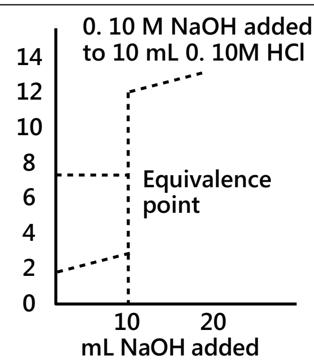
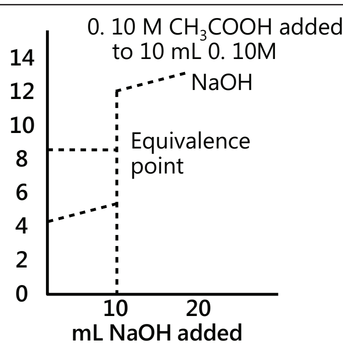
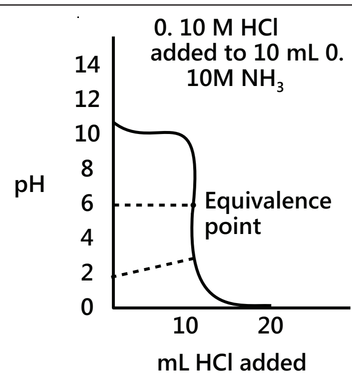
This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i. e., pH is not reached to 8. 3. Thus, the solution 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.

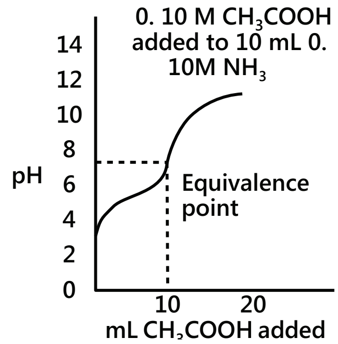
- Phenolphthalein and thymophthalein are suitable indicators for weak acids and strong base titrations.
- Methyl orange, bromocresol green and methyl red are suitable indicators for strong acid and weak base titrations.
- Bromothymol blue, phenolphthalein and methyl orange are suitable indicators for 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 $NaOH + HCl \rightarrow NaCl + H_2O$		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 (pH = 7)
Strong Base and Strong acid $NaOH + HCl \rightarrow NaCl + H_2O$		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 (pH = 7)
Weak Acid and Strong Base $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$		Curve begins at a higher acidic pH and ends at high basic pH. The pH change at the equivalence point (pH > 7) is not so great.
Weak Base and Strong Acid $NH_3 + HCl \rightarrow NH_4Cl$		Curve begins at low pH and ends at a less high basic pH. The pH change at the equivalence point (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 $CH_3COOH + HN_3 \rightarrow CH_3COONH_4$		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 is a very difficult titration to perform.

Tirations of a weak polyprotic acid

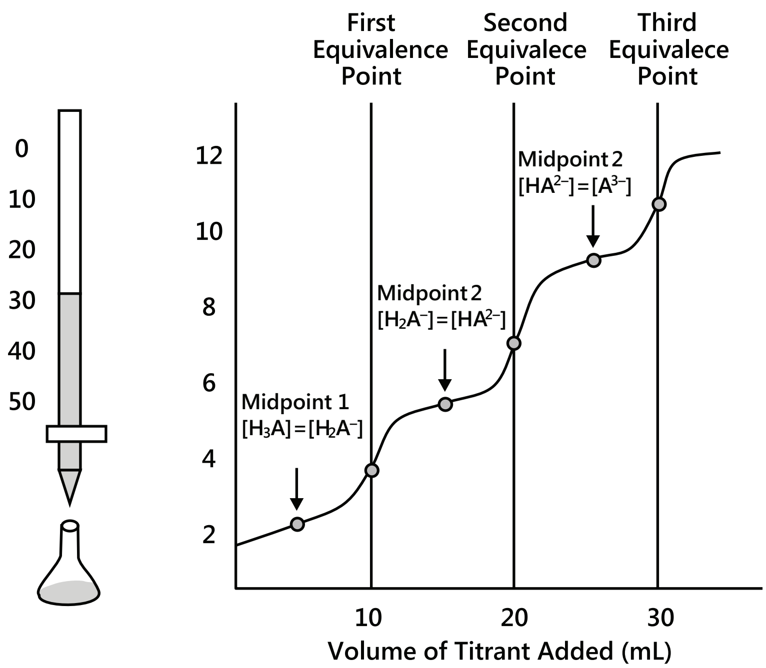


Figure 6.3 Titration of a Weak Polyprotic Acid.

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 α 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 α (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 α is very small, we can calculate α 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) $[A^+]_{left} = \dfrac{K_{sp}[AB]}{[B^-]}$

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

(iii) $[A^{n+}]^m_{left} = \dfrac{K_{sp}[A_mB_n]}{[B^{m-}]^n}$

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

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 Bronsted Lowry theory Lewis concept	(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 (i) A Bronsted acid is proton donor (ii) Bronsted base is proton acceptor. (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 $[H^+]$ Autoinization 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 = 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. $H^+ = \sqrt{K_1c_1 + K_2c_2}$ (f) Buffer solutions: $pH = pK_a + \log\left(\frac{salt}{acid}\right)$ $pOH = pK_b + \log\left(\frac{salt}{base}\right)$ (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 $\{M^{n+}\ mLig \leftrightharpoons [M(Lig)m]^{n+1}\}$ $\left\{K_{sb} = \frac{[M(Lig)m]^{n+1}}{[M^n(Lig)m]}\right\}$
Heterogeneous equilibrium	Solubility of sparingly soluble salt' $(AB, AB_2, A_xB_y) K_{sp} = (S^{x+y})X^xY^y$

Solubility Product	$K_{sp} = [xS]^x [yS]^y = x^x . y^y (S)^{x+y}$ **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: AlI_3, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$,etc. $S = \sqrt[4]{K_{sp}/27}$ In presence of common ion effect – $K_{sp} = S'(S' + c)$ (i) $[A^+]_{left} = \frac{K_{sp}[AB]}{[B^-]}$ (ii) $[Ca^{2+}]_{left} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}$ (iii) $[A^{n+}]^m_{left} = \frac{K_{sp}[A_mB_n]}{[B^{m-}]^n}$ Percentage precipitation of an ion = $\left[\frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}}\right] \times 100$

Solved Examples

JEE Main/Boards

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

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

Ksp =S (S+c)

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

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

$$AgCNS \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{CNS}$$

$$AgBr \rightleftharpoons \underset{b}{Ag^+} + \underset{b}{Br^-}$$

$[Ag^+] = a + b$, $[CNS^-] = a$ and

$[Br^-] = b$

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

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

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

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

Dividing eq. (i) by (ii),

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

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

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

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

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

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

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

Example 2: $MgSO_4$ gives a precipitate with NH_4OH but not with NH_4Cl and NH_4OH. Why?

Sol: No doubt NH_4OH is weak base but it provides appreciable OH^- ion to exceed the product of ionic concentration of Mg^{2+} and OH^- than their K_{sp} and thus $MgSO_4$ is precipitated out as $Mg(OH)_2$. On the other hand the dissociation of NH_4OH is suppressed in presence of NH_4Cl and thus $[OH^-]$ diminishes to the extent that $[Mg^{2+}][OH^-]^2 < K_{sp}$. Thus, $MgSO_4$ is not precipitated.

Example 3: An aqueous solution contains 0. 1 M of Ba^{2+} and 0. 1 M Ca^{2+}. Calculate the maximum concentration of Na_2SO_4 at which one of them is completely precipitated almost completely. What % of that ion is precipitated?

K_{sp} of $BaSO_4 = 1.5 \times 10^{-9}$;

K_{sp} of $CaSO_4 = 2 \times 10^{-4}$.

Sol: $[SO_4^-]$needed for precipitation of $[Ba^{2+}]$as $BaSO_4$

$$= \frac{K_{sp}}{Bs^{2+}} = \frac{1.5\times10^{-9}}{0.1} = 1.5 \times 10^{-8}$$

$[SO_4^{2-}]$ needed for precipitation of $[Ca^{2+}]$ as $CaSO_4$

$$= \frac{2\times10^{-4}}{0.1} = 2\times 10^{-3}.$$

Thus, $[SO_4^{2-}]$ required for precipitation of $BaSO_4$ is less and thus $BaSO_4$ will precipitate first. The precipitation of $BaSO_4$ will start when $[Na_2SO_4]$ is 1.5×10^{-8} and will be maximum when $[Na_2SO_4]$ is 2×10^{-3} .

Thus, maximum $[Na_2SO_4]$ required for precipitation of $Ba^{2+} = 2 \times 10^{-3}$ M. At this conc, of SO_4^{2-}, $[Ba^{2+}]$ left in solution is

$$[Ba^{2+}]_{left} = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{1.5\times10^{-9}}{2\times10^{-3}} = 7.5 \times 10^{-7}$$

$$\therefore \% \text{ of } Ba^{2+} \text{ left} = \frac{7.5\times10^{-7}\times100}{0.1} = 7.5\times10^{-4}\%$$

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

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

Example 4: Will a precipitate of $Mg(OH)_2$ be formed in a 0. 001 M solution of $Mg(NO_3)_2$, if the pH of solution is adjusted to 9?

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

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

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

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

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

0. 001 $MMg(NO_3)_2$ is present in a solution of $[OH^-]= 10^{-5}$

Then product of ionic concentration for $Mg(OH)_2$

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

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

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

Therefore, $Mg(OH)_2$ will not precipitate out.

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

Sol: Solution Let solubility of AgCN be a mol litre^{-1}

$AgCN \rightleftharpoons Ag^+ + CN^-$

a a (After reaction)

However, the CN^- formed will react with H* to form HCN

$CN^- + H^+ \rightarrow HCN$

a 10^{-3} (Before reaction)

0 10^{-3} a (After reaction)

(buffer)

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

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

Now HCN $H^+ + CN^-$

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

$$\text{or } [CN^-] = \frac{K_a[HCN]}{[H^+]} = \frac{a\times(4.8\times10^{-10})}{10^{-3}}$$

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

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

$$1.2 \times 10^{-16} = \frac{a\times a\times 4.8\times10^{-10}}{10^{-3}}$$

$$\because a^2 = \frac{1.2\times10^{-16}\times10^{-3}}{4.8\times10^{-10}}$$

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

Example 6: The dissociation constant for aniline, acetic acid and water at 25 C are 3. 83×10^{-10}, 1.75×10^{-5} and 1. 008×10^{-14} respectively. calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report its Ph.

Sol:

	$Aniline^+$	$+ Acetate^-$	$+H_2O \rightleftharpoons$ Aniline	+ Acetic Acid
Before hydrolysis	1	1	0	0
After hydrolysis	$(1 - h)$	$(1 - h)$	h	h

Let concentration of salt be c mol $litre^{-1}$

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

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

$$= \sqrt{\frac{1.008\times10^{-14}}{1.75\times10^{-5}\times3.83\times10^{-10}}}$$

$\therefore h$ = 54. 95%

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

$$= \frac{1}{2}\log\left[3.83\times10^{-10}\right] - \log\left[1.008\times10^{-14}\right]$$

$$-\log\left[1.\ 75\times10^{-5}\right] = 4.\ 6683$$

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^{2+} and 0. 05M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution.

K_{sp} of $Mg(OH)_2$ =9. 0×10^{-12} and

K_b of NH_3 =1. 8×10^{-5}

Sol: Suppose V mL of solution containing 0. 1 M Mg^{2+} and 0. 8 M NH_4Cl. Now V mL of NH_3 of a M is added to it in order to have just precipitation of $Mg(OH)_2$, then

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

$$\text{or}\left[\frac{0.1\times V}{2V}\right][OH^-]^2 = 1.\ 4\times10^{-5}$$

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

$\therefore [OH^-]$ = 1. 67 × 10^{-5}M

The solution must therefore, contain $[OH^-]$ equal to = 1. 67×10^{-5}M. Which are obtained by buffer solution of NH_3 and NH_4Cl

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

or – log[1. 67 × 1 0^{-5}]

$$= -\log[1.\ 8\times10^{-5}] + \log\frac{(0.8\times V)/2V}{(a\times V)/2V}$$

$\therefore a$ = 0. 7421 M

$$\therefore [NH_3] \text{ in solution } = \frac{0.7421\times V}{2V} = 0.\ 3710\ M.$$

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

CH_3COOH (aq) + NaOH (aq) $\rightarrow$ Na^+(aq) + CH_3COOHa (aq) + H_2O (l)

Sol: Strategy:

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

$$25.\ 19\ mL \times \frac{1L}{1000mL} = 0.\ 02519\ L$$

$$0.\ 02519\ L \times \frac{0.1025 mol}{1L} = 0.\ 002582 \text{ mol NaOH}$$

2. Use the balanced chemical equation to calculate the moles of analyte (in this case, the acid) present. 0. 002582 mol

$$NaOH \times \frac{1mol\ CH_3COOH}{1mol\ NaOH} = 0.\ 002582 \text{ mol } CH_3COOH$$

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

$$34.\ 57\ ml \times \frac{1L}{1000mL} = 0.\ 03457\ L$$

$$\frac{0.002582\ mol\ CH_3COOH}{0.03457L} = 0.\ 07469\ M\ CH_3COOH$$

Example 9: Calculate the dissociation constant of NH_4OH at 25°C, if $\Delta H°$ and $\Delta S°$ for the given changes are as follows:

$NH_3 + H^+ \rightleftharpoons NH_4^+$; $\Delta H° = -52.2$ kJ mol^{-1}; $\Delta S° = +1.67$ JK^{-1} mol^{-1}

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H° = 56.6$ kJ mol^{-1}; $\Delta S° = -78.2$ JK^{-1} mol^{-1};

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

$\Delta G° = \Delta H° - TDS°$

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

$NH_3 + H^+ \rightleftharpoons NH_4^+$; $\Delta H° = -52.2kJ$

Adding,

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H° = +56.6$ kJ

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$;

$\Delta H° = +4.4$ kJ mol^{-1}

Similarly, $\Delta S°$ for the change = –76. 53 Jk^{-1} mol^{-1} or for the change

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$;

$\Delta H° = 4.4$ kJ mol^{-1} and $\Delta S° = -76.53$ jk^{-1} mol^{-1}

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

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

Also, $\Delta G° = -2.303\ RT \log K_b$

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

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

JEE Advanced/Boards

Example 1: Prove that the degree of dissociation of a weak monoprotic acid is given by $\alpha = \dfrac{1}{1+10^{(pK_a - pH)}}$ where K_a is the dissociation constant of the acid.

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

$$HA \rightleftharpoons H^+ + A^-$$

Initial molar conc. C

Molar conc. C –Cα Cα Ca

After dissociation = C (1 – α)

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

Or $C = \dfrac{K_a(1-\alpha)}{\alpha^2}$ .... (i)

Also, $[H^+] = C\alpha$ .... (ii)

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

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

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

Or $pH = pK_a - \log(1-\alpha) - \log a$

Or $\log \dfrac{1-\alpha}{\alpha} = pK_a - pH$

Or $\dfrac{1-\alpha}{\alpha} = 10^{pk_a - pH}$

Or $\dfrac{1}{\alpha} - 1 = 10^{pk_a - pH}$

Or $\dfrac{1}{\alpha} = 1 + 10^{pk_a - pH}$

Or $\alpha = \dfrac{1}{1+10^{pK_a - pH}}$

Example 2: The solubility of $Mg(OH)_2$ is increases by the addition of NH_4^+ ion. Calculate K_c for,

$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$

$K_{spMg(OH)_2} = 6 \times 10^{-12}$, $K_{bNH_3} = 1.8 \times 10^{-5}$.

Sol: The given reaction is:

$Mg(OH)_2 + 2NH_4^+\ 2NH_3 + 2H_2O + Mg^{2+}$

$\therefore K_c = \dfrac{[NH_3]^2[Mg^{2+}]}{[NH_4^+]^2}$

$= \dfrac{[NH_4OH]^2[Mg^{2+}]}{[NH_4^+]^2}$ .... (i)

For NH_4OH, a weak base

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$ .... (ii)

By Eqs. (i) and (ii)

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

$= K_{spMg(OH)_2}$

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

Example 3: 0.1 M CH_3COOH solution is titrated against 0.05 M NaOH solution. Calculate pH at ¼ th and th stages of neutralization of acid. The pH for 0.1 M CH_3COOH is 3.

Sol: Given pH for 0. 1 M $CH_3COOH = 3$

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

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

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

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

Case I: At 1/4th neutralization of acid

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

	CH_3COOH	CH_3COONa
Before addition of NaOH	0. 1	
After addition of NaOH	$0.1\times(3/4)$	$0.1\times(1/4)$

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

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

Case II:

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

	CH_3COOH	CH_3COONa
After 3/4 neutralization	$0.1\times(1/4)$	$0.1\times(3/4)$

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

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 1.75×10^{-5} mol L^{-1}]

Sol: (i) Meq. of $CH_3COOH = 500 \times 0.2 = 100$

Meq. of HCl = 500 × 0. 2 = 100

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

$[CH_3COOH] = \dfrac{100}{1000} = 0.1$

For CH_3COOH:

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

	CH_3COOH	CH_3COO^-	H^+
Before dissociation (from HCl)	0. 1	0	0. 1
After dissociation	(0. 1 – X)	X	(0. 1 + X)

$\therefore K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \dfrac{X(0.1+X)}{(0.1-X)}$

Due to common ion effect dissociation of CH_3COOH is very small in presence of HCl.

Therefore, (0. 1 +X) = 0. 1 and (0. 1 – X) = 0. 1

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

$\therefore X = K_a = 1.75\times10^{-5}$

Thus, degree of dissociation

$\alpha = \dfrac{X}{0.1} = \dfrac{1.75\times10^{-5}}{0.1} = 1.75\times10^{-4}$

= 0. 000175 = 0. 0175%

Also, $[H^+] = 0.1 + X = 0.1 (X << 0.1)$

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

(ii) Eq. of NaOH or mole of NaOH added = 6/40 = 0. 15

Therefor, new equilibrium will have,

$$CH_3COOH + HCl + NaOH \rightarrow CH_3COONa + NaCl + H_2O$$

CH_3COOH	HCl	NaOH	CH_3COONa	NaCl	H_2O
0. 1	0. 1	0. 15	0	0	0
0. 05	0	0	0. 05	0	0

Thus, the solution will act as acidic buffer having

$[CH_3COOH] = \dfrac{0.05}{1000}$

and $[CH_3COONa] = \dfrac{0.05}{1000}$

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

$= -\log[1.75\times10^{-5}] + \log\dfrac{[0.05/1000]}{[0.05/1000]} = 4.757$

Example 5: The average concentration of 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 SO_2 in water at 298 K is 1.3653 mol $litre^{-1}$ and the pK_a of H_2SO_4 is 1.92. Estimate the pH of rain on that day.

Sol: Use henry's law to find out $[SO_2]$ dissolved in water. Concentration of SO_2 in air is 10 ppm or 10 mole in 10^6 mole air or 10^{-5} mole SO_2 per mol of air. The concentration of 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 SO_2 before it reaches earth.

Now the given concentration or solubility of SO_2 at 298 K is 1. 3653 M.

This value of solubility corresponds when P_{SO_2} = 1 atm

Thus, according to Henry's law

$[SO_2]$ dissolved in water $\propto P_{SO_2}$ in gas phase

$[SO_2]$ dissolved in water $\propto P_{SO_2}$ in air

$\therefore [SO_2]$ dissolved in water = 1. 3653 × 10^{-5}M

$SO_2 + H_2O \rightleftharpoons H + HSO_3^-$

1 0 0

$(1 - \alpha)$ a a

$\therefore K_a = 10^{-1.92} = \dfrac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \dfrac{c\alpha^2}{1-\alpha}$ (α is small)

or 0. 012 = $\dfrac{1.3653 \times 10^{-5} \times \alpha^2}{1-\alpha}$

($\because pK_b$ = 1. 92, $\therefore K_b$ = 0. 012)

$\therefore$ 1. 3653 × $10^{-5}\alpha^2$ + 0. 012 α – 0. 012 = 0

$\therefore \alpha = 1$

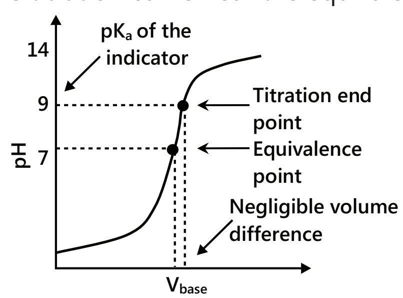
(Solving quadratic equation)

$\therefore [H^+] = c\,\alpha$ = 1. 3653 × 1 = 1. 3653

$\therefore$ 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} M HCl (b) 0. 0001 M NaOH

(c) 0. 0001 M H_2SO_4

Sol: (a) HCl is a strong electrolyte and is completely ionised.

HCl $H^+ + Cl^-$

So, $[H^+] = 10^{-3}$ M

pH = – log$[H^+]$ = – log(10^{-3}) = 3

(b) NaOH is a strong electrolyte and is completely ionized.

NaOH $Na^+ + OH^-$

So, $[H^+]$ = 0. 0001 M = 10^{-4} M

pOH = – log(10^{-4}) = 4

As pH + pOH = 14

So, pH + 4 = 14 s

or pH = 10

Alternative method:

$[OH^-] = 10^{-4}$ M

We know that, $[H^+][OH^-]$ = 1. 0 × 10^{-14}

So, $[H^+] = \dfrac{1.0 \times 10^{-14}}{10^{-4}} = 10^{-10}$ M

pH = –log$[H^+]$ = –log(10^{-10})= 10

(c) H_2SO_4 is a strong electrolyte and is ionized completely.

H_2SO_4 $2H^+ + SO_4^{2-}$

One molecule of H_2SO_4 furnishes $2H^+$ ions.

So, $[H^+]$ = 2 × 10^{-4} M

pH = – log$[H^+]$ = – log(2 × 10^{-4}) = 3. 70

Example 8: If very small amount of phenolphthalein is added to 0. 15 mol litre^{-1} solution of sodium benzoate what fraction of the indicator will exist in the coloured from? State any assumption that you make.

K_a (Benzoic acid) = 6. 2 × 10^{-5},

K_w (H_2O) = 1 × 10^{-14},

K_{In} (Phenolphthalein) = 3. 16 × 10^{-10}

Sol: Use the following expression to find out pH of salt hydrolysis and pH of indicator.

Formula for pH of salt hydrolysis:

pH = $\dfrac{1}{2}[pK_w + pK_a + \log C]$

Formula for pH of indicator:

pH = $pK_{In} + \log_{10}\dfrac{[In^-]}{[HIn]}$

Substitute the values in the above equation,

For pH of salt hydrolysis:

$= \dfrac{1}{2}[14 - \log_{10} 6.2 \times 10^{-5} + \log 0.15]$ = 8. 6918

For pH of indicator:

8. 6918 = – $\log_{10}$ (3. 16 × 10^{-10}) + $\log_{10}\dfrac{[In^-]}{[HIn]}$

0. 16 = $[In^-]/[HIn]$ = 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 1.32×10^{-2}. At what concentration of nitrous acid, its degree of dissociation will be same as that of acetic acid?

$K_a(HNO_2) = 4 \times 10^{-4}$

Q.2 How many times is the H^+ concentration in the blood (pH = 7. 36) greater than in the spinal fluid (pH = 7. 53)?

Q.3 A 0. 400 M formic acid solution freezes at – 0. 758°C. Calculate the K_a of the acid at that temperature. (Assume molarity equal to molality). K_f (H_2O) is 1.86°mol^{-1} kg.

Q.4 A sample of AgCl was treated with 5 mL of 1. 5 M Na_2CO_3 solution to give Ag_2CO_3 the remaining solution contained 0.0026 g/litre Cl^- ion. Calculate the solubility of AgCl.

Q.5 100 mL of solution S_1 contains 0. 17 mg of $AgNO_3$. 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} AgCl = 10^{-10} 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 NH_4Cl; determine the degree of hydrolysis of this salt in 0. 01 M solution and the pH of the solution. $K_b(NH_4OH) = 1.8 \times 10^{-5}$

Q.8 Calculate the pH of 0. 1 M acetic acid solution if its dissociation constant is 1.8×10^{-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 CH_3COOH. To what volume at 25°C must one dm^3 of this solution be diluted in order to (a) double the pH; (b) double the hydroxide-ion concentration. Given that $K_a = 1.8 \times 10^{-5}$M.

Q.11 The solubility of $Mg(OH)_2$ is increased by addition of NH_4^+ ion.

$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$

If K_{sp} of $Mg(OH)_2 = 1 \times 10^{-11}$, K_b for $NH_4OH = 1.8 \times 10^{-5}$ 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 cm^3 of NaOH solution, pH of solution is 5. 8 and after the addition of 20. 0 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 mol dm^3 is saturated with H_2S. Calculate

(i) pH at which the MnS will form a precipitate

(ii) Conc, of Zn^{+2} ions remaining.

Given: $[H_2S]$ = 0. 1 mol/lit,

$K_{sp}(ZnS) = 1 \times 10^{-22} mol^2\,lit^{-2}$,

$K_{sp}(MnS) = 5.6 \times 10^{-16} mol^2\,lit^{-2}$.

K_1 and K_2 for H_2S are 1×10^{-7} and 1.1×10^{-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 4.0×10^{-3} mol/dm^3 hydrogen ion concentration.

Q.15 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of 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 H_2S is 1.2×10^{-13}. Calculate the concentration of S^{2-} under both conditions.

Q.16 The ionization constant of acetic acid is 1.74×10^{-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 TlOH dissolved in water to give 500 ml of solution.

(ii) 0. 3 g of Ca $(OH)_2$ 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 1×10^{-11}, what will be the weight of $Ag_2C_2O_4$ 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. $K_a(HCN) = 7.2 \times 10^{-10}$. $K_b(NH_3)=1.8\times10^{-5}$

Q.22 Assuming that the buffer in blood is $CO_3^- - HCO_3^-$, calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH, 7. 4 K_1 (H_2CO_3)= 4. 5×10^{-7}.

Q.23 How many moles of sodium hydroxide can be added to 1. 0 L of a solution 0. 10 M in NH_3 and 0. 10 M in NH_4Cl without changing the pOH by more than 1 unit. Assume no change in volume. K_b= 1.8×10^{-5}

Exercise 2

Single Correct Choice Type

Q.1 The conjugate acid of NH_2^- is

(A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4

Q.2 Out of the following, amphiprotic species are

I. HPO_3^{2-} II. OH^- III. $H_2PO_4^-$ IV. 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°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 $\frac{M}{200}$ H_2SO_4 is mixed with 40 ml of $\frac{M}{200}$ H_2SO_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° C is 10. 83, the ionisation constant of hydrofluoric acid in water at this temperature is:

(A) 1.74×10^{-5} (B) 3.52×10^{-3}

(C) 6.75×10^{-4} (D) 5.38×10^{-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 H_3PO_4 and $K_1 >> K_2$ which is incorrect.

(A) $[H^+] = [H_2PO_4^-]$ (B) $[H^+] = K_1[H_3PO_4]$

(C) $K_2 = [HPO_4^-]$ (D) $[H^+] = 3[PO_4^{3-}]$

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 1.3×10^{-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 ≈ 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

$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$

Is 1. 8 × 10^{-5}, equilibrium constant for

$CH_3COOH + OH^-$ $CH_3COO^- + H_2O$ is

(A) 1.8 × 10^{-9} (B) 1.8 × 10^{-9}

(C) 5.55× − 10^{-9} (D) 5.55 × 10^{10}

Q.14 The pK_a of a weak acid, HA, is 4. 80. The 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 X^- Na^+ (0. 1 M, 10 ml) with 0. 1 M HCl should be (Given: $K_{b(X^-)} = 10^{-6}$)

(A) 2-3 (B) 3-5 (C) 6-8 (D) 8-10

Q.16 The solubility of A_2X_3 is y 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 $HgSO_4$ is 6. 4 × 10^{-5}, then solubility of this substance in mole per m^3 is

(A) 8 × 10^{-3} (B) 6. 4 × 10^{-5}

(C) 8 × 10^{-6} (D) None of these

Q.18 The solubility of a sparingly soluble salt AB_2 in water is 1. 0 × 10^{-5} mol L^{-1}. Its solubility product is:

(A) 10^{-15} (B) 10^{-10} (C) 4 × 10^{-15} (D) 4 × 10^{-10}

Q.19 Which of the following is most soluble in water?

(A) MnS (K_{sp} = 8 × 10^{-37}) (B) ZnS(K_{sp} =7 × 10^{-16})

(C) Bi_2S_3 (K_{sp} =1 × 10^{-72}) (D) $Ag_3(PO_4)$ (K_{sp} =1. 8 × 10^{-18})

Q.20 When equal volumes of the following solutions are mixed, precipitation of AgCl (K_{sp} =1. 8 × 10^{-10}) will occur only with:

(A) 10^{-4}M (Ag^+) and 10^{-4} M (Cl^-)

(B) 10^{-5}M (Ag^+) and 10^{-5} M (Cl^-)

(C) 10^{-6}M (Ag^+) and 10^{-6} M (Cl^-)

(D) 10^{-10}M (Ag^+) and 10^{-10} M (Cl^-)

Q.21 The precipitate of CaF_2 (K_{sp} = 1. 7 × 10^{-10}) is obtained when equal volumes of the following are mixed

(A) 10^{-4} M Ca^{3+}+ 10^{-4} M F^-

(B) 10^{-2} M Ca^{2+}+ 10^{-3} M F^-

(C) 10^{-5} M Ca^{2+}+ 10^{-3} M F^-

(D) 10^{-3} M Ca^{2+}+ 10^{-5} M F^-

Q.22 50 litre of a solution containing 10^{-5} mole of Ag^+ is mixed with 50 litre of a 2 × 10^{-7} M HBr solution. [Ag^+] in resultant solution is: [Given: K_{sp}(AgBr) = 5 × 10^{-13}]

(A) 10^{-5} M (B) 10^{-6} M

(C) 10^{-7} 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 AgA(s). Given: $K_a(HA) = 10^{-10}$

(A) 1.1 × 10^{-11} (B) 1.1 × 10^{-10}

(C) 10^{-12} (D) None of these

Q.24 The solubility of metal sulphides in saturated solution of H_2S {[H_2S]= 0. 1 M} can be represented by

$MS + 2H^+ \rightarrow M^{2+} + H_2S$;

$$K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$$

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 [H^+]= 1M in saturated H_2S solution.

$$K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$$

Mns	ZnS	CoS	PbS
3×10^{10}	3×10^{-2}	3	3×10^{-7}

(A) MnS, ZnS, CoS (B) PbS, ZnS, CoS

(C) PbS, ZnS (D) PbS

Q.25 Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4}M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $BaCO_3$, = 5. 1 × 10^{-9})

(A) 4. 1 × 10^{-5}M (B) 5. 1 × 10^{-5}M

(C) 8. 1 × 10^{-8}M (D) 8. 1 × 10^{-7}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 2.7×10^{-31}. What is its solubility in moles/litre. ***(2004)***

(A) 1×10^{-8} (B) 8×10^{-8}

(C) 1.1×10^{-8} (D) 0.18×10^{-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 1×10^{-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

$$\begin{bmatrix} 4Na + O_2 \rightarrow 2Na_2O \\ Na_2O + H_2O \rightarrow 2NaOH \end{bmatrix}$$ ***(2002)***

(A) Acidic (B) Basic (C) Amphoteric (D) Neutral

Q.6 The dissociation of water at 25°C is 1.9×10^{-7}% and the density of water is 1. 0 g/cm^3. The ionisation constant of water is ***(1995)***

(A) 3.42×10^{-6} (B) 3.42×10^{-8}

(C) 1.00×10^{-14} (D) 2.00×10^{-16}

Q.7 Which of the following statement (s) is (are) correct ***(1998)***

(A) The pH of 1.0×10^{-8}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_{p_1} and K_{p_2} for the reaction $x \rightleftarrows 2Y$ and $Z \rightleftarrows P + Q$, 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 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120g of 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) 1.2×10^{-10} g (B) 1.2×10^{-9} g
(C) 6.2×10^{-5} g (D) 5.0×10^{-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 CO^{2-}_3 is 0.034 M.
(B) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(C) The concentration of H^+ and HCO_3^- are approximately equal.
(D) The concentration of H^+ is double that of HCO_3^-

Q.15 At 25^0C, the solubility product of $Mg(OH)^2$ is 1.0×10^{-11}. At which precipitating in the from of $Mg(OH)_2$ from a solution 0.001 M Mg^{2+} ***(2010)***

(A) 9 (B) 10 (C) 11 (D) 8

Q.16 The strongest acid amongst the following compounds is: ***(2011)***

(A) HCOOH (B) $CH_3CH_2CH(CI)CO_2H$
(C) $CICH_2CH_2CH_2COOH$ (D) CH_3COOH

Q.17 A vessel at 1000 K contains CO_2 with a Pressure of 0.5 atm. Some of the 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, Ka of this acid is: ***(2012)***

(A) 3×10^{-1} (B) 1×10^{-3} (C) 1×10^{-5} (D) 1×10^{-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 $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in 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 H^+ present in one ml of solution whose pH is 13.

Q.2 Calculate change in concentration of H^+ ion in one litre of water, when temperature changes from 298 K to 310 K.

Given $K_w(298) = 11^{-14}$ (310) = 2.56×10^{-14}.

Q.3 (i) K_w for H_2O is 9.62×10^{-14} at 60°C.

What is pH of water at 60°C.

(ii) What is the nature of solution at 60°C whose

(a) pH = 6. 7 (b) pH = 6. 35

Q.4 The value of K_w at the physiological temperature (37°C) is 2.56×10^{-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 H_2SO_4 (50 ml) + 0. 4 M HCl 50 (ml)

(b) 0. 1 M HA + 0. 1 M HB

[K_a(HA) = 2×10^{-5} ; K_a (HB) = 4×10^{-5}]

Q.6 What are the concentration of H^+, $H_2C_2O_4$, $H_2C_2O_4^-$ and $C_2O_4^{2-}$ in a 0. 1 M solution of oxalic acid?
[$K_1 = 10^{-2}$ M and $K_1 = 10^{-5}$M]

Q.7 What are the concentrations of H^+, HSO_4^- SO_4^{2-} and H_2SO_4 in a 0. 20 M solution of sulphuric acid?

Given: $H_2SO_4 \rightarrow H^+ + HSO_4^-$; strong $HSO_4^- \rightarrow$ 1 H^++ SO_4^{2-} ; $K_2 = 1.3 \times 10^{-2}$ 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 MNH_3.

[$pk_a[NH_4^+]$=9.26]

Q.9 Calculate the pH of a solution made by mixing 50. 0 ml of 0. 2M NH_4Cl & 75. 0 ml of 0. 1 M NaOH.

[pk_a[NaOH]=0.2]

Q.10 What indicator should be used for the titration of 0. 10 M KH_2BO_3 with 0. 10 M HCl? $K_a(H_3BO_3) = 7.2 \times 10^{-10}$

Q.11 An acid indicator has a K_a of 3×10^{-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 form 75% red to 75% blue?

Q.12 What is the OH^- concentration of a 0. 08 M solution of CH_3COONa. [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$]

Q.13 Calculate the pH of a 2. 0 M solution of NH_4Cl.

[$K_b(NH_3)=1.8 \times 10^{-5}$]

Q.14 Calculate 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. [K_a for the acid = 1.9×10^{-5}]

Q.15 Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22. 0 mL of 0. 10M acetic acid, CH_3COOH, with 22. 0 mL of 0. 10 M NaOH. [$K_a = 1.8 \times 10^{-5}$]

Q.16 The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18}. Which salt is more soluble? Explain your answer.

Q.17 Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 1.1×10^{-12} K_{sp}(AgBr) = 5×10^{-13}.

Q.18 A solution contains HCl, $Cl_2HCCOOH$ & CH_3COOH at concentrations 0. 09 M in HCl, 0. 09 M in $Cl_2HCCOOH$ & 0. 1 M in CH_3COOH. pH for the solution is 1. Ionization constant of $CH_3COOH = 10^{-5}$. What is the magnitude of K for dichloroacetic acid?

Q.19 Determine the [S^{2-}] in a saturated (0. 1M) H_2S solution to which enough HCl has been added to produce a [H^+] of 2×10^{-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? pK_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. 16M 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 1.80×10^{-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 H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively The overall dissociation constant of the acid will be:

(A) 5.0×10^{-5} (B) 5.0×10^{15}

(C) 5.0×10^{-15} (D) 0.2×10^{5}

Q.3 An aqueous solution contains 0. 01 M RNH_2

($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH.

The concentration of OH is nearly:

(A) 2.414×10^{-4} (B) 10^{-4} M

(C) 1.414×10^{-4} (D) 2×10^{-4}

Q.4 The degree of hydrolysis of a salt of weak acid and weak base in it's 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

$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$

Is 1. 8 × 10^{-5}, equilibrium constant for

$CH_3COOH + OH^{-1} \rightarrow CH_3COO^- + H_2O$ is

(A) 1. 8 × 10^{-9} (B) 1. 8 × 10^{9}

(C) 5. 55 × 10^{-9} (D) 5. 55 × 10^{10}

Q.7 The pK_a, of a weak acid, HA, is 4. 80. The 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 $Na^+ A^-$ to make the pH of solution 5.5. Given pk_a(HA)= 5. (Use antilog (0. 5) = 3. 16)

(A) 2.08 × 10^{-1} (B) 3.05 × 10^{-3}

(C) 2.01 × 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 [K_a = 2 × 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 pH < 7

(B) Not a buffer solution with pH > 7

(C) A buffer solution with pH < 7

(D) A buffer solution with pH > 7

Q.11 The 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:

$$\underset{A}{\left[Cu(H_2O)_3(OH)\right]^+} + \underset{B}{\left[Al(H_2O)_6\right]^{3+}} \rightleftharpoons \underset{C}{\left[Cu(H_2O)_4\right]^{2+}} + \underset{D}{\left[Al(H_2O)_5(OH)\right]^{2+}}$$

(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) NaH_2PO_2 (B) Na_2HPO_3 (C) Na_2HPO_4 (D) $NaHCO_3$

Q.14 pH of the following solution is affected by dilution:

(A) 0. 01 M CH_3COONa

(B) 0. 01 M $NaHCO_3$

(C) Buffer of 0. 01 M CH_3 COONa and 0. 01 M CH_3COOH

(D) 0. 01 M CH_3COONH_4

Q.15 Which of the following mixtures does not constitute a buffer?

(A) CH_3COOH + CH_3 COONa (B) $Na_2CO_3 + NaHCO_3$

(C) NaCl + HCl (D) $NH_4Cl + (NH_4)_2SO_4$

Q.16 Which of the following mixtures constitute a buffer?

(A) Na_2CO_3 + HCl (B) NaOH + CH_3COOH

(C) $NH_3 + CH_3COONH_4$ (D) NaOH + $BaCl_2$

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 NH_3 and 0. 1 M$(NH_4)_2SO_4$

(B) 0. 1 M NaH_2PO_4 and 0. 1 M Na_2HPO_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 1.0×10^{-8} 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 titrated again a strong base, at half neutralization point pH = (1/2) pKa.

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 $\left(\frac{1}{5}\right)^{th}$ 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°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 NH_4OH (aq).

(B) An acid-base indicator in a buffer solution of pH = pK_{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

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

(D) When Na_3PO_4 (aq) is titrated with HCl (aq), the pH of solution at second equivalent point is calculated by $\frac{1}{2}[pK_{a1} + pK_{a2}]$

Q.21 Which of the following is true for alkaline aqueous solution?

(A) pH > $\frac{pK_w}{2}$ (B) pH > pOH

(C) pOH < $\frac{pK_w}{2}$ (D) pH < pOH

Q.22 An acid-base indicator has a Ka of 3.0×10^{-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

$HONO(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + ONO^-(aq)$ is $1.1 \times 10^{+6}$.

From the magnitude of this Keq one can conclude that

(A) CN^- is stronger base than ONO^-

(B) HCN is a stronger acid than HONO

(C) The conjugate base of HONO is ONO^-

(D) The conjugate acid of CN^- is HCN

Q.24 Which of the following are acid-base conjugate pairs:

(A) HF,F^- (B) H_3O^+, OH^-

(C) $CH_3NH_3^+$, CH_3NH_2 (D) HS^-, S_2^-

Q.25 Which of the following will suppress the ionization of phthalic acid in an aqueous solution.

(A) KCl (B) H_2SO_4 (C) HNO_3 (D) NaOH

Match the Columns

Q.26 Match the following

List I	**List II weak**
(A) CH_3COOH	(p) Base
(B) H_2SO_4	(q) Weak acid
(C) NaOH	(r) Strong acid
(D) 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 H_2SO_4 solution (specific gravity 1. 225 containing 25% H_2SO_4 by weight) + 800 ml of 0. 525 M strong triacidic base X $(OH)_3$	(p) Phenol Red (6.8 to 8.4)
(B) 50 ml of 0. 1 M HCO_3^- +50 ml of 0. 8 M CO_3^{2-} (H_2CO_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 HA(aq) ($K_a = 10^{-5}$) + 50 ml of 0.1 M HCl(aq) + 100 ml of 0.13M NaOH (aq)	(r) Phenolphtalein (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 (α) is appreciable. At equilibrium $N_2 + 3H_2 \rightleftharpoons NH_3$ ***(1984)***

(A) K_p does not change significantly with pressure

(B) α does not change with pressure

(C) Concentration of 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 X^- and HX. The K_b for 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 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is ***(1984)***

(A) 1.0×10^{-4} (B) 1.0×10^{-10}

(C) 1.0×10^{10} (D) 1.0×10^{14}

Q.4 Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol. dm^{-3}) of the salts at temperature 'T' are in the order ***(2008)***

(A) MX > MX_2 > M_3X (B) M_3X > MX_2 > MX

(C) MX_2 > M_3X >MX (D) MX > M_3X > MX_2

Q.5 2. 5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) ***(2008)***

(A) 3.7×10^{-13} M (B) 3.2×10^{-7} M

(C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

Q.6 Aqueous solutions of HNO_3 KOH, CH_3COOH, and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) ***(2010)***

(A) HNO_3 and CH_3COOH

(B) KOH and CH_3COONa

(C) HNO_3 and CH_3COONa

(D) CH_3COOH and CH_3COONa

Q.7 The equilibrium 2 Cu^I Cu^0 + Cu^{II} in aqueous medium at 25°C shifts towards the left in the presence of. ***(2011)***

(A) NO_3^- (B) Cl^- (C) SCN^- (D) CN^-

Q.8 The solubility of $Mg(OH)_2$ in pure water is 9. 57 × 10^{-3} g/L. Calculate its solubility (in g/L) in 0. 02M $Mg(NO_3)_2$ solution. ***(1986)***

Q.9 What is the pH of the solution when 0. 20 moles of 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 = 1.8×10^{-5} ***(1987)***

Q.10 At a certain temperature, equilibrium constant (K_c) is 16 for the reaction;.

$SO_2(g) + NO_2(g) \rightleftarrows SO_3(g) + NO(g)$

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 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 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}(AgCl) = 1.6 x 10^{-10}], 0.1 mol of CuCl [K_{sp}(CuCl) =1.0x10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6 x 10^{-x}. The value of "x" is ***(2011)***

Q.14 The solubility product (K_{sp}; mol^3dm^{-9}) of MX_2 at 298 based on the information available the given concentration cell is (take 2.303× ×298/F=0.059 V) ***(2012)***

(A) 1×10^{-15} (B) 4×10^{-15}

(C) 1×10^{-12} (D) 4×10^{-12}

Q.15 The compound that does NOT liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is ***(2013)***

(A) Benzoic acid (B) Benzenesulphonic acid

(C) Salicylic acid (D) Carbolic 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° C. The Ka of HA is ***(2013)***

(A) 1×10^{-4} (B) 1×10^{-5}

(C) 1×10^{-6} (D) 1×10^{-3}

Q.17 The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298K.The solubility (in mol/L) of Ag_2CrO_4 in a 0.1M$AgNO_3$ solution is ***(2013)***

(A) 1.1×10^{-11} (B) 1.1×10^{-10}

(C) 1.1×10^{-12} (D) 1.1×10^{-9}

Paragraph 1: Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation: $X_2(g) \rightleftharpoons 2X(g)$

The standard reaction Gibbs energy, $\Delta_e G^o$ of this reaction is positive. At the start of the reaction, there is one mole of 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 L bar K_{-1} mol_{-1})

Q.18 The equilibrium constant K_p for this reaction at 298 K, in terms of $b_{\text{equilibrium}}$, is ***(2016)***

(A) $\dfrac{8\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (B) $\dfrac{8\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

(C) $\dfrac{4\beta^2_{\text{equilibrium}}}{2-\beta^2_{\text{equilibrium}}}$ (D) $\dfrac{4\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

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 2.3mol/lit

Q.2. 1.5 times

Q.3 1.44×10^{-4}

Q.4 2×10^{-8}

Q.5 No

Q.6 4.11×10^{-4} M

Q.7 5.6×10^{-10}, 2.4×10^{-4}, 5.63

Q.8 1.3

Q.9HZ< HY< HX , K_a(HY) = 10^{-5} M, K_a(HZ)= 10^{-9} M

Q.10 (a) 3.72×10^4 dm^3 (b) 4 dm^3

Q.11 K_c = 3.02×10^{-2} , S = 0.123 M

Q.12 6.1

Q.13 (i) pH = 4.35 (ii) 1.79×10^{-9} mol/lit

Q.14 (i) 28.6%

Q.15 [HS^-] 9.54×10^{-5} ,in 0.1 M HCl[HS^-] = 9.1×10^{-8} M, [S^{2-}] = 1.2×10^{-13} M, in 0.1 M HCl [S^{2-}] = 1.09×10^{-19} M

Q.16 [Ac^-] = 0.00093, pH = 3.03

Q.17 [A^-] = 7.08×10^{-5} M, K_a= 5.08×10^{-7}, pK_a= 6.29

Q.18 (i) 2.52 (ii) 2.30 (ii) 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 0.0 82 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 6.022×10^{7}

Q.2 1.6×10^{-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 ΔpH = 0.95

Q.12 $[OH^-] = 6.664 \times 10^{-6}$

Q.13 pH = 4.477

Q.14 5.12×10^{-6}M

Q.15 8.86

Q.16 QX_2 is more soluble

Q.17 4×10^{-7}mol/LAgBr, 9×10^{-7}mol/LAgSCN

Q.18 $K_a = 1.25 \times 10^{-2}$

Q.19 $[S^{2-}] = 2.5 \times 10^{-15}$

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 $\rightarrow$ q; B $\rightarrow$ r; C $\rightarrow$ s; D $\rightarrow$ p **Q.27** A $\rightarrow$ s; B $\rightarrow$ s; C $\rightarrow$ 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** 8.7×10^{-4} gL^{-1} **Q.9** (i) 4.56 (ii) 1 **Q.10** [NO] = 0.80M; [NO_2] = 0.20M **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: $\alpha = \sqrt{\frac{K_a}{C}}$

$\because \alpha$ will be equal, equate the terms on R.H.S. for both the acids.

CH_3COOH	HNO_2
$\frac{K_a}{C}$	$\frac{K_a}{C}$

Sol 2:

Blood	Spinal fluid
$[H^+] = 10^{-7.36}$ $= 4.36\times10^{-8}$	$[H^+] = 10^{-7.53}$ $= 2.95\times10^{-8}$

Sol 3: The freezing point depression is given by $\Delta T = K_f \times m$

1.86 K mol^{-1} kg x m = 0.758 K so, m = 0.40752 mol kg^{-1}. If this can be taken to be 0.40752 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: $HCOOH \rightleftharpoons HCOO^- + H^+$

If the initial concentration before ionization is 0.400 mol L^{-1} and x mol L^{-1} ionizes then the final number of particles in the solution is

(0.400 mol L^{-1} - x mol L^{-1}) + 2x mol L^{-1} = 0.400 mol L^{-1} + x mol L^{-1}.

Now, 0.400 mol L^{-1} + x mol L^{-1} = 0.40752 mol L^{-1}

x mol L^{-1} = 7.52 $\times$ 10^{-3} mol L^{-1} = [H$^+$] = [HCOO$^-$]

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{[7.52\times10^{-3}\,molL^{-1}]}{[0.400-7.52\times10^{-3}]molL^{-1}}$$

$$= 1.44\times10^{-4}$$

Sol 4: $2AgCl(s) + CO_2^{2-} \rightleftarrows Ag_2CO_3(S) + 2Cl^-$

$$K = \frac{[Cl^-]}{[CO_3^{2-}]} = \frac{[Cl^-]^2}{[CO_3^{2-}]} \times \frac{[Ag^+]^2}{[Ag^+]^2} = \frac{[K_{sp}(AgCl)]^2}{K_{sp}(Ag_2CO_3)}$$

$$[Cl^-] = \frac{0.0026}{35.5}M = 7.5\times10^{-5}M$$

The above concentration of Cl^- indicates that $[CO_3^{2-}]$ remains almost unchanged.

$$\Rightarrow \frac{7.3\times10^{-5}}{1.5} = \frac{[K_{sp}(AgCl)]^2}{8.2\times10^{-12}} \Rightarrow K_{sp}(AgCl) = 2\times10^{-8}$$

Sol 5: Intial $[Na_2CO_3] = [CO_3^{2-}] = 1.5$ M

$$\text{Equilibrium } [Cl^-] = [NaCl] = \frac{0.0026}{35.5} = 0.0000732M$$

$$2AgCl(s) + \underset{\substack{(1.5-0.0000366)\\=1.5M}}{\overset{1.5M}{Na_2CO_3}} \rightleftharpoons Ag_2(CO)_3(s) + \underset{0.0000732\text{ M} - \text{eqb. conc.}}{\overset{0-\text{initial conc}}{2NaCl}}$$

$$[Ag^+] = \sqrt{\frac{K_{sp}(Ag_2CO_3)}{[CO_3^{2-}]}} = \sqrt{\frac{8.2\times10^{-12}}{1.5}}$$

$= 2.338\times10^{-6}$M

$\therefore K_{sp} = [Ag^+][Cl^-] = (2.338\times10^{-6})(0.0000732)$

$= 1.71\times10^{-10}$

Precipitate of AgCl will not be formed.

Sol 6: The hydrogen ion concentrations of the given pH range are

$pH = 3.1 = -\log\left\{\left[H^+\right]/M\right\}$

i.e. $\log\left\{\left[H^+\right]/M\right\} = -3.1 = \bar{4}.9$

Hence, $\left[H^+\right] = 7.9\times10^{-4}$M

$pH = 4.5$ i.e $\log\left\{\left[H^+\right]/M\right\} = -4.5 = \bar{5}.5$

Hence, $\left[H^+\right] = 3.2\times10^{-5}$ M

The average of these two hydrogen ion concentration is

$$\frac{7.9\times10^{-4}M + 3.2\times10^{-5}M}{2} = 4.11\times10^{-4}M$$

At this H^+ concentration,

$$\left[In^-\right] = \left[HIn\right]$$

Therefore, $pH = pK_{HIn}$

Or $\left[H^+\right] = K_{HIn} = 4.11\times10^{-4}$M

Sol 7: $K_b(NH_4OH) = 1.8\times10^{-5}; C = 0.01M$

$\frac{K_w}{K_b} = cx^2$ (x = degree of hydrolysis)

$K_h = cx^2$ (K_h = hydrolysis constant)

$pH = \frac{1}{2}(pK_w - pK_b - \log C)$

Sol 8: C = 0.1 M

$K_a = 1.8\times10^{-5}$

$$\underset{0.1}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COO^-} + \underset{x}{H^+}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}\ ;\ 1.8\times10^{-5} = \frac{x^2}{0.1}$$

(i) $[H^+] = x \therefore pH = -\log[H^+]$

(ii) Vol. of CH_3COOH = 1L

Addition of 0.05 mole of HCl increases the concentration of CH_3COOH by 0.05 and reduces the conc. of $CH_3COO^{\ominus}$ by 0.05 mol / L.

$\therefore [CH_3COOH] = 0.1 + 0.05 = 0.15$ M

$[CH_3COO^-] = 1.34\times10^{-3} - 0.05 = 0.05134$ M

$$pH = pK_a + \log\frac{[salt]}{[acid]} = -\log1.8\times10^{-5} + \log\frac{0.05134}{0.15}$$

pH=1.3

Sol 9: The pH of NaX is 7, thus the acid HX must be a strong acid. The ions Y^- and Z^- undergo hydrolysis $Y^- + H_2O \rightleftarrows HY + OH^-$ and $Z^- + H_2O \rightleftarrows HY + OH^-$.
The stronger the base, larger the OH^- concentration and thus larger the pH of the solution. Thus Z^- is stronger base then Y^- and thus conjugate acid HZ will be weaker than HY. Hence, the correct order is $HX > HY > HZ$

Sol 10 : We have

$$HA \rightleftarrows H^+ + A^-$$

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]} = \frac{\left[H^+\right]^2}{\left[HA\right]_0 - \left[H^+\right]} \simeq \frac{\left[H^+\right]^2}{\left[HA\right]_0}$$

Or $\left[H^+\right] = \sqrt{K_2\left[HA\right]_0} = \left[\left(1.8\times10^{-5}M\right)\left(0.5M\right)\right]^{1/2}$

$= 3.0\times10^{-3}$M

(a) Now to double the pH, we will have

$$\left[H^+\right] = \text{antilog}\ \left(-2\times2.523\right) = 9.0\times10^{-6}M$$

Now from the expression

$$K_a = \frac{\left[H^+\right]^2}{\left[HA\right]_0 - \left[H^+\right]} \text{ we get}$$

$$1.8\times10^{-5}M = \frac{\left(9.0\times10^{-6}M\right)^2}{\left[HA\right]_0 - \left(9.0\times10^{-6}M\right)}$$

$$[HA]_0 = \frac{\left(9.0\times10^{-6}M\right)^2\left(1.8\times10^{-5}M\right)}{\left(1.8\times10^{-5}M\right)}$$

This given $= \dfrac{8.0\times10^{-11}M^2 + 1.62\times10^{-10}M^2}{1.8\times10^{-5}M}$

$$= \frac{2.42\times10^{-10}M^2}{1.8\times10^{-5}M} = 1.344\times10^{-5}M$$

Dilution factor $= \dfrac{0.5M}{1.344\times10^{-5}M} = 3.72\times10^{4}$

(b) To double the[OH-], we have

$$\left[H^+\right] = \frac{1}{2}\times3.0\times10^{-3}M$$

Hence, $[HA]_0 = \dfrac{\left[H^+\right]^2}{K_a} = \dfrac{\left(1.5\times10^{-3}M\right)^2}{\left(1.8\times10^{-5}M\right)} = 0.125M$

Dilution factor $= \dfrac{0.5M}{0.125M} = 4$

Sol 11: $K_c = \dfrac{K_{sp}}{{K_b}^2} = \dfrac{10^{-11}}{(1.8\times10^{-5})^2} = 3.02\times10^{-2}$

Sol 12: $pH = pK_a^0 + \log\dfrac{[salt]}{[acid]}$

We get $5.8 = pK_a^0 + \log\left[\dfrac{(10mL)M_2}{VM_1 - (10mL)M_2}\right]$

$$6.402 = pK_a^0 + \log\left[\frac{(20mL)M_2}{VM_1 - (20mL)M_2}\right]$$

Subtracting Eq. (i) from Eq. (ii), we get

$$6.402 = \left[\frac{(20mL)M_2}{VM_1 - (20mL)M_2}\,\frac{VM_1 - (10mL)M_2}{(10mL)M_2}\right]$$

Or $\dfrac{2\left[VM_1 - (10mL)M_2\right]}{VM_1 - (20mL)M_2} = 4$

or $\dfrac{VM_1}{M_2} = \dfrac{60mL}{2} = 30mL$

3

Substituting this in either Eq. (i) or Eq. (ii) we get

$$pK_a^0 = 5.8 - \log\left(\frac{10}{30-10}\right) = 5.8 + 0.30 = 6.1$$

Sol 13: The minimum of concentration S^{2-} ion to start of the precipitation is obtained from the K_{tp} with $\left[Mn^{2+}\right] = 0.01M$. Therefore, we have

$$\left[S^{2-}\right] = \frac{K_{sp}(MnS)}{\left[Mn^{2+}\right]} = \frac{5.6\times10^{-16}M^2}{(0.01M)} = 5.6\times10^{-14}M$$

The H^+ concentration of the solution having the above $\left[S^{2-}\right]$ can be computed from the expression of H_2S equilibrium:

$$\frac{\left[H^+\right]^2\left[S^{2-}\right]}{\left[H_2S\right]} = \frac{\left[H^+\right]^2\left(5.6\times10^{-14}M\right)}{(0.10M)} = 1.1\times10^{-21}M^2$$

This gives

$$\left[H^+\right] = 4.43\times10^{-5}M \text{ or } pH = 4.35$$

If the $\left[H^+\right] > 4.43\times10^{-5}M$, then the $\left[S^{2-}\right]$ will be less than 5.6×10^{-14} M and MnS will no longer precipitate from the solution.

The concentration of Zn^{2+} ion remaining in the solution can be calculated from the solubility product of ZnS:

$$\left[Zn^{2+}\right] = \frac{K_{sp}(ZnS)}{\left[S^{2-}\right]} = \frac{1.0\times10^{-22}\ M^2}{\left(5.6\times10^{-14}\ M\right)} = 1.79\times10^{-9}M$$

Thus, by properly adjusting the $\left[H^+\right]$ in the solution, it is possible to precipitate effectively all of zinc ions from the solution without precipitating any Mn^{2+} ion.

Sol 14: Since at pH = 2.0, half of the indicator is present in the unionized from, therefore

$$[HIn] = \left[In^-\right]$$

Using $pH = pK_{In} + \log\dfrac{\left[In^-\right]}{[HIn]}$

$pK_{In} = pH = 2.0$

pH of the solution containing $4.0\times10^{-3}M$ of H^+ is

$$pH = -\log\left(4.0\times10^{-3}\right) = 2.4$$

Thus, $\log\left(\dfrac{\left[In^-\right]}{[HIn]}\right) = pH - pK_{In} = 2.4 - 2.0 = 0.4$

Or $\dfrac{\left[In^-\right]}{[HIn]} = 2.5$

Adding 1 on both sides, we get

$$\frac{\left[In^-\right]+\left[HIn\right]}{\left[HIn\right]}=3.5$$

or $$\frac{\left[HIn\right]}{\left[In^-\right]+\left[HIn\right]}=\frac{1}{3.5}=0.286$$

Thus, the percentage of indicator in the unionized from = 28.6

Sol 15: dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^2 under both conditions.

Ans. To calculate $\left[HS^-\right]$

	$H_2S \rightleftarrows$	H^+ +	HS^-
Initial	0.1M	x	x
After disso.	0.1-x		
	$\simeq 0.1$		

$$K_a=\frac{x\times x}{0.1}=9.1\times10^{-8}\quad\text{or}\quad x^2=9.1\times10^{-9}$$

or' $x=9.54\times10^{-5}$

In presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium,

$\left[H_2S\right]=0.1-y\simeq0.1,\left[H^+\right]$

$=0.1+y\simeq0.1,\left[HS^-\right]=yM$

$$K_a=\frac{0.1\times y}{0.1}=9.1\times10^{-8}\text{(Given) or } y=9.1\times10^{-8}\,M$$

To calculate $\left[S^{2-}\right]$

$$H_2S\xrightleftharpoons{K_{a_1}}H^++HS^-;\ HS^-\xrightleftharpoons{K_{a_2}}H^++S^{2-}$$

For the overall reaction,

$$H_2S\rightleftarrows 2H^++S^{2-}$$

$K_a=K_{a_1}\times K_{a_2}=9.1\times10^{-8}\times1.2\times10^{-13}$

$=1.092\times10^{-20}$

$$K_a=\frac{\left[H^+\right]^2\left[S^{2-}\right]}{\left[H_2S\right]}$$

In the absence of 0.1 MHCl, $\left[H^+\right]=2\left[S^{2-}\right]$

Hence, if $\left[S^{2-}\right]=x,\left[H^+\right]=2x$

$$\therefore\ \frac{(2x)^2x}{0.1}=1.092\times10^{-20}\text{ or } 4x^3$$

$=1.092\times10^{-21}=273\times10^{-24}$

$3\log x=\log\ 273-24=2.4362-24$

$\log x=0.8127-8=\bar{8}.8127,$

Or $x=\text{Antilog }\bar{8}.8127=273\times10^{-24}$

$=6.497\times10=6.5\times10^{-8}M$

In presence of 0.1 M HCl , suppose $\left[S^{2-}\right]=y$, then

$\left[H_2S\right]=0.1-y\simeq0.1M,\ \left[H^+\right]=0.1+y\simeq0.1M$

$$K_a=\frac{(0.1)^2\times y}{0.1}=1.09\times10^{-20}\text{ or } y=1.09\times10^{-19}M.$$

Sol 16: $K_a=1.74\times10^{-5}\quad\sqrt{\frac{K_a}{C}}=\alpha$

Sol 17: $\underset{0.01}{RCOOH}\rightleftharpoons\underset{(0.01-\alpha)}{RCOO^{\ominus}}+\underset{(0.01-\alpha)}{H^{\oplus}}$

pH = 4.15

conc. = 0.01 M

Get conc. of $H^{\oplus}$ from pH. Calculate α and K_a.

Sol 18: (i) pH of 0.003 M HCl

$\left[H^+\right]=0.003M;\ pH=-\log(0.003)=2.52$

(ii) pH of 0.005 M NaOH

$\left[OH^+\right]=0.005M;\ pOH=-\log(0.005)=2.30$

(iii) pH of 0.002 M HBr

$\left[H^+\right]=0.002M;\ pH=-\log(0.002)=2.70$

(iv) pH of 0.002 M KOH

$\left[OH^-\right]=0.002M;\ pOH=-\log(0.002)=2.70$

Sol 19: Calculate $H^{\oplus}$ / $OH^{\ominus}$ 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:

$$K_h = \frac{K_w}{K_a \times K_b} = \frac{10^{-14}}{7.2\times10^{-10}\times1.8\times10^{-5}} = 0.772$$

$$h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}} = \frac{\sqrt{0.772}}{1+\sqrt{0.772}} = \frac{0.878}{1.878} = 0.467$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7.0 + \frac{9.14}{2} - \frac{4.74}{2} = 9.20$$

Sol 22: CO_2 with H_2O forms H_2CO_3.

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.5\times10^{-7}$$

Now, $pH = -\log[H^+] = 7.4;\ [H^+] = 4\times10^{-8}$

Thus, $\frac{[HCO_3^-]}{[CO_2]} = \frac{4.5\times10^{-7}}{4\times10^{-8}} = 11$

Sol 23: The original $pOH = 4.75$. The pOH after addition of NaOH cannot be less than 3.75.

$$pOH = 3.75 = 4.75 + \log\frac{[NH_4^+]}{[NH_3]}$$

$$\log\frac{[NH_4^+]}{[NH_3]} = -1.00 \quad \text{so} \quad \frac{[NH_4^+]}{[NH_3]} = 0.10$$

Hence NaOH can be added until the ration of $[NH_4^+]$ to $[NH_3]$ is 0.10. Initially $[NH_4^+]+[NH_3] = 0.200$

Although the reaction with OH^- converts NH_4^+ into NH_3, the sum of these two concentrations remains 0.200.

$$[NH_4^+]+[NH_3] = 0.200$$

$$[NH_4^+] = 0.10[NH_3] \text{ (From above)}$$

$$0.10[NH_3]+[NH_3] = 0.200$$

so $1.10[NH_3] = 0.200$ and $[NH_3] = 0.182M$

Hence $[NH_4^+] = 0.018M$ Assuming no change in volume, $0.100 - 0.018 = 0.082$ mol of NaOH can be added without changing the pOH by more than 1.00 pOH unit.

Exercise 2

Single Correct Choice Type

Sol 1: (A) The conjugate acid has one proton (H^+) more. Hence, for NH_2^- the conjugate acid would be NH_3 (the positive charge of $H^+$and the negative charge of NH_2^- cancel each other out).

Sol 2: (C) $H_2PO_4^-$ And HCO_3^- are amphoteric in nature.

$$HCl + H_2PO_4^- \rightarrow H_3PO_4 + Cl^{-1}$$

$$NaOH + H_2PO_4^- \rightarrow HPO_4^{-2} + H_2O$$

Sol 3: (C) Halides and alkaline metals dissociate and do not affect the H^+ as the cation does not alter the H^+ and the anion does not attract the H^+ from water. This is why NaCl is a neutral salt. But pH of water **decreases** as the temperature **increases**. So option C is correct

Sol 4: (C) No' moles HCl $= \frac{(1 \text{ x } 0.1)}{1000} = 10^{-4}$

Volume = 1dm^3 Concentration = moles/volume

$= \frac{10^{-4}}{1} = 10^{-4}$ This gives a pH of 4 so option (C) is correct.

Sol 5: (B)

We have 50mL of $\frac{M}{200}$ H_2SO_4

$\frac{M}{200} =$ 0.005M solution

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

Then $[H^+] = 2\times0.005\text{ M} = 0.01M$

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

$pH = -\log 0.01M$

$pH = 2.00$

Sol 6: (C) The equation for the dissociation of HF is as follow:

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

Here $pK_b = 10.83$

$\Rightarrow -\log K_b = 10.83$

Hence, $K_b = 1.48\times10^{-11}$

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 6.76×10^{-4}

Sol 7: (C) $\left[H_3O^+\right] = C\alpha = 0.1 \times \frac{1}{100} = 1 \times 10^{-3}$

$pH = -\log\left[H_3O^+\right] = -\log 10^{-3} = 3$

Sol 8: (D)

$H_3PO_4 = H^+ + H_2PO_4^- \ldots\ldots K_1$

$H_2PO_4^- = H^+ + HPO_4^{2-} \ldots\ldots K_2$

$HPO_4^{2-} = H^+ + PO_4^{3-} \ldots\ldots K_3$

$K_3 = [HPO_4^{2-}]$

$H^+ = [PO_4^{3-}]$

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,

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

$$= \frac{1.0 \times 10^{-14} \times 80}{1.3 \times 10^{-9}}$$

$$= \sqrt{6.16 \times 10^{-4}}$$

$$= 2.48 \times 10^{-2}$$

$\therefore$ Percentage hydrolysis of NaCN in N / 80 Solution is 2.48

Sol 11: (D) Sodium acetate undergoes anionic hydrolysis

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

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)

$$A_2X_3 \rightleftharpoons 2A^{+3} + 3X^{-2}$$

2y 3y

$$Ksp = [A^{+3}]^2[B^{-2}]^3 = (2y)^2(3y)^3 = 108\,y^5$$

Sol 17: (A) Solubility $= \sqrt{K_{sp}} = \sqrt{6.4 \times 10^{-5}} = 8 \times 10^{-3}$

Sol 18: (C)

$$AB_2 \rightleftharpoons A^{+2} + 2B^-$$

S 2S

$$Ksp = [A^{+2}]^2[B^-]^2 = (S)(2S)^2 = 4(1 \times 10^{-5})^3 = 4 \times 10^{-15}$$

Sol 19: (A) (AB, AB_2, A_xB_y)Ksp = $(S^{x+y})X^xY^y$

Sol 20: (B) Precipitation takes place when the ionic product of a salt is greater than the solubility product. Solubility product of AgCl is 1.8×10^{-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 1×10^{-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 1.7×10^{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:

$$= \left[Ca^{2+}\right] \times \left[F\right]^2$$

On using the values given option (A), the ionic product of CaF_2 comes out to be 1×10^{12}, while using the values given in option (C), we get 1×10^{11} as the answer. However, on using the values given in option (B), the ionic product comes out to be

$=\left[10^{2}\right]\times\left[10^{3}\right]^{2}$

$=10^{2}\times10^{6}$

$=10^{8}$

Thus, in this case, the ionic product of CaF_2 is greater than solubility product. Hence the correct answer is option (b) 10^2 M Ca^{2+} and 10^3 MF.

Sol 22: (C)

$K_{sp}(AgBr)=5\times10^{-13}$

$$AgBr \rightleftharpoons \underset{[S]}{Ag^{+}} + \underset{[S]}{Br^{-}}$$

$K_{sp}=S^{2}$; $S=\sqrt{K_{sp}}$ ..... (1)

$$\underset{\frac{10^{-5}\text{ mol}}{50\text{ L}}}{Ag^{+}} + \underset{\frac{2\times10^{-7}\text{ mol}}{50\text{ L}}}{HBr} \longrightarrow AgBr + H^{\oplus}[Ag^{+}]$$

M = mole / V

The obtained $[Ag^{+}]$ should be subtracted from the available 50 L Ag^{+} solution.

Sol 23: (A) pH (HA) = 9 $\Rightarrow [H^{+}]=10^{-9}$

$K_{sp}(AgA) = [Ag^{+}]\,[A^{-}]$

K_a (HA) = 10^{-10}

$$HA \rightleftharpoons H^{\oplus} + A^{\Theta}$$

$K_a=\dfrac{[H^{+}][A^{-}]}{[HA]}$. Get conc. of $[A^{-}]$

Thus, calculate $K_{sp.}$

Sol 24: (D) Na_2CO_3 is salt of weak acid H_2CO_3 and strong base NaOH therefore, it has a pH more than 7. Also, it dissociates to give two moles of NaOH.

Sol 25: (B)

Concentration of $Na_2CO_3=[CO_3^{2-}]=1.0\text{x}10^{-4}$M

ksp of $BaCO_3=5.1\text{x}10^{-9}$

Reaction : $Ba^{2+}+CO_3^{2-}\rightarrow BaCO_3$

$Ksp=[Ba^{2+}]\,[CO_3^{2-}]$

$$[Ba^{2+}]=\frac{Ksp}{[CO_3^{2-}]}=\frac{5.1\text{x}10^{-9}}{1.0\text{x}10^{-4}}$$

$=5.1\text{x}10^{-5}$

Sol 26: (A) $MX_4 \rightleftharpoons M^{4+}+4X^{-}$

$\therefore K_{sp}=[S][4S]^{4}=256$

$$S=\left(\frac{K_{sp}}{256}\right)^{1/4}$$

Previous Years' Questions

Sol 1: (C)

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

(0.004 –x) 2x x

Since both the solution are isotonic 0.004 + 2x = 0.01

$x = 3\times10^{-3}$

Percent dissociation $=\dfrac{3\times10^{-3}}{0.004}\times100=75\%$

Sol 2: (A)

(a) $Cr(OH)_3 \rightarrow Cr^{+3} + 3OH^{-}$

x 3x

$K_{sp} = x.(3x)^3 = 27x^4$

$x=\sqrt[4]{\dfrac{K_{sp}}{27}}$; $x=\sqrt[4]{\dfrac{2.7\times10^{-31}}{27}}$

$x = 1\times10^{-8}$ mole/litre.

Sol 3: (A)

(a) pH = $7+\dfrac{1}{2}[pK_a+\log C]$

$=7+\dfrac{1}{2}[4.74+\log10^{-2}]$

$=7+\dfrac{1}{2}[4.74-2]$

$=7+\dfrac{2.74}{2}=8.37$

Sol 4: (B)

$X^{-}+H_2O \rightleftharpoons HX+OH^{-}$

$K_h=\dfrac{10^{-14}}{10^{-5}}$ so $h=\sqrt{\dfrac{10^{-9}}{10^{-1}}}=10^{-4}$

$100\times10^{-4}=10^{-2}$

So% of hydrolysis = 0.01%.

Sol 5: (B) Na_2O from NaOH. So that it is basic oxide.

Sol 6: (D) $\alpha = 1.9 \times 10^{-9}$; $C = \frac{1000}{18}$

$$K = \frac{[H^+][OH^-]}{(H_2O)} = c\alpha^2$$

$$= 1.9 \times 10^{-9} \times 1.9 \times 10^{-9} \times \frac{1000}{18} = 2.0 \times 10^{-16}$$

Sol 7: (B, C) pH of 1×10^{-8} M is below to7

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

Conjugate base of $H_2PO_4^-$ acid

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

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

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

[Salt] = [Acid] $\therefore$ pH = 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 HNO_3 than in water because carbonate is a weak base and reacts with the H^+ ion of HNO_3 causing the barium salt to dissociate.

$$BaCO_3 + HNO_3 \rightarrow Ba(NO_3)_2 + CO_2 + H_2O$$

Sol 10: (A) (a) The conjugate base of $CHCl_3$ is more stable than conjugate base of $CHF_3(CF_3)$. CCl_3 stabilized by –I effect of chlorine atoms as well as by the electrons. But conjugate base of $CH_3(CH_3)$ is stabilized only by –I effect of flourine 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

$$\left[H^+\right] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$pH = 7.01$$

Sol 12: (A) $X \rightleftarrows 2Y$

$$\begin{array}{ll} x & \rightleftarrows 2Y \\ 1 & 0 \\ (1-x) & 2x \end{array}$$

$$k_{p_1} = \frac{(2x)^2}{(1-x)}\left(\frac{P_1}{1+x}\right)^1$$

$$\begin{array}{lll} z & \rightleftarrows P & + \ Q \\ 1 & 0 & 0 \\ (1-x) & x & x \end{array}$$

$$k_{p_2} = \frac{x^2}{(1-x)}\left(\frac{P_2}{1+x}\right)^1$$

$$\frac{4 \times P_1}{p_2} = \frac{1}{9} \Rightarrow \frac{p_1}{p_2} = \frac{1}{36}$$

Sol 13: (B) $Ag^+ + Br^- \rightleftarrows AgBr$

Precipitation starts when ionic product just exceeds solubility product

$$K_{sp} = \left[Ag^+\right]\left[Br^-\right]$$

$$\left[Br^-\right] = \frac{K_{sp}}{\left[Ag+\right]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1 L $AgNO_3$ solution. No of miles of KBr to be added $= 10^{-11}$

$$= 10^{-11} \times 120$$

$$= 1.2 \times 10^{-9}\ g$$

Sol 14: (C)

$$A \rightarrow H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad K_1 = 4.2 \times 10^{-7}$$

$$B \rightarrow HCO^-_3 \rightleftarrows H^+ + CO_3^{-2} \qquad K_2 = 4.8 \times 10^{-11}$$

As $K_2 << 1$

All major $\left[H^+\right]_{total} \approx \left[H^+\right]_A$

Sol 15: (B) $Mg^{2+} + 2OH^- \rightleftarrows Mg(OH)_2$

$$K_{sp} = \left[Mg^{2+}\right]\left[OH^-\right]^2$$

$$\left[OH^-\right] = \sqrt{\frac{K_{sp}}{\left[Mg^{2+}\right]}} = 10^{-4}$$

$\therefore$ pOH = 4 and 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 17.9×10^{-5}

K_a of $CH_3CH_2\underset{\substack{| \\ Cl}}{C}H-COOH$ is 139×10^{-5}

Sol 17: (D)

	$CO_2(g)+C \rightleftarrows$	$2CO(g)$
Initial moles	p	0
Equilibrium moles	p – x	2x

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) $\left[H^+\right] = \sqrt{K_a.C} \Rightarrow 10^{-3} = \sqrt{K_a.10^{-1}}$

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

Sol 19: (D) $pH = 1 \left[H^+\right] = 10^{-1} = 0.1 \text{ M}$

$pH = 2 \left[H^+\right] = 10^{-2} = 0.01 \text{ M}$

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)

	A	+	B	$\rightleftarrows$ C	+	D
t=0	1		1	1		1
t_{eq}	1 – x		1 – x	1 + x		1 + x

$\Rightarrow \frac{(1+x)^2}{(1-x)^2} = 100$ $\qquad \Rightarrow \frac{1+x}{1-x} = 10$

$\Rightarrow 1 + x = 10 - 10x$ $\qquad \Rightarrow 11x = 9$

$\Rightarrow x = \frac{9}{11}$

$\Rightarrow \left[D\right] = 1 + \frac{9}{11}; \Rightarrow \left[D\right] = 1.818$

JEE Advanced/Boards

Exercise 1

Sol 1: pH = 13

$\therefore C = [H^+] = 10^{-13}$

$n = \frac{C}{V} = \frac{10^{-13}}{10^3} = 10^{-16}$

No. of H^+ ions $= n \times N_A = 10^{-16} \times 6.023 \times 10^{23}$

$= 6.022 \times 10^7$

Sol 2: $K_w = \left[H^+\right]\left[OH^-\right]$

Substitute in the value for K_w at 298 K:

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

Since $\left[H^+\right] = \left[OH^-\right]$

$10^{-14} = \left[H^+\right]$

Take the root of both sides of the equation to find $\left[H^+\right]$:

$\sqrt{10^{-14}} = \left[H^+\right]$

$\left[H^+\right] = 10^{-7} \text{M}$ at 298K

Similarly At 310 K,

$2.56 \times 10^{-14} = \left[H^+\right]^2$

$\left[H^+\right] = \sqrt{2.56 \times 10^{-14}} = 1.6 \times 10^{-7} \text{M}$ at 310 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: $K_w = 2.56 \times 10^{-14} \longrightarrow 60°C$

$pK_w = -\log(2.56 \times 10^{-14}) = 13.58$

Apply $pH = \frac{1}{2}(pK_w) = \frac{13.58}{2} = 6.79$

Sol 5:

(a) Since H_2SO_4 dissociates as $H_2SO_4 \rightleftharpoons \underset{0.2}{2H^+} + SO_4^-$

$$H_3O^+ = \frac{(50\times 0.2)+(50\times 0.4)}{50+50} = \frac{30}{100} = 0.3$$

$$pH = -\log(0.3) = 0.522$$

(b) 0.1 M HA + 0.1 M HB

$K_a = 2\times 10^{-5}$ $K_a = 4\times 10^{-5}$

$$[H^+] = \sqrt{K_{a(HA)}\times C_1 + K_{a(HB)}\times C_2}$$

$$= \sqrt{2\times 10^{-5}\times 0.1 + 4\times 10^{-5}\times 0.1}$$

$= 0.00244$

$pH = -\log[H^+] = -\log(0.00244) = 2.61$

Sol 6: Since the solution is fairly concentrated and $K_2/K_1 \simeq 10^{-3}\left(K_2 << K_1\right)$, we can use the expression:

$$K_1 = \frac{\left[H_3O^+\right]^2}{\left[H_2A\right]_0 - \left[H_3O^+\right]} \qquad \text{(Eq.1.10.10)}$$

Which gives

$$\left[H_3O^+\right] = \frac{-K_1\sqrt{K_1^2 + 4\left[H_2A\right]_0 K_1}}{2}$$

Substituting the given values of K_1 and $\left[H_2A\right]_0$ in the above expression, we get

$$\left[H_3O^+\right] = \frac{-\left(5.9\times 10^{-2}M\right)+\sqrt{\left(5.9\times 10^{-2}M\right)^2 + 4\left(0.1M\right)\left(5.9\times 10^{-2}M\right)}}{2}$$

$$= \frac{-\left(5.9\times 10^{-2}M\right)+\left(1.645\times 10^{-1}M\right)}{2}$$

$= 0.0528M$

We can obtain the concentrations of $H_2C_2O_4$ $HC_2O_4^-$ and $C_2O_4^{2-}$ in 0.1 M solution of oxalic acid from the following relations:

$$\left[H_2C_2O_4\right] = \frac{\left[H_2A\right]_0}{1+\frac{K_1}{\left[H_3O^+\right]}} = \frac{0.1M}{1+\left(\frac{5.9\times 10^{-2}M}{5.28\times 10^{-2}M}\right)}$$

$$= \frac{0.1M}{1+1.118} = 0.0472M$$

$$\left[HC_2O_4^-\right] = \frac{\left[H_2A\right]_0}{\frac{\left[H_3O^+\right]}{K_1}+1} = \frac{0.1M}{\left(\frac{5.28\times 10^{-2}M}{5.90\times 10^{-2}M}\right)+1}$$

$$= \frac{0.1M}{0.8949+1} = 0.0528M$$

$$\left[C_2O_4^{2-}\right] = \frac{\left[H_2A_o\right]}{\frac{\left[H_3O^+\right]^2}{K_1K_2}+\frac{\left[H_3O^+\right]}{K_2}}$$

$$= \frac{0.1\,M}{\frac{\left(5.28\times 10^{-2}M\right)^2}{\left(5.9\times 10^{-2}M\right)\left(6.4\times 10^{-5}M\right)}+\frac{5.28\times 10^{-2}M}{6.4\times 10^{-5}M}}$$

$$= \frac{0.1M}{738.3+825.0} = 0.000064M$$

Sol 7: Since the dissociation is strong, therefore, the $\left[H^+\right]$ due to this dissociation is 0.20 M.

Let x be the amount of H^+ due to this dissociation Hence,

$$\left[H^+\right]_{total} = 0.20M + x$$

This in equilibrium gives

$$\underset{(0.20M-x)}{HSO_4^-} \rightleftarrows \underset{(o.20M+x)}{H^+} + \underset{x}{SO_4^{2-}}$$

$$K_2 = \frac{\left[H^+\right]\left[SO_4^{2-}\right]}{\left[HSO_4^-\right]} = \frac{(0.20M+x)(x)}{(0.20M-x)} = 1.3\times 10^{-2}M$$

Or $\left(0.20M+x\right)\left(x\right) = \left(1.3\times 10^{-2}M\right)\left(0.20M-x\right)$

$$x^2 + \left(0.20M + 1.3\times 10^{-2}M\right)$$

$$x - \left(1.3\times 10^{-2}M\right)\left(0.20M\right) = 0$$

This is eadratic equation in x, which gives

$$x = \frac{-0.213M + \sqrt{\left\{0.213^2 + 4\left(1.3\times 10^{-2}\left(0.20\right)\right)M^2\right\}}}{2}$$

$$= \frac{-0.213M + 0.2362M}{2} = 0.0116M$$

Thus, $\left[H^+\right]_{total} = \left(0.2M + x\right) = 0.211\ 6M$

$$\left[HSO_4^-\right] = 0.2M - x = 0.1884M$$

$$\left[SO_4^{2-}\right] = x = 0.0116M$$

$$\left[H_2SO_4\right] = 0$$

Sol 8:

$pK_a\left(NH_4^+\right) = 9.26$

$\therefore \quad pK_b\left(NH_3\right) = 14 - 9.26 = 4.74$

	NH_3	+ HCl	$\rightleftarrows$ NH_4Cl
Initial	20	15	0
After	5	0	15

Mixture is a buffer containing 5 millimol of NH_3 (base)

And 15 millimol of NH_4^+ (conjugate acid)

$$\therefore \quad pOH = pK_b + \log\frac{\left[NH_4^+\right]}{\left[NH_3\right]}$$

$$= 4.74 + \log\ 3$$

$$\therefore \quad pH = 14 - pOH$$

$$= 9.26 - \log 3$$

$$= 9.26 - 0.48 = 8.78$$

Sol 9: $pOH = pk_b + \log\frac{[Salt]}{[Base]}$

Final Volume of NaOH after reaction =50+75=125 ml

$M_1V_1=M_2V_2$

$$M_2 = \frac{0.1\times 50}{125} = 0.04M$$

Final Volume of NH_4Cl = 25 ml

$M_1V_1=M_2V_2$

$$M_2 = \frac{0.2\times 50}{25} = 0.4M$$

$$pOH = 0.2 + \log\frac{[0.4]}{[0.04]} = 0.2 + 1 = 1.2$$

pH=14-1.2=12.8

Sol 10: Methyl red, one with pH = 5.22 as midpoint of colour range.

Sol 11: $pH = pK_a + \log\frac{\left[In^-\right]}{\left[HIn\right]}$

Initial concentration of $\left[HIn\right] = 75\%$

Initial concentration of $\left[In^-\right] = 25\%$

Final concentration of $\left[HIn\right] = 25\%$

Initial concentration of $\left[In^-\right] = 75\%$

Thus,

$$pH_1 = -\log\left(3^*10\,^\wedge 5\right) + \log 75/25$$

$$pH_1 = 5$$

$$\left[H^+{}_1\right] = 10^{-5}M$$

$$pH_2 = -\log\left(3^*10\,^\wedge 5\right) + \log 25/75 = -4.045$$

$$\left[H^+{}_2\right] = 8.91\times 10^{-5}M$$

$$\left[H^+{}_2\right] = 8.91\times 10^{-5}M$$

$$\left[H^+{}_2\right] - \left[H^+{}_1\right] = 7.91\times 10^{-5}M$$

Sol 12: $K_a(CH_3COOH) = 1.8\times 10^{-5}$

$CH_3COONa(0.08\ M)$

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

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

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

$$\frac{1}{K_a} = \frac{[HA]}{[H^+][A^-]}$$

$$K_b = K_w \times K_a$$

$$K_w = 1\times 10^{-14}$$

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

$$K_b = 5.6\times 10^{-20} = \frac{x^2}{(0.08 - x)} = \frac{x^2}{(0.08)}$$

$$x = [OH^-] = 0.669\times 10^{-5}M$$

Sol 13: $K_b(NH_3) = 1.8\times10^{-5}$

2M NH_4Cl solution of strong acid and weak base.

$pH = \frac{1}{2}[pK_w - pK_b - \log C]$ **=**4.477

Sol 14: $pH = \frac{1}{2}\left[pk_w + pk_a + \log\ C\right]$

Sol 15: $pH = \frac{1}{2}\left[pk_w + pk_a + \log\ C\right] = 8.86$

Sol 16:

$MX \rightleftarrows M^{n+} + X^{n-} \qquad K_{sp} = \left[M^{n+}\right]\left[X^{n-}\right] = 4.0\times10^{-18}$

$QX_2 \rightleftarrows Q2n^{+} + 2X^{n-} \qquad K_{sp} = \left[Q^{2n+}\right]\left[X^{n-}\right]^2 = 4.0\times10^{-18}$

Solving yield $\left[M^{n+}\right] = 2.0\times10^{-9} \qquad \left[Q^{2n+}\right] = 1.0\times10^{-6}$

Soluble.

Sol 17: Let the simultaneous solubilities of AgSCN and AgBr be s_1 and s_2 mole per litre

$\left[Ag^{+}\right] = s_1 + s_2, \left[SCN^{-}\right] = s_1$ and $\left[Br^{-}\right] = s_2$

$$K_{sp}(AgSCN) = \left[Ag^{+}\right]\times\left[SCN^{-}\right]$$

$1.0\times10^{-12} = (s_1 + s_2)\times s_1$ .... (i)

$5.0\times10^{-13} = (s_1 + s_2)s_2$ .... (ii)

Dividing Equation (i) by Equation (ii), we get

$$\frac{s_1}{s_2} = 2$$

Or $s_1 = 2s_2$

Substituting this value in Equation (ii)

$$5.0\times10^{-13} = 3s_2^2$$

$$s_2 = 4.08\times10^{-7}$$

$$\therefore \quad = 8.16\times10^{-7}$$

This simultaneous solubilities of AgSCN and AgBr are 8.16×10^{-17} mole per litre and 4.08×10^{-7} mole per litre respectively.

Sol 18: pH will be decided by $\left[H^{+}\right]$ furnished by HCl and $CHCl_2COOH.CH_3COOH$ being weak does not dissociate due to common ion effect.

$$CHCl_2COOH \rightleftarrows CHCl_2COO^{-} + H^{+}$$

Initial conc.	0.09	0	0.09(from HCl)
Final conc.	$(0.09 - x)$	x	$(0.09 = x)$

$\therefore \quad \left[H^{+}\right] = 0.09 + x;$

But $pH = 1$

$\therefore \quad \left[H^{+}\right] = 10^{-1} = 0.1$

$\therefore \quad 0.09 + x = 0.1$

$\therefore \quad x = 0.01$

K_a for $CHCl_2COOH$ can be given as:

$$K_a = \frac{\left[H^{+}\right]\left[CHCl_2COO^{-}\right]}{\left[CHCl_2COOH\right]}$$

$$= \frac{0.1\times0.01}{(0.09 - 0.01)} = 1.25\times10^{-2}$$

Sol 19: $H_2S \rightleftharpoons H^{+} + HS^{-}$

$K_{a_1} = \frac{[H^{+}][HS^{-}]}{[H_2S]}$ .... (i)

Further $HS^{-} = H^{+} + S^{2-}$

$K_{a_2} = \frac{[H^{+}][S^{2-}]}{[HS^{-}]}$ .... (ii)

Multiplying both the equations

$$K_{a_1} \times K_{a_2} = \frac{[H^{+}]^2[S^{2-}]}{[H_2S]}$$

Due to common ion, the ionization of H_2S is suppressed and the $[H^{+}]$ in solution is due to the presence of 0.3 M HCl.

$$\left[S^{2-}\right]\frac{K_{a_1}\times K_{a_2}[H_2S]}{[H^{+}]^2} = \frac{10^{-7}\times10^{-14}\times(0.1)}{(2\times10^{-4})^2} = 2.5\times10^{-15}$$

Sol 20: Use pH = - log $[H^{+}]$ for 1 M.

$$\underset{1-x}{\overset{1}{CH_3COOH}} \rightleftharpoons \underset{x}{CH_3COO^{-}} + \underset{x}{H^{+}}$$

$$K_a = \frac{x^2}{1-x} = x^2 = 1.8\times10^{-5}; x = 4.2\times10^{-3} = [H^{+}]$$

$$\therefore pH = -\log[H^{+}] = -\log(4.2\times10^{-3}) = 2.37$$

Now, let 1 litre of 1 M CH_3COOH 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, $\underset{(c-x')}{\overset{c}{CH_3COOH}} \rightleftharpoons \underset{x'}{CH_3COO^-} + \underset{x'}{H^+}$

$K_a = \frac{x'.x'}{(c-x')} = 1.8\times10^{-5}$ ...(i);

Further $pH = -\log x' = 2\times2.37 = 4.74$ (pH doubles on dilution)

Or $\log x' = -4.74 = \bar{5}.26$; $x' = 1.8\times10^{-5}$.

Sub. x′ in (1) we get, $c = 3.6\times10^{-5}$

As the number of moles of CH_3COOH before and after dilution will be the same.

$\therefore$ Moles of CH_3COOH = Molarity × Volume in litres.

$\therefore\ 3.6\times10^{-5}\times V = 1\times1\begin{pmatrix}\text{Initial molarity}=1\\ \text{Initial volume}=1\end{pmatrix}$

$V = 2.78\times10^4$ 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

= m.e. of NaOH $= 0.1\times36.12 = 3.612$

(Since salt formed will be univalent and so for such salts m.m. = m.e.)

m.e. (millimole) of HCl added $= 0.1\times18.06 = 1.806$

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.

$\therefore$ m.e. (millimole) of the unknown acid = 1.806

And m.e. (or millimole) of the salt = 3.612 – 1.8006 = 1.806.

Using,

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

Sol 23: Let us find $[H^+]$ of HCOOH before adding HCOONa.

For the equilibrium,

$HCOOH \rightleftharpoons H^+ + HCOO^-$

$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{[H^+]^2}{[HCOOH]}$

$(\because\ [H^+] = [HCOO^-])$

$\therefore [H^+] = \sqrt{K_a.[HCOOH]} = \sqrt{1.8\times10^{-4}\times0.2} = 6\times10^{-3}$

Now, on the addition of sodium formate in the acid, we have,

$[H^+] = \frac{[acid]}{[salt]} = 1.8\times10^{-4}\times\frac{0.2}{0.1} = 3.6\times10^{-4}$

Calculate pH.

Exercise 2

Single Correct Choice Type

Sol 1: (A) $pH = -\log[4^+] = \frac{1}{\log_{10}[4^+]}$ or

$[4^+] = 10^{-pH}$

$\therefore [4^+] = 10^{-2}$ and $[H^+] = 10^{-6}$

$10^{-2} = 10^{-6}$

$\therefore$ Factor $= 10^4$

Sol 2: (C) Overall dissociation

Constant $= 1.0\times10^{-5}\times5.0\times10^{-10}$

Acid $(H_2A) = 5.0\times10^{-15}$

Sol 3: (D) $k_b = 2\times10^{-6}$; 0.01 M RNH_2

10^{-4} M NaOH

$$\begin{array}{llll} RNH_2 + H_2O & \rightleftharpoons & R\overset{\oplus}{N}H_3 & + \overset{\ominus}{O}H \\ 1 & & 0 & 0 \\ 1-\alpha & & \alpha & \alpha \end{array}$$

Common ion effect due to NaOH

$k_b = \frac{[R\overset{\oplus}{N}H_3][OH^-]}{[RNH_2]}$

pOH= $-\log k_b + \log\frac{[C.A]}{[Base]}$

$= -\log(2\times10^{-6}) + \log\frac{(0.01)}{10^{-4}}$

= - log 2 + 6 + log 0.01 + 4

= 10 – 2 – 0.3010 = 7.699

POH = - log $[OH^-]$

$[OH^-] = 10^{-7.699}$

Sol 4: (B) Salt of WB & WA

Degree of hydrolysis = 50 % ; M = 0. 1 M

$M_2 = 0.2$ M

% hydrolysis of salt = ?

$h_1 = \sqrt{\frac{K_h}{C_1}}$ $\quad h_2 = \sqrt{\frac{K_h}{C_2}}$

$h_1^2\ C_1 = K_h$ $\quad h_2^2\ C_2 = K_h$

$h_1^2\ C_1 = h_2^2\ C_2$

Sol 5: (B) $\underset{0.1N}{NH_4OH} + \underset{0.1N}{HCl} \longrightarrow NH_4Cl + H_2O$

$K = \frac{x^2}{(0.1-x)^2}$; $\sqrt{K} = \frac{x}{0.1-x}$

$\frac{12}{12} = 1$

Sol 6: (D) $CH_3COOH + H_2O \longrightarrow CH_3COO^{\ominus} + H_3O^{\oplus}$

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

$CH_3COOH + OH^- \longrightarrow CH_3COO^{\ominus} + H_2O$

$k_b = \frac{Kw}{Ka} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$

Sol 7: (C) $pK_a = 4.80$; $pK_b = 4.78$

$pH = \frac{1}{2}(pR_w + pK_a - pK_b)$

Sol 8: (B) $(x^{\oplus}Na^+)$ 0.1M 10 ml

HCl 0.1M

$k_b(x^{\oplus}) = 10^{-6}$

$K_a \times K_b = K_w$

$k_a = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

$K_{In} = K_a = \frac{[H^+][In^-]}{[H_{In}]} = \frac{[H^+]\,[base]}{[acid]}$

$[H^+] = K_a = \frac{[acid]}{[base]} = 10^{-9}\frac{[0.1]}{[0.1]}$

$pH = \frac{1}{2}(pK_w - pK_b - \underbrace{\log a}_{pK_a})$

Sol 9: (A) Vol. of buffer soln. = 100 ml

$M_{buffer} = 0.1M$

$pH = 5.5$

$pK_a(HA) = 5$

$NaOH + \underbrace{(\underset{0.1M}{HA} + \underset{0.1M}{NaA})}_{\substack{pK_a=5 \\ 100\ ml}} = pH\ (5.5)$

$pH = pK_a + \log\frac{[salt]}{[acid]} = 5 + \log\frac{[0.1]}{[0.1]} = 5$

Contributing $pH = 0.5$ by NaOH

$0.5 = -\log[H^+]$

A log (-0.5)= $[H^+]$

$[H^+] = 3.16$

$[OH^-] = 10.84 = \frac{\text{no. of moles}}{\text{vol.}}$

Sol 10: (D)

KOH	HCOOH
0.2M	0.1M
40ml	160ml

$K_a = 2 \times 10^{-4}$

No. of Millimoles = M × Vol

∴ Milimoles of KOH = 0.2 × 40=8

Milimoles of HCOOH = 0.1 × 160=16

Milimoles of HCOOK produced = 8

Milimoles of HCOOH remained = 16 - 8 = 8

$pH = pK_a + \log\frac{\text{millimoles of salt}}{\text{milimoles of acid}}$

$= -\log(2 \times 10^{-4}) + \log\frac{8}{8} = 4 - 0.3010 = 3.699$

$pOH = 14 - 3.699 = 10.3$

Sol 11: (A) For buffer solution

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} = 4.5 + \log\frac{[Salt]}{[Acid]}$$

As H A is 50% ionized, $[Salt] = [Acid]$

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 $[Salt] \neq [Acid]$.

$pH = 4.5$

$pH + pOH = 14$

or $pOH = 14 - 4.5 = 9.5$

Sol 12: (A) C is the conjugate acid of A, and D is the conjugate base of B

Sol 13: (A) NaH_2PO_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) $\underset{\text{Acid}}{H_2PO_4^-} \rightleftharpoons \underset{\text{Conjugate Base}}{HPO_4^{2-}} + H^+$

(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) pH > $\frac{pK_w}{2}$

(B) pH > pOH

(C) pOH < $\frac{pK_w}{2}$

Sol 22: (A, B) $pH = pk_a + \log\frac{[In^-]}{[HIn]}$

Initial concentration of [HIn] = 75%

Initial concentration of [In-] = 25%

Final concentration of [HIn] = 25%

Final concentration of [In-] = 75%

$$pH_1 = -\log(3\times10^{-5}) + \log\frac{75}{25} = 5$$

$$[H_1^+] = 10^{-5}M$$

$$pH_2 = -\log(3\times10^{-5}) + \log\frac{25}{75} = 4.05$$

Sol 23: (A, C, D) A very high value of equilibrium constant indicates that the forward is almost complete. Thus CN^- is stronger base than ONO^-. (C) and (D) are factual.

Sol 24: (A, D)

$$\underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Conjugate Base}}{F^-} + H^+$$

$$\underset{\text{Acid}}{HS^-} \rightleftharpoons \underset{\text{Conjugate Base}}{S^{2-}} + H^+$$

Sol 25: (B, C, D) H_2SO, HNO_3, NaOH all of them will suppress the ionization of phthalic acid in an aqueous solution.

Match the Columns

Sol 26: A $\rightarrow$ q; B $\rightarrow$ r; C $\rightarrow$ s; D $\rightarrow$ p

(A) CH_3COOH- Weak acid

(B) H_2SO_4- Strong acid

(C) NaOH –Strong base

(D) NH_3-Weak base

Sol 27: A $\rightarrow$ s; B $\rightarrow$ s; C $\rightarrow$ 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 (HX) = $\frac{K_w}{K_b}$ = 10^{-4}

$$\Rightarrow pH = pK_a + \log\frac{[X^-]}{[HX]}$$

$= pK_a$

$[\because [X^-] = [HX]] = 4$

Sol 3: (C) The reaction of HA with strong base is :

$$HA + OH^- \rightleftharpoons H_2O + A^-$$

$$K = \frac{[A^-]}{[HA][OH^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

Sol 4: (D) MX: $K_{sp} = S^2 = 4 \times l0^{-8} \Rightarrow S = 2 \times 10^{-4}$

$MX_2 : K_{sp} = 4S^3 = 3.2 \times 10^{-4} \Rightarrow 5 = 2 \times 10^{-5}$

$M_3 X : K_{sp} = 27S^4$

$= 2.7 \times 10^{-15}$

$\Rightarrow S = 10^{-4}$

Order of solubility is:

$MX > M_3X > MX_2$

Sol 5: (D) $BOH + Ha \rightarrow Ba + H_2O.B^+ + H_2O \rightleftarrows \underset{ch}{BOH} + \underset{ch}{H^+}$

For titration $N_{acid_1} \; V_{acid_1} = N_{acid_2} V_{acid_2}$

$$\frac{2}{15} \times v = 2.5 \times \frac{2}{5}$$

v = vol g HCI7.5mL

In resulting solution, conc. of salt

$$\left[BCI\right] = \frac{\frac{2}{5} \times 2.5}{10} = 0.1$$

$$\because \frac{ch^2}{1-h} = \frac{k_w}{k_b} \text{ or } h = \sqrt{\frac{k_w}{k_b \times c}} = \sqrt{\frac{10^{-19}}{16^{-12} \times 0.1}}$$

$$h = \sqrt{\frac{1}{10}} \text{ how}$$

$$\left[H^+\right] = ch = 0.1 \times \sqrt{\frac{1}{01}} = 3.16 \times 10^{-2} M \quad = 3.2 \times 10^{-2} M$$

Sol 6: (C, D) In HNO_3 and CH_3COONa combination, if HNO_3 is present in limiting amount, it will be neutralised completely, leaving behind some excess of CH_3COONa :

$$CH_3COONa + HNO_3 \rightarrow CH_3COOH + NaNO_3$$

Buffer combination

Sol 7: (B, C, D) Cl^-, CN^- and 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 = $\frac{9.57}{58} \times 10^{-3}$

$= 1.65 \times 10^{-4}$ M

$K_{sp} = 4S^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$

In 0.02 M $Mg(NO_3)_2$;

solubility of $Mg(OH)_2 = \sqrt{\frac{K_{sp}}{[mg^{2+}]}} \times \frac{1}{2}$

$= 1.5 \times 10^{-5}$ mol L^{-1}

$= 1.5 \; 10^{-5} \times 58g \; L^{-1}$

$= 8.7 \times 10^{-4}$ g L^{-1}

Sol 9: (i) 0.20 mole HCl will neutralise 0.20 mole CH_3COONa, producing 0.20 mol CH_3COOH. Therefore, in the solution

moles of $CH_3COOH = 1.20$

moles of $CH_3COONa = 0.80$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{(0.80)}{1.20} = 4.56$$

(ii) $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

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 CH_3COOH can be ignored (common mainly due to HCl.

$\Rightarrow [H^+] = 0.10$

$\Rightarrow pH = -\log (0.10) = 1.0$

Sol 10: $SO_2(g) + NO_2(g)$ ƒ $SO_3(g) + NO(g)$

$1 - x \quad 1 - x \quad x \quad x$

$Q_c = l < K_c$, ie, reaction proceed in forward direction to attain equilibrium.

$$\Rightarrow 16 = \left(\frac{x}{1-x}\right)^2$$

$\Rightarrow \quad x = 0.80$

$\Rightarrow \quad [NO] = 0.80$ M, $[NO_2] = 0.20$ M

Sol 11: (C) H_3BO_3 (orthoboric acid) is a weak lewis acid.

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^{\oplus}$$

It does not donate proton rather it acceptors 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 $\Delta G^o > 0$ ($\Rightarrow$ Kp < 1).

$\therefore$ Therefore, option (C) is incorrect.

Sol 13:

Let the solubility of AgCl is x mollitre $\quad AgCl \rightleftarrows \underset{x}{Ag^+} + \underset{x}{Cl^-}$

Let the solubility of AgCl is x mollitre $\quad CuCl \rightleftarrows \underset{y}{Cu^+} + \underset{y}{Cl^-}$

$\therefore$ K_{sp} of AgCl = $[Ag^+][Cl^{-1}]$

$1.6 \times 10^{-10} = x(x + y)$ ... (i)

Similarly K_{sp} of CuCl = $[Cu^+][Cl^-]$

$1.6 \times 10^{-6} = y(x + y)$ ... (ii)

On solving (i) and (ii)

$[Ag^+] = 1.6 \times 10^{-7}$

$\therefore$ x = 7

Sol 14: (B)

$$M\left|M^{2+}(aq)\right\|\underset{0.001\text{ M}}{M^{2+}(aq)}\Big|\,M$$

$$\begin{aligned}&\text{Anode:} && M \rightarrow M^{2+}(aq) + 2e^-\\ &\text{Cathode:} && M^{2+}(aq) + 2e^- \rightarrow M\\ & && \overline{M2+(aq)c \rightleftharpoons M^{2+}(aq)_a}\end{aligned}$$

$$E_{cell} = 0 - \frac{0.059}{2}\log\left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\}$$

$$0.059 = -\frac{0.059}{2}\log\left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\} \quad -2 = \log\left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\}$$

$$10^{-2}\times 10^{-3} = M^{2+}(aq)_a = \text{solubility} = s$$

$$K_{sp} = 4S^3 = 4\times(10^{-5})^3 = 4\times 10^{-15}$$

Sol 15: (D) pKa of PhOH (carbolic acid) is 9.98 and that of carbonic acid (H_2CO_3) is 6.63 thus phenol does not give effervescence with HCO_3^- ion.

Sol 16: (A) Rate in weak acid = $\frac{1}{100}$ (rate in strong acid)

$\therefore \quad \left[H^+\right]_{\text{weak acid}} = \frac{1}{100}\left[H^+\right]_{\text{strong acid}}$

$\therefore \quad \left[H^+\right]_{\text{weak acid}} = \frac{1}{100}M = 10^{-2}M$

$\therefore \quad C\alpha = 10^{-2}$

$\therefore \quad K_a = 10^{-4}$

Option (A) is correct.

Sol 17: (B) $K_{sp} = 1.1\times 10^{-12} = \left[Ag^+\right]^2\left[CrO_4^{-2}\right]$

$1.1\times 10^{-12} = \left[0.1\right]^2\left[s\right]$

$s = 1.1\times 10^{-10}$

Sol 18: (B)

	$X_{2(g)} \rightarrow$	$2X_{(g)}$
t = 0 (No. of moles)	1	0
t = t	$1-\frac{\beta}{2}$	β
$t = t_{eq}$	$\left(1-\frac{\beta_{eq}}{2}\right)$	β_{eq}

$$P_x = 2\left(\frac{\beta_{eq}}{1+\frac{\beta_{eq}}{2}}\right) \qquad nTotal = 1-\frac{\beta_{eq}}{2}+\beta_{eq} = \left(1+\frac{\beta_{eq}}{2}\right)$$

$$Px_2 = 2\left(\frac{1-\beta_{eq/2}}{1+\beta_{eq/2}}\right)$$

$$K_P = \frac{(Px)^2}{Px_2} = \frac{\left[2\left(\frac{\beta_{eq}}{1+\beta_{eq}/2}\right)\right]^2}{\left[2\left(\frac{1-\beta_{eq}/2}{1+\beta_{eq}/2}\right)\right]^2} = \frac{2\beta_{eq}^2}{1-\frac{\beta_{eq}^2}{4}} = \frac{8\beta_{eq}^2}{4-\beta_{eq}^2}$$