UNIT 8

Equilibrium-II

(Ionic Equilibrium in Solutions)

SYLLABUS

Equilibria involving ions, various concepts of acids and bases—Arrehenius, Bronsted—Lowry and Lewis, dissociation of acids and bases, acid-base equilibria, ionization of water, pH scale, hydrolysis of salts, pH calculation of salt solutions, acid—base titration using indicator, solubility equilibria—solubity of sparingly soluble salts, solubility equilibrium and solubility product, common ion effect, elementary idea of buffer solutions.

8.1. Strong and Weak Electrolytes and Ionic Equilibrium

On the basis of conduction of their solutions, Faraday in 1824 classified all substances into two categories viz electrolytes and non-electrolytes.

***An electrolyte is defined as a compound whose aqueous solution or melt conducts electricity. On the other hand, a compound whose aqueous solution or melt does not conduct electricity is called a* non-electrolyte.**

For example, aqueous solutions of sugar, urea etc. do not conduct electricity. Hence they are non-electrolytes whereas solutions of inorganic acids, bases and salts conduct electricity. Hence, they are electrolytes.

Arrhenius in 1880 explained that the conductance by an electrolyte is due to the presence of ions produced by the dissociation of the substance. However, different electrolytes dissociate to different extents.

***The fraction of the total number of molecules which dissociates into ions is called the* degree of dissociation *and is usually represented by* α.**

$$i.e. \quad \alpha = \frac{\textbf{No. of moles dissociated}}{\textbf{Total no. of moles taken}}$$

Depending upon the degree of dissociation, Faraday further classified the electrolytes into two categories, called 'strong electrolytes' and 'weak electrolytes'.

A strong electrolyte is defined as a substance which dissociates almost completely into ions in aqueous solution and hence is a very good conductor of electricity. e.g.* $NaOH$, KOH, HCl, H_2SO_4, $NaCl$, KNO_3 *etc.

A weak electrolyte is defined as a substance which dissociates to a small extent in aqueous solution and hence conducts electricity also to a small extent. e.g.* NH_4OH, CH_3COOH *etc.

As strong electrolytes are completely ionised in the aqueous solution, therefore, their ionisation is represented by putting a single arrow pointing towards right *e.g.*

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$NaOH + aq \longrightarrow Na^+\ (aq) + OH^-\ (aq) \text{ etc.}$$

In case of weak electrolytes, as they are partly ionized, an equilibrium is set up between the ions and the unionized electrolyte. Hence their ionization is represented by putting double arrows ($\rightleftharpoons$) in between *e.g.*

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

$$NH_4OH + aq \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq) \text{ etc.}$$

In general, the ionisation of a weak electrolyte, AB, is represented as follows :

$$AB\ (s) + aq \rightleftharpoons A^+\ (aq) + B^-\ (aq)$$

Such an equilibrium is called **ionic equilibrium** between the ions and the undissociated electrolyte.

Applying the law of chemical equilibrium to the above equilibrium we get

$$\frac{[A^+][B^-]}{[AB]} = K_i, \text{ called } \textbf{ionisation constant.}$$

Difference between 'dissociation' and 'ionization'. When an ionic compound is dissolved in water, the ions which are already present in the solid compound separate out. The process is called **dissociation.** On the other hand, when a neutral molecule like HCl (*i.e.* a polar covalent compound) which does not contain ions but when 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.

8.2. Ionisation of Weak Electrolytes—Ostwald's Dilution Law

When acetic acid (a weak electrolyte) is dissolved in water, it dissociates partly into H^+ or H_3O^+ and CH_3COO^- ions and the following equilibrium is obtained :

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

Applying law of chemical equilibrium,

$$K = \frac{[CH_3COO^-] \times [H_3O^+]}{[CH_3COOH] \times [H_2O]}$$

In dilute solution, $[H_2O]$ is constant. The product of K and constant $[H_2O]$ is denoted as K_a, *the ionization constant or dissociation constant of the acid.* Thus

$$K_a = \frac{[CH_3\,COO^-] \times [H_3O^+]}{[CH_3COOH]} \quad ...(i)$$

If 'C' represents the initial concentration of the acid in moles L^{-1} and α, the degree of dissociation, then equilibrium concentration of the ions (CH_3COO^- and H_3O^+) is equal to $C\alpha$ and that of the undissociated acetic acid = $C(1-\alpha)$ *i.e.* we have

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

	CH_3COOH	CH_3COO^-	H_3O^+
Initial conc.	C	0	0
Concs. at eqm.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Substituting the values of the equilibrium concentrations in equation (*i*), we get

$$K_a = \frac{C\alpha\,.\,C\alpha}{C(1-\alpha)} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \quad ...(ii)$$

In case of weak electrolytes, the value of α is very small and can be neglected in comparison to 1 *i.e.* $1-\alpha = 1$. Hence, we get

$$K_a = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}} \quad ...(iii)$$

The degree of dissociation, α can therefore be calculated at a given concentration, C if K_a is known. Further, if V is the volume of the solution in litres containing 1 mole of the electrolyte, $C = 1/V$. Hence we have $\alpha = \sqrt{K_a V}$ ...(*iv*)

Similarly, for a weak base like NH_4OH, we have $\alpha = \sqrt{K_b/C} = \sqrt{K_b V}$ ...(*v*)

The above equationss lead to the following result :

For a weak electrolyte, the degree of ionisation is inversely proportional to the square root of molar concentration or directly proportional to the square root of volume containing one mole of the solute.

This is called **Ostwald's dilution law.**

REMEMBER

(*i*) The approximation $1-\alpha \simeq 1$ can be applied only if $\alpha < 5\%$. If on solving a problem by applying the 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.*

$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

(*ii*) Ostwald's dilution law is applicable only to weak electrolytes because for strong electrolytes, $\alpha \simeq 1$ *i.e.* $K_a \to \infty$.

PROBLEMS ON CALCULATION OF DEGREE OF DISSOCIATION

Calculate the degree of dissociation and concentration of H_3O^+ ions in 0.01 M solution of formic acid. $K_a = 2.1 \times 10^{-4}$ at 298 K.

Solution. Formic acid is weak electrolyte and ionizes in water to give H_3O^+ ions according to the equation

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

Let α be the degree of ionization. Then the concentration of the various species present at equilibrium would be as under :

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

Initial conc.	0.01	0	0
Conc. at eqm.	$0.01(1-\alpha)$ $\simeq 0.01$	0.01α	0.01α

[$\because$ α is very small and can be neglected in comparison to 1]

Thus $K_a = \dfrac{0{\cdot}01\,\alpha \times 0{\cdot}01\,\alpha}{0{\cdot}01}$

$= 0{\cdot}01 \times \alpha^2 = 2{\cdot}1 \times 10^{-4}$

[$K_a = 2{\cdot}1 \times 10^{-4}$, given]

or $\alpha^2 = \dfrac{2{\cdot}1 \times 10^{-4}}{0{\cdot}01} = 2{\cdot}1 \times 10^{-2}$

$\therefore$ Degree of ionisation, α

$= \sqrt{2{\cdot}1 \times 10^{-2}} = 0{\cdot}14$

Concentration of H_3O^+ ions

$= C\alpha = 0{\cdot}14 \times 0{\cdot}01$

$= 1{\cdot}4 \times 10^{-3}$ mol L^{-1}

PROBLEMS FOR PRACTICE

1. Calculate the degree of ionization and $[H_3O^+]$ of 0.01 M CH_3COOH solution. The equilibrium constant of acetic acid is 1.8×10^{-5}

   [Ans. 4.24×10^{-2}, 4.24×10^{-4} mol L^{-1}]

2. A 0.01 M solution of acetic acid is 1.34% ionised (degree of dissociation = 0.0134) at 298 K. What is the ionization constant of acetic acid ?

   [Ans. 1.80×10^{-6}]

3. What will be the percentage of dissociation in 1.0 M CH_3 COOH at equilibrium having dissociation constant of 1.8×10^{-5} ?

   [Ans. 0.424]

HINTS FOR DIFFICULT PROBLEMS

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

Initial conc.	C mol L^{-1}	0	0
At. eqm.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_c = \frac{C\alpha \,.\, C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{0{\cdot}01 \times (0{\cdot}0134)^2}{1-0{\cdot}01} = 1{\cdot}8 \times 10^{-6}$$

3. As in Problem 2,

$$K_c = \frac{C\alpha^2}{1-\alpha} \quad i.e.\ 1{\cdot}8 \times 10^{-5} = \frac{1 \times \alpha^2}{1-\alpha} \approx \alpha^2$$

or $\alpha = \sqrt{1{\cdot}8 \times 10^{-5}} = 4{\cdot}24 \times 10^{-3}$

% dissociation = $(4{\cdot}24 \times 10^{-3}) \times 100 = 0{\cdot}424$

ADD TO YOUR KNOWLEDGE

1. Except $HgCl_2$ and $CdBr_2$, all salts are strong electrolytes.
2. If the concentration of common ions in the solutions of two electrolytes (*e.g.* OH^- ion concentration in $Ca(OH)_2$ and $Ba(OH)_2$ solutions) is same, then on mixing them there is no change in the degree of dissociation of either of the electrolytes. Such solutions are called **isohydric solutions.**

8.3. Various Concepts of Acids and Bases

Throughout the history of chemistry, various acid-base concepts have been proposed and used. In this section, we shall briefly discuss the different concepts put forth from time to time. Each of these can be applied with advantage in appropriate circumstances. In a given situation, the chemist uses the concept that suits his purpose best.

(1) Classical Concept of Acids and Bases. The earliest classification of substances into acids and bases was based upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possessed the following characteristic properties :

(*i*) conducts electricity,

(*ii*) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(*iii*) turns blue litmus red.

(*iv*) has a sour taste.

(*v*) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties :

(*i*) conducts electricity,

(*ii*) turns red litmus blue,

(*iii*) has a bitter taste,

(*iv*) has a soapy (slippery) touch

(*v*) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called *operational definitions as they are based upon certain operations (i.e. tests)* to be performed on the substances. However, these have been replaced by *conceptual definitions* (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behaviour, based upon structure and composition of the substances.

(2) Arrhenius Concept of Acids and Bases. To explain the observed properties of electrolytes, Arrhenius in 1884 put forward a theory, popularly known as *'Arrhenius theory of ionization'*. The main idea contained in this theory was that when an electrolyte is dissolved in water, it dissociates into positively and negatively charged ions.

Based upon this theory, Arrhenius gave the definitions of acids and bases as follows :

An acid *is defined as a substance which contains hydrogen and which when dissolved into water gives hydrogen ions (H⁺).*

Examples. Substances like HCl, HNO_3 and H_2SO_4, containing hydrogen, when dissolved in water dissociate completely into H^+ ions and the negative ions as follows :

$$HCl \xrightarrow{\text{Water}} H^+ + Cl^-$$

$$HNO_3 \xrightarrow{\text{Water}} H^+ + NO_3^-$$

$$H_2SO_4 \xrightarrow{\text{Water}} 2H^+ + SO_4^{2-}$$

Such acids are called **strong acids.**

Substances like acetic acid (CH_3COOH), carbonic acid (H_2CO_3), phosphoric acid (H_3PO_4), etc., when dissolved in water dissociate into ions to a small extent. Thus an equilibrium is set up between the ions and the undissociated molecules as follows :

$$CH_3COOH \xrightleftharpoons{\text{Water}} CH_3COO^- + H^+$$

$$H_2CO_3 \xrightleftharpoons{\text{Water}} 2H^+ + CO_3^{2-}$$

$$H_3PO_4 \xrightleftharpoons{\text{Water}} 3H^+ + PO_4^{3-}$$

Such acids are called **weak acids.**

In general, we can write

$$\underset{\text{(Acid)}}{HA} \xrightleftharpoons{\text{Water}} H^+ + A^-$$

In fact, all the properties of an acid are due to the H^+ ions which it furnishes in aqueous solution.

A base is defined as a substance which contains hydroxyl groups and which when dissolved in water gives hydroxyl ions (OH⁻).

Examples. Substances like NaOH and KOH containing the $-OH$ groups, when dissolved into water, dissociate completely to give OH^- ions as follows :

$$NaOH \xrightarrow{\text{Water}} Na^+ + OH^-$$

$$KOH \xrightarrow{\text{Water}} K^+ + OH^-$$

These are called **strong bases.**

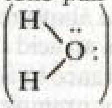
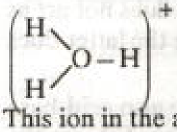
Substances like NH_4OH, $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$ etc. dissociate to a small extent as follows :

$$NH_4OH \overset{\text{Water}}{\rightleftharpoons} NH_4^+ + OH^-$$

$$Ca(OH)_2 \overset{\text{Water}}{\rightleftharpoons} Ca^{2+} + 2OH^-$$

$$Al(OH)_3 \overset{\text{Water}}{\rightleftharpoons} Al^{3+} + 3OH^-$$

These are called **weak bases.**

Existence of H^+ ion and OH^- ion in aqueous solution. H^+ ion is simply a proton which is very small in size (radius $\simeq 10^{-13}$ cm). It has a strong electric field. It takes up a lone pair of electrons from water molecule  to form  *i.e.* H_3O^+, called **hydronium ion.** This ion in the aqueous solution can combine with more of H_2O molecules (a process called hydration) to form species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Hence we simply represent it as H_3O^+ *(aq)*. Similarly, OH^- ions in aqueous solution can combine with one or more H_2O molecules to form species like $H_3O_2^-$, $H_5O_3^-$, $H_7O_4^-$ etc. Hence we generally represent it as OH^- *(aq)*. Thus the dissociation of an acid in water may be represented as

$$HCl + Water \longrightarrow H^+(aq) + Cl^-(aq)$$

$$CH_3COOH + Water \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

or $$HCl + H_2O \longrightarrow H_3O^+(aq) + Cl^-$$

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Similarly, the dissociation of a base may be represented as

$$NaOH + Water \longrightarrow Na^+(aq) + OH^-(aq)$$

$$NH_4OH + Water \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Arrhenius described* neutralization *as the process in which hydrogen ions and hydroxide ions combine to form unionized molecules of water.

$$NaOH \longrightarrow Na^+ + OH^-$$

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

or $$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O$$

or $$H^+ + OH^- \longrightarrow H_2O$$

As a result of this process, the characteristic properties of acids and bases are destroyed.

Utility and Limitations of Arrhenius Concept. The Arrhenius concept of acids and bases was able to explain a number of phenomena like neutralization, salt hydrolysis, strength of acids and bases etc. However, it was found to have the following limitations :

(i) Nature of H^+ ions and OH^- ions : According to Arrhenius concept, acids and bases were defined as substances which gave H^+ ions and OH^- ions respectively in aqueous solution. But as discussed above, these ions cannot exist as such in the aqueous solution but exist as hydrated ions, written as H^+ *(aq)* and OH^- *(aq)*.

(ii) Inability to explain acidic and basic character of certain substances : Arrhenius concept demands that an acid must contain hydrogen and a base must contain hydroxyl (OH^-) groups. However, a number of substances like NH_3, Na_2CO_3, CaO etc. are known to be basic but do not contain any hydroxyl groups. Similarly, a number of substances like CO_2, SO_2, SO_3 etc. are known to be acidic but do not contain any hydrogen.

This limitation is, however, overcome if water is supposed to play an important role. This is clear from the following reactions :

$$NH_3(g) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$Na_2CO_3(s) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq) + 2Na^+(aq)$$

$$CaO + H_2O \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

$$CO_2 + H_2O \rightleftharpoons CO_3^{2-}(aq) + 2H^+(aq)$$

$$SO_3 + H_2O \rightleftharpoons SO_4^{2-}(aq) + 2H^+(aq)$$

(iii) Inability to explain the reaction between an acid and base in absence of water : Two important examples are :

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

$$CaO(s) + SO_3(g) \longrightarrow CaSO_4(s)$$

(3) Bronsted-Lowry Concept of Acids and Bases. To overcome the limitations of Arrhenius concept, Bronsted (a Danish chemist) and Lowry (an English chemist) independently and simultaneously, in the year 1923, proposed a broader concept of acids and bases. According to this concept :

An acid is defined as a substance which has the tendency to give a proton (H^+) and a base is defined as a substance which has a tendency to accept a proton. In other words, an acid is a proton donor whereas a base is a proton acceptor.

The above definition may be explained with the help of the following examples :

(*a*) $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

(*b*) $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

(*c*) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

(*d*) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

(*e*) $HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$

The following important results may be derived from these equations :

(*i*) HCl and CH_3COOH are acids because they donate a proton to H_2O.

(*ii*) NH_3 and CO_3^{2-} are bases because they accept a proton from water.

(*iii*) Not only molecules but even the ions can act as acids or bases *e.g.*, CO_3^{2-} ion in the above case is acting as a base.

(*iv*) In the first two reactions, water is accepting a proton and hence is base. In the next two reactions, water is donating a proton and hence is acting as an acid. Thus water acts both as an acid as well as a base and hence is called **amphoteric** or **amphiprotic.***

(*v*) The reaction (*e*) above indicates that Bronsted- Lowry definitions of acids and bases are not restricted to aqueous solutions. In this reaction, HCl is acid because it gives a proton and NH_3 is a base because it accepts the proton.

(*vi*) The presence of hydroxyl (OH^-) groups is not essential for a substance to act as a base. The only requirement is that it should have a tendency to accept a proton.

(*vii*) The above reactions indicate that a substance acts as an acid *i.e.* gives a proton only when another substance to accept the proton, *i.e.* a base, is present. For example, acetic acid does not act as an acid in benzene solution because the latter does not accept the proton.

(*viii*) The reverse reactions are also acid-base reactions. For example, in reaction (*a*), in the reverse process, H_3O^+ can give a proton and hence is an acid while Cl^- can accept the proton and hence is a base. Thus there are two acid-base pairs in reaction (*a*). These are $HCl - Cl^-$ and $H_3O^+ - H_2O$. These acid-base pairs are called *conjugate acid- base pairs*. Obviously,

A conjugate pair of acid and a base differs by a proton only i.e.
Conjugate acid $\rightleftharpoons$ Conjugate base + H^+

The conjugate acid-base pairs in reactions (*a*) to (*e*) may be represented as follows :

Conjugate Pair I

Conjugate Pair II

$Acid_1$		$Base_2$		$Acid_2$		$Base_1$
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-
HCl	+	NH_3	$\rightleftharpoons$	NH_4^+	+	Cl^-

Note. According to this concept if two acids (which are acids with respect to water) are mixed, the weaker acid will act as a base with respect to the stronger acid *e.g.*

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*Amphoteric is a general term for a substance acting as an acid as well as a base. When acid base behaviour is restricted to proton transfer, it is called amphiprotic.

$$\underset{\text{Acid}_1}{HClO_4} + \underset{\text{Base}_2}{H_2SO_4} \rightleftharpoons \underset{\text{Acid}_2}{H_3SO_4^+} + \underset{\text{Base}_1}{ClO_4^-}$$

(Perchloric acid)

Thus H_2SO_4 is a amphoteric or amphiprotic.

Advantages of Bronsted-Lowry concept over Arrhenius concept :

(*i*) Bronsted-Lowry concept is not limited to molecules but includes even the ionic species to act as acids or bases.

(*ii*) It can explain the basic character of the substances like Na_2CO_3, NH_3 etc. (which do not contain OH^- group and hence were not bases according to Arrhenius definition) on the basis that they are proton acceptors.

(*iii*) It can explain the acid-base reactions in the non-aqueous medium or even in the absence of a solvent (e.g. between HCl and NH_3).

Limitations of Bronsted-Lowry concept. Although Bronsted-Lowry concept has a wider scope than the Arrhenius concept but it has some limitations *e.g.*,

(*i*) It cannot explain the reactions between acidic oxides like CO_2, SO_2, SO_3 etc. and the basic oxides like CaO, BaO, MgO etc. which take place even in the absence of the solvent, e.g.

$$CaO + SO_3 \longrightarrow CaSO_4$$

Obviously, there is no proton transfer involved in this reaction.

(*ii*) Substances like BF_3, $AlCl_3$ etc., do not have any hydrogen and hence cannot give a proton but are known to behave as acids.

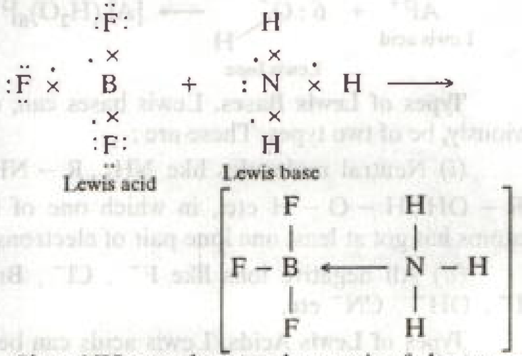
(4) Lewis Concept of Acids and Bases. Bronsted-Lowry concept of acids and bases was broader than Arrhenius concept in the sense that it could explain not only all the Arrhenius acids and bases but included many more substances as bases. However, it did not much enlarge the scope of acids as this concept also emphasized the presence of hydrogen in an acid like the Arrhenius concept.

G.N. Lewis (an American chemist) in the same year *i.e.* 1923, proposed a broader concept of acids and bases. This concept eliminated the necessity of the presence of hydrogen in an acid and this included many more substances as acids and bases. According to this concept (also called *electronic concept*) :

An acid is defined as substance (atom, ion or molecule) which is capable of accepting a pair of electrons and a base is defined as a substance which is capable of donating an unshared pair of electrons. In other words, an acid is an electron pair acceptor while a base is an electron pair donor.

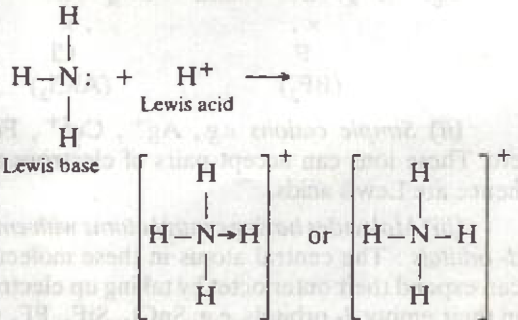
Obviously, the reaction between an acid and a base, according to this concept, amounts to the formation of a co-ordinate bond or dative bond between them.

Examples. (*i*) *Reaction between BF_3 and NH_3 :*

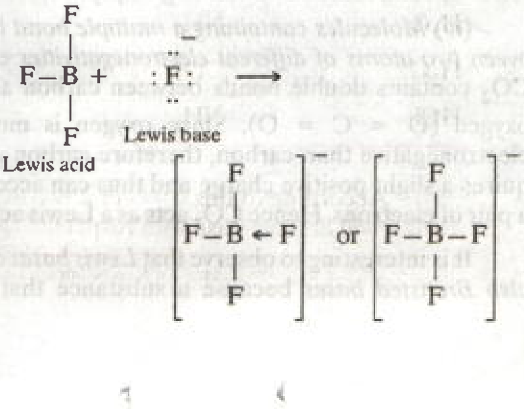


Since NH_3 can donate a lone pair of electrons while BF_3 (in which boron atom has only 6 electrons in the outermost orbit) can accept a pair of electrons, NH_3 is a base and BF_3 is an acid.

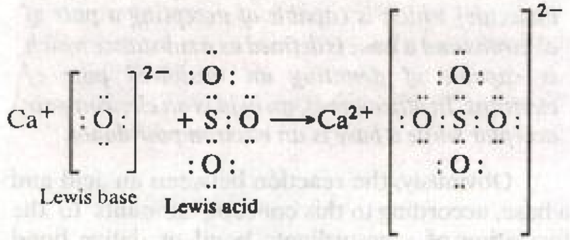
(*ii*) *Reaction between NH_3 and H^+ ion*



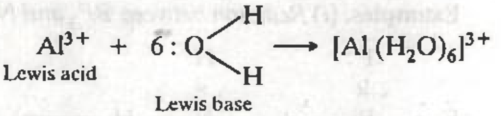
(*iii*) *Reaction between BF_3 and F^- ion*



(iv) Reaction between CaO and SO_3



(v) Hydration of metal ions



Types of Lewis Bases. Lewis bases can, obviously, be of two types. These are :

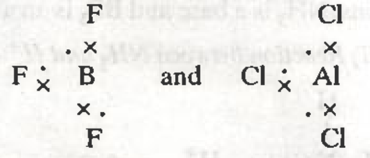
(*i*) Neutral molecules like NH_3, $R-NH_2$, $R-OH$, $H-O-H$ etc., in which one of the atoms has got at least one lone pair of electrons.

(*ii*) All negative ions like F^-, Cl^-, Br^-, I^-, OH^-, CN^- etc.

Types of Lewis Acids. Lewis acids can be of four types. These are :

(*i*) *Molecules having a central atom with incomplete octet :*

e.g.



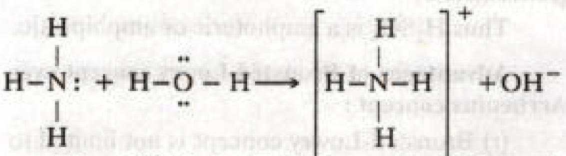
(BF_3) and ($AlCl_3$)

(*ii*) *Simple cations e.g.*, Ag^+, Cu^{2+}, Fe^{3+} etc. These ions can accept pairs of electrons and hence are Lewis acids.

(*iii*) *Molecules having central atoms with empty d- orbitals :* The central atoms in these molecules can expand their outer octet by taking up electrons in their empty *d*- orbitals, e.g. $SnCl_4$, SiF_4, PF_5 etc. have the central atoms containing empty *d*-orbitals.

(*iv*) *Molecules containing a multiple bond between two atoms of different electronegativities* e.g. CO_2 contains double bonds between carbon and oxygen (O = C = O). Since oxygen is more electronegative than carbon, therefore carbon acquires a slight positive charge and thus can accept a pair of electrons. Hence CO_2 acts as a Lewis acid.

It is interesting to observe that *Lewis bases are also Bronsted bases* because a substance that is capable of giving an electron pair has the tendency to accept a proton. For example, consider the reaction



$$H_3N: + H-\ddot{O}-H \longrightarrow [NH_4]^+ + OH^-$$

Here NH_3 is Lewis base as well as Bronsted base. However *Bronsted acid may not be a Lewis acid.* For example, in the above case, H_2O is Bronsted acid because it is giving a proton but is not a Lewis acid because it is electronically satisfied.

Usefulness and Limitations of Lewis concept. No doubt, Lewis concept is the most general out of all the concepts and can explain the acidic and basic nature of all those substances which could not be explained by the earlier concepts. Similarly, it could explain even those acid-base reactions which could not be explained by the other concepts. However, it suffered from some serious drawbacks as follows :

(*i*) Lewis concept is so general that it considers every reaction forming a co-ordinate bond to be acid-base reaction. This however, may not be always true. [For example, according to this concept, even some metals are acids *e.g.* nickel is acid because it forms the co-ordination compound with CO *i.e.* $Ni(:C\equiv O:)_4$, called nickel tetracarbonyl].

(*ii*) The necessary requirement in Lewis concept is the formation of a co-ordinate bond between the acid and base. However, the well known acids like HCl and H_2SO_4 do not form any co-ordinate bond and, therefore, should not be acids according to this concept.

(*iii*) Acid-base reactions are usually fast but formation of co-ordination compound is slow. Hence it does not fit in the acid-base concept.

(*iv*) The catalytic activity of an acid is due to H^+ (*aq*) ion. Since the presence of hydrogen is not an essential requirement for a Lewis acid, many Lewis acids will not have this property.

(*v*) Arrhenius concept and Bornsted concept can explain the strengths of acids and bases (as discussed in the next section) but Lewis concept cannot.

It may be pointed out here that, no doubt, Bronsted concept is more general than Arrhenius concept and the Lewis concept is the most general out of all but still Arrhenius concept continues to be most important in explaining a number of phenomena.

8.4. Dissociation of Acids and Bases

Acids like HCl, HNO_3 and H_2SO_4 when dissolved in water dissociate almost completely thus producing a large number of H^+ ions. Hence these acids are called ***strong acids***. On the other hand, acids like CH_3COOH, HF, H_2CO_3, H_3PO_4 etc. dissociate only to a small extent in the aqueous solution giving small amount of H^+ ions and hence are called ***weak acids***. Similarly, bases like NaOH and KOH dissociate almost completely in the aqueous solution producing a large number of OH^- ions and are called ***strong bases***, whereas bases like NH_4OH, $Ca(OH)_2$, $Al(OH)_3$ etc. dissociate only to a small extent in the aqueous solution and are, therefore, called ***weak bases***.

Thus the dissociation of weak acids or weak bases in water can be represented as an equilibrium process. For example,

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- (aq) + H_3O^+ (aq)$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ (aq) + OH^- (aq) \text{ etc.}$$

In general, if a weak acid is represented by HA, its dissociation in water can be represented by the equilibrium

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

Applying the law of chemical equilibrium, the expression for equilibrium constant will be

$$K = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

As H_2O is solvent, its concentration is large and remains almost constant (= 55·5 mol L^{-1})*.

We put K $[H_2O]$ = K_a, called dissociation constant of the acid. Thus $K_a = \frac{[A^-][H_3O^+]}{[HA]}$

Alternatively, we write

$$HA + aq \rightleftharpoons H^+ (aq) + A^- (aq)$$

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

Knowing the value of the dissociation constant of the acid, K_a and the concentration (C) of the weak acid HA taken, the concentration of H_3O^+ or H^+ (*aq*) in the solution can be calculated as follows :

	HA + *aq*	$\rightleftharpoons H^+ (aq)$	$+ A^- (aq)$
Initial conc.	C mol L^{-1}	0 M	0 M
Concs. at eqm.	(C−*x*) M	*x* M	*x* M

$$\therefore \quad K_a = \frac{[H^+ (aq)][A^- (aq)]}{[HA]} = \frac{x \times x}{C - x}$$

As usually *x* is very small as compared to the initial concentration C, *x* can be neglected in comparison to C. Hence the equation is simplified to the form

$$K_a = \frac{x^2}{C} \quad \text{or} \quad x = \sqrt{K_a \times C}$$

However, it may be pointed outer that if *x* is more than 5% of C, *x* cannot be neglected in comparison to C and the equation has to be solved as a quadratic equation to get the value of *x*.

Similarly, the dissociation of a weak base in water can be represented by the equilibrium

$$BOH + aq \rightleftharpoons B^+ (aq) + OH^- (aq)$$

The dissociation constant of the weak base, represented by K_b, will be given by

$$K_b = \frac{[B^+ (aq)][OH^- (aq)]}{[BOH]}$$

SOLVED EXAMPLE

EXAMPLE. *Calculate the H^+ ion concentration in 0·10 M acetic acid solution. Given that the dissociation constant of acetic acid in water is $1{\cdot}8 \times 10^{-5}$.*

Solution. Suppose at equilibrium,

$[H^+ (aq)]$ = *x* mol L^{-1}. Then

	$CH_3COOH + aq$	$\rightleftharpoons CH_3COO^-(aq)$	$+ H^+ (aq)$
Initial conc.	0·10 M	0 M	0 M
Concs. at eqm.	(0·10 − *x*) M	*x* M	*x* M

---

*Density of H_2O = 1 g/cm^3. Mass of 1 L of H_2O = 1000 g. Therefore, number of moles in 1 L of H_2O = 1000/18 = 55·5 moles.

$$K_a = \frac{[CH_3COO^- (aq)]\,[H^+ (aq)]}{[CH_3COOH]}$$

$$1\cdot8 \times 10^{-5} = \frac{x \times x}{0\cdot10 - x} \approx \frac{x^2}{0\cdot10}$$

or $$x^2 = (1\cdot8 \times 10^{-5}) \times 0\cdot10$$

$$= 1\cdot8 \times 10^{-6}$$

or $$x = \sqrt{1\cdot8 \times 10^{-6}}$$

$$= 1\cdot34 \times 10^{-3}\ \text{M}$$

i.e. $$[H^+] = 1\cdot34 \times 10^{-3}\ \text{M}$$

PROBLEMS FOR PRACTICE

Calculate the concentration of $H^+ (aq)$ in 0·2 M solution of HCN. Given that the dissociation constant of HCN in water is $4\cdot9 \times 10^{-10}$. **[Ans. $9\cdot9 \times 10^{-6}$ M]**

8.5. Strengths of Acids and Bases

According to Arrhenius concept, an acid is defined as a substance which when dissolved in water gives H^+ ions and a base is defined as a substance which when dissolved in water gives OH^- ions. Thus

Greater the number of H^+ ions produced in the aqueous solution, the stronger is the acid. Similarly, greater the number of OH^- ions produced in the aqueous solution, stronger is the base.

Now, as greater is the dissociation constant of the weak acid (K_a), greater is the amount of $H^+ (aq)$ produced, therefore stronger is the acid. Thus K_a values give a measure of the relative strengths of the weak acids. Similarly, K_b values give a measure of the relative strengths of the weak bases. The K_a values of some common weak acids are given in Table 8.1.

TABLE 8.1. Dissociation or Ionization constants (K_a) of some weak monobasic acids at 298K.

Acid	Formula	Dissociation constant (K_a)
Formic acid	HCOOH	$1\cdot7 \times 10^{-4}$
Acetic acid	CH_3COOH	$1\cdot8 \times 10^{-5}$
Benzoic acid	C_6H_5COOH	$6\cdot5 \times 10^{-5}$
Phenol	C_6H_5OH	$1\cdot3 \times 10^{-10}$
Hydrofluoric acid	HF	$6\cdot8 \times 10^{-4}$
Hydrocyanic acid	HCN	$4\cdot9 \times 10^{-10}$
Hypochlorous acid	HClO	$3\cdot2 \times 10^{-8}$
Hypobromous acid	HBrO	$2\cdot1 \times 10^{-9}$
Hypoiodous acid	HIO	$2\cdot3 \times 10^{-11}$
Nitrous acid	HNO_2	$4\cdot5 \times 10^{-4}$

The relative strengths of two weak acids can, however, be compared in a quantitative manner as follows :

Suppose the weak acid is represented as HA. Suppose the initial concentration of HA is C moles/litre and α its degree of dissociation. Then we can write

$$HA + \text{Water} \rightleftharpoons H^+ (aq) + A^- (aq)$$

	HA	$H^+ (aq)$	$A^- (aq)$
Initial conc.	C	0	0
Conc. at eqm.	$C - C\alpha = C(1-\alpha)$	$C\alpha$	$C\alpha$

Applying the law of chemical equilibrium, we get

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

where K_a is called the dissociation constant (or ionization constant) of the acid.

$$\therefore \quad K_a = \frac{C\alpha \,.\, C\alpha}{C\,(1-\alpha)} = \frac{\alpha^2 C}{1-\alpha}$$

As the degree of dissociation (α) of a weak acid is very small, we can take $1 - \alpha \simeq 1$.

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

Thus if two acids of equimolar concentration are taken (so that C is constant),

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

But degree of dissociation is a measure of the strength of an acid. Hence we can say

$$\frac{\text{Strength of the acid } HA_1}{\text{Strength of the acid } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Thus *the relative strengths of two acids of equimolar concentration can be compared by taking square root of the ratio of their dissociation constants.*

e.g. K_a for $CH_3COOH = 1{\cdot}8 \times 10^{-5}$

K_a for $HCN = 4{\cdot}9 \times 10^{-10}$

$$\therefore \frac{\text{Strength of } CH_3\,COOH}{\text{Strength of HCN}} = \sqrt{\frac{1{\cdot}8 \times 10^{-5}}{4{\cdot}9 \times 10^{-10}}}$$

$$= \sqrt{3{\cdot}67 \times 10^4} = 1{\cdot}92 \times 10^2 = 192$$

Hence, CH_3OOH *is nearly 192 times stronger than HCN.*

Similarly, the relative strengths of two weak bases of equimolar concentrations can be compared by taking the square root of the ratio of their dissociation constants, *i.e.*,

$$\frac{\text{Strength of base } (BOH)_1}{\text{Strength of base } (BOH)_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

where K_{b_1} and K_{b_2} are the dissociation constants of the two bases.

The dissociation constants of a few bases at 298K are given in Table 8.2 below :

TABLE 8.2. Dissociation or Ionization constants (K_b) of some weak bases at 298K

Base	Formula	Dissociation constant (K_b)
	Inorganic Bases	
Ammonia	NH_3	$1{\cdot}77 \times 10^{-5}$
Hydroxylamine	NH_2OH	$1{\cdot}1 \times 10^{-8}$
Hydrazine	NH_2NH_2	$1{\cdot}7 \times 10^{-6}$
	Organic Bases	
Methyl amine	CH_3NH_2	$3{\cdot}7 \times 10^{-4}$
Dimethylamine	$(CH_3)_2NH$	$5{\cdot}4 \times 10^{-4}$
Triethylamine	$(CH_3)_3N$	$6{\cdot}45 \times 10^{-5}$
Aniline	$C_6H_5NH_2$	$4{\cdot}27 \times 10^{-10}$
Pyridine	C_5H_5N	$1{\cdot}77 \times 10^{-9}$

It must be remembered that since the ionization of an acid or a base increases with dilution, the strength of the acid or the base increases with dilution.

Note that K_a and K_b are taken as dimensionless quantities (as already explained in unit 7) because the standard state concentration of all the species involved is taken as 1 mol L^{-1}.

Polyprotic acids and Polyacidic bases. Some acids like sulphuric acid (H_2SO_4), carbonic acid (H_2CO_3), oxalic acid ($(COOH)_2$), phosphoric acid (H_3PO_4) etc. contain more than one ionizable proton. Such acids are called **polybasic** or **polyprotic acids.** They ionize in steps. For example, the dibasic acid (H_2X) may ionize in two steps as follows :

$$H_2X\,(aq) \rightleftharpoons H^+\,(aq) + HX^-\,(aq)$$

$$HX^-\,(aq) \rightleftharpoons H^+\,(aq) + X^{2-}\,(aq)$$

Their ionization constants, K_{a_1} and K_{a_2} called the first and the second ionization constant respectively, will be given by the equations

$$K_{a_1} = \frac{[H^+]\,[HX^-]}{[H_2X]},\; K_{a_2} = \frac{[H^+]\,[X^{2-}]}{[HX^-]}$$

The overall equilibrium may be btained by adding the stepwise dissociation equilibria. Thus for the above process, the overall equilibrium will be

$$H_2X\,(aq) \rightleftharpoons 2\,H^+\,(aq) + X^{2-}\,(aq)$$

$$K_a = \frac{[H^+]^2\,[X^{2-}]}{[H_2X]}$$

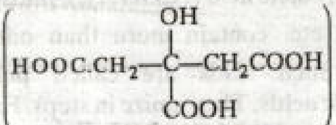
Evidently, $K_a = K_{a_1} \times K_{a_2}$

Similarly, a tribasic acid like H_3PO_4 has three ionization constants. The overall ionization constant (K_a) will be the product of the ionization constants of the three steps *i.e.*

$$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$$

The ionization constants of some polyprotic acids are given in Table 8.3 below :

TABLE 8.3. Dissociation or Ionization constants of some polyprotic acids at 298K

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Sulphuric acid (H_2SO_4)	very high	$1{\cdot}2 \times 10^{-2}$	
Sulphurous acid (H_2SO_3)	$1{\cdot}7 \times 10^{-2}$	$6{\cdot}4 \times 10^{-8}$	
Oxalic acid $(COOH)_2$	$5{\cdot}9 \times 10^{-2}$	$6{\cdot}4 \times 10^{-5}$	
Carbonic acid (H_2CO_3)	$4{\cdot}3 \times 10^{-7}$	$5{\cdot}6 \times 10^{-11}$	
Phosphoric acid (H_3PO_4)	$7{\cdot}5 \times 10^{-3}$	$6{\cdot}2 \times 10^{-8}$	$4{\cdot}2 \times 10^{-13}$
Arsenic acid (H_3PO_4)	$5{\cdot}0 \times 10^{-3}$	$8{\cdot}3 \times 10^{-8}$	6×10^{-10}
Citric acid  $\left(HOOC.CH_2-\overset{\overset{\large OH}{\vert}}{\underset{\underset{\large COOH}{\vert}}{C}}-CH_2COOH\right)$	$7{\cdot}4 \times 10^{-4}$	$1{\cdot}7 \times 10^{-5}$	$4{\cdot}0 \times 10^{-7}$

It may be noted from the above table that $K_{a_1} > K_{a_2} > K_{a_3}$

Similarly, polyacidic bases also ionize in steps with ionization constants $K_{b_1}, K_{b_2}, K_{b_3}$ etc.

According to Bronsted-Lowry concept, the relative strengths of two acids are compared by comparing their tendencies to donate protons. Simiarly, the relative strengths of two bases are compared by comparing their tendencies to accept protons.

The relative strengths of the two acids or the two bases involved in the two acid-base conjugate pairs can be found out if we know whether forward reaction is favoured or backward reaction is favoured. For example, consider the reaction

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

Here, the forward reaction proceeds almost to completion. We must, therefore, conclude that HCl is a stronger acid than H_3O^+ (*i.e.* HCl has a stronger tendency to give proton than H_3O^+). Similarly, H_2O is a stronger base than Cl^-. Thus *the strong acid (HCl) has a weak conjugate base* (Cl^-).

Again, consider the reaction

$$\underset{Acid_1}{CH_3COOH} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Acid_2}{H_3O^+} + \underset{Base_1}{CH_3COO^-}$$

Here, backward reaction is favoured. This shows that H_3O^+ is stronger acid than CH_3COOH. Similarly, CH_3COO^- is a stronger base than H_2O. Thus we again observe that the *strong acid* (H_3O^+) *has the weak conjugate base* (H_2O). To sum up

A strong acid has a weak conjugate base and vice versa.

Thus the relative strengths of some acids and their conjugate bases may be represented as follows :

Strongest ⟶ weakest

Acid : $HIO_3 > HNO_2 > HF > HCOOH > HCN > H_2O$

Conjugate Base : $IO_3^- < NO_2^- < F^- < HCOO^- < CN^- < OH^-$

Weakest ⟵ Strongest

Conversely, if we know with respect to water the relative strengths of two acids or bases involved in the conjugate pair in the acid-base reaction, we can find out whether the forward reaction will be favoured or the backward reaction will be favoured.

8.6. Acid-base Equilibria

An acid when dissolved in water gives H^+ ions and the corresponding *anion.* Similarly, when a base is dissolved in water, it gives OH^- ions and the corresponding *cation.* These anions or cations further interact with water. The reaction of the ion with water is called *hydrolysis*. The following three different possibilities arise :

1. The ions simply get hydrated. The cations of strong bases such a NaOH, KOH etc. and the anions of strong acids like HCl, HNO_3 etc. simply undergo hydration *i.e.* surrounded by water molecules attracted by intermolecular forces. This is because these ions are such weak acids or bases that they cannot react with water by splitting it into H^+ and OH^- ions. Examples of some ions that simply undergo hydration in aqueous solution are

$$Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-, Na^+, K^+ \text{ etc.}$$

2. Negative ions of weak acids react with water molecules, setting up acid-base equilibria and giving alkaline solution. The general equation for anion hydrolysis may be written as

$$\underset{\text{Base}}{X^-} + \underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{HX} + \underset{\text{Base}}{OH^-}$$

$$e.g.\ CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \text{ etc.}$$

Anions that undergo hydrolysis as above are the anions of the weak acids. In other words, they are stronger bases than water (conjugate acid-base concept). Examples of some strongly basic anions are

$$CO_3^{2-}, HCO_3^-, S^{2-}, HS^-, CN^-, CH_3COO^-, PO_4^{3-} \text{ etc.}$$

3. Positive ions of weak bases react with water molecules setting up acid-base equilibria and giving acidic solution. The most common example is that of NH_4^+ cation (obtained from the weak base NH_4OH). Its hydrolysis may be represented as

$$\underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_3O^+}$$

As only the cations obtained from weak bases undergo hydrolysis as above, it can be said that these are those cations that are stronger acids than water. A few examples of such cations are

$$NH_4^+, Be^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+} \text{ etc.}$$

Acid-base equilibria are also set up when salts are dissolved in water. The reaction of salts with water is called **'salt hydrolysis'** and has been discussed in section 8.10.

ADD TO YOUR KNOWLEDGE

1. H^+ ion (which is barely a proton) is so small in size that it cannot exist as such in the aqueous solution. It combines with four H_2O molecules surrounded tetrahedrally and exists as $H_9O_4^+$ ion ($H^+ + 4H_2O \longrightarrow H_9O_4^+$).

2. Like H_2O, many other liquids also undergo auto-protolysis *e.g.*

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

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-.$$

3. **Classification of solvents**

	Name	Characteristic	Examples
(*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

8.7. Dissociation Constant and Ionic Product of Water

Pure water is poor conductor of electricity. This shows that water is a weak electrolyte *i.e.*, it is ionized to a very small extent as

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

or more accurately, it may be written as

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \quad ...(i)$$

This ionization is called *self-ionization of water*.

Applying the law of chemical equilibrium to the above equilibrium, we get

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

or $$\frac{[H_3O^+][OH^-]}{[H_2O]^2} = K \qquad ...(ii)$$

where K is the dissociation constant of water.

Since water is ionized to a very small extent, this means that out of millions of water molecules, only a few are dissociated into H_3O^+ and OH^- ions. Thus the concentration of unionized water molecules *i.e.* $[H_2O]$ remains almost constant (being equal to 1000/18 = 55.55 moles per litre, because 1 litre of water = 1000 cc = 1000 g and molar mass of H_2O = 18 g mol^{-1}) *i.e.*

$$[H_2O] = \text{constant}$$

Equation (*ii*) may be rewritten as

$$\begin{aligned}[H_3O^+][OH^-] &= K[H_2O]^2\\ &= \text{constant} \times \text{constant}\\ &= K_w, \text{ another constant,}\end{aligned}$$

called ionic product of water. Hence

Ionic product of water *may be defined as the product of the molar concentration of H_3O^+ ions and OH^- ions (or H^+ ions and OH^- ions).*

The dissociation constant of water, as given by eqn. (*ii*), can be calculated by substituting the values of $[H_3O^+]$, $[OH^-]$ and $[H_2O]$. Thus, we get

$$K = \frac{10^{-7} \times 10^{-7}}{55 \cdot 55} = 1 \cdot 8 \times 10^{-16}$$

Note carefully that dissociation/ionization constant of water (K) is different from ionic product of water (K_w). The two are related as

$$K = \frac{K_w}{55 \cdot 55} \quad \text{or} \quad K_w = K \times 55 \cdot 55$$

Further, it must be noted that ionic product of water is constant only at constant temperature. Its value at 25°C (298 K) is found to be 1.008×10^{-14}. However, for simplicity, the value of K_w at 298 K is usually taken as

$$K_w = 1.00 \times 10^{-14}$$

Effect of temperature on K_w. The ionic product of water (K_w) increases with increase of temperature (as shown by the values given in Table 8.2). This is obviously because of the fact that with increase of temperature, the degree of ionization of water increass. In other words, more of H_2O molecules dissociate into H^+ (or H_3O^+) ions and OH^- ions. Thus the concentration of H^+ (or H_3O^+) ions and OH^- ions increases and hence the ionic product also increases.

TABLE 8.4. Values of K_w at different temps.

Temperature (°C)	K_w
0	0.1×10^{-14}
10	0.3×10^{-14}
25	1.0×10^{-14}
30	1.5×10^{-14}
40	3.0×10^{-14}
50	5.5×10^{-14}
60	9.6×10^{-14}

H_3O^+ Ion and OH^- ion concentrations in pure water at 298 K : Pure water ionizes as

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

Obviously, for any degree of ionization, we will always have

$$[H_3O^+] = [OH^-]$$

But at 298 K, we know that

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$\therefore \quad [H_3O^+][H_3O^+] = 1.0 \times 10^{-14}$$

or $$[H_3O^+]^2 = 1.0 \times 10^{-14}$$

or $$[H_3O^+] = \sqrt{1 \cdot 0 \times 10^{-14}} = 1 \cdot 0 \times 10^{-7} \text{ moles/litre}$$

Thus in pure water at 25°C,

$$[H_3O^+] = [OH^-] = 1 \cdot 0 \times 10^{-7} \text{ M}$$

8.8. H_3O^+ Ion and OH^- Ion Concentrations in Aqueous Solutions of Acids and Bases

As already explained above, for pure water at 298 K

$$[H_3O^+] = [OH^-] = 10^{-7} \text{ M}$$

Now, if some acid (say HCl) is added to the pure water, then

$$[H_3O^+] > 10^{-7} \text{ M}$$

However, experiments show that the equation $K_w = [H_3O^+][OH^-]$ is still valid. Thus the $[OH^-]$ decreases and may be calculated as

$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

Again, if some base (say NaOH) is added to pure water, then

$$[OH^-] > 10^{-7}\,M$$

But the equation $K_w = [H_3O^+]\,[OH^-]$ is still found to hold good. Hence $[H_3O^+]$ decreases and may be calculated as

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

The increase or decrease of the H_3O^+ ion concentration in an aqueous solution of an acid or a base may be explained qualitatively on the basis of Le Chatelier's principle (or common ion effect) as follows :

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

If some acid is added to pure water, H_3O^+ ion concentration increases, therefore the equilibrium shifts in the backward direction (or ionization of H_2O is suppressed). Thus the OH^- ion concentration decreases. Similarly, if a base added, OH^- ion concentration increases. Again, the equilibrium shifts in the backward direction (or the ionization of H_2O is suppressed) and hence the H_3O^+ ion concentration decreases.

8.9. pH—A Convenient Representation of H_3O^+ Ion Concentration

It has already been discussed above that a solution may be neutral, acidic or alkaline, the equation

$$K_w = [H_3O^+]\,[OH^-]$$
$$= 1.0 \times 10^{-14} \text{ at } 298\text{ K}$$

always holds good. Thus if H_3O^+ ion concentration of a solution is known, OH^- ion concentration is automatically fixed. Thus to express the acidity or alkalinity of a solution, it is sufficient to express only the H_3O^+ ion concentration. Since the product of $[H_3O^+]$ and $[OH^-]$ is always 1.0×10^{-14}, the concentration of H_3O^+ ions may vary from 10^0 *i.e.* 1 M to 10^{-14} M. Thus a solution may have $[H_3O^+] = 2.5 \times 10^{-5}$ M or which may be written as 0.000025 M. Obviously, such a method of expressing the H_3O^+ ion concentration is quite cumbersome. Sorensen, in 1909, suggested a convenient method of expressing the H_3O^+ ion concentration in terms of pH The symbol has been taken from the Danish word *potenz de hydrogen ion* which means power of Hydrogen ions. The following different definitions of pH are used to express the H_3O^+ ion concentration.

(i) pH of a solution is defined as the magnitude of the negative power to which 10 must be raised to express the hydronium ion (H_3O^+) concentration*.

Thus if in a solution

$$[H_3O^+] = 10^{-x} \qquad ...(i)$$
$$pH = x$$

However, this definition can be used only where the $[H_3O^+]$ can be expressed as a power of 10. In many cases, it may not be easy to do so, e.g., a solution may have $[H_3O^+] = 2.5 \times 10^{-5}$ M.

A more general definition may be arrived at from equation (*i*) as follows :

Taking logarithm of both sides of equation (*i*), we get

$$\log [H_3O^+] = \log 10^{-x}$$
$$= -x \log 10$$
$$\text{or} \quad = -x \qquad (\log 10 = 1)$$
$$\text{or} \quad x = -\log [H_3O^+]$$
$$i.e. \quad \boxed{pH = -\log [H_3O^+]} \quad ..(ii)$$

This is the most common form used in numerical problems. Thus

(ii) pH may be defined as negative logarithm of hydronium ion concentration.

Equation (*ii*) may be rewritten as

$$pH = \log [H_3O^+]^{-1}$$
$$\text{or} \quad pH = \log \frac{1}{[H_3O^+]}. \text{ Hence}$$

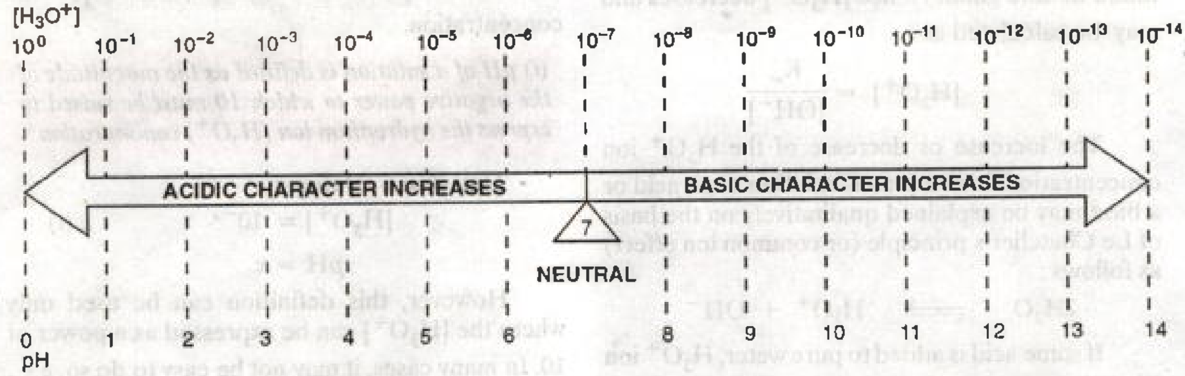
(iii) pH may also be defined as logarithm of the reciprocal of H_3O^+ ion concentration.

pH scale : Theoretically, a solution may have any H_3O^+ ion concentration and hence may have any pH value. However, practically, the solutions having H_3O^+ ion or OH^- ion concentration more than 10^0 (= 1 M) and hence OH^- ion or H_3O^+

---

*Strictly seaking, in place of molar concentrations, activities of H^+ ions (a_{H^+}) are used. However, at low concentrations, the two are equal.

ion conc. less than 10^{-14} M are not common. This is because such solutions are not easy to obtain and moreover as the concentration increases, the degree of dissociation of the acid or the base decreases enormously. Hence the pH range is taken as 0 to 14 for most of the practical purposes. The acidity or the alkalinity of a solution may be represented on the pH scale as follows :



Relationship between pH and pOH. Just as $pH = -\log[H^+]$, similarly, $pOH = -\log[OH^-]$

Since $[H_3O^+]\ [OH^-] = K_w = 10^{-14}$ at 25° C

$$\therefore \log[H_3O^+] + \log[OH^-] = \log K_w = \log 10^{-14} = -14$$

$$\text{or } -\log[H_3O^+] - \log[OH^-] = -\log K_w = 14$$

$$\text{or } \boxed{pH + pOH = pK_w = 14}$$

Relationship between pK_a and pK_b values (*i.e. between ionization constant of a weak acid and that of its conjugate base*).

Consider the weak acid HF. Its conjugate base is F^-. They dissociate as follows :

$$HF \rightleftharpoons H^+ + F^-,$$

$$K_a = \frac{[H^+][F^-]}{[HF]} \quad ...(i)$$

$$F^- + H_2O \rightleftharpoons OH^- + HF,$$

$$K_b = \frac{[OH^-][HF]}{[F^-]} \quad ...(ii)$$

Multiplying eqns. (*i*) and (*ii*), we get

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

$$i.e. \quad \boxed{K_a \times K_b = K_w}$$

$$\therefore \log K_a + \log K_b = \log K_w$$

$$\text{or} \quad -\log K_a - \log K_b = -\log K_w$$

$$i.e. \quad \boxed{pK_a + pK_b = pK_w.}$$

Limitations of pH scale.

(*i*) The pH values of the solutions do not give the exact idea of their relative strength. For example,

(*a*) A solution of pH = 1 has hydrogen ion concentration 100 times than that of a solution of pH = 3, and not 3 times.

(*b*) A 4×10^{-5} N HCl solution is twice concentrated as compared to 2×10^{-5} N HCl solution but the pH values of these solutions are 4·4 and 4·7 respectively, and not double.

(*ii*) pH = 0 is obtained in 1N solution of a strong acid and for concentration 2N, 3N, 10N etc. the value can be negative too. Similarly, for a concentrated solution of a strong base (> 1 M), pH can be greater than 14.

(*iii*) A 10^{-8} M solution of acid can not have pH = 8. The value will be close to but < 7 (see solved example under 'Type VIII' page 8/26).

Measurement of pH. Though accurate measurement of pH of a solution is done with the help of an instrument, called pH-meter, approximate pH (within the range of 0·5) can be determined with the help of pH papers which show different colours when dipped in solutions of different pH.

PROBLEMS ON CALCULATION OF $[H_3O^+]$, $[OH^-]$ & pH

TYPE I. On the calculation of $[H_3O^+]$ and $[OH^-]$

EXAMPLE 1. *Calculate the H_3O^+ and OH^- ion concentrations at 25° C in*

(i) 0.02 N HCl solution

(ii) 0.005 N NaOH solution

Solution. (*i*) HCl completely ionizes as

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$\therefore \quad [H_3O^+] = [HCl] = 0.02\text{ N} \quad (\textit{Given})$$

$$= 0.02\text{ M} \quad (\because \text{HCl is monobasic})$$

$$= 2 \times 10^{-2}\text{ M}$$

Now as $[H_3O^+][OH^-] = K_w = 10^{-14}$

$$\therefore \quad [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{2 \times 10^{-2}}$$

$$= \mathbf{5 \times 10^{-13}\ M}$$

(*ii*) NaOH completely ionizes as

$$NaOH \longrightarrow Na^+ + OH^-$$

$$\therefore [OH^-] = [NaOH] = 0{\cdot}005\text{ N} \ (\textit{Given})$$

$$(\because \text{NaOH is monoacidic})$$

$$= 5 \times 10^{-3}\text{ M}$$

Now as $[H_3O^+][OH^-] = K_w = 10^{-14}$

$$\therefore [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{5 \times 10^{-3}}$$

$$= \mathbf{2 \times 10^{-12}\ M}$$

EXAMPLE 2. *Calculate the concentration of H_3O^+ ions in a mixture of 0·02 M acetic acid and 0·2 M sodium acetate. Given that the ionization constant (K_a) for acetic acid is $1{\cdot}8 \times 10^{-5}$.*

Solution. Acetic acid ionizes to a small extent whereas sodium acetate (being a salt) ionizes completely. Suppose acetic acid ionized at equilibrium $= x$ moles. Then

	$CH_3COOH + H_2O \rightleftharpoons$	CH_3COO^-	$+ H_3O^+$
Initial moles	0·02	0	0
Moles at eqm.	$0{\cdot}02 - x$	x	x

	$CH_3COONa \longrightarrow$	CH_3COO^-	$+ Na^+$
Initial moles	0·2	0	0
Moles at eqm.	0	0·2	0·2

Thus in the mixture solution

$$[CH_3COO^-] = 0{\cdot}2 + x \simeq 0.2\text{ M}$$

(CH_3COO^- are obtained mainly from CH_3COONa, therefore $x << 0{\cdot}2$)

$$[CH_3COOH] = 0{\cdot}02 - x \simeq 0{\cdot}02\text{M}$$

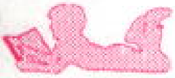
$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$1{\cdot}8 \times 10^{-5} = \frac{0{\cdot}2 \times [H_3O^+]}{0.02}$$

$$\text{or} \quad [H_3O^+] = \frac{1{\cdot}8 \times 10^{-5} \times 0{\cdot}02}{0{\cdot}2}$$

$$= \mathbf{1{\cdot}8 \times 10^{-6}\ M}$$

PROBLEMS FOR PRACTICE



If hydrogen ion concentration in a solution is 1×10^{-5} moles/litre, calculate the concentration of OH^- ion in this solution ($K_w = 10^{-14}$ moles^2 / litre^2) **[Ans. 10^{-9} moles/litre]**

Note. Since the calculation of H_3O^+ ion concentration is usually the first step towards the calculation of pH, therefore the numericals of this type are automatically included in the various types that follow.

TYPE II. On the calculation of pH of completely ionized acids

EXAMPLE 1. *Calculate the pH value of*

(i) 10^{-2} *molar* HNO_3 *solution*

(ii) 0.03 N HCl solution

(iii) 0.001 N H_2SO_4 *solution.*

Solution. (*i*) HNO_3 completely ionizes as

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

$$\therefore [H_3O^+] = [HNO_3] = 10^{-2}\,M \text{ (Given)}$$

$$pH = -\log[H_3O^+] = -\log(10^{-2})$$

$$= -(-2\log 10) = 2$$

(*ii*) HCl completely ionizes as

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$\therefore [H_3O^+] = [HCl] = 0.03\,N \quad \text{(Given)}$$

$$= 3 \times 10^{-2}\,N = 3 \times 10^{-2}\,M$$

(HCl is monobasic)

$$\therefore \quad pH = -\log[H_3O^+]$$

(Eq. mass = Mol. mass)

$$= -[\log 3 \times 10^{-2}]$$

$$= -(\log 3 + \log 10^{-2})$$

$$= -(0.4771 - 2) = \mathbf{1.5229}$$

(*iii*) H_2SO_4 completely ionizes as

$$H_2SO_4 + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$$

$$[H_3O^+] = 2 \times [H_2SO_4]$$

[1 molecule of H_2SO_4 gives 2 H_3O^+ ions]

But $H_2SO_4 = 0.001\,N = 0.001 \times 49$ g/litre

(Eq. mass of H_2SO_4 = 49)

$$= \frac{0{\cdot}001 \times 49}{98} \text{ moles/litre}$$

($\because$ Mol. mass of H_2SO_4 = 98)

$$= 0{\cdot}0005\,M$$

$$\therefore [H_3O^+] = 2 \times [H_2SO_4]$$

$$= 2 \times 0{\cdot}0005\,M$$

$$= 0.001\,M = 10^{-3}\,M$$

$$\therefore \quad pH = -\log[H_3O^+]$$

$$= -\log(10^{-3}) = 3$$

EXAMPLE 2. *The concentration of hydronium ions in a cup of black coffee is* $1{\cdot}3 \times 10^{-5}$ *M. Find the pH of the coffee. Is this coffee acidic or alkaline ?*

Solution. Here we are given that

$$[H_3O^+] = 1.3 \times 10^{-5}$$

$$pH = -\log[H_3O^+] = -\log(1.3 \times 10^{-5})$$

$$= -(\log 1.3 + \log 10^{-5})$$

$$= -0.1139 + 5 = 4.8861$$

$$= \mathbf{4.89}$$

As pH is less than 7, the black coffee is *acidic.*

EXAMPLE 3. *A solution is found to contain 0.63 g of nitric acid per 100 ml of the solution. What is the pH of the solution if the acid is completely dissociated ?*

Solution. Concentration of HNO_3 solution = 0.63 g per 100 ml (*Given*)

$$= 6.3 \text{ g per litre} = \frac{6{\cdot}3}{63} \text{ moles/litre}$$

$$= 10^{-1}\,M$$

($\because$ Mol. mass of HNO_3 = 63)

Now, HNO_3 completely ionizes as

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

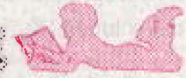
$$\therefore [H_3O^+] = [HNO_3]$$

$$= 10^{-1}\,M$$

$$\therefore \quad pH = -\log[H_3O^+]$$

$$= -\log 10^{-1} = 1$$

PROBLEMS FOR PRACTICE



1. Calculate the pH value of 0.001 N HNO_3 solution [Ans. 3]
2. Calculate the pH value of 10^{-3} M HCl solution [Ans. 3]
3. What is the pH of a solution whose H^+ ion concentration is 2×10^{-5} g ions/litre ? [Ans. 4.699]
4. 0.049 g of H_2SO_4 is dissolved per litre of the given solution. Calculate the pH of the solution. [Ans. 3.0]

PRACTICE PROBLEMS CONTD.

5. Calculate the pH of a solution which is 1×10^{-3} M with respect to sulphuric acid. [Ans. 2.699]

6. 13.5 g of an acid HA, of molecular mass 135 was dissolved in 10 litres of aqueous solution. Calculate the pH of the solution, assuming the acid to be completely dissociated. [Ans. 2]

7. Calculate the pH value of a 4.9×10^{-4} N monobasic acid solution assuming complete ionization. [Ans. 3.31]

8. Calculate the pH of a solution obtained by diluting 25 ml of N/100 HCl to 500 ml. [Ans. 3.301]

9. 1 ml of 13·6 M HCl is diluted with water to give 1 litre of the solution. Calculate pH of the resulting solution. [Ans. 1·67]

HINTS FOR DIFFICULT PROBLEMS

4. $[H_2SO_4] = \frac{0 \cdot 049}{98} \text{ mol L}^{-1} = 5 \times 10^{-4}$ M.

As $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$,

$$[H^+] = 2 \times (5 \times 10^{-4}) = 10^{-3} \text{ M}$$

6. $[HA] = \frac{13 \cdot 5}{135 \times 10} \text{ mol L}^{-1} = 10^{-2}$ M.

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

8. $N_1V_1 = N_2V_2$, $25 \times 1/100 = N_2 \times 500$

or $N_2 = 5 \times 10^{-4}$ N

$$[H^+] = [HCl] = 5 \times 10^{-4} \text{ M}$$

$$pH = -\log(5 \times 10^{-4})$$
$$= 4 - \log 5 = 4 - 0 \cdot 6990 = 3 \cdot 301.$$

TYPE III. On the calculation of pH of completely ionized alkalies

EXAMPLE 1. *Calculate the pH of N/1000 sodium hydroxide solution assuming complete ionization* ($K_w = 1.0 \times 10^{-14}$).

Solution. NaOH completely ionizes as

$$NaOH \longrightarrow Na^+ + OH^-$$

$$\therefore \quad [OH^-] = [NaOH] = \frac{N}{1000}$$
$$= 10^{-3} \text{ N} = 10^{-3} \text{ M}$$

($\because$ Eq. mass = Mol. mass in case of NaOH)

Now as $[H_3O^+][OH^-] = 10^{-14}$

$$\therefore [H_3O^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-3}} = 10^{-11}$$

$$\therefore pH = -\log [H_3O^+]c = -\log 10^{-11} = 11$$

EXAMPLE 2. *4.0 g of NaOH are dissolved per litre. Find (i) molarity of the solution (ii) OH^- ion concentration (iii) pH value of the solution (At. masses : Na = 23, O = 16, H = 1).*

Solution. (*i*) *Calculation of molarity :*

Mass of NaOH dissolved = 4.0 g/litre

Mol. mass of NaOH = 40

$\therefore$ Molarity of the solution

$$= \frac{\text{Strength in g/ litre}}{\text{Mol. mass}} = \frac{4 \cdot 0}{40} = 0 \cdot 1 \text{ M}$$

(*ii*) *Calculation of the OH^- ion conc.*

NaOH completely ionizes as

$$NaOH \longrightarrow Na^+ + OH^-$$

$$\therefore [OH^-] = [NaOH] = 0.1 \text{ M} = 10^{-1} \text{ M}$$

(*iii*) *Calculation of pH :*

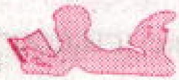
We know that

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$\therefore [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \cdot 0 \times 10^{-14}}{10^{-1}}$$
$$= 10^{-13} \text{ M}$$

$$\therefore \quad pH = -\log [H_3O^+]$$
$$= -\log 10^{-13} = 13.$$

PROBLEMS FOR PRACTICE



1. Calculate the pH value of (a) 0.0001 M NaOH (*b*) 0.01 M NaOH and (c) 0.04 M NaOH solution at 25°C. [Ans. (*a*) 10 (*b*) 12 (*c*) 12.60]

2. Calculate the pH of a solution containing 2 g caustic soda/litre of water. [Ans. 12.699]

3. How many grams of sodium hydroxide must be dissolved in one litre of water to prepare its N/10 solution ? What will be its pH value ? [Ans. 4 g, 13]

4. Calculate the pH of the following solutions :

Base	**Amount dissolved**	**Volume of sol. made**
(*a*) TlOH	2 *g*	2 L
(*b*) $Ca(OH)_2$	0·3 *g*	500 *m*L
(*c*) NaOH	0·3 *g*	200 *m*L

(Atomic masses : Tl = 204, Ca = 40, Na = 23)

(N.C.E.R.T.) [Ans. **(*a*) 11·70 (*b*) 12·21 (*c*) 12·57]**

5. The solubility of $Sr(OH)_2$ at 298K is 19·23 *g*/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution. (Atomic mass of Sr = 87 cdot 6) *(N.C.E.R.T.)*

[Ans. **$[Sr^{2+}]$ = 0·1581 M, $[OH^-]$ = 0·3162 M, pH = 13·50]**

6. If 0·561 *g* KOH is dissolved in water to give 200 mL of solution at 298 K, calculate the concentration of potassium, hydrogen and hydroxyl ions. What is its pH ? *(N.C.E.R.T.)*

[Ans. **$[K^+] = [OH^-]$ = 0·05 M, $[H^+] = 2{\cdot}0 \times 10^{-13}$ M]**

HINTS FOR DIFFICULT PROBLEMS

2. $[NaOH] = \frac{2}{40} \text{ mol L}^{-1} = 5 \times 10^{-2}$ M

i.e. $[OH^-] = 5 \times 10^{-2}$ M

$$\therefore \quad [H_3O^+] = \frac{10^{-14}}{5 \times 10^{-2}} = 2 \times 10^{-13}.$$

$$pH = -\log(2 \times 10^{-13})$$

3. For 1 L of 1 N NaOH solution, NaOH dissolved = 1 g eq. = 40 g

∴ For 1 L of N/10 NaOH sol., NaOH dissolved

$$= 40 \times \frac{1}{10} = 4\ g$$

$[OH^-] = 10^{-1}$ M

$\therefore\ [H_3O^+] = 10^{-13}$ M.

$$pH = -\log 10^{-13} = 13$$

4. (*b*) Molarity of $Ca(OH)_2$ sol.

$$= \frac{0{\cdot}3}{74} \times \frac{1000}{500} = 8{\cdot}11 \times 10^{-3}$$

$$[OH^-] = 2 \times [Ca(OH)_2] = 16{\cdot}22 \times 10^{-3}$$

$$\therefore \quad pOH = -\log(16{\cdot}22 \times 10^{-3})$$
$$= 3 - 1{\cdot}2101 = 1{\cdot}79$$

$$\therefore \quad pH = 14 - pOH = 14 - 1{\cdot}79 = 12{\cdot}21.$$

6. $[KOH] = \frac{0{\cdot}561}{56} \times \frac{1000}{200}\ M = 0{\cdot}050\ M$

As KOH $\longrightarrow K^+ + OH^-$,

$\therefore \quad [K^+] = [OH^-] = 0{\cdot}05$ M

$$[H^+] = K_w/[OH^-]$$
$$= 10^{-14}/0{\cdot}05 = 10^{-14}/(5 \times 10^{-2})$$
$$= 2{\cdot}0 \times 10^{-13}\ M.$$

TYPE IV. On the calculation of pH of acids and bases not completely ionized

EXAMPLE 1. *Calculate the pH of a 0.01 N solution of acetic acid. K_a for CH_3COOH is 1.8×10^{-5} at 25°C.*

Solution. CH_3COOH ionizes as

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

Applying the law of chemical equilibrium, we get

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

But $[CH_3COO^-] = [H_3O^+]$

$$\therefore \quad K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

[∵ one molecule of CH_3COOH gives one CH_3COO^- ion and one H^+ ion or H_3O^+ ion]

or $\quad [H_3O^+] = \sqrt{K_a\ [CH_3COOH]}$

But $\quad K_a = 1{\cdot}8 \times 10^{-5}$

and $\quad [CH_3COOH] = 0{\cdot}01\ M = 10^{-2}\ M$

$$\therefore \quad [H_3O^+] = \sqrt{(1{\cdot}8 \times 10^{-5}) \times (10^{-2})}$$
$$= \sqrt{1{\cdot}8 \times 10^{-7}} = \sqrt{18 \times 10^{-8}}$$
$$= \sqrt{18} \times 10^{-4} \text{ g ions/litre}$$
$$= 4{\cdot}242 \times 10^{-4} \text{ g ions/litre}$$

$$\therefore \quad pH = -\log[H_3O^+]$$
$$= -\log(4{\cdot}242 \times 10^{-4})$$
$$= -(0{\cdot}6276 - 4) = 3{\cdot}3727 = 3{\cdot}37.$$

• **EXAMPLE 2.** *Calculate the pH of 0.1 M solution of acetic acid if the degree of dissociation of the acid is 0.0132.*

Solution. Acetic acid dissociates as

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

If C moles/litre is the initial concentration and α is the degree of dissociation, we can write

	$CH_3COOH + H_2O$	$\rightleftharpoons$	CH_3COO^-	$+ H_3O^+$
Initial conc.	C			
Conc. at eqm.	$C - C\alpha$		$C\alpha$	$C\alpha$

$$\text{Thus } [H_3O^+] = C \times \alpha$$
$$= 0.1 \times 0.0132$$
$$= 1.32 \times 10^{-3}\ M$$
$$\therefore\ pH = -\log [H_3O^+]$$
$$= -\log (1.32 \times 10^{-3})$$
$$= -\ \log 1.32 +\ \log 10^{-3}$$
$$= -\ 0.1206 - 3$$
$$= \mathbf{2.8794.}$$

EXAMPLE 3. *Calculate the pH of 10^{-3} M aniline solution. Given that its ionization constant, $K_b = 4 \cdot 27 \times 10^{-10}$. Also calculate its degree of ionization and ionization constant of its conjugate acid.*

Solution.

	$C_6H_5NH_2 + H_2O$	$\rightleftharpoons$	$C_6H_5NH_3^+$	$+ OH^-$
Initial	C mol L^{-1}			
After disso.	$C - x \simeq C$		x	x

$$K_b = \frac{x^2}{C}$$
$$\text{or } x = \sqrt{K_b \times C} = \sqrt{(4 \cdot 27 \times 10^{-10})\,(10^{-3})}$$
$$= 6 \cdot 53 \times 10^{-7}$$
$$\text{i.e. } [OH^-] = 6 \cdot 53 \times 10^{-7}\ M$$
$$\therefore [H^+] = K_w/[OH^-] = 10^{-14}/(6 \cdot 53 \times 10^{-7})$$
$$= 1 \cdot 53 \times 10^{-8}\ M$$
$$pH = -\log [H^+]$$
$$= -\log (1 \cdot 53 \times 10^{-8}) = \mathbf{7 \cdot 81}$$
$$\text{Degree of ionization } (\alpha) = \sqrt{K_b \times C}$$
$$= \sqrt{(4 \cdot 27 \times 10^{-10}) \times 10^{-3}}$$
$$= 6 \cdot 53 \times 10^{-4}$$
$$\left(\text{or directly } \alpha = \frac{x}{C} = \frac{6 \cdot 53 \times 10^{-7}}{10^{-3}} = 6 \cdot 53 \times 10^{-4}\right)$$
$$K_a = K_w/K_b = 10^{-14}/(4 \cdot 27 \times 10^{-10})$$
$$= \mathbf{2 \cdot 34 \times 10^{-5}.}$$

PROBLEMS FOR PRACTICE

1. Acetic acid has a dissociation constant of 1.8×10^{-5}. Calculate the pH value of the decinormal solution of acetic acid. **[Ans. 2.87]**
2. A 0.05 N solution of acetic acid is found to be 1.9% ionized at 25°C. Calculate (*i*) K_a for acetic acid and (*ii*) the pH of the solution. **[Ans. (i) 1.8×10^{-5} (ii) 3.0223]**
3. Calculate the pH value of a solution of 0.1 M NH_3 ($K_b = 1.8 \times 10^{-5}$) **[Ans. 11·12]**
4. A sample of sour milk was found to be 0.1 M solution of lactic acid $CH_3CH(OH)COOH$. What is the pH of the sample of milk ? K_a for lactic acid at 25°C is 1.37×10^{-4}. **[Ans. 2.43]**
5. Calculate the pH of 0.15 M solution of hypochlorous acid HClO ($K_a = 9 \cdot 6 \times 10^{-7}$). **[Ans. 3.42]**

HINTS FOR DIFFICULT PROBLEMS

2. Amount of acetic acid dissociated
$= 0.05 \times 1.9 / 100 = 0.00095$
∴ Concs. at equilibrium :
$[CH_3COOH] = 0.05 - 0.00095$ M.
$[CH_3COO^-] = [H^+] = 0.00095$ M

3. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[OH^-]^2}{[NH_3]}$$
$$\therefore [OH^-] = \sqrt{K_b \times [NH_3]}$$
$$[H^+] = \frac{K_w}{[OH^-]},\ pH = -\log [H^+]$$

TYPE V. On the calculation of pH of mixtures of acids and bases

• EXAMPLE 1. *What would be the pH of a solution obtained by mixing 100 ml of 0.1 N HCl and 9.9 ml of 1.0 N NaOH solution ?*

Solution. Vol. of 0.1 N HCl taken = 100 ml

Vol. of NaOH mixed = 9.9 ml of 1.0 N

= 99 ml of 0.1 N

∴ Amount of HCl left unneutralized

= (100 – 99) ml of 1.0 N = 1 ml of 0.1 N

As the total volume of the solution after mixing = 100 + 9.9 ml = 109.9 ml ≃ 110 ml, it means that 1 ml of 0.1 N HCl has been diluted 110 times

∴ Conc. of HCl in the solution after mixing

$$= 0.1/110 = 9.09 \times 10^{-4}\ \text{M}$$

As HCl completely ionizes as

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$\therefore \quad [H_3O^+] = [HCl] = 9.09 \times 10^{-4}\ \text{M}$$

$$\begin{aligned} pH &= -\log [H_3O^+] \\ &= -\log (9.09 \times 10^{-4}) \\ &= -[\log 9.09 + \log 10^{-4}] \\ &= -[0.9546 - 4] \\ &= 3.0454 = \mathbf{3.05} \end{aligned}$$

Alternatively, 100 ml of 0·1 N HCl

= 100 × 0·1 milli eq. = 10 milli eq.

9·9 ml of 1 N NaOH

= 9·9 × 1 milli eq. = 9·9 milli eq.

∴ HCl left unneutralized

= 10 – 9·9 = 0·1 milli eq.

Volume of solution = 100 + 9·9 = 109·9 ml

∴ Normality of HCl in resulting solution

$$= \frac{0 \cdot 1}{109 \cdot 9} \approx \frac{0 \cdot 1}{110} = 0 \cdot 09 \times 10^{-4}\ \text{N}$$

$$= 9 \cdot 09 \times 10^{-4}\ \text{M}$$

• EXAMPLE 2. *Calculate the pH of a solution obtained by mixing equal volumes of the solutions with pH = 3 and pH = 5.*

Solution. pH = 3 means $[H^+] = 10^{-3}$ M and pH = 5 means $[H^+] = 10^{-5}$ M. On mixing equal volumes, in the final solution,

$$[H^+] = (10^{-3} + 10^{-5})/2$$

$$= \frac{10^{-3}(1 + 10^{-2})}{2} = \frac{1 \cdot 01 \times 10^{-3}}{2}$$

$$= 0 \cdot 505 \times 10^{-3}\ \text{M} = 5 \cdot 05 \times 10^{-4}\ \text{M}$$

$$\therefore \quad pH = -\log (5 \cdot 05 \times 10^{-4}) = 4 - 0 \cdot 7033$$

$$\approx \mathbf{3 \cdot 3}$$

EXAMPLE 3. *Equal volumes of solutions with pH = 4 and pH = 10 are mixed. Calculate the pH of the resulting solution ?*

Solution. pH = 4 means $[H^+] = 10^{-4}$ M and pH = 10 means $[H^+] = 10^{-10}$ M

or $[OH^-] = 10^{-4}$ M. Thus they will exactly neutralise each other and pH of the resulting solution will be = 7.

• EXAMPLE 4. *Calculate the pH of the solution obtained by mixing 100 cm³ of solution with pH = 3 with 400 cm³ of solution with pH = 4.*

Solution. 100 cm³ of solution with pH = 3 contains $H^+ = \frac{10^{-3}}{1000} \times 100 = 10^{-4}$ mole

400 cm³ of solution with pH = 4 contains

$$H^+ = \frac{10^{-4}}{1000} \times 400 = 4 \times 10^{-5}\ \text{mole}$$

$$\text{Total } H^+ = 10^{-4} + 4 \times 10^{-5}$$

$$= 10^{-4}(1 + 0 \cdot 4) = 1 \cdot 4 \times 10^{4}.$$

Total volume = 500 cm³

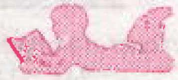
$$\therefore \quad [H^+] = \frac{1 \cdot 4 \times 10^{-4}}{500} \times 1000\ \text{M}$$

$$= 2 \cdot 8 \times 10^{-4}\ \text{M}$$

$$pH = -\log (2 \cdot 8 \times 10^{-4})$$

$$= 4 - 0 \cdot 4472 \approx \mathbf{3 \cdot 55}$$

PROBLEMS FOR PRACTICE



1. Calculate the pH of a solution obtained by mixing 50 ml of 0.2 M HCl with 49.9 ml of 0.2 M NaOH solution [Ans. 3.699]
2. Calculate the pH of a solution obtained by mixing equal volumes of N/10 NaOH and N/20 HCl. [Ans. 12.398]
3. Calculate the pH value of a mixture containing 50 ml of 1 N HCl and 30 ml of 1 N NaOH solution, assuming both to be completely dissociated. [Ans. 0.6021]
4. A 50 ml solution of pH = 1 is mixed with 50 ml solution of pH = 2. What will be the pH of the mixture ? [Ans. 1·26]

HINTS FOR DIFFICULT PROBLEMS

1. 49·9 ml of 0·2 M NaOH will neutralise 49·9 ml of 0·2 M HCl. Hence HCl left unneutralised = 0·1 ml of 0·2 M. Volume after mixing = 99·9 ml = 100 ml. Hence applying $N_1V_1 = N_2V_2$, $0·1 \times 0·2 = N_2 \times 100$ or $N_2 = 2 \times 10^{-4}$. In the final solution, $[HCl] = 2 \times 10^{-4}$ M

   i.e. $[H_3O^+] = 2 \times 10^{-4}$ M.

2. Suppose 1 L of N/10 NaOH is mixed with 1 L of N/20 HCl.

   1 L of N/10 NaOH contains NaOH

   $$= \frac{1}{10} \text{ g eq.} = 0·1 \text{ g eq.}$$

   1 L of N/20 HCl contains HCl

   $$= \frac{1}{20} \text{ g eq.} = 0·05 \text{ g eq.}$$

   0·05 g eq. of HCl will neutralise 0·05 g eq. of NaOH.

   ∴ NaOH left unneutralised = 0·05 g eq.

   Volume of solution = 2 L

   ∴ Concentration of NaOH in the final solution

   $$= \frac{0·05}{2} \text{ g eq L}^{-1} = 0·025 \text{ N}$$

   $[NaOH] = [OH^-] = 0·025 \text{ M} = 2·5 \times 10^{-2}$

   ∴ $[H_3O^+] = 10^{-14} / (2·5 \times 10^{-2})$

   $= 4 \times 10^{-13}$ M

4. In the mixture, $[H^+] = (10^{-1} + 10^{-2}) / 2$

   $$= \frac{0·11}{2} = 0·055 = 5·5 \times 10^{-2}$$

   $pH = -\log (5·5 \times 10^{-2}) = 2 - 0·74 = 1·26$

TYPE VI. On the calculation of pH of water from its ionic product

• EXAMPLE. *The value of K_w is 9.55×10^{-14} at a certain temperature. Calculate the pH of water at this temperature.*

Solution. Here we are given

$K_w = 9.55 \times 10^{-14}$

Now, as for water $[H_3O^+] = [OH^-]$

∴ $K_w = [H_3O^+]\,[OH^-]$

$= [H_3O^+]\,[H_3O^+] = [H_3O^+]^2$

i.e. $[H_3O^+]^2 = 9.55 \times 10^{-14}$

or $[H_3O^+] = \sqrt{9·55 \times 10^{-14}}$

$= [H_3O^+]\,[OH^-]$

$= [H_3O^+]\,[H_3O^+] = [H_3O^+]^2$

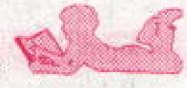
$= 3·09 \times 10^{-7}$ M

∴ $pH = -\log [H_3O^+]$

$= -\log (3·09 \times 10^{-7})$

$= -[\log 3·09 + \log 10^{-7}]$

$= -[0·49 - 7] = 6·51.$



PROBLEMS FOR PRACTICE

1. The value of K_w at a certain temperature is 6.25×10^{-14}. Calculate the pH of water. [Ans. 6.6021]

2. The ionic product of water at 310 K is $2·7 \times 10^{-14}$. What is the pH of neutral water at this temperature ? *(N.C.E.R.T.)* [Ans. 6·78]

TYPE VII. On the calculation of H^+ ion conc. or OH^- ion conc. or ionization constant (K_a or K_b) from given value of pH.

EXAMPLE 1. *Calculate the H_3O^+ ion concentration of a solution having pH 6.58.*

Solution. $pH = -\log [H_3O^+]$

∴ $\log [H_3O^+] = -pH$

$= -6.58$ {pH = 6.58, given}

∴ $[H_3O^+] = \text{antilog} (-6.58)$

$= \text{antilog } \bar{7}.42$

$= 2.63 \times 10^{-7}$ g ions/litre

EXAMPLE 2. *Calculate the mass of HCl to be dissolved per litre of the solution so that its pH value is 1.301.*

Solution. $pH = -\log [H_3O^+]$

$$\therefore \quad \log[H_3O^+] = -pH = -1.301$$

$$[H_3O^+] = \text{antilog}(-1.301)$$

$$= \text{antilog}(\bar{2}.699)$$

$$= 5.0 \times 10^{-2} \text{ g ions/litre}$$

But $[H_3O^+]$ ions are obtained from HCl by its complete ionization as

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$\therefore \quad HCl = [H_3O^+] = 5.0 \times 10^{-2} \text{ M}$$

Molar mass of HCl = 36.5 g mol^{-1}

$\therefore$ 5.0×10^{-2} M HCl

$$= (5.0 \times 10^{-2}) \times 36.5 \text{ g of HCl/lire}$$

$$= \mathbf{1.825\ g/litre}$$

EXAMPLE 3. *How many grams of NaOH must be dissolved in one litre of the solution to give it a pH value of 12 ?*

Solution. $pH = -\log[H_3O^+]$

$$\therefore \quad \log[H_3O^+] = -pH = -12$$

$$\therefore \quad [H_3O^+] = \text{antilog}(-12)$$

$$= \text{antilog}(\bar{1}\bar{2})$$

$$= 10^{-12} \text{ g ions/litre}$$

But we know that

$$[H_3O^+]\,[OH^-] = K_w = 10^{-14}$$

$$\therefore \quad [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{10^{-12}}$$

$$= 10^{-2} \text{ g ions/litre}$$

Since NaOH is a strong electrolyte, it undergoes complete ionization as

$$NaOH \longrightarrow Na^+ + OH^-$$

$$\therefore \quad [OH^-] = [NaOH] = 10^{-2} \text{ M}$$

Mo. mass of NaOH = 40

$\therefore$ Amount of NaOH dissolved per litre

$$= 10^{-2} \times 40 = \mathbf{0.4\ g}$$

• EXAMPLE 4. *The pH of a solution obtained by dissolving 0.1 mole of an acid HA in 100 ml of the aqueous solution was found to be 3.0. Calculate the dissociation constant of the acid.*

Solution. $pH = -\log[H_3O^+]$

$$\therefore \quad \log[H_3O^+] = -pH$$

$$= -3.0 \quad [pH = 3.0, \text{ given}]$$

$$\text{or} \quad [H_3O^+] = \text{antilog}(-3)$$

$$= 10^{-3} \text{ g ions/litre}$$

$$= 0.001 \text{ g ion/litre}$$

Original conc. of the acid HA = 0.1 mole in 100 ml. = 1 mole/litre

HA dissociates as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Initial conc. :	1M	0	0
Conc. at equilibrium :	1–0.001M	0.001M	0.001M

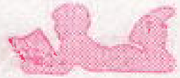
$\therefore$ Dissociation constant (K) will be given by

$$K = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{0{\cdot}001 \times 0{\cdot}001}{1 - 0{\cdot}001} = \frac{10^{-6}}{1} = \mathbf{10^{-6}}$$

(Neglecting 0·001 in comparison to 1)

PROBLEMS FOR PRACTICE



1. Calculate the H_3O^+ ion concentration of a solution having a pH of 10.6. [Ans. **2.512×10^{11} M**]
2. The pH of blood serum is 7.4. What is the hydrogen ion concentration of blood serum ? [Ans. **4×10^{-8} M**]
3. Urine has a pH of 6.0. If a patient eliminates 1300 ml of urine per day, how many gram equivalents of the acid he eliminates per day ? [Ans. **1.3×10^{-6} g equivalents**]
4. A sample of fresh apple juice has a pH of 3.76. Calculate $[H^+]$. [Ans. **1.74×10^{-4}**]
5. Lemon juice has a pH = 2.1. If all the acid in lemon is citric acid (H Cit. $\rightleftharpoons H^+ + Cit^{-1}$) and K_a for citric acid is 8.4×10^{-4} mole/litre, what is the concentration of citric acid in lemon juice ? [Ans. **7.5×10^{-2} M**]
6. Calculate the dissociation constant of an acid, 1 M solution of which has a pH value of 4. [Ans. **10^{-8}**]
7. The pH of 0.1 M solution of an organic acid is 3.0. Calculate the dissociation constant of the acid. [Ans. **10^{-5}**]

PRACTICE PROBLEMS CONTD.

8. 0·01 M solution of an organic acid is found to have a pH of 4·15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

[Ans. $[A^-] = 7 \cdot 08 \times 10^{-5}$ M, $K_a = 5 \cdot 08 \times 10^{-7}, pK_a = 6 \cdot 29$]

9. The pH of 0·005 M codeine ($C_{18}H_{21}NO_3$) solution is 9·95. Calculate its ionization constant and pK_b.

[Ans. $K_b = 1 \cdot 6 \times 10^{-6}, pK_b = 5 \cdot 8$]

10. The pH of 0·1 M solution of cyanic acid (HCNO) is 2·34. Calculate the ionization constant of the acid and its degree of ionization in the solution. *(N.C.E.R.T.)*

[Ans. $K_a = 2 \cdot 09 \times 10^{-4}, \alpha = 0 \cdot 0457$]

11. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below :

(*a*) Human muscle-fluid, 6·83
(*b*) Human stomach fluid, 1·2
(*c*) Human blood, 7·38
(*d*) Human saliva, 6·4 *(N.C.E.R.T.)*

[Ans. (*a*) $1 \cdot 48 \times 10^{-7}$ M (*b*) 0·063 (*c*) $4 \cdot 17 \times 10^{-8}$ M (*d*) $3 \cdot 98 \times 10^{-7}$]

HINTS FOR DIFFICULT PROBLEMS

3. *p*H = 6·0 means $[H_3O^+] = 10^{-6}$ M

i.e. $[\text{Acid}] = 10^{-6}\text{ M} = 10^{-6}\text{ N}$

Thus 1000 ml of the urine contain acid

$= 10^{-6}$ *g* eq.

∴ 1300 ml of the urine will contain acid

$= 1 \cdot 3 \times 10^{-6}$ *g* eq.

5. *p*H = 2·1 *i.e.* $-\log[H^+] = 2 \cdot 1$

or $\log[H^+] = -2 \cdot 1 = \bar{3} \cdot 9$

or $[H^+] = 7 \cdot 943 \times 10^{-3}$

$$\text{HCit} \rightleftharpoons H^+ + \text{Cit}^{-1}$$

$$K_a = \frac{[H^+][\text{Cit}^{-1}]}{[\text{HCit}]}$$

$$8 \cdot 4 \times 10^{-4} = \frac{(7 \cdot 943 \times 10^{-3})(7 \cdot 943 \times 10^{-3})}{[\text{H Cit}]}$$

or $[\text{H Cit}] = 7 \cdot 5 \times 10^{-2}$ M

6. *p*H = 4 means $[H^+] = 10^{-4}$ M

$$\begin{array}{lccccc} & \text{HA} & \rightleftharpoons & H^+ & + & A^- \\ \text{At eqm} & 1 - 10^{-4} \approx 1\text{ M} & & 10^{-4}\text{ M} & & 10^{-4}\text{ M} \end{array}$$

$$K_a = \frac{10^{-4} \times 10^{-4}}{1} = 10^{-8}$$

7. $$\text{RCOOH} \rightleftharpoons \text{RCOO}^- + H^+$$

$[H^+] = [\text{RCOO}^-] = 10^{-3}$ M (∵ *p*H = 3)

$[\text{RCOOH}] = 0 \cdot 1 - 10^{-3} \approx 0 \cdot 1$ M

$$K_a = \frac{[\text{RCOO}^-][H^+]}{[\text{RCOOH}]} = \frac{10^{-3} \times 10^{-3}}{0 \cdot 1} = 10^{-5}.$$

8. pH = 4·15 means — $\log[H^+] = 4 \cdot 15$

or $\log[H^+] = -4 \cdot 15 = \bar{5} \cdot 85$

or $[H^+] = 7 \cdot 08 \times 10^{-5}$ M

$$\text{HA} \rightleftharpoons H^+ + A^-$$

Hence at equilibrium

$$[H^+] = [A^-] = 7 \cdot 08 \times 10^{-5}\text{ M}$$
$$= 7 \cdot 1 \times 10^{-5}\text{ M}$$

$[\text{HA}] = (0 \cdot 01 - 7 \cdot 1 \times 10^{-5})$
$= (0 \cdot 01 - 0 \cdot 000071)\text{ M} = 0 \cdot 009929$ M

$$K_a = \frac{[H^+][A^-]}{[\text{HA}]}$$
$$= \frac{(7 \cdot 1 \times 10^{-5})^2}{9 \cdot 929 \times 10^{-3}} = 5 \cdot 08 \times 10^{-7}$$

$pK_a = -\log K_a = -\log(5 \cdot 08 \times 10^{-7}) = 6 \cdot 29.$

9. Codeine + water $\rightleftharpoons$ codenium ion + OH^-

From given pH, $[H^+] = 1 \cdot 12 \times 10^{-10}$ M

∴ $[OH^-] = K_w/[H^+] = 8 \cdot 93 \times 10^{-5}$ M

$$K_b = \frac{[B^+][OH^-]}{[\text{BOH}]}$$
$$= \frac{(8 \cdot 93 \times 10^{-5})^2}{0 \cdot 005} = 1 \cdot 6 \times 10^{-6}.$$

10. $$\text{HCNO} \rightleftharpoons H^+ + \text{CNO}^-$$

pH = 2·34 means $-\log[H^+] = 2 \cdot 34$

or $\log[H^+] = -2 \cdot 34 = \bar{3} \cdot 66$

or $[H^+] = \text{Antilog } \bar{3} \cdot 66 = 4 \cdot 57 \times 10^{-3}$ M

$[\text{CNO}^-] = [H^+] = 4 \cdot 57 \times 10^{-3}$ M

$$K_a = \frac{(4 \cdot 57 \times 10^{-3})(4 \cdot 57 \times 10^{-3})}{0 \cdot 1} = 2 \cdot 09 \times 10^{-4}$$

$$\alpha = \sqrt{K_a/C} = \sqrt{2 \cdot 09 \times 10^{-4}/0 \cdot 1} = 0 \cdot 0457.$$

TYPE VIII. pH of very dilute acid or alkali solutions

EXAMPLE 1. *Calculate the pH of 10^{-8} M acid solution.*

Solution. **Note.** At the first instance, it appears that as $[H^+] = 10^{-8}$, therefore pH should be 8. But pH cannot be 8 but should be less than 7 because the solution is acidic. The reason is that from H_2O, $[H^+] = 10^{-7}$ M which cannot be neglected in comparison to 10^{-8} M. The pH can be calculated as follows : –

From acid, $[H^+] = 10^{-8}$ M

From H_2O, $[H^+] = 10^{-7}$ M

$$\therefore \quad \text{Total } [H^+] = 10^{-8} + 10^{-7}$$
$$= 10^{-8}(1 + 10)$$
$$= 11 \times 10^{-8} \text{ M}$$

$$\therefore \quad pH = -\log [H^+] = -\log (11 \times 10^{-8})$$
$$= -[\log 11 + \log 10^{-8}]$$
$$= -[1{\cdot}0414 - 8]$$
$$= 6{\cdot}9586 \approx \mathbf{6{\cdot}96}$$

EXAMPLE 2. *Calculate the pH of 10^{-10} M NaOH solution.*

Solution. $[OH^-]$ from NaOH $= 10^{-10}$ M

$[OH^-]$ from $H_2O = 10^{-7}$ M

Total $[OH^-] = 10^{-10} + 10^{-7}$

$$= 10^{-7}(10^{-3} + 1) = 1{\cdot}001 \times 10^{-7} \text{ M}$$

$$\therefore pOH = -\log (1{\cdot}001 \times 10^{-7})$$
$$= 7 - \log 1{\cdot}001 = 7 - 0{\cdot}0004 = 6{\cdot}9986$$

or $pH = 14 - 6{\cdot}9996 = 7{\cdot}0004$

TYPE IX. pH on dilution

• EXAMPLE 1. *An acid having pH = 6 is diluted 1000 times. What will be the pH of the final solution ?*

Solution. pH = 6 means $[H_3O^+] = 10^{-6}$.

After diluting 1000 times,

$$[H_3O^+] = 10^{-6}/1000 \text{ M} = 10^{-9} \text{ M}.$$

$\therefore$ $[H_3O^+]$ from H_2O cannot be neglected.

$$\text{Total } [H_3O^+] = 10^{-9} + 10^{-7}$$
$$= 10^{-7}(10^{-2} + 1) = 10^{-7}(1{\cdot}01)$$

$$\therefore \quad pH = -\log (1{\cdot}01 \times 10^{-7}) = 7 - 0{\cdot}0043$$
$$= \mathbf{6{\cdot}9957.}$$

• EXAMPLE 2. *1 cm³ of 0·01 N HCl is added to one litre of sodium chloride solution. What will be the pH of the resulting solution ?*

Solution. As NaCl solution is neutral, it simply dilutes the HCl solution from 1 cc to 1000 cc.

Now $[H^+] = 0{\cdot}01/1000 = 10^{-5}$ M

$$\therefore \quad pH = 5.$$

PROBLEMS FOR PRACTICE

1. 10^{-6} M NaOH solution is diluted 1000 times. Calculate the *p*H of the diluted base. [Ans. 7·0454]
2. What will be the *p*H of the resulting solution if to a 100 ml of HCl solution of *p*H = 1·0, 900 ml of distilled water is added ? [Ans. 2·0]
3. The *p*H of a solution is 5. Its hydrogen ion concentration is increased 100 times. What is the *p*H of the resulting solution ? [Ans. 3·0]

HINTS FOR DIFFICULT PROBLEMS

1. After dilution, $[OH^-] = 10^{-8}$ M. Hence $[OH^-]$ from H_2O cannot be neglected.
2. 100 ml has been diluted to 1000 ml. Hence dilution = 10 times. Now $[H^+] = 10^{-1}/10 = 10^{-2}$ M

   $\therefore$ pH = 2
3. pH = 5 means $[H^+] = 10^{-5}$ M. On increasing 100 times, new $[H^+] = 10^{-3}$ M. So *p*H = 3.

ADD TO YOUR KNOWLEDGE

1. For a neutral solution, $pH = 7$ at 298 K (25°C). With increase in temperature, as dissociation of H_2O molecules increases *i.e.* $[H^+]$ and $[OH^-]$ increase, so the ionic product increases with increase of temperature. Further, as $[H^+]$ increases, pH decreases with increase of temperature.

   A few interesting results are given below :

   (*i*) At 273 K (0°C), $K_w = 10^{-15}$ so that *p*H of neutral solution at this temperature = 7·5 and *p*H scale is 0 to 15.

   (*ii*) At 333 K (60°C), $K_w = 10^{-13}$, *p*H of neutral solution = 6·5 and *p*H range is 0 to 13.

   (*iii*) At the temperature of the human body which is nearly 37°C, *p*H of neutral solution = 6·8.

2. *p*H values of a few common substances are given below :

Saturated NaOH sol.	~ 15	Black coffee	5·0
0·1 M NaOH sol.	13	Tomato juice	~ 4·2
Lime water, $Ca(OH)_2$	10·5	Vinegar and Soft drinks	~ 3
Milk of magnesia, $Mg(OH)_2$	10	Lemon juice	~ 2·2
Sea water and white of egg	7·8	Gastric juice	~ 1·2
Human blood and Tears	7·4	1 M HCl sol.	~ 0
Milk	6·8	Conc. HCl	~ – 1·0
Human saliva	6·4		

3. *p*H is inversely related to the acidity of a solution. As acidity increases, *p*H decreases.

4. *p*H of the solution of a weak acid or a weak base depends upon its degree of ionization (α). The relationship may be derived as follows taking the example of weak acid HA

$$\begin{array}{llll} & HA & \rightleftharpoons & H^+ + A^- \\ \text{Initial conc.} & C & & \\ \text{Conc. at eqm.} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$[H^+] = C\alpha \quad \therefore \quad pH = -\log[H^+] = -\log C\alpha. \quad \text{But} \quad K_a = C\alpha^2 \quad \text{or} \quad C = K_a/\alpha^2$$

$$\therefore \ pH = -\log(K_a/\alpha)$$

8.10. Salt Hydrolysis

8.10.1. Definition and Examples

Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.

$$\text{Salt} + \text{Water} \longrightarrow \text{Acid} + \text{Base}$$

$$\text{or} \quad \underset{\text{Salt}}{BA} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Acid}}{HA} + \underset{\text{Base}}{BOH}$$

Thus *salt hydrolysis may be considered as reverse of neutralization.*

All salts are strong electrolytes and thus ionize completely in the aqueous solution. If the acid (HA) produced is strong and the base (BOH) produced is weak, we can write the above equation as

$$B^+ + A^- + H_2O \longrightarrow H^+ + A^- + BOH$$

$$\text{or} \quad B^+ + H_2O \longrightarrow H^+ + BOH$$

Thus, in this case the cation reacts with water to give an acidic solution. This is called **cationic hydrolysis.**

Again, if the acid produced is weak and the base produced is strong, we can write

$$B^+ + A^- + H_2O \longrightarrow HA + B^+ + OH^-$$

or $$A^- + H_2O \longrightarrow HA + OH^-$$

Here, the anion reacts with water to give the basic solution. This is called **anionic hydrolysis.**

Hence salt hydrolysis may be defined as the reaction of the cation or the anion of the salt with water to produce acidic or basic solution.

Thus depending upon the relative strengths of the acid and the base produced, the resulting solution is acidic, basic or neutral. On this basis, the salts are divided into four categories :

I. Salts of strong acids and strong bases : Examples are :

$NaCl$, $NaNO_3$, Na_2SO_4, KCl, KNO_3, K_2SO_4

As an illustration, let us discuss the hydrolysis of NaCl. We may write :

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

or $$Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^-$$

or $$H_2O \longrightarrow H^+ + OH^-$$

Thus it involves only ionization and no hydrolysis. Further in the resulting solution, $[H^+] = [OH^-]$. So the solution is **neutral.** Hence it can be generalized that the *salts of strong acids and strong bases* **do not undergo hydrolysis** *and the resulting solution is neutral.*

II. Salts of weak acids and strong bases : Examples are :

CH_3COONa, Na_2CO_3, K_2CO_3, Na_3PO_4 etc.

As an illustration, the hydrolysis of sodium acetate (CH_3COONa) may be represented as follows :

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

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

or $$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

As it produces OH^- ions, the solution of such a salt is **alkaline** in nature.

III. Salts of strong acids and weak bases : Examples are :

NH_4Cl, $CuSO_4$, NH_4NO_3, $AlCl_3$, $CaCl_2$ etc.

As an illustration, the hydrolysis of NH_4Cl may be represented as follows :

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

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

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

As it produces H^+ ions, the solution of such a salt is **acidic** in character.

IV. Salts of weak acids and weak bases : Examples are :

CH_3COONH_4, $(NH_4)_2CO_3$, $AlPO_4$ etc.

As an illustration, the hydrolysis of ammonium acetate may be represented as follows :

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

or $$CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH$$

Thus it involves both anionic and cationic hydrolysis.

The resulting solution may be neutral or slightly acidic or basic depending upon the relative degrees of ionization of the weak acid and the weak base produced. In the present example, the acid (CH_3COOH) and the base (NH_4OH) formed are almost equally weak. Hence the resulting solution is **almost neutral.**

8.10.2. Hydrolysis constant. The general equation for the hydrolysis of a salt (BA) may be written as

$$BA + H_2O \rightleftharpoons HA + BOH$$

Applying the law of chemical equilibrium, we get

$$\frac{[HA]\,[BOH]}{[BA]\,[H_2O]} = K, \text{ the equilibrium constant.}$$

Since water is present in very large excess in the aqueous solution, its concentration $[H_2O]$ may be regarded as constant so that we have

$$\frac{[HA]\,[BOH]}{[BA]} = K\,[H_2O] = K_h$$

where K_h is called the hydrolysis constant.

8.10.3. Degree of Hydrolysis. *The degree of hydrolysis of a salt is defined as the fraction (or percentage) of the total salt which is hydrolysed.*

$$\text{i.e.}\quad h = \frac{\text{No. of moles of the salt hydrolysed}}{\text{Total no. of moles of the salt taken}}$$

8.11. Calculation of Hydrolysis Constant, Degree of Hydrolysis and pH of Salt Solutions

As already explained, salts of strong acid and strong base do not undergo hydrolysis, therefore to talk of K_h or h of such salts is meaningless. The cases of the other three types of salts are discussed below :

I. Salts of weak acid and strong base :

(*a*) **Hydrolysis constant.** Representing the salt by BA as usual, the hydrolysis may be represented as follows :

$$\underset{\substack{\text{Salt}\\ \downarrow}}{BA} + H_2O \rightleftharpoons \underset{\substack{\text{Strong}\\ \downarrow}}{BOH} + \underset{\text{Weak}}{HA}$$

$$\text{or}\quad B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA$$

$$\text{or}\quad A^- + H_2O \rightleftharpoons OH^- + HA$$

i.e. it is a case of *anion hydrolysis*.

The hydrolysis constant K_h for the above reaction will be given by

$$K_h = \frac{[OH^-]\,[HA]}{[A^-]} \qquad \text{...}(i)$$

For the weak acid HA, the dissociation equilibrium is

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

∴ The dissociation constant K_a of the acid HA will be given by

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

Further the ionic product of water, K_w is given by

$$K_w = [H^+]\,[OH^-] \qquad \text{...}(iii)$$

Multiplying equation (*i*) with (*ii*) and dividing by (*iii*), we get

$$\frac{K_h \cdot K_a}{K_w} = \frac{[OH^-]\,[HA]}{[A^-]} \times \frac{[H^+]\,[A^-]}{[HA]} \times \frac{1}{[H^+]\,[OH^-]} = 1$$

$$\text{or}\quad \boxed{K_h = \frac{K_w}{K_a}} \qquad \text{...}(iv)$$

(*b*) **Degree of Hydrolysis.** Suppose the original concentration of the salt in the solution is *c* moles/litre and *h* is its degree of hydrolysis at this concentration. Then we have

$$\begin{array}{lcccc} & A^- + H_2O & \rightleftharpoons & OH^- & + \; HA \\ \text{Original molar conc.} & c & & 0 & 0 \\ \text{Molar conc. at equilibrium} & c\,(1-h) & & ch & ch \end{array}$$

The hydrolysis constant (K_h) will, therefore, be given by

$$K_h = \frac{[OH^-]\,[HA]}{[A^-]} = \frac{ch \,.\, ch}{c\,(1-h)} = \frac{ch^2}{1-h}$$

If *h* is very small as compared to 1, we can take $1 - h = 1$ so that the above expression becomes

$$ch^2 = K_h \quad \text{or} \quad h^2 = \frac{K_h}{c}$$

$$\text{or}\quad \boxed{h = \sqrt{\frac{K_h}{c}}}$$

Substituting the value of K_a from equation (*iv*), we get

$$h = \sqrt{\frac{K_w}{K_a \,.\, c}} \qquad \text{...}(v)$$

(*c*) **pH.** In the present case, we have

$$\begin{array}{lcccc} & A^- + H_2O & \rightleftharpoons & OH^- & + \; HA \\ \text{Original conc. :} & c & & 0 & 0 \\ \text{Conc. at eqm. :} & c\,(1-h) & & ch & ch \end{array}$$

$$\text{i.e.,}\quad [OH^-] = ch$$

$$\therefore\quad [H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

Substituting the value of *h* from equation (*v*), we get

$$[H^+] = \frac{K_w}{c}\sqrt{\frac{K_a \,.\, c}{K_w}}$$

$$\text{or}\quad [H^+] = \sqrt{\frac{K_w \,.\, K_a}{c}}$$

$$\because\quad pH = -\log\,[H^+] = -\log\sqrt{\frac{K_w\,K_a}{c}}$$

$$= -\log\left(\frac{K_w \,.\, K_a}{c}\right)^{1/2}$$

$$\text{or} \quad \boxed{pH = -\frac{1}{2}[\log K_w + \log K_a - \log c]}$$

This equation may be rewritten as

$$pH = \frac{1}{2}[-\log K_w - \log K_a + \log c]$$

$$\text{or} \quad \boxed{pH = \frac{1}{2}[pK_w + pK_a + \log c]}$$

At 298 K, $pK_w = 14$. Hence at 298 K, we have

$$\boxed{pH = 7 + \frac{1}{2}[pK_a + \log c]}$$

Thus knowing the molar concentration c of the solution and the dissociation constant K_a of the weak acid involved, the pH of the solution can be calculated.

II. Salts of strong acid and weak base :

(*a*) **Hydrolysis constant.** For the salt BA, the hydrolysis may be represented as

$$\underset{\underset{\downarrow}{\text{salt}}}{BA} + H_2O \rightleftharpoons \underset{\text{Weak}}{BOH} + \underset{\overset{\text{Strong}}{\downarrow}}{HA}$$

$$\text{or} \quad B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$$

$$\text{or} \quad B^+ + H_2O \rightleftharpoons BOH + H^+$$

i.e., it is a case of *cation hydrolysis*.

The hydrolysis constant K_h will be given by

$$K_h = \frac{[BOH][H^+]}{[B^+]} \quad ...(vii)$$

For the weak base BOH, the dissociation equilibrium is

$$BOH \rightleftharpoons B^+ + OH^-$$

∴ The dissociation constant K_b of the weak base BOH will be given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad ...(viii)$$

The ionic product of water, K_w, is given by

$$K_w = [H^+][OH^-] \quad ...(ix)$$

Multiplying equation (*vii*) with (*viii*) and dividing by (*ix*), we get

$$\frac{K_h K_b}{K_w} = 1$$

$$\text{or} \quad \boxed{K_h = \frac{K_w}{K_b}} \quad ...(x)$$

(*b*) **Degree of Hydrolysis.** Proceeding as in the earlier case, we get the same relationship *viz.*

$$\boxed{h = \sqrt{\frac{K_h}{c}}}$$

Substituting the value of K_h from equation (*x*), we get

$$\boxed{h = \sqrt{\frac{K_w}{K_b c}}} \quad ...(xi)$$

(*c*) **pH.** In this case we have

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

Original conc : c 0   0

Conc. at eqm : $c(1-h)$ ch ch

i.e., $[H^+] = ch$

Substituting the value of h from equation (*xi*), we get

$$[H^+] = c.\sqrt{\frac{K_w}{K_b . c}} = \sqrt{\frac{K_w . c}{K_b}} = \left(\frac{K_w . c}{K_b}\right)^{1/2}$$

$$\therefore \quad pH = -\log[H^+] = -\log\left(\frac{K_w . c}{K_b}\right)^{1/2}$$

$$\text{or} \quad \boxed{pH = -\frac{1}{2}[\log K_w - \log K_b + \log c]} \quad ...(xii)$$

As before, this equation can be rewritten as

$$\boxed{pH = -\frac{1}{2}[pK_w + pK_b + \log c]}$$

At 298 K, $pK_w = 14$. Hence at 298 K, we have

$$\boxed{pH = 7 - \frac{1}{2}[pK_b + \log c]}$$

III. Salts of weak acid and weak base

(*a*) **Hydrolysis constant.** Representing the salt by BA as before, we have

$$\underset{\underset{\downarrow}{\text{Salt}}}{BA} + H_2O \rightleftharpoons \underset{\text{Weak}}{BOH} + \underset{\text{Weak}}{HA}$$

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

i.e., it involves both *anion hydrolysis as well as cation hydrolysis*. Writing the various equations as before, we have

$$K_h = \frac{[BOH]\,[HA]}{[B^+]\,[A^-]} \quad ...(xiii)$$

For the weak acid,

$$HA \rightleftharpoons H^+ + A^-, \text{ so that}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \quad ...(xiv)$$

For the weak base,

$$BOH \rightleftharpoons B^+ + OH^-, \text{ so that}$$

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]} \quad ...(xv)$$

Also, we know that

$$K_w = [H^+]\,[OH^-] \quad ...(xvi)$$

Multiplying equations (*xiii*), (*xiv*), (*xv*) and dividing by equation (*xvi*), we get

$$\frac{K_h \,.\, K_a \,.\, K_b}{K_w} = 1$$

or $$\boxed{K_h = \frac{K_w}{K_a\, K_b}} \quad ...(xvii)$$

(*b*) **Degree of Hydrolysis.** In this case, we have

$$B^+ \; + \; A^- + H_2O \rightleftharpoons BOH + HA$$

Original conc. : c $\quad c$ $\quad 0$ $\quad 0$

Conc. at eqm. : $c\,(1-h)$ $\quad c\,(1-h)$ $\quad ch$ $\quad ch$

$$K_h = \frac{[BOH]\,[HA]}{[B^+]\,[A^-]}$$

$$= \frac{ch\,.\,ch}{c\,(1-h)\,.\,c\,(1-h)} = \frac{h^2}{(1-h^2)} \quad ...(xviii)$$

Here, the relationship between K_h and h does not involve c. Thus the *degree of hydrolysis of such a salt is independent of the concentration of the solution.*

If h is very small in comaprison to 1, we can take $1 - h = 1$ so that equation (*xviii*) becomes

$$K_h = h^2$$

or $$\boxed{h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a . K_b}}} \quad ...(xix)$$

(*c*) **pH.** For the weak acid HA,

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

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

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

$$= K_a \frac{h}{1-h}$$

But from equation (*xviii*),

$$\frac{h}{1-h} = \sqrt{K_h} \text{ so that we have}$$

$$[H^+] = K_a \sqrt{K_h} = K_a \sqrt{\frac{K_w}{K_a . K_b}}$$

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

$$pH = -\log\,[H^+] = -\log \sqrt{\frac{K_a\, K_w}{K_b}}$$

$$= -\log \left(\frac{K_a\, K_w}{K_b} \right)^{1/2}$$

or $$\boxed{pH = -\frac{1}{2}[\log K_a + \log K_w - \log K_b]}$$

or this equation may be written as

$$\boxed{pH = \frac{1}{2}[pK_w + pK_a - pK_b]}$$

or at 298 K, we have

$$\boxed{pH = 7 + \frac{1}{2}[pK_a - pK_b]}$$

PROBLEMS ON THE CALCULATION OF pH OF SALT SOLUTIONS

EXAMPLE 1. *Calculate the hydrolysis constant, degree of hydrolysis and pH of 0·10 M KCN solution at 25°C. For HCN, $K_a = 6{\cdot}2 \times 10^{-10}$.*

Solution. As KCN is a salt of strong base and weak acid,

Hydrolysis constant,

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{6{\cdot}2 \times 10^{-10}} = 1{\cdot}6 \times 10^{-6}$$

Degree of hydrolysis,

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{1{\cdot}6 \times 10^{-5}}{0{\cdot}1}} = 1{\cdot}26 \times 10^{-2}$$

The hydrolysis reaction will be

$$CN^- \; + \; H_2O \rightleftharpoons HCN \; + \; OH^-$$

Initial $\quad c$ M $\quad 0 \quad 0$

At eqm. $\quad c-x \quad x \quad x$

(x = No. of moles of CN^- reacted)

$$K_h = \frac{[HCN]\,[OH^-]}{[CN^-]} = \frac{x \times x}{c - x} \approx \frac{x^2}{c}$$

$$\text{or } x = \sqrt{K_h \times c} = \sqrt{(1{\cdot}6 \times 10^{-5})\,(0{\cdot}1)}$$

$$= 1{\cdot}26 \times 10^{-3}$$

i.e. $[OH^-] = 1{\cdot}26 \times 10^{-3}$

$$\therefore \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1{\cdot}26 \times 10^{-3}}$$

$$= 7{\cdot}94 \times 10^{-12}$$

$$pH = -\log[H^+] = -\log(7{\cdot}94 \times 10^{-12})$$

$$= 12 - 0{\cdot}90 = \mathbf{11{\cdot}1}$$

EXAMPLE 2. *Calculate the pH of 0·10 M solution of NH_4Cl. The dissociation constant (K_b) of NH_3 is $1{\cdot}6 \times 10^{-5}$.*

Solution. As NH_4Cl is a salt of weak base and strong acid,

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1{\cdot}6 \times 10^{-5}} = 6{\cdot}25 \times 10^{-10}$$

The hydrolysis reaction will be

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$\text{or} \quad NH_4^+ \rightleftharpoons NH_3 + H^+$$

Initial conc. c M

At eqm. $c - x$ $\quad x \quad x$

$$K_h = \frac{[NH_3]\,[H^+]}{[NH_4^+]} = \frac{x \times x}{c - x} \approx \frac{x^2}{c}$$

$$\text{or } x = \sqrt{K_h \times c} = \sqrt{(6{\cdot}25 \times 10^{-10}) \times 0{\cdot}1}$$

$$= 7{\cdot}9 \times 10^{-6}\ \text{M}$$

i.e. $[H^+] = 7{\cdot}9 \times 10^{-6}$ M

$$\therefore \quad pH = -\log[H^+] = -\log(7{\cdot}9 \times 10^{-6})$$

$$= 6 - 0{\cdot}90 = \mathbf{5{\cdot}10}$$

Alternatively, applying the formula directly

$$pH = 7 - \frac{1}{2}[pK_b + \log c]$$

$$= 7 - \frac{1}{2}[-\log K_b + \log c]$$

$$= 7 - \frac{1}{2}[-\log(1{\cdot}6 \times 10^{-5}) + \log 0{\cdot}1]$$

$$= 7 - \frac{1}{2}[(5 - 0{\cdot}02041) - 1]$$

$$= \mathbf{5{\cdot}10}$$

EXAMPLE 3. *Calculate the pH of 0·01 M solution of NH_4CN. Given that the dissociation constants are : K_a for HCN = $6{\cdot}2 \times 10^{-10}$ and K_b for $NH_3 = 1{\cdot}6 \times 10^{-5}$.*

Solution. As NH_4CN is a salt of weak acid and weak base

$$K_h = \frac{K_w}{K_a\,K_b} = \frac{10^{-14}}{(6{\cdot}2 \times 10^{-10})\,(1{\cdot}6 \times 10^{-5})} = 1{\cdot}0$$

For such a salt,

$$[H^+] = \sqrt{\frac{K_a\,K_w}{K_b}}$$

$$= \sqrt{\frac{(6{\cdot}2 \times 10^{-10})\,(10^{-14})}{1{\cdot}6 \times 10^{-5}}}$$

$$= \sqrt{3{\cdot}875 \times 10^{-19}}$$

$$= 6{\cdot}22 \times 10^{-10}$$

$$\therefore \quad pH = -\log[H^+] = -\log(6{\cdot}22 \times 10^{-10})$$

$$= 10 - 0{\cdot}79 = \mathbf{9{\cdot}21}$$

Alternatively, applying the formula directly

$$pH = 7 + \frac{1}{2}[pK_a - pK_b]$$

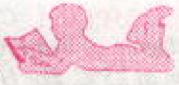
$$= 7 + \frac{1}{2}[-\log K_a + \log K_b]$$

$$= 7 + \frac{1}{2}[-\log(6{\cdot}2 \times 10^{-10}) + \log(1{\cdot}6 \times 10^{-5})]$$

$$= 7 + \frac{1}{2}[(10 - 0{\cdot}7924) + (-5 + 0{\cdot}2041)]$$

$$= \mathbf{9{\cdot}21}$$

PROBLEMS FOR PRACTICE



1. What would be the pH of 0·1 molar sodium acetate solution, given that the dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$ [Ans. **8·87**]
2. The dissociation constant of aniline ($C_6H_5NH_2$) as a base is $5{\cdot}93 \times 10^{-10}$. The ionic product of water at 25°C is $1{\cdot}02 \times 10^{-14}$. Calculate the percentage hydrolysis of aniline hydrochloride in 1·0 N solution at 25°C. Also calculate the pH of the solution. [Ans. **0·415%, 2·38**]
3. At 25°C, the ionisation constant of anilinium hydroxide is $4{\cdot}6 \times 10^{-10}$. Taking ionic product of water as 1×10^{-14}, calculate (a) hydrolysis con-

PRACTICE PROBLEMS CONTD.

stant of anilinium chloride (*b*) the degree of hydrolysis and (*c*) *p*H value of 0·2 molar solution of the salt.

[Ans. (*a*) $2\cdot17 \times 10^{-5}$ (*b*) $3\cdot29 \times 10^{-2}$ (*c*) 3·18]

4. The ionization constant of nitrous acid is $4\cdot5 \times 10^{-4}$. Calculate the *p*H of 0·04 M sodium nitrite solution and also its degree of hydrolysis.

(N.C.E.R.T.) **[Ans. *p*H = 7·97, $\alpha = 2\cdot36 \times 10^{-5}$]**

5. A 0·02 M solution of pyridine hydrochloric has *p*H = 3·44. Calculate the ionization constant of pyridine. *(N.C.E.R.T.)* **[Ans. $1\cdot5 \times 10^{-9}$]**

6. The ionization constant of chloroacetic acid is $1\cdot35 \times 10^{-3}$. What will be the *p*H of 0·1 M acid and its 0·1 M sodium salt solution ? *(N.C.E.R.T.)*

[Ans. 1·94, 7·94]

7. Calculate the *p*H of 0·05 M sodium acetate solution if the pK_a of acetic acid is 4·74. **[Ans. 8·72]**

8. The pK_a of acetic acid and pK_b of ammonium hydroxide are 4·76 and 4·75 respectively. Calculate the hydrolysis constant of ammonium acetate at 298K and also the degree of hydrolysis and *p*H of (*a*) 0·01 M and (*b*) 0·04 M solutions.

[Ans. $K_h = 3\cdot25 \times 10^{-5}$, $h = 5\cdot7 \times 10^{-3}$ and *p*H = 7·005 (same in both cases)]

HINTS FOR DIFFICULT PROBLEMS

1. $$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1\cdot8 \times 10^{-5}} = 5\cdot56 \times 10^{-10}$$

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

$$[OH^-] = \sqrt{K_h \times c}$$
$$= \sqrt{(5\cdot56 \times 10^{-10}) \times 0\cdot1} = 7\cdot46 \times 10^{-6}.$$

$$[H^+] = \frac{10^{-14}}{7\cdot4 \times 10^{-6}} = 1\cdot34 \times 10^{-9}$$

$$pH = -\log(1\cdot34 \times 10^{-9}) = 9 - 0\cdot127$$
$$= 8\cdot873 \approx 8\cdot87$$

2. Aniline hydrochloride ($C_6H_5\overset{+}{N}H_3Cl^-$) is a salt of weak base ($C_6H_5NH_2$) and strong acid (HCl).

$$K_h = \frac{K_w}{K_b} = \frac{1\cdot02 \times 10^{-14}}{5\cdot93 \times 10^{-10}} = 1\cdot72 \times 10^{-5}$$

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

or $$C_6H_5NH_3^+ \rightleftharpoons CH_5NH_2 + H^+$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{1\cdot72 \times 10^{-5}}{1\cdot0}} = 4\cdot15 \times 10^{-3}$$

or $4\cdot15 \times 10^{-3} \times 100\% = 0\cdot415\%$

$$[H^+] = \sqrt{K_h \times c} = \sqrt{1\cdot72 \times 10^{-5} \times 1\cdot0}$$
$$= 4\cdot15 \times 10^{-3}\ M$$

$$pH = -\log(4\cdot15 \times 10^{-3}) = 3 - 0\cdot618$$
$$= 2\cdot382 \approx 2\cdot38$$

4. $$K_h = K_w/K_a = 10^{-14}/(4\cdot5 \times 10^{-4})$$
$$= 2\cdot22 \times 10^{-11}$$

$$h = \sqrt{K_h/c} = \sqrt{2\cdot22 \times 10^{-11}/0\cdot04}$$
$$= \sqrt{5\cdot5 \times 10^{-10}} = 2\cdot36 \times 10^{-5}$$

$$[OH^-] = \sqrt{K_h/c} = \sqrt{(2\cdot22 \times 10^{-11})(0\cdot04)}$$
$$= \sqrt{8\cdot88 \times 10^{-13}} = 9\cdot42 \times 10^{-7}$$

$$pOH = -\log(9\cdot42 \times 10^{-7})$$
$$= 7 - 0\cdot9741 = 6\cdot03$$

$$pH = 14 - pOH = 14 - 6\cdot03 = 7\cdot97.$$

5. Pyridine hydrochloride is a salt of weak base and strong acid. Hence

$$pH = -\frac{1}{2}[\log K_w - \log K_b + \log c].$$

i.e. $$3\cdot44 = -\frac{1}{2}[-14 - \log K_b + \log(2 \times 10^{-2})]$$

or $$6\cdot88 = 14 + \log K_b + 1\cdot70$$

or $$\log K_b = -8\cdot82 = \bar{9}\cdot18$$

or $$K_b = 1\cdot5 \times 10^{-9}.$$

6. $$[H^+] = \sqrt{K_a \times c}$$
$$= \sqrt{1\cdot35 \times 10^{-3} \times 0\cdot1} = 1\cdot16 \times 10^{-2}$$

$$pH = -\log(1\cdot16 \times 10^{-2})$$
$$= 2 - 0\cdot06 = 1\cdot94$$

Sodium salt of chloroacetic acid is a salt of strong base and weak acid. Hence

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log c].$$

8. First calculate K_a and K_b. Then

$$K_b = K_w/(K_a.K_b) \text{ and } h = \sqrt{K_h}.$$

8.12. Acid-base Titration Using Indicator

8.12.1. Definitions

Titration *is the measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant.* As both the reactants are taken in the form of solutions and the titration is the measurement of volume of one solution that must be added to another solution till the reaction is complete, *this method of quantitative analysis is, therefore, called* **volumetric analysis.** Usually the concentration of one of the solutions is known, (called **standard solution**) and it is desired to find the concentration of the other by titration. The apparatus used is shown in Fig. 8.2. A known volume of the solution is taken in the titration flask (with the help of a pipette) and the other solution is taken in the burette which is graduated in cc's and has a stopclock at the bottom to control the amount of flow into the flask. The solution to be titrated (taken in the flask) is called **titrate** and the solution with which the titration is to be done (taken in the burette) is called the **titrant.** *The point at which the required volume of one solution has been added to the other to exactly complete the reaction between the two is called* **end point or equivalence point.**

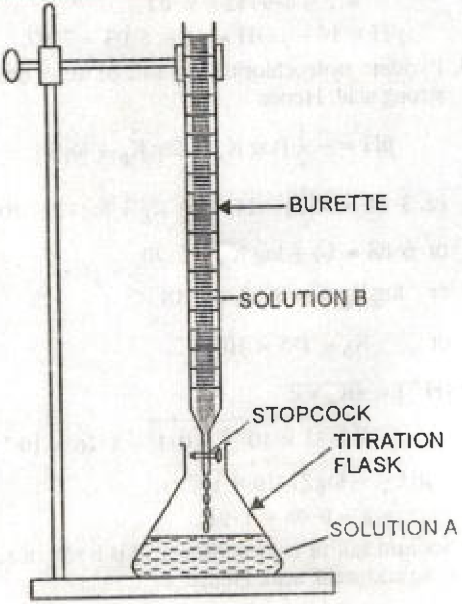


FIGURE 8.2. Apparatus for titration.

There are many types of titrations such as redox titrations (involving oxidation and reduction), acid-base tittrations (involving neutraisation), precipitation titrations (*e.g.* NaCl vs $AgNO_3$), complexometric titrations (involving formation of complexes) but here we shall take up a brief discussion of acid-base titrations in aqueous solutions only.

The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator.

8.12.2. Theory of Acid-Base Indicators (Ostwald's theory). According to this theory

(1) Acid-base indicators are mostly complex organic molecules which are either weak acids or weak bases. For example, phenolphthalein is a weak organic acid which may be represented in a simple way as HPh and methyl orange is a weak organic base which may be represented as MeOH.

(2) They dissociate in aqueous solution as follows :

$$\left\{\begin{array}{lll} \underset{(Colourless)}{HPh} \rightleftharpoons \underset{(Colourless)}{H^+} + \underset{(Pink)}{Ph^-} & \ldots(i) \\ \underset{(Yellow)}{MeOH} \rightleftharpoons \underset{(Red)}{Me^+} + \underset{(Colourless)}{OH^-} & \ldots(ii) \end{array}\right.$$

The unionized form has one colour and the ions have different colour. For example, HPh is colourless while Ph ions have pink colour. Similarly MeOH has yellow colour while Me^+ ions have red colour.

(3) As the medium changes from acidic to basic or vice versa, the equilibrium shifts either towards right or towards left and so the colour changes. For example, in acidic medium (*i.e.* in presence of excess of H^+ ions), equilibrium (*i*) is towards left and the solution is colourless. While in basic medium, OH^- ions will combine with the H^+ ions to form unionized H_2O molecules, the equilibrium shifts towards right and the solution has pink colour. Similarly, in case of methyl orange, in basic medium (*i.e.* in presence of excess of OH^- ions) the equilibrium (*ii*) is towards left and the colour is yellow while in acidic medium, H^+ ions combine with the OH^- ions and the equilibrium (*ii*) shifts towards right and the colour is red.

Phenolphthalein cannot be used as indicator if the base is weak e.g. NH_4OH. This is because the OH^- ions produced from the weak base are insufficient to shift the equilibrium (*i*) towards right substantially. Similarly, *methyl orange is not a suitable indicator if the acid is weak* like acetic acid

(CH_3COOH). This is because the H^+ ions produced are insufficient to combine with the OH^- ions and shift the equilibrium (*ii*) towards right significantly.

8.12.3. pH at the End-Point of Acid-Base Titrations. One often assumes that the pH at the end point of an acid-base titration must be 7. However, we must remember that what we have at the end point is an aqueous solution of a salt formed as a result of neutralisation of the acid by the base. If strong acid has been titrated with a strong base, the pH at the end point is, of course, 7. But it a weak acid or a weak base is involved in the titration, pH at the end point depends upon the hydrolysis of the salt formed. However, in any type of acid-base titration, it is found that there is a sudden change in the *p*H value at the end point.

As the titration proceeds, if the *p*H values of the solution are measured (say with the help of a *p*H meter) or calculated theoretically and then plotted against the volume of the solution added, the curve obtained is called **titration curve.** The titration curves of strong acid against strong base (*e.g.* HCl versus NaOH), weak acid against strong base (*e.g.* CH_3COOH versus NaOH), weak base against strong acid (*e.g.* NH_4OH versus HCl) and weak acid against a weak base (*e.g.* CH_3COOH versus NH_4OH) are shown in Fig. 8.3(*a*), (*b*), (*c*) and (d) respectively. The point at which there is a sudden change in *p*H when a very small amount of the titrant is added to the titrate is called **point of inflection.**

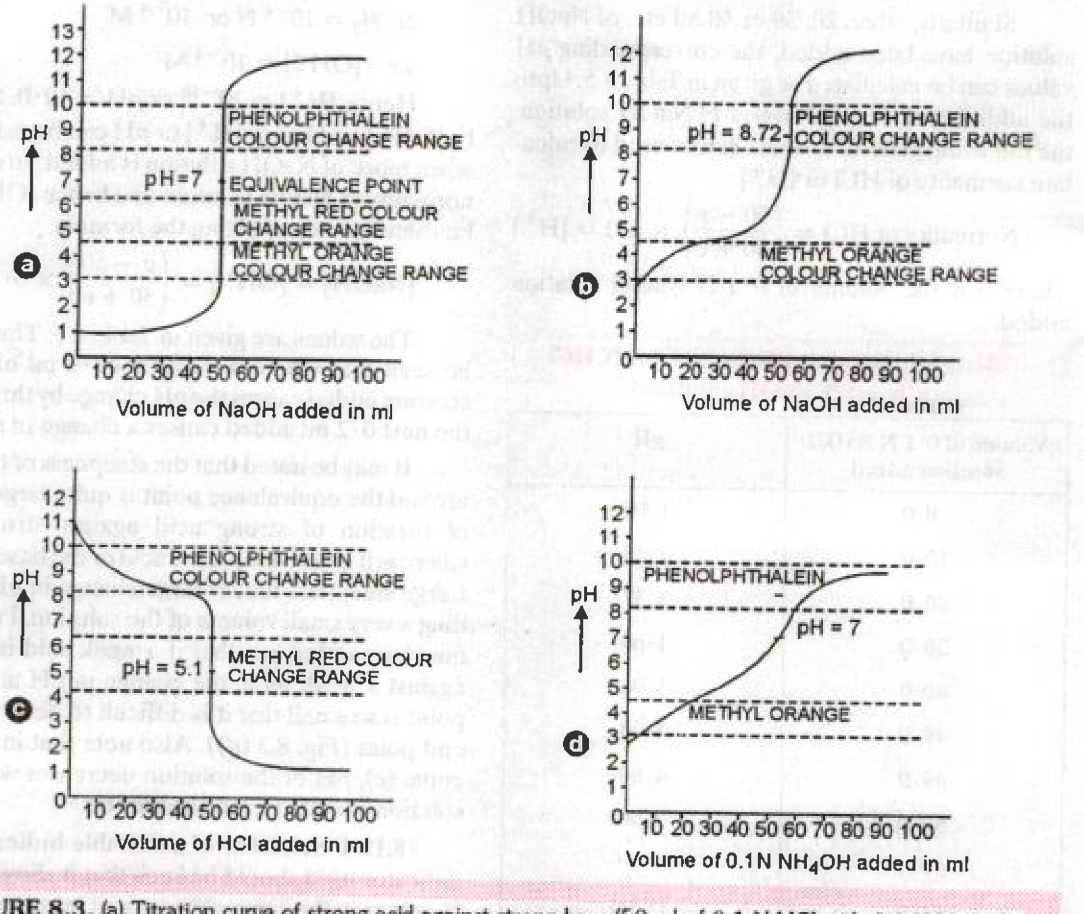


FIGURE 8.3. (a) Titration curve of strong acid against strong base (50 ml of 0.1 N HCl with 0.1 N NaOH)
(b) Titration curve of weak acid against strong base (50 ml of 0.1 N CH_3COOH with 0.1 N NaOH)
(c) Titration curve of weak base with against strong acid (50 ml of 0.1 N NH_4OH with 0.1 N HCl)
(d) Titration curve of a weak acid against weak base (50 ml of 0.1 N CH_3COOH with 0.1 N NH_4OH).

To understand how *p*H changes during acid-base titration, let us consider the titration of 50·0 ml of 0·1 N HCl against 0·1 N NaOH solution. The *p*H at different additions of NaOH solution may be calculated theoretically as follows :

Initially, as the solution taken in the flask is 0·1 M HCl, $[H^+] = 10^{-1}$, $pH = 1\cdot 0$. After 10 ml of 0·1 N NaOH has been added, it will neutralize 10 ml of 0·1 N HCl so that HCl left in the solution = 40 ml of 0·1 N and total volume of solution = 60 ml. To calculate normality of HCl in the final solution, apply $N_1 \times V_1 = N_2 \times V_2$ *i.e.* $0\cdot 1 \times 40 = N_2 \times 60$ or $N_2 = 0\cdot 0667$ N or 0·0667 M

i.e. $[H^+] = 6\cdot 67 \times 10^{-2}$ M.

Hence $pH = 1\cdot 18$.

Similarly, when 20, 30 or 40 ml etc. of NaOH solution have been added, the corresponding *p*H values can be calculated as given in Table 8.5. Upto the addition of 49·9 ml of 0·1 N NaOH solution, the following general formula can be used to calculate normality of HCl or $[H^+]$

$$\text{Normality of HCl} = \left(\frac{50 - v}{50 + v}\right) \times 0\cdot 1 = [H^+]$$

where *v* is the volume of 0·1 N NaOH solution added.

TABLE 8.5. Titration 50·0 ml of 0·1 N HCl with 0·1 N NaOH solution

Volume of 0·1 N NaOH solution added	pH
0·0	1·00
10·0	1·18
20·0	1·37
30·0	1·60
40·0	1·96
49·0	3·00
49·9	4·00
50·0	7·00
50·1	10·00
51·0	11·00
60·0	11·96
70·0	12·22

When 50 ml of 0·1 N NaOH solution has been added, the end point of the titration is reached. All the acid is neutralized. The solution contains NaCl only. Hence $pH = 7\cdot 0$. Thus *p*H of the solution has suddenly increased from 4·0 to 7·0.

Further addition of even a very small amount of NaOH solution (say 0·1 ml) increases the *p*H of the solution very rapidly. This may be seen as follows : –

Now, volume of the solution
$= 50 + 50\cdot 1 = 100\cdot 1$ ml

0·1 N NaOH solution left unneutralized
$= 0\cdot 1$ ml

To calculate normality of NaOH in the final solution, apply

$N_1V_1 = N_2V_2$ *i.e.* $0\cdot 1 \times 0\cdot 1 = N_2 \times 100\cdot 1$

or $N_2 = 10^{-4}$ N or 10^{-4} M

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

Hence $[H^+] = 10^{-10}$ or $pH = 10\cdot 0$. Similarly, $[OH^-]$ and hence $[H^+]$ or *p*H can be calculated when more of NaOH solution is added. In general, normality of NaOH solution and hence $[OH^-]$ can be calculated by applying the formula

$$[NaOH] = [OH^-] = \left(\frac{v - 50}{50 + v}\right) \times 0\cdot 1\ M$$

The values are given in Table 8.5. Thus it may be seen that whereas the first 49·9 ml of NaOH solution added causes the *p*H change by three units, the next 0·2 ml added causes a change of six units.

It may be noted that the steepness of the slope around the equivalence point is quite large in case of titration of strong acid against strong base whereas it is less steep if the acid or the base is weak. Large steepness means large change in *p*H on adding a very small volume of the solution. Further, it may be pointed out that if a weak acid is titrated against a weak base, the change in *p*H at the end point is so small that it is difficult to determine the end point (Fig. 8.3 (*d*)). Also note that in titration curve (*c*), *p*H of the solution decreases when HCl solution is added from the burette.

8.12.4. Selection of a suitable indicator. The indicator used should be such that it shows change in colour in the same pH range as required around the equivalence point. A number of indicators are available for the entire pH range. These are given in Table 8.6. below.

TABLE 8.6. Common acid-base indicators and their colour changes

Indicator	pH-range	Acidic colour	Alkaline colour
Methyl violet	0—2	Yellow	Violet
Methyl yellow	1·2—2·3	Red	Yellow
Methyl orange	3·1—4·5	Red	Yellow
Bromocresol green	3·8—4·6	Yellow	Blue
Methyl red	4·2—6·2	Red	Yellow
Litmus	4·5—8·3	Red	Blue
Bromothymol blue	6·0—7·5	Orange	Blue
Phenol red	6·4—8·2	Yellow	Red
Cresol red	7·2—8·8	Yellow	Red
Thymol blue	8·0—9·6	Yellow	Blue
Phenolphthalein	8·3—10·0	Colourless	Red
Thymolphthalein	9·3—10·5	Colourless	Blue
Alizarin yellow	10·1—12·0	Yellow	Violet
Trinitrobenzene	12·0—14·0	Colourless	Orange

From the titration curves, it may be observed that

(*i*) For titration of a strong acid against a strong base, any indicator out of methyl orange, methyl red and phenolphthalein can be used to determine the end point.

(*ii*) For titration of weak acid like acetic acid against a strong base like NaOH solution, only phenolphthalein is a suitable indicator.

(*iii*) For titration of weak base like NH_4OH against strong acid like HCl, only methyl red can be used as an indicator.

8.12.5. To prove that for the colour change $pK_{\text{indicator}}$ = pH at the equivalence point

As already mentioned, acid-base indicators are weak organic acids or weak organic bases. Suppose we consider an indicator which is a weak organic acid. Let it be represented by H*In*. In aqueous solution,it dissociates as

$$HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$$

H*In* and *In*$^-$ have different colours. The equilibrium constant for the above reaction is

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

The exact point of the colour change will be at the *p*H when [H*In*] = [In$^-$]. Substituting this value, we get

$$K_{In} = [H^+] \text{ or } -\log K_{In} = -\log [H^+]$$

i.e. $$pK_{In} = pH$$

Thus for a particular, tittration, the indicator selected should be such for which $pK_{In} = pH$ of the solution at the equivalence point. For example, in the titration of HF with NaOH, *p*H at the equivalence point is 8.1. pK_{In} for cresol red is 8.1. Hence cresol red should be used as indicator in this titration.

8.12.6. Explanation of the pH range of 2 units of indicators. From Table 8.6, it may be seen that most of the indicators have a useful colour change over a *p*H range of 2 units.For example, the most common indicator, phenolphthalein, changes from colourless to pink in the *p*H range from 8·3 to 10·0. This solves the problem for the fact that we may not have an indicator for which pK_{In} is exactly equal to the *p*H at the equivalence point. The explanation for the *p*H range of 2 units is as follows :

For the indicator HIn,

$$HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$$

HIn and In$^-$ have different colours. The equilibrium constant is

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \qquad ...(i)$$

Our eye can detect the change in colour if the concentration of one of the coloured form is at least 10 times greater than the concentration of the other. Thus to see the acidic colour

$$\frac{[In^-]}{[HIn]} = \frac{1}{10}$$

and to see the alkaline colour

$$\frac{[In^-]}{[HIn]} = \frac{10}{1}$$

Rearranging eqn. (*i*), we get

$$[H^+] = \frac{[H\,In]}{[In^-]} K_{In}$$

$\therefore$ For acidic colour to be visible

$$[H^+] = 10\,K_{In}$$

or $$-\log[H^+] = -\log 10 - \log K_{In}$$

i.e. $$pH = pK_{In} - 1$$

For alkaline colour to be visible

$$[H^+] = \frac{1}{10}K_{In}$$

or $$-\log[H^+] = \log 10 - \log K_{In}$$

i.e. $$pH = pK_{In} + 1$$

Thus for colour change of an indicator

$$pH = pK_{In} \pm 1$$

i.e. pH range for colour change is from $pK_{In} - 1$ to $pK_{In} + 1$ *i.e.* a pH range of 2 units.

8.12.7. Calculation of pK_b or pK_a values from pH of equivalence point. The pK of a weak acid or weak base can be determined from the measurement of pH at the equivalence point from the titration curve. For example, for a weak acid, HA

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

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

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

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

i.e. $$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

The half-equivalence point is the point in the neutralisation at which one half of HA has been neutralised in the reaction

$$HA + OH^- \rightleftharpoons H_2O + A^-$$

At this point, $[HA] = [A^-]$

$\therefore$ $pH = pK_a - \log 1 = pK_a$.

Thus at the half-equivalence point (half-neutralisation)

$$pH = pK_a$$

8.12.8. Formula for calculation of volumetric analysis. The basic principle is that the reactants react with each other in equivalent amounts.

Suppose the two reactants involved are A and B. Further suppose V_1 cc of the solution of reactant A having normality N_1 react exactly with V_2 cc of the solution of reactant B having normality N_2.

Number of gram equivalents of A reacted

$$= \frac{N_1}{1000} \times V_1$$

Number of gram equivalents of B reacted

$$= \frac{N_2}{1000} \times V_2$$

As the reactants react in equivalent amounts,

$$\frac{N_1 \times V_1}{1000} = \frac{N_2 \times V_2}{1000}$$

or $$\boxed{N_1 \times V_1 = N_2 \times V_2} \quad ...(i)$$

This is called normality equation.

In terms of molarities, as

Normality of an acid (N_a)

= Molarity (M_a) × Basicity of the acid (n_a)

and Normality of a base (N_b)

= Molarity (M_b) × Acidity of the base (n_b)

the equation $N_a \times V_a = N_b \times V_b$ can be written as

$$\boxed{n_a M_a V_a = n_b M_b V_b} \quad ...(ii)$$

Thus if both acid and base have same basicity and acidity *i.e.* $n_a = n_b$, we can write

$$\boxed{M_a V_a = M_b V_b} \quad ...(iii)$$

Equation (*ii*) and (*iii*) are called **molarity equations.** These equations may also be written as

$$n_1 M_1 V_1 = n_2 M_2 V_2$$

and $$M_1 V_1 = M_2 V_2.$$

ADD TO YOUR KNOWLEDGE

1. **Indicators used in different titrations**

	Type of titration	*Indicator used*
(*i*)	Strong acid vs strong base	Phenolphthalein or Methyl orange or Methyl red, Bromothymol and thymolphthalein
(*ii*)	Weak acid vs strong base	Phenolphthalein and Thymolphthalein
(*iii*)	Strong acid vs weak base	Methyl orange or Methyl red and Bromocresol green

2. **Universal indicator.** It is a mixture of a number of indicators which shows colour changes over different pH ranges

pH :	2	4	6	8	10	12
Colour :	Red	Orange	Yellow	Green	Blue	Purple

8.13. Solubility Equilibrium and Solubility Product

If a sparingly soluble salt like AgCl is stirred with water, only a small amount of it goes into solution (and makes the solution saturated) while most of the salt remains undissolved. But whatever little amount of the salt dissolves, it gets completely dissociated into ions. In other words, when a sparingly soluble salt is added to water, there exists a *dynamic equilibrium* between the undissolved solid salt and the ions which it furnishes in solution.

At equilibrium the solid AgCl continues to dissolve at the same rate at which the opposite process of precipitation takes place. Thus, the equilibrium can be represented by a reversible equation as shown below :

$$AgCl(s) \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} AgCl\,(aq) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

or we may write directly as

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

Applying law of chemical equilibrium, we have

$$K = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

Since concentration of the undissociated solid remains almost constant, we may write

$$[Ag^+]\,[Cl^-] = K \times [AgCl] = K_{sp}$$

where K_{sp} is called solubility product and is equal to ionic product $[Ag^+]\ [Cl^-]$ for a saturated solution.

Similarly, the solubility products of $BaSO_4$, $Al\,(OH)_3$ and $Ca_3(PO)_4$ may be represented as

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}\ ;$$

$$K_{sp} = [Ba^{2+}]\ [SO_4^{2-}]$$

$$Al\,(OH)_3\,(s) \rightleftharpoons Al^{3+} + 3OH^-\ ;$$

$$K_{sp} = [Al^{3+}]\,[OH^-]^3$$

$$Ca_3\,(PO_4)_2\,(s) \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}\ ;$$

$$K_{sp} = [Ca^{2+}]^3\ [PO_4^{3-}]^2$$

In general, for any electrolyte $A_x\,B_y$, the equilibrium may be represented as

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

Thus the solubility product for $A_x\,B_y$ may be written as $K_{sp} = [A^{y+}]^x \times [B^{x-}]^y$

where *x* and *y* represent the number of ions in the formula of the electrolyte. Thus

Solubility product of an electrolyte at a specified temperature may be defined as the product of the molar concentrations of its ions in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

The values of solubility products of some common sparingly soluble salts are listed in the following table :

TABLE 8.7. Solubility products of some common sparingly soluble salts at 298 K

Salt	K_{sp}	Salt	K_{sp}
$AgCl$	$1\cdot8 \times 10^{-10}$	$SrSO_4$	$3\cdot2 \times 10^{-7}$
$AgBr$	$5\cdot0 \times 10^{-13}$	SrF_2	$2\cdot5 \times 10^{-9}$
AgI	$8\cdot3 \times 10^{-17}$	$SrCO_3$	$1\cdot1 \times 10^{-10}$
Ag_2CrO_4	$1\cdot1 \times 10^{-12}$	CdS	$8\cdot0 \times 10^{-27}$
Ag_2SO_4	$1\cdot4 \times 10^{-5}$	CuS	$6\cdot3 \times 10^{-36}$
Ag_2CO_3	$8\cdot1 \times 10^{-12}$	HgS	$4\cdot0 \times 10^{-53}$
$BaSO_4$	$1\cdot1 \times 10^{-10}$	MnS	$2\cdot5 \times 10^{-13}$
$BaCrO_4$	$1\cdot2 \times 10^{-10}$	NiS	$4\cdot7 \times 10^{-5}$
BaF_2	$1\cdot0 \times 10^{-6}$	PbS	$8\cdot0 \times 10^{-28}$
$CaSO_4$	$9\cdot1 \times 10^{-6}$	SnS	$1\cdot0 \times 10^{-25}$
CaC_2O_4	$4\cdot0 \times 10^{-9}$	ZnS	$1\cdot6 \times 10^{-24}$
CaF_2	$5\cdot3 \times 10^{-9}$	FeS	$6\cdot3 \times 10^{-18}$
$CaCO_3$	$2\cdot8 \times 10^{-9}$	$CuCl$	$1\cdot7 \times 10^{-6}$
$Ca(OH)_2$	$5\cdot5 \times 10^{-6}$	Hg_2Cl_2	$1\cdot3 \times 10^{-18}$
$Cu(OH)_2$	$2\cdot2 \times 10^{-20}$	$PbCl_2$	$1\cdot6 \times 10^{-5}$
$Al(OH)_3$	$1\cdot3 \times 10^{-33}$	PbF_2	$7\cdot7 \times 10^{-8}$
$Fe(OH)_3$	$1\cdot0 \times 10^{-38}$	$PbBr_2$	$4\cdot0 \times 10^{-5}$
$Mg(OH)_2$	$1\cdot8 \times 10^{-11}$	PbI_2	$7\cdot1 \times 10^{-9}$
$Pb(OH)_2$	$1\cdot2 \times 10^{-15}$	$PbSO_4$	$1\cdot6 \times 10^{-8}$

Difference between Solubility Product and Ionic Product. Both ionic product and solubility product represent the product of the concentrations of the ions in the solution, each raised to the power equal to the number of ions as represented by the dissociation of one molecule of the substance. However, they differ in the following two aspects :

(*i*) The term **ionic product** has a broad meaning since it is applicable to all types of solutions, *may be unsaturated or saturated*. On the other hand, the **solubility product** has *restricted meaning since it applies only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in solution*. Thus the solubility product is in fact the ionic product for a saturated solution.

(*ii*) The solubility product of a salt is constant at constant temperature whereas ionic product depends upon the concentrations of ions in the solution.

Determination of Solubility Product. The solubility product of a sparingly soluble salt at a particular temperature can be calculated from a knowledge of the solubility of the salt in water at that particular temperature. This is illustrated with the help of the following examples :

EXAMPLE 1. *The solubility of AgCl in water at 25°C is found to be 1.06 × 10^{-5} moles per litre. Calculate the solubility product of AgCl at this temperature.*

Solution. AgCl ionizes completely in the solution as

$$AgCl \longrightarrow Ag^+ + Cl^-$$

i.e. 1 mole of AgCl in the solution gives 1 mole of Ag^+ ions and 1 mole of Cl^- ions.

Now, as the solubility of AgCl

$$= 1.06 \times 10^{-5} \text{ moles per litre}$$

$$\therefore \quad [Ag^+] = 1.06 \times 10^{-5} \text{ moles/litre}$$

$$\text{and} \quad [Cl^-] = 1.06 \times 10^{-5} \text{ moles/litre}$$

$$\therefore \quad K_{sp} \text{ for } AgCl = [Ag^+][Cl^-]$$

$$= 1.06 \times 10^{-5} \times 1.06 \times 10^{-5}$$

$$= \mathbf{1.1 \times 10^{-10}}$$

EXAMPLE 2. *The solubility of $Mg(OH)_2$ is 8.352 × 10^{-3} g/litre at 290°C. Find out its K_{sp} at this temperature.*

Solution. Mg $(OH)_2$ ionizes completely in the solution as

$$Mg(OH)_2 \longrightarrow Mg^{+2} + 2OH^-$$

$$\therefore \quad [Mg^{2+}] = [Mg(OH)_2]$$

$$\text{and} \quad [OH^-] = 2 \times [Mg(OH)_2]$$

But Molar mass of $Mg(OH)_2$ = 58 g mol^{-1}

$$\therefore [Mg(OH)_2] = \frac{\text{Strength in g/litre}}{\text{Molar mass}}$$

$$= \frac{8\cdot352 \times 10^{-2}}{58}$$

$$= 1\cdot44 \times 10^{-4} \text{moles/litre}$$

$$\therefore \quad [Mg^{2+}] = 1\cdot44 \times 10^{-4} \text{ moles/litre}$$

$$\text{and} \quad [OH^-] = 2 \times 1.44 \times 10^{-4}$$

$$= 2.88 \times 10^{-4} \text{ moles/litre}$$

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

(By definition)

$$= (1.44 \times 10^{-4}) \times (2.88 \times 10^{-4})^2$$

$$= \mathbf{1.194 \times 10^{-11}}$$

PROBLEMS FOR PRACTICE

1. Calculate the solubility product of silver bromide if the solubility of the salt in saturated solution is 5.7×10^{-7} moles/litre. [Ans. 3.25×10^{-13}]

2. A saturated solution of sparingly soluble lead chloride on analysis was found to contain 11.84 g/litre of the salt at room temperature. Calculate the solubility product constant at room temperature. (At. wt. : Pb = 207, Cl = 35.5) [Ans. 3.09×10^{-4}]

3. The solubility of lead iodide in water is 0.63 g/litre. Calculate the solubility product of lead iodide. (At mass of Pb = 207, I = 127) [Ans. 10^{-8}]

HINTS FOR DIFFICULT PROBLEMS

2. Solubility of $PbCl_2$

$$= \frac{11 \cdot 84}{207 + 2 \times 35 \cdot 5} \text{ mol L}^{-1}$$

$$= 4 \cdot 259 \times 10^{-2} \text{ mol L}^{-1}$$

$PbCl_2 \longrightarrow Pb^{2+} + 2Cl^-$,

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$= (4 \cdot 259 \times 10^{-2})(2 \times 4 \cdot 259 \times 10^{-2})^2$$

$$= 3 \cdot 09 \times 10^{-4}$$

8.14. Common Ion Effect

If to an ionic equilibrium, $AB \rightleftharpoons A^+ + B^-$, a salt containing a common ion (e.g. AC or BD) is added, the equilibrium shifts in the backward direction. This is called common ion effect.

The results can be easily explained on the basis of Le Chatelier's principle.

Examples. (*i*) Acetic acid, being a weak acid, ionizes to a small extent as follows :

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad ...(i)$$

To this solution suppose the salt of this weak acid with a strong base (*e.g.* CH_3COONa) is added. It ionizes almost completely in the solution as follows and provides the common acetate ions

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

As a result, the concentration of CH_3COO^- ions increases and by Le Chatelier's principle, the dissociation equilibrium (*i*) shifts backwards *i.e.* dissociation of acetic acid is further suppressed.

(*ii*) To the solution of the weak base, NH_4OH, if NH_4Cl is added which provides the common NH_4^+ ions, dissociation of NH_4OH is suppressed

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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

(*iii*) To the solution of silver chloride in water, (being a saturated solution because solubility of AgCl in water is very small), if NaCl is added which provides the common Cl^- ions, the solubility of AgCl decreases.

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

$$NaCl \longrightarrow Na^+ + Cl^-$$

This is again because by Le Chatelier's principle, increase in the concentration of Cl^- ions shifts the equilibrium in the backward direction *i.e.* some solid AgCl separates out. Similarly, solubility of lead iodide (PbI_2) in water decreases if KI is added to it.

Thus 'common ion effect' may also be defined as follows :

If to the solution of a weak electrolyte (e.g. acetic acid or ammonia), which ionizes to a small extent, a strong electrolyte having a common ion is added which ionizes almost completely, the ionization of the weak electrolyte is further suppressed. Similarly, if to the solution of a sparingly soluble salt (like AgCl, PbI_2 etc.), if a soluble salt having a common ion is added, the solubility of the sparingly soluble salt further decreases.

Remembering that the solubility product of a salt is constant irrespective of the source of the ions, the solubility of a sparingly soluble salt in the presence of a soluble salt having common ion can be calculated. (See solved example 3 on page of 8/44).

PROBLEMS ON INFLUENCE OF COMMON ION EFFECT ON DEGREE OF IONISATION OF ACIDS AND BASES

Basic Principle. The ionization constant of an acid HX ($HX \rightleftharpoons H^+ + X^-$) which is given by

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

is constant at constant temperature irrespective of the source of H^+ or X^- ions. The degree of ionization is given by

$$\alpha = \sqrt{K_a/c} \qquad \textit{(Refer to page 8/10)}$$

where c is the molar concentration of HX. However, degree of ionization is affected if extra H^+ or X^- (from any other source) are present.

Similarly, for a base MOH ($MOH \rightleftharpoons M^+ + OH^-$) the ionization constant K_b is constant at constant temperature irrespective of the source of M^+ or OH^- ions. The degree of ionization is given by

$$\alpha = \sqrt{K_b/c}$$

However, degree of ionization is affected if extra M^+ or OH^- (from any other source) are also present.

EXAMPLE 1. *The ionization constant of propionic acid is $1\cdot32 \times 10^{-5}$. Calculate the degree of ionization if its solution is $0\cdot05$ M. What will be its degree of ionization if the solution is $0\cdot01$ M in HCl also ?* **(N.C.E.R.T.)**

Solution. As already discussed on page 8/10

$$\alpha = \sqrt{K_a/c}$$

$$= \sqrt{(1\cdot32 \times 10^{-5}) \times 0\cdot05} = \mathbf{1\cdot62 \times 10^{-2}}$$

$$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$$

In presence of HCl, equilibrium will shift in the backward direction *i.e.* concentration of CH_3CH_2COOH will decrease. If c is the initial concentration and x is the amount now dissociated, then at equilibrium

$$[CH_3CH_2COOH] = c - x,$$

$$[CH_3CH_2COO^-] = x, [H^+] = 0\cdot01 + x$$

$$\therefore K_a = \frac{x\,(0\cdot01 + x)}{c - x} \simeq \frac{x\,(0\cdot01)}{c}$$

$$\text{or } \frac{x}{c} = \frac{K_a}{0\cdot01} = \frac{1\cdot32 \times 10^{-5}}{10^{-2}} = 1\cdot32 \times 10^{-3}$$

$$\alpha = \mathbf{1\cdot32 \times 10^{-3}}.$$

EXAMPLE 2. *The ionization constant of phenol is $1\cdot0 \times 10^{-10}$. What is the concentration of phenate ion in $0\cdot05$ M solution of phenol ? What will be its degree of ionization if the solution is also $0\cdot01$ M in sodium phenate ?* **(N.C.E.R.T.)**

Solution.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Initial: $0\cdot05$ M

After disso.: $0\cdot05 - x$, x, x

$$\therefore K_a = \frac{x \times x}{0\cdot05 - x} = 1\cdot0 \times 10^{-10} \; \textit{(Given)}$$

$$\text{or } \frac{x^2}{0\cdot05} = 1\cdot0 \times 10^{-10} \qquad (\text{Taking } 0\cdot05 - x \simeq 0\cdot05)$$

$$\text{or } x^2 = 5 \times 10^{-12} \text{ or } x = \mathbf{2\cdot2 \times 10^{-6}\ M}$$

In presence of $0\cdot01$ C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$$[C_6H_5OH] = 0\cdot05 - y \simeq 0\cdot05,$$

$$[C_6H_5O^-] = 0\cdot01 + y \simeq 0\cdot01\text{ M}, [H^+] = y\text{ M}$$

$$\therefore K_a = \frac{(0\cdot01)\,(y)}{0\cdot05} = 1\cdot0 \times 10^{-10} \; \textit{(Given)}$$

$$\text{or } y = 5 \times 10^{-10}$$

$$\therefore \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = \mathbf{10^{-8}}.$$

EXAMPLE 3. *The first ionization constant of H_2S is $9\cdot1 \times 10^{-8}$. Calculate the concentration of HS^- ions in its $0\cdot1$ M solution and how will this concentration be affected if the solution is $0\cdot1$ M in HCl also ? If the second dissociation constant of H_2S is $1\cdot2 \times 10^{-13}$, calculate the concentration of S^{2-} under both conditions.* **(N.C.E.R.T.)**

Solution. To calculate $[HS^-]$

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

Initial: $0\cdot1$ M

After disso.: $0\cdot1 - x \simeq 0\cdot1$, x, x

$$K_a = \frac{x \times x}{0\cdot1} = 9\cdot1 \times 10^{-8}$$

$$\text{or } x^2 = 9\cdot1 \times 10^{-9} \text{ or } x = 9\cdot54 \times 10^{-5}.$$

In presence of $0{\cdot}1$ M HCl, suppose H_2S dissociated is y. Then at equilibrium

$$[H_2S] = 0{\cdot}1 - y \simeq 0{\cdot}1,$$

$$[H^+] = 0{\cdot}1 + y \simeq 0{\cdot}1, [HS^-] = y \text{ M}$$

$$K_a = \frac{0{\cdot}1 \times y}{0{\cdot}1} = 9{\cdot}1 \times 10^{-8} \textit{ (Given)}$$

or $y = 9{\cdot}1 \times 10^{-8}$ M

To calculate $[S^{2-}]$

$$H_2S \overset{K_{a_1}}{\rightleftharpoons} H^+ + HS^-$$

$$HS^- \overset{K_{a_2}}{\rightleftharpoons} H^+ + S^{2-}$$

For the overall reaction,

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

$$K_a = K_{a_1} \times K_{a_2} = 9{\cdot}1 \times 10^{-8} \times 1{\cdot}2 \times 10^{-13}$$

$$= 1{\cdot}092 \times 10^{-20}$$

$$K_a = \frac{[H^+]^2 [S^{2-}]}{[H_2S]}$$

In the absence of $0{\cdot}1$ M HCl,

$$[H^+] = 2[S^{2-}]$$

Hence if $[S^{2-}] = x$, $[H^+] = 2x$

$$\therefore \quad \frac{(2x)^2 x}{0{\cdot}1} = 1{\cdot}092 \times 10^{-20}$$

or $4x^3 = 1{\cdot}092 \times 10^{-21}$

or $x^3 = 0{\cdot}273 \times 10^{-21} = 273 \times 10^{-24}$

$$3 \log x = \log 273 - 24 = 2{\cdot}4362 - 24$$

$$\log x = 0{\cdot}8127 - 8 = \bar{8}{\cdot}8127$$

or $x = \text{Antilog } \bar{8}{\cdot}8127$

$$= 6{\cdot}497 \times 10^{-8} = 6{\cdot}5 \times 10^{-8} \text{ M.}$$

In presence of $0{\cdot}1$ M HCl,

suppose $[S^{2-}] = y$, then

$$[H_2S] = 0{\cdot}1 - y \simeq 0{\cdot}1 \text{ M},$$

$$[H^+] = 0{\cdot}1 + y \simeq 0{\cdot}1 \text{ M}$$

$$K_a = \frac{(0{\cdot}1)^2 \times y}{0{\cdot}1} = 1{\cdot}09 \times 10^{-20}$$

or $y = 1{\cdot}09 \times 10^{-19}$ M.

PROBLEMS FOR PRACTICE

1. The pK_a value of acetic acid is $4{\cdot}74$. Calculate degree of ionization of $0{\cdot}05$ M acetic acid solution. How is the degree of ionization affected if its solution is also (*a*) $0{\cdot}01$ M (*b*) $0{\cdot}1$ M in HCl ?
[Ans. **0·019, (*a*) 0·0018 (*b*) 0·00018 *i.e.* each case, it decreases by a factor of 10]**

2. Calculate the degree of ionization of $0{\cdot}02$ M dimethyl amine solution. Given that its ionization constant is $5{\cdot}4 \times 10^{-4}$. What percentage of dimethyl amine is ionized if the solution is also $0{\cdot}1$ M in NaOH ? [Ans. **0·164, 0·0054]**

HINTS FOR DIFFICULT PROBLEMS

1. $pK_a = 4{\cdot}74$ means $-\log K_a = 4{\cdot}74$

or $\log K_a = \bar{5}{\cdot}26$

or $K_a = 1{\cdot}8 \times 10^{-5}$.

$$\alpha = \sqrt{K_a/c} = \sqrt{1{\cdot}8 \times 10^{-5}/0{\cdot}05}$$

$$= 1{\cdot}9 \times 10^{-2} = 0{\cdot}019.$$

Further proceed as in solved example 1.

2. $\alpha = \sqrt{K_b/c} = \sqrt{5{\cdot}4 \times 10^{-4}/0{\cdot}02} = 0{\cdot}164$

In presence of $0{\cdot}1$ M NaOH, if x is the amount of dimethyl amine dissociated.

$$[MOH] = 0{\cdot}02 - x \simeq 0{\cdot}02 \text{ M},$$

$$[OH^-] = 0{\cdot}1 + x \simeq 0{\cdot}1, [M^+] = x \text{ M}$$

$$\therefore \quad K_b = \frac{x \times (0{\cdot}1)}{0{\cdot}02} = 5{\cdot}4 \times 10^{-4} \textit{ (Given)}$$

or $x = 1{\cdot}08 \times 10^{-4}$ M

$$\therefore \quad \alpha = \frac{x}{c} = \frac{1{\cdot}08 \times 10^{-4}}{0{\cdot}02} = 0{\cdot}0054.$$

8.15. Applications of Solubility Product and Common Ion Effect

Some of the important applications are discussed below :

(1) Calculation of solubility of sparingly soluble salts. Knowing the solubility product of a sparingly soluble salt at any given temperature, we can very easily calculate its solubility.

The relationship between solubility (s) in mol L^{-1} and solubility product (K_{sp}) depends upon the nature of the salt. For example,

(*i*) For salts of the type AB (*e.g.* AgCl, $BaSO_4$, $PbSO_4$, $AlPO_4$ etc.)

$$\underset{s}{AB} \rightleftharpoons \underset{s}{A^+} + \underset{s}{B^-}$$

$$K_{sp} = [A^+][B^-] = s \times s = s^2$$

(*ii*) For salts of the type AB_2 (*e.g.* $PbCl_2$, CaF_2 etc.)

$$\underset{s}{AB_2} \rightleftharpoons \underset{s}{A^{2+}} + \underset{2s}{2B^-}$$

$$K_{sp} = [A^+][B^-]^2 = s \times (2s)^2 = 4s^3$$

Similarly for salts of the type A_2B (e.g. Ag_2CrO_4, Ag_2SO_4 etc.) also, $K_{sp} = 4s^3$.

(*iii*) For salts of the type AB_3 (*e.g.* $Fe(OH)_3$, $Al(OH)_3$ etc.)

$K_{sp} = s \times (3s)^3 = 27s^4$ and so on.

EXAMPLE 1. *The solubility product for silver chloride is 1.2×10^{-10} at 298 K. Calculate the solubility of silver chloride at 298 K.*

Solution. Silver chloride dissociates according to the equation

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

Let s be the solubility of AgCl in moles per litre.

Consequently, the molar concentration of Ag^+ and Cl^- will also be x each. Substituting in the expression for solubility product of AgCl

$$K_{sp} = [Ag^+][Cl^-]$$
$$= s \times s = s^2$$

But $K_{sp} = 1.2 \times 10^{-10}$ (*Given*)

$\therefore$ $x^2 = 1 \cdot 2 \times 10^{-10}$

or $s = \sqrt{1 \cdot 2 \times 10^{-19}}$

$$= \mathbf{1 \cdot 1 \times 10^{-5}\ mol\ L^{-1}}$$

EXAMPLE 2. *Lead chloride has a solubility product of 1.7×10^{-5} at 298 K. Calculate its solubility at this temperature.*

Solution. The solubility equilibrium for $PbCl_2$ may be represented as :

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq)$$

Let the solubility of $PbCl_2$ be s moles/litre. Then the solution will contain s moles of Pb^{2+} ions and $2s$ moles of Cl^- ions respectively per litre. Hence, the solubility product, K_{sp} of $PbCl_2$, would be given by the expression,

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$
$$= s \times (2s)^2 = 4s^3$$

But the vlaue of $K_{sp} = 1.7 \times 10^{-5}$ (Given)

$$4s^3 = 1.7 \times 10^{-5}$$

or $s^3 = \dfrac{1 \cdot 7 \times 10^{-5}}{4} = 0 \cdot 425 \times 10^{-5}$

or $s = (0.425 \times 10^{-5})^{1/3}$

$= (4.25 \times 10^{-6})^{1/3}$

Let $x = (4.25)^{1/3}$

$\therefore$ $\log x = 1/3 \log 4.25 = 1/3\,(0.6284)$

$= 0.2095$

$x = \text{Antilog}\ 0.2095 = 1.620$

Hence $s = \mathbf{1.620 \times 10^{-2}\ mol\ L^{-1}}$

EXAMPLE 3. *The solubility product of AgCl in water is $1 \cdot 5 \times 10^{-10}$. Calculate its solubility in $0 \cdot 01$ M NaCl aqueous solution.* **(Roorkee 1995)**

Solution. As NaCl dissociates completely, therefore in $0 \cdot 01$ M NaCl solution, $[Cl^-] = 0.01$ M

If solubility of AgCl in 0.01 M NaCl solution is s mol L^{-1}, then from AgCl that dissolves,

$$[Ag^+] = [Cl^-] = s\ mol\ L^{-1}$$

$\therefore$ Total $[Cl^-] = 0 \cdot 01 + s \simeq 0 \cdot 01$ M

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

$= s \times 0 \cdot 01 = 0 \cdot 01\,s$

$\therefore$ $0 \cdot 01\,s = 1 \cdot 5 \times 10^{-10}$

or $s = \mathbf{1 \cdot 5 \times 10^{-8}\ M}$

EXAMPLE 4. *What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298K. For calcium sulphate, $K_{sp} = 9 \cdot 1 \times 10^{-6}$.*

(N.C.E.R.T.)

Solution.

$$CaSO_4\,(s) \rightleftharpoons Ca^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

If s is the solubility of $CaSO_4$ in moles L^{-1}, then

$$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = s^2$$

or $s = \sqrt{K_{sp}} = \sqrt{9 \cdot 1 \times 10^{-6}}$

$$= 3\cdot02 \times 10^{-3}\ \text{mol L}^{-1}$$
$$= 3\cdot02 \times 10^{-3} \times 136\ \text{g L}^{-1}$$
$$= 0\cdot411\ \text{g L}^{-1}$$

(Molar mass of $CaSO_4$ = 136 g mol^{-1})

Thus for dissolving 0·411 g, water required = 1 L

∴ For dissolving 1 g, water required

$$= \frac{1}{0\cdot411}\ \text{L} = 2\cdot43\ \text{L}.$$

PROBLEMS FOR PRACTICE

1. Calculate the solubility of silver chloride in water at room temperature if the solubility product of AgCl is 1.6×10^{-10}

[Ans. 1.26×10^{-5} mol L^{-1}]

2. If solubility product for CaF_2 is 1.7×10^{-10} at 298 K, calculate the solubility in mol L^{-1}.

[Ans. 3.5×10^{-4}]

3. How many moles of AgBr ($K_{sp} = 5 \times 10^{-13}$ mol^{-2} L^{-2}) will dissolve in 0·01 M NaBr solution?

[Ans. 5×10^{-11} mol L^{-1}]

4. Calculate the solubilities of silver chromate and mercurous iodide in water at 298K. Given that their solubility products are $1{\cdot}1 \times 10^{-12}$ and $4{\cdot}5 \times 10^{-29}$ respectively. Also calculate the molarities of their individual ions.

[Ans. Solubility of $Ag_2CrO_4 = 6\cdot5 \times 10^{-5}$ M
Molarity of $Ag^+ = 1\cdot30 \times 10^{-4}$ M
Molarity of $CrO_4^{2-} = 6\cdot5 \times 10^{-5}$ M
Solubility of $Hg_2I_2 = 2\cdot24 \times 10^{-10}$ M
Molarity of $Hg_2^{2+} = 2\cdot24 \times 10^{-10}$ M
Molarity of $I^- = 4\cdot48 \times 10^{-10}$ M]

5. The solubility of product constants of Ag_2CrO_4 and AgBr are $1{\cdot}1 \times 10^{-12}$ and $5{\cdot}0 \times 10^{-13}$ respectively. Calculate the ratio of molarities of their saturated solutions. (*N.C.E.R.T.*)

[Ans. 9·15]

HINTS FOR DIFFICULT PROBLEMS

3. Suppose solubility of AgBr in 0·01 M NaBr = s mol L^{-1}. Then as

$$AgBr \longrightarrow Ag^+ + Br^-$$

$[Ag^+] = s$ mol L^{-1} and

Total $[Br^-] = 0\cdot01 + s \approx 0\cdot01$ M

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

i.e. $5 \times 10^{-13} = s \times 0\cdot01$

or $\quad s = 5 \times 10^{-11}$ mol L^{-1}

4. $$\underset{s}{Hg_2I_2} \rightleftharpoons \underset{s}{Hg_2^{2+}} + \underset{2s}{2I^-}$$

$K_{sp} = s \times (2s)^2 = 4s^3$ or $s^3 = 4\cdot5 \times 10^{-29}/4$

or $\quad 3 \log s = \log 4\cdot5 - 29 - \log 4 = -28\cdot9489$

or $\quad \log s = -9\cdot6496 = \overline{10}\cdot3504$

or $\quad s = \text{Antilog}\ \overline{10}\cdot3504 = 2\cdot24 \times 10^{-10}$.

5. Calculate their solubilities separately and then calculate the ratio.

(2) Predicting ionic or precipitation reaction. The solubility product represents the upper limit for ionic product in a saturated solution of any sparingly soluble salt. In other words,

> ***If the ionic product i.e., the product of the concentration of ions in the solution exceeds the value of the solubility product of a sparingly soluble salt, the excess ions will combine resulting in the formation of precipitate.***

Thus, having a knowledge of solubility product of any sparingly soluble salt, we can predict whether the salt will precipitate out or not when two solutions containing a known concentration of its ions are mixed together. This is illustrated by the following example.

- **EXAMPLE 1.** *Given that the solubility product of $BaSO_4$ is 1×10^{-10}. Will a precipitate form when*

(i) Equal volumes of 2×10^{-3} M $BaCl_2$ solution and 2×10^{-4} M Na_2SO_4 solution are mixed ?

(ii) Equal volumes of 2×10^{-8} M $BaCl_2$ solution and 2×10^{-3} M Na_2SO_4 solution are mixed ?

Solution. (*i*) $BaCl_2$ ionizes completely in the solution as

$$BaCl_2 \longrightarrow Ba^{2+} + 2Cl^-$$

$$[Ba^{2+}] = [BaCl_2] = 2 \times 10^{-3}\ M \quad \text{(Given)}$$

Na_2SO_4 ionizes completely in the solution as

$$Na_2SO_4 \longrightarrow 2\,Na^+ + SO_4^{2-}$$

$$\therefore [SO_4^{2-}] = [Na_2SO_4] = 2 \times 10^{-4}\ M \text{ (Given)}$$

Since equal volumes of the two solutions are mixed together, therefore, the concentrations of Ba^{2+} ions and SO_4^{2-} ions after mixing will be

$$[Ba^{2+}] = \frac{2 \times 10^{-3}}{2} = 10^{-3}\ M$$

$$\text{and} \quad [SO_4^{2-}] = \frac{2 \times 10^{-4}}{2} = 10^{-4}\ M$$

$$\therefore \text{Ionic product of } BaSO_4 = [Ba^{2+}][SO_4^{2-}]$$

$$= 10^{-3} \times 10^{-4} = 10^{-7}$$

which is greater than the solubility product (1×10^{-10}) of $BaSO_4$. Hence a precipitate of $BaSO_4$ will be formed.

(*ii*) Here, the concentrations before mixing are :

$$[Ba^{2+}] = [BaCl_2] = 2 \times 10^{-8}\ M \text{ (Given)}$$

$$[SO_4^{2-}] = [Na_2SO_4] = 2 \times 10^{-3}\ M \text{ (Given)}$$

$\therefore$ Concentrations after mixing equal volumes will be

$$[Ba^{2+}] = \frac{2 \times 10^{-8}}{2} = 10^{-8}\ M$$

$$\text{and} \quad [SO_4^{2-}] = \frac{2 \times 10^{-3}}{2} = 10^{-3}\ M$$

$$\therefore \text{Ionic product of } BaSO_4 = [Ba^{2+}][SO_4^{2-}]$$

$$= 10^{-8} \times 10^{-3} = 10^{-11}$$

which is less than the solubility product (1×10^{-10}). Hence no ppt. will be formed in this case.

EXAMPLE 2. *What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide ? For iron sulphide, $K_{sp} = 6 \cdot 3 \times 10^{-18}$.* **(N.C.E.R.T.)**

Solution. Suppose the concentration of each of $FeSO_4$ and Na_2S is x mol L^{-1}. Then after mixing equal volumes, $[FeSO_4] = [Na_2S] = \frac{x}{2}$ M

$$\text{i.e.} \quad [Fe^{2+}] = [S^{2-}] = \frac{x}{2}\ M$$

$$K_{sp} \text{ for } FeS = [Fe^{2+}][S^{2-}]$$

$$\text{i.e.} \quad 6 \cdot 3 \times 10^{-18} = \frac{x}{2} \times \frac{x}{2}$$

$$\text{or} \quad x^2 = 25 \cdot 2 \times 10^{-18}$$

$$\text{or} \quad x = 5 \cdot 02 \times 10^{-9}\ M.$$

- EXAMPLE 3. *The concentration of sulphide ion in 0·1 M HCl solution saturated with hydrogen sulphide is $1 \cdot 0 \times 10^{-19}$ M. If 10 mL of this solution is added to 5 mL of 0·04 M solution of $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CaCl_2$, in which solutions precipitation will take place ? Given K_{sp} for $FeS = 6 \cdot 3 \times 10^{-18}$, $MnS = 2 \cdot 5 \times 10^{-13}$, $ZnS = 1 \cdot 6 \times 10^{-24}$ and $CdS = 8 \cdot 0 \times 10^{-27}$.* **(N.C.E.R.T.)**

Solution. Precipitation will take place in the solution for which ionic product is greater than solubility product. As 10 mL of solution containing S^{2-} ion is mixed with 5 mL of metal salt solution, after mixing

$$[S^{2-}] = 1 \cdot 0 \times 10^{-19} \times \frac{10}{15} = 6 \cdot 67 \times 10^{-20},$$

$$[Fe^{2+}] = [Mn^{2+}] = [Zn^{2+}] = [Cd^{2+}]$$

$$= \frac{5}{15} \times 0 \cdot 04 = 1 \cdot 33 \times 10^{-2}\ M$$

$\therefore$ Ionic product for each of these will be

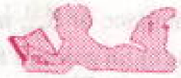
$$= [M^{2+}][S^{2-}]$$

$$= (1 \cdot 33 \times 10^{-2})(6 \cdot 67 \times 10^{-20})$$

$$= 8 \cdot 87 \times 10^{-22}$$

As this is greater than the solubility product of ZnS and CdS, therefore, $ZnCl_2$ and $CdCl_2$ solutions wil be precipitated.

PROBLEMS FOR PRACTICE



1. Predict whether a precipitate will be formed or not on mixing 20 ml of 0.001 N NaCl solution with 80 ml of 0.01 N $AgNO_3$ solution. K_{sp} for AgCl = 1.5×10^{-10} [Ans. **Yes, ppt. will be formed]**

2. If 20 ml of 2×10^{-5} $BaCl_2$ solution is mixed with 20 ml of 1×10^{-5} M Na_2SO_4 solution, will a ppt. form ? ($K_{s.p.}$ for $BaSO_4$ is 1.0×10^{-10}) [Ans. **No]**

3. 0.03 mole of Ca^{2+} ions is added to a litre of 0.01 M SO_4^{2-} solution. Will it cause precipitation of $CaSO_4$? K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$

[Ans. **Precipitation of $CaSO_4$ will occur]**

4. $PbCl_2$ has a solubility product of 1.7×10^{-8}. Will a precipitate of $PbCl_2$ form, when 0.010 mole of lead nitrate and 0.010 mole of potassium chloride are mixed and water added upto 1 litre ?

[Ans. **Yes]**

5. Equal volumes of 0·002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate ? For copper iodate, $K_{sp} = 7{\cdot}4 \times 10^{-8}$.

(N.C.E.R.T.) [Ans. **No precipitation]**

HINTS FOR DIFFICULT PROBLEMS

1. After mixing, total volume of the solution = 100 ml

20 ml of 10^{-3} M NaCl sol ≡ 100 ml of ? M

Molarity of NaCl solution in the final solution

$$= \frac{20 \times 10^{-3}}{100} = 2 \times 10^{-4}\ M$$

or $[Cl^-] = 2 \times 10^{-4}$ M

80 ml of 10^{-2} M $AgNO_3$ sol ≡ 100 ml of ? M

Molarity of $AgNO_3$ solution in the final solution

$$= \frac{80 \times 10^{-2}}{100} = 8 \times 10^{-3}\ M$$

or $[Ag^+] = 8 \times 10^{-3}$

∴ Ionic product $= [Ag^+][Cl^-] = 16 \times 10^{-7}$

$= 1{\cdot}6 \times 10^{-8}$ which is greater than the solubility product. Hence ppt. will be formed.

3. In the final solution, $[Ca^{2+}] = 0{\cdot}03$ M and $[SO_4^{2-}] = 0{\cdot}01$ M. Hence ionic product of $CaSO_4$

$= (0{\cdot}03\ (0{\cdot}01) = 3 \times 10^{-4}$ which is greater than K_{sp}. Hence precipitation will occur.

4. As final volume of the solution = 1 L, therefore

$[Pb^{2+}] = 0{\cdot}01\ M = 10^{-2}\ M$

$[Cl^-] = 0{\cdot}01\ M = 10^{-2}\ M.$

Ionic product of $PbCl_2 = [Pb^{2+}][Cl^-]^2$

$$= (10^{-2})(10^{-2})^2 = 10^{-6}$$

which is greater than K_{sp}. Hence ppt. of $PbCl_2$ will be formed.

5. $2\ NaIO_3 + CuCrO_4 \longrightarrow Na_2CrO_4 + Cu(IO_3)_2$

After mixing, $[NaIO_3] = [IO_3^-]$

$$= \frac{2 \times 10^{-3}}{2} = 10^{-3}\ M$$

$$[CuCrO_4] = [Cu^{2+}] = \frac{2 \times 10^{-3}}{2} = 10^{-3}\ M$$

Ionic product of $Cu(IO_3)_2 = [Cu^{2+}][IO_3^-]^2$

$$= (10^{-3})(10^{-3})^2 = 10^{-9}$$

As ionic product is less than K_{sp}, no precipitation will occur.

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(3) In explaining salting out or precipitation of soluble salts. For example, on passing hydrochloric acid gas through a saturated solution of sodium chloride, the concentration of chloride ions will be increased. This increases the ionic product of NaCl and the solid salt will be precipitated.

Similarly, soap (which is sodium salt of higher fatty acids) is precipitated out from its solution by stirring with sodium chloride. The process is called 'salting out'.

Alternatively, it may be pointed out that K_{sp} is for the concentrations in equilibrium (in the saturated solution). It is constant for a particular salt at a particular temperature irrespective of the source of ions. Thus in the presence of some common ion produced from any other substance in the solutions, the concentration of ions are disturbed and in place of K_{sp}, we use the symbol Q_{sp} (just as we use Q_c in place of K_c). The concept is applicable even to soluble salts like NaCl except that we use activities in place of molar concentrations (due to high concentration of their ions). Thus in case of NaCl,

$$NaCl\,(s) \rightleftharpoons Na^+\,(aq) + Cl^-\,(aq)$$

$$K_{sp} = [Na^+\,(aq)]\,[Cl^-\,(aq)]$$

If HCl gas is passed through the saturated solution of NaCl, Cl^- ion concentration will increase so that $Q_{sp} > K_{sp}$. In order that Q_{sp} may become equal to K_{sp}, equilibrium will shift in the backward direction *i.e.* pure solid NaCl will precipitate out.

(4) **In Qualitative Analysis.** The separation and identification of various basic radicals into different groups is based upon

(*a*) *Solubility product principle,* according to which 'a precipitate is formed if ionic product is greater than the solubility product'.

(*b*) *Common ion effect*, according to which 'if to the solution of a weak electrolyte (like NH_4OH), a strong electrolyte having a common ion (like NH_4Cl) is added, the ionization of the weak electrolyte is further suppressed.

A brief description of the separation of basic radicals into different groups is given below :

(i) Precipitation of sulphides of group II. Sulphides of group II are precipitated by passing H_2S gas through the solution of these cations in presence of dil HCl.

H_2S being a weak electrolyte ionizes only slightly, while HCl being a strong electrolyte is almost completely ionized.

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

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

Thus the common ion effect takes place. As a result, the degree of dissociation of H_2S decreases sufficiently and the concentration of S^{2-} ions in the solution becomes very small. But with this low concentration of S^{2-} ions, the ionic product of the cations of second group and the sulphide ions exceeds the very low solubility products of their corresponding sulphides. Therefore, the cations of group II get precipitated as their insoluble sulphides.

On the other hand, the sulphides of the cations of the other groups (III, IV, V and Mg) are not precipitated under these conditions because their solubility products are quite high.

(ii) Precipitation of the hydroxides of group III. Hydroxides of group III are precipitated by adding an excess of solid NH_4Cl to the solutions of these cations followed by the addition of excess of NH_4OH. Being a weak electrolyte, NH_4OH is only slightly ionised, whereas NH_4Cl, being a strong electrolyte, ionizes almost completely to give a large concentration of NH_4^+ ions.

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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

Due to the *common ion effect*, the degree of dissociation of NH_4OH gets suppressed and hence the concentration of OH^- ions in solution decreases appreciably. But even with this low conc. of OH^- ions, the ionic products of the cations of group III and OH^- ions exceed the low values of the solubility products of their corresponding metal hydroxides. As a result, the cations of group III get precipitated as their insoluble hydroxides.

On the other hand, cations of groups IV, V and Mg, which require a large conc. of OH^- ions due to their high solubility products will not be precipitated.

(iii) Precipitation of sulphides of group IV. The sulphides of group IV are precipitated by passing H_2S through ammoniacal solution of these cations.

Both H_2S and NH_4OH, being weak electrolytes, ionize only slightly as :

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

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

The H^+ ions and OH^- ions combine to produce practically unionised molecules of water

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

As a result, the above dissociation equilibrium reactions get shifted in the forward direction, so that the concentration of S^{2-} ions goes on increasing. Ultimately, the ionic products of the cations of group IV and S^{2-} ions exceed the solubility products of their corresponding metal sulphides and hence get precipitated.

(iv) Precipitation of Carbonates of Group V. The carbonates of group V are precipitated by adding $(NH_4)_2\ CO_3$ solution to the solution of these cations in the presence of NH_4Cl and NH_4OH. $(NH_4)_2CO_3$, being a weak electrolyte ionises only slightly to give a small concentration of CO_3^{2-} ions.

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{2-}$$

On the other hand, NH_4Cl being a strong electrolyte, ionises almost completely to give a large concentration of NH_4^+ ions. Due to the common ion effect, the dissociation of $(NH_4)_2CO_3$ is suppressed and hence the concentration of CO_3^{2-} ions in the solution decreases considerably. But even with this low concentration of CO_3^{2-} ions, the ionic products of these cations and CO_3^{2-} ions exceed the low values of the solubility products of their corresponding metal carbonates and thus get precipitated.

However, under these conditions, Mg salts do not get precipitated as $MgCO_3$ since its solubility product is comparatively high and thus requires a high concentration of CO_3^{2-} ions for precipitation. The carbonates of Na^+, K^+ and NH_4^+ ions are also not precipitated because they are quite soluble.

The necessity of adding NH_4OH arises due to the fact that $(NH_4)_2CO_3$ solution usually contains a large amount of NH_4HCO_3. Thus the cations of group V will form not only insoluble carbonates but soluble bicarbonates as well. As a result, the precipitation will not be complete. In order to convert NH_4HCO_3 to $(NH_4)_2\ CO_3$, NH_4OH is always added.

$$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2\ CO_3 + H_2O$$

(5) In fractional precipitation. Fractional precipitation is a technique of separating two or more ions from a solution by adding a suitable reactant that precipitates first one ion, then another and so on. For example, suppose we have a solution which is 0·1 M in Ba^{2+} and 0·1 M in Sr^{2+}. When a concentrated K_2CrO_4 solution is added to it slowly, Ba^{2+} ions precipitate out first. When most of the Ba^{2+} ions (almost whole of it) have precipitated out, Sr^{2+} ions start precipitating out. The reason for this may be explained on the basis of their solubility products as follows :

$$K_{sp} \text{ for } BaCrO_4 = 1{\cdot}2 \times 10^{-10}$$

$$K_{sp} \text{ for } SrCrO_4 = 3{\cdot}5 \times 10^{-5}$$

Assuming volume change of the solution to be negligible due to addition of concentrated K_2CrO_4 solution, $[CrO_4^{2-}]$ required to start precipitation of 0·1 M Ba^{2+} may be calculated as follows :

$$[Ba^{2+}]\,[CrO_4^{2-}] = K_{sp} \text{ for } BaCrO_4$$

$$(0{\cdot}1)\,[CrO_4^{2-}] = 1{\cdot}2 \times 10^{-10}$$

$$\text{or } [CrO_4^{2-}] = \frac{1{\cdot}2 \times 10^{-10}}{0{\cdot}1} = 1{\cdot}2 \times 10^{-9} \text{ M}$$

Similarly $[CrO_4^{2-}]$ required to start precipitation of 0·1 M Sr^{2+} can be calculated as follows :

$$[Sr^{2+}]\,[CrO_4^{2-}] = K_{sp} \text{ for } SrCrO_4$$

$$(0{\cdot}1)\,[CrO_4^{2-}] = 3{\cdot}5 \times 10^{-5}$$

$$\text{or } [CrO_4^{2-}] = \frac{3{\cdot}5 \times 10^{-5}}{0{\cdot}1} = 3{\cdot}5 \times 10^{-4} \text{ M}$$

Thus $BaCrO_4$ starts precipitating first because CrO_4^{2-} concentration required to precipitate $BaCrO_4$ is much smaller than that required for the precipitation of $SrCrO_4$.

8.16. Buffer Solutions and Buffer Action

It is sometimes necessary that a solution of definite pH be prepared and stored. The preservation of such a solution is even more difficult than its preparation. If the solution comes in contact with air, it will absorb carbon dioxide (an acidic anhydride) and becomes more acidic. If the solution is stored in a glass bottle, the alkaline impurities present in glass may dissolve into the solution and may alter its pH.

A buffer solution is defined as a solution which resists any change in its pH value (i.e. whose pH remains preactically constant) even when small amounts of the acid or the base are added to it.

Types of Buffer solutions. There are two types of buffer solutions. These are :

(i) Solutions of single substances. The solution of the salt of a weak acid and a weak base *e.g.* ammonium acetate (CH_3COONH_4) acts as a buffer.

***(ii)* Solutions of Mixtures.** These are further of two types :

***(a)* Acidic Buffer.** It is the solution of a mixture of a weak acid and a salt of this weak acid with a strong base (*e.g.* $CH_3COOH + CH_3COONa$).

***(b)* Basic Buffer.** It is the solution of a mixture of a weak base and a salt of this weak base with a strong acid. (*e.g.* $NH_4OH + NH_4Cl$).

Buffer Action. ***The property of a buffer solution to resist any change in its pH value even when small amounts of the acid or the base are added to it is called 'Buffer action'.***

The buffer action of different types of buffers may be explained as follows :

Buffer Action of Ammonium Acetate Solution. Ammonium acetate like all other salts, is almost completely dissociated in the aqueous solution as follows :

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

Thus in the solution there is excess of CH_3COO^- ions and NH_4^+ ions.

When a few drops of an acid (say HCl) are added to the above solution, the H_3O^+ ions given by the acid combine with the CH_3COO^- ions to form weakly ionized molecules of CH_3COOH.

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

Thus the H_3O^+ ion concentration of the solution does not change practically and hence the pH of the solution remains almost constant. Similarly, when a few drops of a base (say NaOH) are added to the above solution, the OH^- ions given by the base combine with the NH_4^+ ions to form weakly ionized molecules of NH_4OH.

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

Thus the OH^- ion concentration and hence the H_3O^+ ion concentration or the pH of the solution remains almost consant.

On the contrary, the solution of a substance like NaCl cannot act as a buffer because NaCl dissociates completely to give Na^+ and Cl^- ions. These may combine with the base or the acid added to form NaOH or HCl. But these ionize completely to give back the OH^- ions or H_3O^+ ions. Thus the H_3O^+ ions concentration of the solution changes and hence the pH of the solution changes.

Buffer Action of Acidic Buffer. For example, let us consider the buffer action of the acidic buffer containing CH_3COOH and CH_3COONa. Acetic acid dissociates to a small extent whereas sodium acetate is almost completely dissociated in the aqueous solution as follows :

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \quad ...(i)$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad ...(ii)$$

By *'common ion effect'*, the ionization of CH_3COOH is further suppressed. Thus in the solution, there are excess of acetate (CH_3COO^-) ions and a small amount of H_3O^+ ions.

When a few drops of an acid are added to the above mixture solution, the H_3O^+ ions given by the acid combine with the CH_3COO^- ions to form weakly ionized molecules of CH_3COOH.

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

Thus the H_3O^+ ion concentration and hence the pH of the solution remains almost constant.

Similarly, when a few drops of a base are added, the OH^- ions given by the base combine with the H_3O^+ ions already present to form weakly ionized molecules of H_2O.

$$\underset{\text{[From (i)]}}{H_3O^+} + \underset{\text{[Given by the base]}}{OH^-} \longrightarrow 2H_2O$$

As the H_3O^+ ions are consumed, the equilibrium (*i*) shifts towards right (according to Le Chatelier's principle). Thus more of CH_3COOH dissociates to make up the loss of H_3O^+ ions. Hence the H_3O^+ ion concentration or the pH of the solution does not change.

Buffer Action of Basic Buffer. The buffer action of a basic buffer *e.g.* $NH_4OH + NH_4Cl$ may be explained as follows :

NH_4OH dissociates to a small extent whereas NH_4Cl dissociates completely in the aqueous solution as follows :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad ...(i)$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \quad ...(ii)$$

By common ion effect, the ionization of NH_4OH is further suppressed. Thus in the solution, there are excess of NH_4^+ ions and a small amount of OH^- ions.

When a few drops of a base are added, the OH^- ions given by it immediately combine with NH_4^+ ions to form the weakly ionized NH_4OH.

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

Thus the H_3O^+ ion concentration or the pH of the solution remains unaffected.

Similarly, when a small amount of an acid is added, the H_3O^+ ions given by it combine with the OH^- ions already produced by NH_4OH in equilibrium (*i*).

$$\underset{\text{[Given by the acid]}}{H_3O^+} + \underset{\text{[Given by (i)]}}{OH^-} \longrightarrow 2H_2O$$

As the OH^- ions are consumed, the equilibrium (*i*) shifts in the forward direction. Thus more of NH_4OH dissociates to produce more of OH^- ions which makes up the loss of OH^- ions. Hence the OH^- ion concentration and, therefore, the H_3O^+ ion concentration or the pH of the solution remains fairly constant.

Note. (*i*) From titration curves given in Fig. 8.3, it may be seen that some portions of the titration curves are flat. *i.e.* the *p*H of the titration mixtures changes very little even on adding acid or base. These portions are generally mixtures of acid and salt or base and salt. Thus they correspond to buffer mixtures.

(*ii*) *A solution of a strong acid (e.g. HCl) of reasonable concentration (~ 0·1 M) also acts as a buffer.* The acid is completely dissociated and all the H^+ ions are present in the free form. From the titration curve, it may be seen that initial *p*H increases only by 0·3 even after half of the acid is neutralized.

Calculation of pH of a buffer mixture

(*a*) For acidic buffer mixture (Henderson-Hasselbalch equation)

If the weak acid is HA and its salt is BA, then

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$BA \longrightarrow B^+ + A^-$$

$$\therefore \quad K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

$$\text{or} \quad [H_3O^+] = K_a \frac{[HA]}{[A^-]} \qquad \ldots(i)$$

But $[A^-] = [BA]$, therefore

$$[H_3O^+] = K_a \frac{[HA]}{[BA]} = K_a \frac{[\text{Acid}]}{[\text{Salt}]} \qquad \ldots(ii)$$

$$\therefore \quad pH = -\log\,[H_3O^+] \qquad \ldots(iii)$$

$$= -\log\left\{K_a \frac{[\text{Acid}]}{[\text{Salt}]}\right\}$$

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

$$\text{or} \quad \boxed{pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}} \qquad \ldots(iv)$$

or substituting the value of $[H_3O^+]$ from eqn. (*i*) in eqn. (*iii*), we get

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

$$\text{or} \quad pH = pK_a + \log \frac{[A^-]}{HA}$$

$$\text{or} \quad \boxed{pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}} \qquad \ldots(v)$$

It is interesting to observe that if [Salt]/[Acid] = 10, $pH = pK_a + 1$ and if [Acid]/[Salt] = 10, $pH = pK_a - 1$. Thus if the ratio of the conjugate acid-base pair is changed by 10 times, pH changes by ± 1.

(*b*) **For basic buffer mixture** like BOH + BA, in a similar manner,

$$\boxed{pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}} \qquad \ldots(vi)$$

As pH + pOH = 14, pH can be calculated.

Alternatively, the above equation can be expressed in a different form as follows :

$$pH + pOH = 14$$

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

$$\text{Also} \quad pK_a + pK_b = 14$$

$$\text{or} \quad pK_b = 14 - pK_a$$

Substituting these values in eqn. (*vi*), we get

$$14 - pH = 14 - pK_a + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{or} \quad pH = pK_a - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

or $$\boxed{pH = pK_a + \log \frac{[\text{Base}]}{[\text{Salt}]}} \quad ...(vii)$$

where K_a is the ionization constant of the conjugate acid of the base (*e.g.* in the buffer $NH_4OH + NH_4Cl$, NH_4^+ is the conjugate acid of the base NH_3 and K_a represents the ionization constant of the reaction

$$NH_4^+ (aq) + H_2O (l) \rightleftharpoons NH_3 (aq) + H^+ (aq)$$

Thus for this basic buffer, the above equation implies that

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$i.e.\ \boxed{pH = pK_a + \log \frac{[\text{Base}]}{[\text{Conjugate acid}]}} \quad ...(viii)$$

Buffer capacity or Buffer index. *It is defined as the number of moles of an acid or a base required to be added to one litre of the buffer solution so as to change its pH by one unit.* Thus

Buffer capacity

$$= \frac{\text{No. of moles of the acid or base added to 1 litre of the buffer}}{\text{Change in pH}} = \frac{dn}{d\,pH}$$

Buffer capacity of a buffer is maximum when the concentration of the weak acid and its salt or weak base and its salt are equal *i.e.* when $pH = pK_a$ or $pOH = pK_b$. (Refer to Henderson equation).

Importance of Buffer Solutions :

(1) In biological processes. The pH of our blood is maintained constant (at about 7·4) inspite of various acid and base-producing reactions going on in our body. In the absence of its buffer nature, we could not eat a variety of foods and spices.

(2) In Industrial processes. The use of buffers is an important part of many industrial processes, *e.g.*,

(*i*) In electroplating ;

(*ii*) in the manufacture of leather, photographic materials and dyes ;

(*iii*) in analytical chemistry ;

(*iv*) to calibrate the pH metres ;

(*v*) in bacteriological research-culture media are generally buffered to maintain the pH required for the growth of the bacteria being studied.

PROBLEMS ON BUFFER SOLUTIONS

FORMULAS AND UNITS

By Henderson equation, pH of an acid buffer is given by

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

Similarly, for a basic buffer

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

$pH + pOH = 14$ *i.e.* $pH = 14 - pOH$.

● EXAMPLE 1. *Calculate the pH of a buffer which is 0·1 M in acetic acid and 0·15 M in sodium acetate. Given that the ionization constants of acetic acid is $1{\cdot}75 \times 10^{-5}$. Also calculate the change in pH of the buffer if to 1 litre of the buffer*

(i) 1 cc of 1 M NaOH are added

(ii) 1 cc of 1 M HCl are added.

Assume that the change in volume is negligible.

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

$$= -\log (1{\cdot}75 \times 10^{-5}) + \log \frac{0{\cdot}15}{0{\cdot}10}$$

$$= (5 - 0{\cdot}2430) + 0{\cdot}1761$$

$$= 4{\cdot}757 + 0{\cdot}1761 = \mathbf{4{\cdot}933}.$$

(*i*) 1 cc of 1 M NaOH contains NaOH $= 10^{-3}$ mol. This will convert 10^{-3} mol of acetic acid into the salt so that salt formed $= 10^{-3}$ mol

Now $[\text{Acid}] = 0{\cdot}10 - 0{\cdot}001 = 0{\cdot}099$ M

$[\text{Salt}] = 0{\cdot}15 + 0{\cdot}001 = 0{\cdot}151$ M

$$pH = 4{\cdot}757 + \log \frac{0{\cdot}151}{0{\cdot}099}$$

$$= 4{\cdot}757 + 0{\cdot}183 = \mathbf{4{\cdot}940}$$

$\therefore$ Increase in $pH = 4 \cdot 940 - 4 \cdot 933 = 0 \cdot 007$ which is negligible.

(*ii*) 1 cc of 1 M HCl contains HCl $= 10^{-3}$ mol. This will convert 10^{-3} mol CH_3COONa into CH_3COOH.

$$\therefore \text{Now } [\text{Acid}] = 0 \cdot 10 + 0 \cdot 001 = 0 \cdot 101 \text{ M}$$

$$[\text{Salt}] = 0 \cdot 15 - 0 \cdot 001 = 0 \cdot 149 \text{ M}$$

$$\therefore pH = 4 \cdot 757 + \log \frac{0 \cdot 149}{0 \cdot 101}$$

$$= 4 \cdot 757 + 0 \cdot 169 = \mathbf{4 \cdot 926}$$

$\therefore$ Decrease in $pH = 4 \cdot 933 - 4 \cdot 926 = 0 \cdot 007$ which is again negligible.

• **EXAMPLE 2.** *Calculate the pH of a solution obtained by mixing 5 mL of 0·1 M NH_4OH with 250 mL of 0·1 M NH_4Cl solution. K_b for $NH_4OH = 1 \cdot 8 \times 10^{-5}$.*

Solution. 5 mL of 0·1 M $NH_4OH = 5 \times 0 \cdot 1$ millimole $= 0 \cdot 5$ millimole

250 mL of 0·1 M NH_4Cl

$= 250 \times 0 \cdot 1$ millimole $= 25$ millimoles

Total volume of solution after mixing = 255 mL

$$\therefore \quad [\text{Salt}] = [NH_4Cl] = \frac{25}{255} \text{ M}$$

$$[\text{Base}] = [NH_4OH] = \frac{0 \cdot 5}{255} \text{ M}$$

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

$$= -\log (1 \cdot 8 \times 10^{-5}) + \log \frac{25/255}{0 \cdot 5/255}$$

$$= (5 - 0 \cdot 2553) + 1 \cdot 6990 = 6 \cdot 4437$$

$$pH = 14 - 6 \cdot 4437 = \mathbf{7 \cdot 5563}$$

Note. For more solved examples, see problem 5, page 8/66 and problems 10, 14, 24 and 31, pages 8/70, 71, 74 and 75, given under **CBSE-PMT (Mains) Special** and **IIT (Mains) Special.**

PROBLEMS FOR PRACTICE

1. How much volume of 0·1 M HAc should be added to 50 mL of 0·2 M NaAc solution if we want to prepare a buffer solution of *p*H 4·91. Given pK_a for acetic acid is 4·76. **[Ans. 70·92 *m*L]**
2. How much of 0·3 M ammonium hydroxide should be mixed with 30 mL of 0·2 M solution of ammonium chloride to give a buffer solution of *p*H 10. Given pK_b for NH_4OH is 4·75. **[Ans. 112·5 mL]**
3. The ionization constant of formic acid is $1 \cdot 8 \times 10^{-4}$. Calculate the ratio of sodium formate and formic acid in a buffer of pH 4·25. **[Ans. 3·24]**

HINTS FOR DIFFICULT PROBLEMS

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

i.e. $4 \cdot 91 = 4 \cdot 76 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

or $\log \frac{[\text{Salt}]}{[\text{Acid}]} = 0 \cdot 15$

or $\frac{[\text{Salt}]}{[\text{Acid}]} = \text{Antilog } 0 \cdot 15 = 1 \cdot 41$

$$\frac{\text{Moles of Salt}}{\text{Moles of Acid}} = 1 \cdot 41$$

i.e. $\dfrac{\frac{0 \cdot 2}{1000} \times 50}{\frac{0 \cdot 1}{1000} \times V} = 1 \cdot 41$ or $\dfrac{0 \cdot 01}{0 \cdot 0001\,V} = 1 \cdot 41$

or $V = 100/1 \cdot 41$

$= 70 \cdot 92$ *m*L.

2. $pOH = 14 - pH = 14 - 10 = 4$

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

$$4 = 4 \cdot 75 + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

or $\log \frac{[\text{Salt}]}{\text{Base}} = -0 \cdot 75 = \bar{1} \cdot 25$

or $\frac{[\text{Salt}]}{[\text{Base}]} = 0 \cdot 1778$

i.e. $\frac{\text{Moles of salt}}{\text{Moles of base}} = 0 \cdot 1778$

or $\dfrac{\frac{0 \cdot 2}{1000} \times 30}{\frac{0 \cdot 3}{1000} \times V} = 0 \cdot 1778$ or $V = 112 \cdot 5$ ml

3. $pK_a = -\log (1 \cdot 8 \times 10^{-4}) = 3 \cdot 74$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = pH - pK_a = 4 \cdot 25 - 3 \cdot 74 = 0 \cdot 51$$

or $[\text{Salt}]/[\text{Acid}] = \text{Antilog } 0 \cdot 51 = 3 \cdot 24$.

ADD TO YOUR KNOWLEDGE

1. pH of a buffer solution does not change on dilution or on keeping for long time or on adding small amounts of an acid or a base.
2. pH of a buffer changes with temperature because K_w changes. pH decreases with increase of temperature.
3. Buffer solutions can also be obtained by mixing an acid salt and a normal salt of a polybasic acid *e.g.* $Na_2HPO_4 + Na_3PO_4$.

Conceptual Questions

Q. 1. How does the degree of ionization of a weak electrolyte vary with concentration ? Give exact relationship. What is this law called ?

Ans. $\alpha = \sqrt{K_i / C}$. It is called Ostwald's dilution law (K_i is ionization constant and C is molar concentration of the electrolyte).

Q. 2. 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.

(*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^-**

Ans. (*i*) HCl (*aq*) — Acid (Arrhenius concept and Bronsted — Lowry concept)

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

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

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

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

(*vi*) BF_3 — Acid (Lewis concept)

(*vii*) Ag^+ — Acid (Lewis concept)

(*viii*) CN^- — Base (Lewis concept)

(*ix*) H_2O — Both acid and base *i.e.* amphoterric (Bronsted concept)

(*x*) H_2SO_4 — Both acid and base *i.e.* amphoterric (Bronsted concept)

(*xi*) HCO_3^- — Both acid and base *i.e.* amphoteric (Bronsted concept)

(*xii*) SiF_4 — Acid (Lewis concept)

Q. 3. Write down the conjugate acid and conjugate base of

(*i*) H_2O **(*ii*) HSO_4^-** **(*iii*) NH_3** **(*iv*) HS^-**

Ans. (*i*) H_3O^+ , OH^- (*ii*) H_2SO_4 , SO_4^{2-} (*iii*) NH_4^+ , NH_2^- (*iv*) H_2S , S^{2-}

Note. To write the conjugate acid of the given species, add H^+ ion. To write the conjugate base of the given species, subtract H^+ ion.

Q. 4. Write the conjugate acid/base for the following species :

HNO_2 , CN^- , $HClO_4$, F^- , OH^- , CO_3^{2-} , S^{2-}. (*N.C.E.R.T.*)

Ans. NO_2^- , HCN , ClO_4^- , HF , H_2O , HCO_3^- , HS^-.

Q. 5. Which of the following are Lewis acids ? H_2O , BF_3 , H^+ , NH_4^+. *(N.C.E.R.T.)*

Ans. BF_3, H^+ and NH_4^+ (Remember that all cations are Lewis acids).

Q. 6. Classify the following into Lewis acids and Lewis bases, OH^- , F^- , H^+ , BCl_3.

Ans. OH^- and F^- are Lewis bases because they can donate a pair of electrons while H^+ and BCl_3 are Lewis acids because they can accept a lone pair of electrons (In BCl_3, B is electron deficient).

Q. 7. Which concept can justify that $CaO + SO_3 \longrightarrow CaSO_4$ is an acid-base reaction ?

Ans. Lewis concept.

Q. 8. Ionization constants K_a for formic acid and acetic acid are $17 \cdot 7 \times 10^{-5}$ and $1 \cdot 77 \times 10^{-5}$. Which acid is stronger and how many times the other if equimolar concentrations of the two are taken ?

Ans. K_a for HCOOH > K_a for CH_3COOH. Hence formic acid is stronger.

Further $\dfrac{\text{Strength of HCOOH}}{\text{Strength of } CH_3COOH} = \sqrt{\dfrac{K_{HCOOH}}{K_{CH_3COOH}}} = \sqrt{10} = 3 \cdot 16$ **times.**

Q. 9. Fill in the blanks :

A strong acid has a weak.......and a weak base has a strong.......

Ans. Conjugate base, conjugate acid.

Q. 10. Out of CH_3COO^- and OH^- which is stronger base and why ?

Ans. OH^- ions can combine with H^+ ions more readily than CH_3COO^- ions can do. Hence OH^- is a stronger base.

Q. 11. What will be the *p*H of 1 M $NaNO_3$ solution at 25°C ?

Ans. $NaNO_3$ is a salt of strong acid and strong base. Hence its solution will be neutral. At 25°C, its *p*H will be = 7.

Q. 12. How is the degree of dissociation of a weak base related to its molarity ?

Ans. $\alpha = \sqrt{K_b / C} = \sqrt{K_b / M}$ where M = molarity

Q. 13. What is the effect of temperature on ionic product of water and why ?

Ans. Ionic product of water (K_w) increases with increase of temperature because $K_w = [H_3O^+][OH^-]$ and dissociation of H_2O to give H_3O^+ and OH^- increases with increase of temperature.

Q. 14. What happens to the ionic product of water if some acid is added into water ?

Ans. If remains unchanged.

Q. 15. What is pK_w ? What is its value at 25°C ?

Ans. $pK_w = -\log K_w = -\log 10^{-14} = 14$

Q. 16. What are pH and pOH values of a neutral solution at a temperature at which $K_w = 10^{-13}$?

Ans. pK_w = pH + pOH. But pK_w = 13. Also, for neutral solution, *p*H = *p*OH. Hence pH = pOH = 6·5.

Q. 17. The ionization constants of HF is $6 \cdot 8 \times 10^{-4}$. Calculate the ionization constant of the corresponding conjugate base. *(N.C.E.R.T.)*

Ans. $K_b = K_w / K_c = 10^{-14} / (6 \cdot 8 \times 10^{-4}) = 1 \cdot 47 \times 10^{-11} \simeq 1 \cdot 5 \times 10^{-11}$.

Q. 18. What pH do you expect for 10^{-8} M solution of an acid ?

Ans. Close to 7 but < 7. (Refer to solved example on page 8/26).

Q. 19. **Predict the acidic, basic or neutral nature of the solutions of the following salts :**

$NaCl$, KBr, $NaCN$, NH_4NO_3, $NaNO_2$, KF. *(N.C.E.R.T.)*

Ans. $NaCN$, $NaNO_2$, KF solutions are basic

$NaCl$, KBr solutions are neutral

NH_4NO_3 solution is acidic.

Q. 20. **What is the difference between ionic product and solubility product ?**

Ans. Solubility product is the product of the molar concentrations of the ions in a **saturated solution** but ionic product is for any solution.

Q. 21. **When is a precipitate formed when solutions of $BaCl_2$ and Na_2SO_4 are mixed ?**

Ans. When in the final solution after mixing, the ionic product $[Ba^{2+}]\,[SO_4^{2-}] > K_{sp}$ for $BaSO_4$.

Q. 22. **Will AgCl be more soluble in aqueous solution or NaCl solution and why ?**

Ans. $AgCl \rightleftharpoons Ag^+ + Cl^-$

In NaCl solution, $[Cl^-]$ will increase. As $[Ag^+]\,[Cl^-] = K_{sp}$ remains constant, $[Ag^+]$ will decrease *i.e.* the solubility will be less in NaCl solution than in water.

Q. 23. **Why solid NaCl starts separating out from a saturated solution of NaCl if HCl gas is passed through it ?**

Ans. HCl in the solution provides Cl^- ions. This increases the ionic product of NaCl and so the solid NaCl starts separating out.

Q. 24. **Why common salt is added to precipitate out soap from the solution during its manufacture ?**

Ans. Soap is sodium salt of higher fatty acids (RCOONa). On adding common salt, Na^+ ion concentration increases. Hence the equilibrium $RCOONa\,(s) \rightleftharpoons RCOO^- + Na^+$ shifts in the backward direction *i.e.* soap precipitates out.

Q. 25. **Through a solution containing Cu^{2+} and Ni^{2+}, H_2S gas is passed after adding dil HCl, which will precipitate out and why ?**

Ans. Cu^{2+} will precipitate out because in the acidic medium, only ionic product $[Cu^{2+}]\,[S^{2-}]$ exceeds the solubility product of CuS.

Q. 26. **Why in Group V of qualitative analysis, sufficient NH_4OH solution should be added before adding $(NH_4)_2CO_3$ solution ?**

Ans. This is done to convert NH_4HCO_3 usually present in large amounts alongwith $(NH_4)_2CO_3$ to $(NH_4)_2CO_3$

$$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$$

Q. 27. **What is pH of our blood ? Why does it remain almost constant inspite the variety of foods and spices we eat ?**

Ans. pH of our blood is about 7·4. It remains constant because it is a buffer.

Q. 28. **The *p*H of an enzyme catalysed reaction has to be maintained between 7 and 8. What indicator should be used to monitor and control the *p*H ?** *(N.C.E.R.T.)*

Ans. Bromothymol blue or Phenol red or Cresol red (see Table 8.6 Page 8/37).

Q. 29. **The pK_{In} of an indicator is 10·5. For which *p*H transition range is the indicator most suitable ?** *(N.C.E.R.T.)*

Ans. $pK_{In} \pm 1$ *i.e.* 9·5 to 11·5.

Q. 30. **Benzoic acid is a monobasic acid. When 1·22 g of its pure sample are dissolved in water and titrated against base, 50 ml of 0·2 M NaOH are used up. Calculate the molar mass of benzoic acid.** *(N.C.E.R.T.)*

Ans. 1000 ml of 1 M NaOH will neutralize acid $= \dfrac{1 \cdot 22}{50 \times 0 \cdot 2} \times 1000 = 122\ g$

But 1000 ml of 1 M NaOH contain 1 mole of NaOH and will neutralize 1 mole of monobasic acid. Hence molar mass of benzoic acid $= 122\ g\ mol^{-1}$.

Q. 31. **A solution gives yellow colour with methyl orange, methyl red and phenol red. What is the *p*H of the solution ?**

Ans. Yellow colour with methyl orange means $pH > 4{\cdot}5$

Yellow colour with methyl red means $pH > 6{\cdot}2$

Yellow colour with phenol red means $pH < 6{\cdot}4$. Hence the solution has pH between $6{\cdot}2$ to $6{\cdot}4$.

Q. 32. The ionization constant of formic acid is $1{\cdot}8 \times 10^{-4}$. Around what pH will its mixture with sodium formate give buffer solution of highest capacity ?

Ans. Buffer solution of highest capacity is formed at which $pH = pK_a = -\log(1{\cdot}8 \times 10^{-4}) = 3{\cdot}74$.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. What is the law called which gives relationship between degree of dissociation of a weak electrolyte and its concentration in the solution ?

Ans. Ostwald's dilution law.

Q. 2. What is the difference between a conjugate acid and a conjugate base ?

Ans. A conjugate acid and base differ by a proton (Conjugate acid $\rightleftharpoons$ Conjugate base + H^+)

Q. 3. Write the expression for comparison of relative strengths of two weak acids in terms of their ionization constants.

Ans. $\dfrac{\text{Strength of Acid}_1}{\text{Strength of Acid}_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$

Q. 4. What is the active mass of water ?

Ans. $55{\cdot}5 \text{ mol L}^{-1}$

Q. 5. How can we predict whether a precipitate will be formed or not on mixing two solutions ?

Ans. A precipitate will be formed if ionic product > solubility product

Q. 6. What happens when HCl gas is passed through saturated NaCl solution ?

Ans. NaCl will be precipitated out.

Q. 7. What is the function of adding NH_4OH in group V ?

Ans. It converts any NH_4HCO_3 present into $(NH_4)_2CO_3$.

Q. 8. What happens to the pH if a few drops of acid are added to CH_3COONH_4 solution ?

Ans. pH will remain almost constant (being a buffer solution).

Q. 9. Which indicator should preferably be used for titration of NH_4OH with HCl solution ?

Ans. Methyl orange.

Q. 10. What is the relationship between pK_{In} and pH at the equivalence point ?

Ans. $pK_{In} = pH$ at the equivalence point.

Q. 11. At half-neutralisation of a weak acid with a strong base, what is the relationship between pH and dissociation constant (K_a) of the weak acid ?

Ans. At half-neutralisation, $pH = pK_a$.

Q. 12. What is the range of a pH indicator in terms of its dissociation constant (K_{In}) ?

Ans. $pH = pK_{In} \pm 1$.

Q. 13. What happens to the solubility of AgCl in water if NaCl solution is added to it ?

Ans. Solubility of AgCl decreases due to common ion effect.

Q. 14. What is the relationship between pK_a and pK_b values where K_a and K_b represent ionization constants of the acid and its conjugate base respectively ?

Ans. $pK_a + pK_b = pK_w = 14$.

Q. 15. What is the relationship between pH and pOH ?

Ans. $pH + pOH = pK_w = 14$.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 8.1. to 8.2. **1.** What are strong and weak electrolytes ? Derive an expression for the calculation of the degree of ionization of a weak electrolyte.

2. Derive and define Ostwald's Dilution Law.

Sec. 8.3. **3.** Define the following giving examples :

(*i*) Bronsted-Lowry acid (*ii*) Bronsted-Lowry base (*iii*) Conjugate acid (*iv*) Conjugate base (*v*) Lewis acid (*vi*) Lewis base

4. Discuss the proton transfer theory (Bronsted Lowry theory) of acids and bases.

5. What is meant by the conjugate acid-base pair ?

6. Discuss Lewis definition of acids and bases. How is it more useful than the Bronsted definition ?

7. Define the terms 'acid' and 'base' according to each of the following concepts :

(*i*) Arrhenius (*ii*) Bronsted-Lowry (*iii*) Lewis

8. Derive expression for dissociation constants of weak acids and weak bases.

Sec. 8.4. to 8.5. **9.** How do you explain the strengths of acids and bases on the basis of Arrhenius theory ?

10. Discuss the strengths of acids and bases in terms of their dissociation or ionization constants.

11. Justify the statement that a strong acid has a weak conjugate base and strong base has a weak conjugate acid.

Sec. 8.6. **12.** What happens when the ions of weak or strong acid or base are allowed to interact with water ?

Sec. 8.7. to 8.8. **13.** What do you understand by the term 'ionic product of water' ? How has this concept been useful in defining the acidity and basicity of a solution ?

14. Explain the term 'ionic product of water'

15. Explain the significance of K_w.

16. How does K_w vary with temperature and why ?

Sec. 8.9. **17.** Briefly explain the term 'pH'.

18. What do you understand by 'pH scale' ? Can a solution have pH less than 0 or more than 14 ? Explain your answer, giving suitable reasons.

Sec 8.10. to 8.11. **19.** Derive expression for the calculation of pH of a solution of a salt of weak acid with a strong base or weak base with a strong acid.

20. Prove that the degree of hydrolysis of the solution of a salt of weak acid with a weak base (*e.g* CH_3COONH_4) is independent of the concentration of the solution.

21. Derive that for the solution of a salt of strong acid with a weak base (having concentration $= c$ mol L^{-1})

$$pH = -\frac{1}{2}[\log K_w - \log K_b + \log c]$$

Sec. 8.12. **22.** Briefly explain why phenophthalein is not a suitable indicator when the base is weak acid why methyl orange is not suitable when the acid is weak.

23. Is pH of the end point of acid-base titration always equal to 7 ? Explain why or why not.

24. Prove that for the colour change $pK_{\text{indicator}} \equiv pH$ at the equivalence point.

25. Why most of the indicators have a useful colour change over a *p*H range of 2 units ? Prove mathematically.

26. How is *p*K of a weak acid or a weak base determined from the titration curve ? Derive the result mathematically.

27. Derive normality equation, $N_1V_1 = N_2V_2$ and the molarity equation, $n_1 M_1 V_1 = n_2 M_2 V_2$

where n_1 and n_2 are the acidity and basicity of the base and the acid respectively.

Sec. 8.13. to 8.15. **28.** Explain the terms

(*i*) Solubility product (*ii*) Common ion effect

29. How does solubility product differ from ionic product ? Discuss two important applications of solubility product.

30. Give reasons for the following :

(*i*) Zinc sulphide is precipitated by hydrogen sulphide from an ammoniacal solution but not from a strong hydrochloric acid solution.

(*ii*) The precipitation of Mg $(OH)_2$ is prevented by the addition of NH_4Cl prior to the addition of NH_4OH but its precipitation by NaOH is not prevented by the prior addition of NaCl.

(*iii*) In qualitative analysis, NH_4Cl is added before adding NH_4OH solution for testing

Fe^{3+}, Cr^{3+} and Al^{3+}

or Discuss the use of ammonium chloride in group III of the inorganic analysis.

31. Define the term 'solubility product'. How would you use this concept to separate the sulphides of copper from that of zinc?

32. How is concept of solubility product utilized in qualitative analysis ?

Sec. 8.16. **33.** What is the Buffer solution ? Give an example of an acidic buffer and explain its buffer action.

34. Derive Henderson-Hasselbalch equation.

Long Answer Questions CARRYING 5 or more MARKS

Sec. 8.1. to 8.2. **1.** What are strong and weak electrolytes ? Define the term 'degree of ionization' and derive how the degree of ionization is related to the concentration of the solution of the electrolyte.

Sec. 8.3. **2.** What are acids and bases according to

(*i*) Arrhenius concept (*ii*) Bronsted-Lowry concept ? In what respects (*ii*) is superior to (*i*) ?

3. What is Lewis concept of Acids and Bases ? Classify the following into Lewis acids or Lewis bases giving reasons : H_2O , BF_3 , NH_3 , SiF_4 , Ag^+ , Cl^- , CO_2

What are the advantages and limitations of this concept over the earlier concepts ?

Sec. 8.4. to 8.5. **4.** Derive expression relating the strengths of monobasic acids of same molar concentration to the ionization constants of the acids.

Sec. 8.6. **5.** Briefly explain Aid-Base equilibria taking suitable examples.

Sec. 8.7. to 8.9. **6.** Explain the terms 'Ionic Product of Water' and 'pH value'. How does the former change with temperature ? What is pH scale ?

Sec 8.10. to 8.11. **7.** Briefly explain the terms—Salt hydrolysis, hydrolysis constant and degree of hydrolysis. Derive expressions for the calculation of pH of

(*a*) salt of strong acid with weak base (*b*) salt of weak acid with weak base.

Sec. 8.12. **8.** Describe Ostwald's theory of Acid-Base indicators.

9. Explain the different types of acid-base titration curves. How is a suitable indicator selected for a particular titration ?

Sec. 8.13. to 8.15. **10.** Briefly explain the term 'Solubility product.' Discuss its application

(*i*) in calculation of solubility of a sparingly soluble salt (*ii*) in qualitative analysis.

11. Explain 'Common Ion Effect'.

Sec. 8.16. **12.** What is a 'Buffer solution' ? What are different types of buffers ? Discuss their buffer action. What is the importance of buffers in biological processes ?

13. Derive expressions for the pH of (*a*) an acidic buffer mixture (*b*) a basic buffer mixture

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Levelling effect of water and differentiating solvents. As already explained, acids like HCl, HNO_3, H_2SO_4 etc. when dissolved in water dissociate almost completely *i.e.* their dissociation equilibrium is almost completely to the right (*e.g.* $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$ or may be written simply as $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$). These acids behave as equally strong in water. In fact, in aqueous solution, all acids stronger than H_3O^+ appear equally strong. Similarly, a number of strong bases behave as equally strong in water. This is called the **levelling effect** of water because the solvent 'water' levels them to the same strength. Thus to compare the relative strength of strong acids or strong bases, the solvent selected should be such that it ionizes the acids and bases to different extents. Such a solvent is called **differentiating solvent.** For example, acetic acid acts as a differentiating solvent for strong acids like $HClO_4$, HCl, HBr, HI, H_2SO_4 and HNO_3. This is because acetic acid is a poor proton acceptor. It accepts protons to different extents from these strong acids and an equilibrium exists which may be represented in general as

$$HA\,(aq) + CH_3COOH\,(aq) \rightleftharpoons A^-\,(aq) + CH_3COOH_2^+\,(aq)$$

$$[e.g.\ HClO_4\,(aq) + CH_3COOH\,(aq) \rightleftharpoons ClO_4^-\,(aq) + CH_3COOH_2^+\,(aq)$$

$$HNO_3\,(aq) + CH_3COOH\,(aq) \rightleftharpoons NO_3^-\,(aq) + CH_3COOH_2^+\,(aq)]$$

Their equilibrium constants can be determined and hence their relative strength can be found. For example, in case of the acids mentioned above, the strengths are found to be in the order

$$HClO_4 > H_2SO_4 > HI > HBr > HCl > HNO_3$$

Lastly, it may be mentioned that in water, as strong acids and strong bases dissociate almost completely, K_a or K_b has no meaning.

2. An interesting observation on change in pH on dilution or mixing with another solution.

If a solution of pH = 2 is diluted with water so that the volume becomes double, the pH of the diluted solution can be calculated as follows : $pH = 2$ means $[H_3O^+] = 10^{-2}$ M

After dilution to double the volume, $[H_3O^+] = \frac{10^{-2}}{2}\ M = 5 \times 10^{-3}$ M

$$pH = -\log(5 \times 10^{-3}) = 3 - \log 5 = 3 - 0{\cdot}699 = 2{\cdot}3$$

If a solution of pH = 2 is mixed with an equal volume of a solution of pH = 5, the pH of the final solution can be calculated as follows :

ADDITIONAL USEFUL INFORMATION contd.

After mixing, for solution with $pH = 2$, $[H_3O^+] = \frac{10^{-2}}{2} = 5 \times 10^{-3}$ M

and for solution with $pH = 5$, $[H_3O^+] = \frac{10^{-5}}{2} = 5 \times 10^{-6}$ M

$$\text{Total } [H_3O^+] = 5 \times 10^{-3} + 5 \times 10^{-6}$$
$$= 5 \times 10^{-3}\,(1 + 0{\cdot}001) = 5 \times 1{\cdot}001 \times 10^{-3}$$
$$= 5{\cdot}005 \times 10^{-3}$$
$$pH = -\log (5{\cdot}005 \times 10^{-3}) = 3 - \log 5{\cdot}005 \approx 2{\cdot}3$$

Thus we observe that the solution of $pH = 2$ when diluted with water to double the volume, pH changes to 2·3. Again when the solution of $pH = 2$ is mixed with equal volume of solution of $pH = 5$, pH again changes to 2·3. It means that the solution of $pH = 2$ being strong enough, the other solutions of $pH = 5$ or $pH = 7$ *i.e.* water have no role to play. However when the acid is diluted so that its concentration of H_3O^+ ions falls below 10^{-7}, then it is the $[H_3O^+]$ of water which retains the pH below 7. Similarly in case of a very dilute solution of a base *e.g.* 10^{-10} M NaOH solution, it is the $[OH^-]$ from H_2O which helps to retain the pH of the solution above 7. (Refer to solved examples of Type VIII and IX on page 8/26)

3. Double indicator. In the acid-base titrations, generally the indicators used are phenolphthalein and methyl orange. As they give end point at different pH ranges, hence it is important to remember the following :

(*i*) For titration of a base such as Na_2CO_3 against a strong acid (HCl), if phenolphthalein is used as indicator, the end point is indicated only for half neutralization of Na_2CO_3 (*i.e.* upto $NaHCO_3$), $Na_2CO_3 + H^+ \longrightarrow NaHCO_3 + Na^+$. If methyl orange is used, the end point is indicated when all the alkali is completely neutralized.

(*ii*) For titration of a mixture of Na_2CO_3 + NaOH vs HCl, there are two ways to carry out the titration :

(*a*) *Phenolphthalein may be used first to get first end point followed by methyl orange to get second end point.*

Then Acid used upto 1st end point = Complete neutralization of NaOH + $\frac{1}{2}$ neutralization of Na_2CO_3

Acid used from 1st end point to 2nd end point = $\frac{1}{2}$ neutralization of Na_2CO_3

(*b*) *Titration may be carried out first using phenolphthalein and then with same volume of fresh sample using methyl orange.*

Acid used with phenolphthalein as indicator = Complete neutralization of NaOH + $\frac{1}{2}$ neutralization of Na_2CO_3

Acid used with methyl orange as indicator = Complete neutralization of NaOH + Complete neutralization of Na_2CO_3. See solved example 40, page 8/79.

4. Acidic and Basic salts. The salts obtained during the intermediate stages of neutralization of a polyprotic acid are called **acidic salts.** The salt obtained on complete reaction of the acid with the base is called **normal salt.** For example, in the neutralization of H_3PO_4 with KOH, the salts KH_2PO_4 and K_2HPO_4 are acidic salts while K_3PO_4 is normal salt. Similarly $NaHSO_4$, $NaHCO_3$ etc. are acidic salts while Na_2SO_4, Na_2CO_3 etc. are normal salts.

Basic salts are salts that contain oxygen or hydroxyl groups in addition to the usual anions. Basic salts may be considered as the products of intermediate neutralization of bases *e.g.*

$$\underset{\text{Lead hydroxy nitrate}}{Pb(OH)NO_3} \quad \text{from } Pb(OH)_2 + HNO_3$$

or as the products of the loss of water from salts containing hydroxide ion *e.g.*

ADDITIONAL USEFUL INFORMATION contd.

$BiOCl$ from $Bi(OH)_2Cl$ by loss of H_2O.
Bismuth oxychloride

5. Effect of pH on solubility. The solubility of a salt of weak acid increases if the solution is made more acidic (*i.e.* *p*H is decreased). For example, the solubility equilibrium of CaF_2 may be represented as

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

On making the solution more acidic, H^+ ions will combine with the F^- ions. As a result, equilibrium will shift forward *i.e.* solubility will increase.

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS

Q. 1. What are the conjugate bases of the following ?

CH_3OH, HN_3, $[Al(H_2O)_6]^{3+}$.

Ans. CH_3O^-, N_3^-, $[Al(H_2O)_5OH]^{2+}$.

methoxide ion, azide ion

Q. 2. Why is ammonia termed as a base though it does not contain OH^- ions ?

Ans. : NH_3 is termed as a base on the basis of Lewis concept because it can donate a lone pair of electrons.

Q. 3. Glycine is an α-amino acid which exists in the form of Zwitter ion as $\overset{+}{N}H_3CH_2COO^-$. Write the formula of its conjugate acid and conjugate base.

Ans. Conjugate acid $= \overset{+}{N}H_3CH_2COO^- + H^+$

$$= \overset{+}{N}H_3CH_2COOH$$

Conjugate base $= \overset{+}{N}H_3CH_2COO^- - H^+$

$$= NH_2CH_2COO^-.$$

Q. 4. Write reaction for autoprotolysis of water. How is ionic product of water related to ionization constant of water ? Derive the relationship.

Ans. Autoprotolysis of H_2O takes place as follows :

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

For ionization of H_2O,

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

$$K_i = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_w}{[H_2O]} = \frac{K_w}{55\cdot55\ \text{mol L}^{-1}}$$

or $K_w = K_i \times 55\cdot55$.

Q. 5. Give reason for the following :

(i) Zinc is not precipitated as $Zn(OH)_2$ on adding NH_4OH to a zinc salt solution containing NH_4Cl.

(ii) $BaSO_4$ precipitate is washed with water containing a small amount of H_2SO_4 in gravimetric analysis.

(iii) CO_2 is more soluble in aqueous NaOH solution than in water.

(iv) A brown precipitate in a bottle containing aqueous $FeCl_3$ solution appears on standing.

Ans. (*i*) NH_4Cl suppresses the ionization of NH_4OH due to common ion effect. Hence concentration of OH^- decreases such that the ionic product $[Zn^{2+}][OH^-]^2$ does not exceed solubility product. Hence $Zn(OH)_2$ is not precipitated.

(*ii*) $BaSO_4$ dissociates as $BaSO_4\,(s) \overset{aq}{\rightleftharpoons} Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$. Addition of H_2SO_4 gives common SO_4^{2-} ions which suppresses the dissociation of $BaSO_4$ and thus helps in the complete precipitation.

(*iii*) In water, CO_2 dissoves to form carbonic acid (H_2CO_3)

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

As the reaction is reversible, the solubility is low. In aqueous NaOH, CO_2 reacts to form sodium carbonate

$$2\,NaOH\,(aq) + CO_2\,(g) \longrightarrow Na_2CO_3\,(aq) + H_2O\,(l)$$

As the reaction is irreversible, the solubility is more.

(*iv*) $FeCl_3$ undergoes hydrolysis forming a brown precipitate of ferric hydroxide

$$FeCl_3 + 3\,H_2O \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3} + 3\,HCl$$

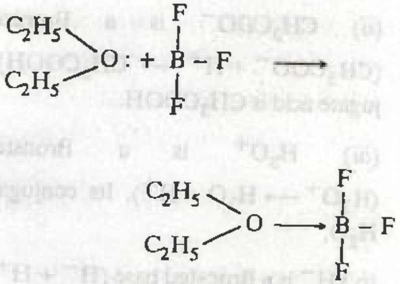
Q. 6. Why PO_4^{3-} ion is not amphiprotic ?

(B.I.T. Ranchi, 1990)

Ans. An amphiprotic ion is one which can donate proton as well as accept proton. PO_4^{3-} ion can accept proton(s) but cannot donate any proton. Hence PO_4^{3-} is not amphiprotic.

Q. 7. In the reaction between BF_3 and $C_2H_5OC_2H_5$ which one of them will act as an acid ? Justify your answer. ***(I.S.M. Dhanbad 1990)***

Ans. The reaction between BF_3 and $C_2H_5OC_2H_5$ is



As BF_3 accepts a pair of electrons, hence BF_3 is the Lewis acid.

Q. 8. Give reason in one or two sentences for the following :

Ammonium chloride is acidic in liquid ammonia solvent ***(I.I.T. 1991)***

Ans. In solution of NH_4Cl in liquid NH_3, the following reaction takes place

$$NH_4^+ + NH_3 \rightleftharpoons NH_3 + NH_4^+$$

Thus NH_4Cl gives proton. Hence it is acidic.

Q. 9. Arrange the following in order of their increasing basicity

$$\mathbf{H_2O,\ OH^-,\ CH_3OH,\ CH_3O^-}$$

(I.I.T. 1992)

Ans. $H_2O < CH_3OH < OH^- < CH_3O^-$

Q. 10. The following can act as both Bronsted acid and Bronsted base. Write the formula in each case (of the product)

(*i*) HCO_3^- (*ii*) $H_2PO_4^-$

(*iii*) NH_3 (*iv*) HS^-

(I.S.M. Dhanbad 1992)

Ans. (*i*) CO_3^{2-}, H_2CO_3

(*ii*) HPO_4^-, H_3PO_4

(*iii*) NH_2^-, NH_4^+

(*iv*) S^{2-}, H_2S.

Q. 11. NaCl solution is added to a saturated solution of $PbCl_2$. What will happen to the concentration of Pb^{2+} ions ?

Ans. Pb^{2+} ion concentration will decrease to keep K_{sp} constant.

Q. 12. Which is a stronger base in each of the following pairs and why ?

(*i*) H_2O, Cl^-

(*ii*) CH_3COO^-, OH^-

Ans. (*i*) H_2O

(*ii*) OH^-.

Refer to Bronsted-Lowry concept for relative strengths.

Q. 13. Between Na^+ and Ag^+ which is stronger Lewis acid and why ? ***(I.I.T. 1997)***

Ans. Ag^+. This is because Ag^+ has a pseudo noble gas configuration which makes it more polarizing.

Q. 14. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (Ionization energy for Al = 5137 kJ mol^{-1}, $\Delta H_{hydration}$ for Al^{3+} = − 4665 kJ mol^{-1}, $\Delta H_{hydration}$ for Cl^- = − 381 kJ mol^{-1}).

(I.I.T. 1997)

Ans. Total energy released due to hydration of ions $= -4665 - 3 \times 381 = -5808$ kJ mol^{-1}. This energy is greater than the ionisation energy of Al which is 5137 kJ mol^{-1}. Hence it would be ionic in the solution.

Q. 15. Classifly the following species as Lewis acids and Lewis bases

NH_3, BF_3, $SnCl_4$, C_5H_5N, CO, Ni^{2+}

(Bihar 1997)

Ans. Lewis acids : BF_3, $SnCl_4$, Ni^{2+}

Lewis bases : NH_3, C_5H_5N, CO.

Q. 16. Give reasons for the following :

(*i*) The solubility of calcium acetate decreases while that of lead nitrate increases with increase in temperature.

(ii) Magnesium is not precipitated from a solution of its salt by NH_4OH in the presence of NH_4Cl. ***(Roorkee 2000)***

Ans. (*i*) This is explained on the basis of Le Chatelier principle. Dissolution of lead nitrate is endothermic while that of calcium acetate is exothermic *i.e.*

$$Pb(NO_3)_2 + aq \rightleftharpoons Pb(NO_3)_2\,(aq) - \text{Heat}$$

$$CaAc_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + 2\,CH_3COOH$$

$$Ca(OH)_2 + aq \rightleftharpoons Ca(OH)_2\,(aq) + \text{Heat.}$$

(*ii*) The solubility product of $Mg(OH)_2$ is high. Presence of NH_4Cl suppresses the dissociation of NH_4OH due to common ion effect thus giving low concentration of $[OH^-]$. The ionic product, therefore, cannot exceed the solubility product.

Q. 17. **Explain why pH of 0·1 molar solution of acetic acid will be higher than that of 0·1 molar solution of HCl ?** ***(Bihar C.E.C.E. 2000)***

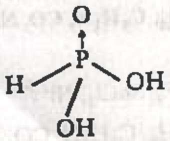
Ans. Acetic acid is a weak electrolyte. It is not completely ionized and hence gives less H^+ ion concentration. HCl is a strong acid. It is completely ionized giving more H^+ ion concentration. As $pH = -\log[H^+]$; less the $[H^+]$, greater will be the pH.

Q. 18. **Will the pH of water be same at 4°C and 25°C ? Explain.** ***(I.I.T. 2003)***

Ans. No, pH of water is not same at 4°C and 25°C. This is because with increase in temperature, dissociation of H_2O molecules increases. Hence $[H^+]$ will increase *i.e.* pH decreases. Thus pH at 4°C will be more than at 25°C.

Q. 19. **What type of salts are Na_2HPO_3 and NaHS ?** ***(West Bengal J.E.E. 2003)***

Ans. Na_2HPO_3 is obtained by reaction between NaOH and H_3PO_3 (a dibasic acid)



Both displaceable hydrogens are replaced by Na. No acidic hydrogen is left. Hence Na_2HPO_3 is a *normal salt.* NaHS is obtained by replacement of one acidic hydrogen of H_2S by Na (on reaction with NaOH). Hence NaHS is an *acidic salt.*

Q. 20. **Classify the following as acid or base according to Bronsted–Lowry theory and name their corresponding conjugate base or acid**

(i) NH_3 **(ii) CH_3COO^-**

(iii) H_3O^+ **(iv) H^-**

(v) HOO^- **(vi) $S_2O_8^{2-}$**

(West Bengal J.E.E. 2004)

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

(*i*) NH_3 is a Bronsted base ($NH_3 + H^+ \longrightarrow NH_4^+$). Its conjugate acid is NH_4^+.

(*ii*) CH_3COO^- is a Bronsted base ($CH_3COO^- + H^+ \longrightarrow CH_3COOH$). Its conjugate acid is CH_3COOH.

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

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

(*v*) HOO^- is a Bronsted acid ($HOO^- \longrightarrow O_2^{2-} + H^+$ in the reaction $HOO^- + H_2O \longrightarrow O_2^{2-} + H_3O^+$). Its conjugate acid is O_2^{2-} (peroxide ion).

(*vi*) $S_2O_8^{2-}$ is a Bronsted base ($S_2O_8^{2-} + 2\,H^+ \longrightarrow 2\,HSO_4^-$ in the reaction $S_2O_8^{2-} + 2\,H_2O \rightleftharpoons 2\,HSO_4^- + OH^-$). Its conjugate acid is HSO_4^-.

Q. 21. **Prove that the degree of dissociation of a weak monoprotic acid is given by**

$$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$

where K_a is the dissociation constant of the acid.

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

	HA	$\rightleftharpoons$	H^+	$+ A^-$
Initial molar conc.	C			
Molar conc. after dissociation	$C - C\alpha$ $= C(1-\alpha)$		$C\alpha$	$C\alpha$

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

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

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

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

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

or $$pH = pK_c - \log(1-\alpha) + \log\alpha$$

or $$\log\frac{1-\alpha}{\alpha} = pK_a - pH$$

or $$\frac{1-\alpha}{\alpha} = 10^{pK_a - pH}$$

or $$\frac{1}{\alpha} - 1 = 10^{pK_a - pH}$$

or $$\frac{1}{\alpha} = 1 + 10^{pK_a - pH}$$

or $$\alpha = \frac{1}{1 + 10^{pK_a - pH}}$$

Q. 22. (a) For an aqueous solution NH_4Cl prove that

$$[H_3O^+] = \sqrt{K_a C}$$

(C.B.S.E. P.M.T. 2004)

Ans. Refer to page 8/30.

Q. 23. Arrange the following compounds in the decreasing order of basicity on the basis of Bronsted-Lowry concept

$BaO, CO_2, SO_3, B_2O_3, Cl_2O_7$.

(I.I.T. 2004)

Ans. $BaO + H_2O \rightleftharpoons Ba(OH)_2$ (Basic)

$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (Weakly acidic)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (Strongly acidic)

$B_2O_3 + 3H_2O \rightleftharpoons 2H_3BO_3$ (Very weakly acidic)

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

Hence in the decreasing order of basicity, we have

$BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$.

B. PROBLEMS

Problem 1. Calculate the degree of dissociation of 0·5 M NH_3 at 25°C in a solution of pH = 12.

Solution.

	$NH_4OH \rightleftharpoons$	NH_4^+	$+ OH^-$
Initial conc.	C mol L^{-1}	0	0
After disso.	$C - C\alpha$	$C\alpha$	$C\alpha$

pH = 12 means $[H^+] = 10^{-12}$ or $[OH^-] = 10^{-2}$

$$\therefore [OH^-] = C\alpha = 10^{-2} \quad \text{or} \quad \alpha = \frac{10^{-2}}{C} = \frac{10^{-2}}{0{\cdot}5}$$

$$= 2 \times 10^{-2} \text{ or } 2\%.$$

Problem 2. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre to that of a solution containing 1 mole of CH_3COONa + 1 mole of CH_3COOH per litre.

Solution. Case I. *Calculation of pH of solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre*

	CH_3COONa	$+ HCl \longrightarrow$	CH_3COOH	$+ NaCl$
Initial moles	1 mole	1 mole	0	0
Moles after reaction	0	0	1	1

i.e. $[CH_3COOH] = 1 \text{ mol } L^{-1}$

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	$+ H^+$
Initial	C mol L^{-1}		
After dissociation	$C - C\alpha$	$C\alpha$	$C\alpha$

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

$$\therefore \quad [H^+] = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a C} = \sqrt{K_a} = K_a^{1/2}$$

$(\because C = 1 \text{ mol } L^{-1})$

$$\therefore \quad -\log[H^+] = -\frac{1}{2}\log K_a$$

i.e. $$(pH)_1 = -\frac{1}{2}\log K_a \quad \text{...}(i)$$

Case II. *Calculation of pH of solution containing 1 mole of CH_3COONa + 1 mole of CH_3COOH per litre*

Applying Henderson equation

$$(pH)_2 = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$= pK_a = -\log K_a \quad \text{...}(ii)$$

$[[Salt] = [Acid] = 1 \text{ mol } L^{-1}]$

From equations (*i*) and (*ii*), $(pH)_1/(pH)_2 = 1/2$.

Problem 3. 0·1 M CH_3COOH (pH = 3) is titrated with 0·05 M NaOH solution. Calculate the pH when

(i) 1/4th of the acid has been neutralized.

(ii) 3/4th of the acid has been neutralized.

Solution. *Calculation of dissociation constant of the acid*

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

As $pH = 3$, $\therefore [H^+] = 10^{-3}$ M,

$$[CH_3COO^-] = [H^+] = 10^{-3} \text{ M}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{10^{-3} \times 10^{-3}}{0{\cdot}1} = 10^{-5}$$

(i) When 1/4th of the acid has been neutralized

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Initial conc. $0.1\ M$

After 1/4th neutralization $0.1 \times \frac{3}{4} = 0.075\ M$ $\quad 0.1 \times \frac{1}{4} = 0.025\ M$

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

$$= -\log 10^{-5} + \log \frac{0.025}{0.075}$$

$$= 5 - 0.4771 = \mathbf{4.5229}$$

(ii) When 3/4th of the acid has been neutralized

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Initial conc. $0.1\ M$

After 3/4th neutralization $0.1 \times \frac{1}{4}\ M = 0.025\ M$ $\quad 0.1 \times \frac{3}{4}\ M = 0.075\ M$

$$\therefore\ pH = -\log 10^{-5} + \log \frac{0.075}{0.025}$$

$$= 5 + 0.4771 = 5.4771.$$

Problem 4. **A sample of hard water contains 100 ppm of $CaSO_4$. What minimum fraction of water should be evaporated off so that solid $CaSO_4$ begins to separate out ? K_{sp} for $CaSO_4$ is 9.0×10^{-6}.**

Solution. Maximum solubility of $CaSO_4$ in water can be calculated from its K_{sp} value as follows :

$$S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$$

$$= 3.0 \times 10^{-3}\ \text{mol L}^{-1}.$$

Suppose the volume of water taken = V litre

As $CaSO_4$ present is 100 ppm *i.e.* 100 *g* per 10^6 *g* of water, therefore, $CaSO_4$ present in V litres ($V \times 10^3$ *g*) of water

$$= \frac{100}{10^6} \times V \times 10^3\ g = 0.1\ V\ g = \frac{0.1\ V}{136}\ \text{moles}$$

(Molar mass of $CaSO_4$ = 136 *g* mol^{-1})

After evaporation, suppose volume of water left = V′ litre

Thus V′ litre of water will now contain $\frac{0.1\ V}{136}$ moles of $CaSO_4$.

This should be equal to the maximum solubility in moles L^{-1}.

$$\therefore\ \frac{0.1\ V}{136} \times \frac{1}{V'} = 3.0 \times 10^{-3}$$

$$\text{or}\quad V' = \frac{0.1\ V}{136 \times 3 \times 10^{-3}} = 0.245\ V$$

∴ Volume of water evaporated

$$= V - V' = V - 0.245\ V = 0.755\ V$$

i.e. **75·5%** of water should be evaporated off.

Problem 5. **A buffer solution with pH 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of $1.0\ M\ NH_4OH$ $\{K_b = 1.8 \times 10^{-5}\}$**

(M.L.N.R. Allahabad 1991)

Solution. For a basic buffer

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Further $\quad pH + pOH = 14$

so that $\quad pOH = 14 - pH = 14 - 9 = 5$

$$pK_b = -\log K_b$$

$$= -\log (1.8 \times 10^{-5}) = 4.7447$$

$$[Base] = [NH_4OH] = 1\ \text{mol L}^{-1}$$

$$\therefore\quad 5 = 4.7447 + \log \frac{[Salt]}{1}$$

or $\log [Salt] = 0.2553$ or $[Salt] = \mathbf{1.8\ mol\ L^{-1}}$

Problem 6. **Calculate the amount of $(NH_4)_2SO_4$ in g which must be added to 500 mL of $0.2\ M\ NH_3$ to yield a solution of pH = 9·35. K_b for $NH_3 = 1.78 \times 10^{-5}$.**

(M.L.N.R. 1992)

Solution. As it is a basic buffer,

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$= -\log K_b + \log \frac{[NH_4^+]}{[NH_4OH]}$$

As $pH = 9.35$, $\therefore pOH = 14 - 9.35 = 4.65$

Milli moles of NH_4OH in solution

$$= 0.2 \times 500 = 100$$

Suppose milli moles of NH_4^+ to be added = x

$$\therefore\ 4.65 = -\log (1.78 \times 10^{-5}) + \log \frac{x/500}{100/500}$$

$$= (5 - 0.2504) + \log \frac{x}{100}$$

$$\text{or}\quad \log \frac{x}{100} = -0.0996 = \bar{1}.0004 = 0.1$$

$$\text{or}\quad \log x = 2.1 \quad \text{or} \quad x = 125.9$$

∴ Milli moles of $(NH_4)_2SO_4$ to be added

$$= \frac{125.9}{2} = 62.95$$

(∵ 1 millimole of $(NH_4)_2SO_7 \equiv 2$ millimoles of NH_4^+)

∴ Mass of $(NH_4)_2SO_4$ to be added

$$= (62 \cdot 95 \times 10^{-3} \text{ moles}) (132 \, g \text{ mol}^{-1})$$

$$= 8 \cdot 3094 \, g.$$

Problem 7. **Given that the solubility product of radium sulphate ($RaSO_4$) is 4×10^{-11}. Calculate the solubility in (*a*) pure water (*b*) 0·10 M Na_2SO_4.** ***(I.S.M. Dhanbad 1992)***

Solution. (*a*) Suppose the solubility of $RaSO_4$ in water $= x$ mol L^{-1}. Then

$$\underset{x \text{ mol } L^{-1}}{RaSO_4} \rightleftharpoons \underset{x \text{ mol } L^{-1}}{Ra^{2+}} + \underset{x \text{ mol } L^{-1}}{SO_4^{2-}}$$

$$K_{sp} = [Ra^{2+}] [SO_4^{2-}]$$

$$= x \times x = x^2$$

or $\quad x^2 = 4 \times 10^{-11}$

or $\quad x = 6 \cdot 66 \times 10^{-6}$ mol L^{-1}

(*b*) $\quad Na_2 SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

As $[Na_2 SO_4] = 0 \cdot 10$ M,

∴ $[SO_4^{2-}]$ from $Na_2 SO_4 = 0 \cdot 10$ M

∴ Total $[SO_4^{2-}] = x + 0 \cdot 1$ M

$$= 6 \cdot 66 \times 10^{-6} + 0 \cdot 1 = 0 \cdot 1$$

Hence $\quad K_{sp} = [Ra^{2+}] [SO_4^{2-}]$

$$4 \times 10^{-11} = [Ra^{2+}] [0 \cdot 1]$$

or $\quad [Ra^{2+}] = 4 \times 10^{-10}$ mol L^{-1}

∴ Sulubility of $RaSO_4$ in 0·1 M Na_2SO_4

$$= 4 \times 10^{-10} \text{ mol } L^{-1}$$

Problem 8. **Calculate the simultaneous solubility of AgSCN and AgBr. K_{sp} for AgSCN and AgBr are $1 \cdot 0 \times 10^{-12}$ and $5 \cdot 0 \times 10^{-13}$ respectively.** ***(M.L.N.R. Allahabad 1995)***

Solution. Suppose the simultaneous solubilities of AgSCN and AgBr are x and y moles L^{-1}. Then as

$$Ag\,SCN \longrightarrow Ag^+ + SCN^-$$

and $\quad AgBr \longrightarrow Ag^+ + Br^-$

∴ $\quad$ Total $[Ag^+] = x + y$ moles L^{-1},

$[SCN^-] = x$ moles L^{-1},

$[Br^-] = y$ moles L^{-1}

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

$= (x + y) x = 1 \cdot 0 \times 10^{-12}$ *(Given)* $\quad$ ...*(i)*

K_{sp} for AgBr $= [Ag^+] [Br^-]$

$= (x + y) y = 5 \cdot 0 \times 10^{-13}$ *(Given)* $\quad$ ...*(ii)*

Dividing (*ii*) by (*i*),

$$\frac{y}{x} = 0 \cdot 5 \quad \text{or} \quad y = 0 \cdot 5 x$$

Putting in (*i*),

$(x + 0 \cdot 5 x) x = 10^{-12}$ or $1 \cdot 5 x^2 = 10^{-12}$

or $\quad x^2 = 0 \cdot 667 \times 10^{-12}$

or $\quad x = 0 \cdot 82 \times 10^{-6}$ mol L^{-1}

∴ $\quad y = 0 \cdot 5 x = 0 \cdot 41 \times 10^{-6}$ mol L^{-1}

Solubility of AgSCN $= 0 \cdot 82 \times 10^{-6}$ mol L^{-1}

Solubility of AgBr $= 0 \cdot 41 \times 10^{-6}$ mol L^{-1} M

Problem 9. **Calculate the hydrolysis constant of the salt containing NO_2^- ions. (Given K_a for $HNO_2 = 4 \cdot 5 \times 10^{-10}$.** ***(M.L.N.R. 1996)***

Solution. For the salt containing NO_2^- ion (*i.e.* salt of weak acid)

$$K_b = \frac{K_w}{K_a} = \frac{10^{-4}}{4 \cdot 5 \times 10^{-10}} = 2 \cdot 2 \times 10^{-5}.$$

Problem 10. **Calculate the degree of hydrolysis of a 0·01 M solution of KCN, K_a for HCN is $6 \cdot 2 \times 10^{-10}$.** ***(Bihar C.E.E. 1998)***

Solution. $h = \sqrt{\frac{K_w}{K_a c}}$

$$= \sqrt{\frac{10^{-14}}{6 \cdot 2 \times 10^{-10} \times 10^{-2}}}$$

$$= 0 \cdot 04 = 4\%.$$

Problem 11. **K_{sp} of Al $(OH)_3$ at 25°C is 5×10^{-33}. Calculate the solubility of Al $(OH)_3$ in moles/litre at 25°C.** ***(Bihar C.E.E. 2000)***

Solution. Suppose the solubility of Al $(OH)_3$

$= s$ moles litre^{-1}

$$Al\,(OH)_3 \xrightarrow{+aq} \underset{s}{Al^{3+}} + \underset{3s}{3\,OH^-}$$

$$K_{sp} = s \times (3s)^3 = 27 s^4 = 5 \times 10^{-33}$$

or $\quad s^4 = \dfrac{5}{27} \times 10^{-33}$

or $\quad 4 \log s = \log 5 - \log 27 - 33$

$$= 0 \cdot 6990 - 1 \cdot 4314 - 33 = 33 \cdot 7324$$

or $\log s = -8\cdot4331 = \bar{9}\cdot5669$

or $s = 3\cdot689 \times 10^{-9}$ M.

Problem 12. **$pH = 7\cdot40$, K_1 of H_2CO_3 $= 4\cdot5 \times 10^{-7}$. What will be the ratio of $[HCO_3^-]$ to $[H_2CO_3]$?** **(C.B.S.E. P.M.T. 2004)**

Solution. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$\therefore \frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H^+]}$$

$pH = 7\cdot40$ means $-\log[H^+] = 7\cdot4$

or $\log[H^+] = -7\cdot4 = \bar{8}\cdot6$

or $[H^+] = 3981 \times 10^{-8}$

$$\therefore \frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4\cdot5 \times 10^{-7}}{3\cdot981 \times 10^{-8}} = 11\cdot3.$$

I.I.T. (MAINS) SPECIAL

Problem 1. **The pH of pure water at 25°C and 35°C are 7 and 6 respectively. Calculate the heat of dissociation of H_2O into H^+ and OH^- ions.**

Solution. The reaction is

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

At 25°C, $pH = 7$ means $[H^+] = 10^{-7}$ M

$\therefore \quad K_w = 10^{-14}$

At 35°C, $pH = 6$ means $[H^+] = 10^{-6}$ M

$\therefore \quad K_w = 10^{-12}$

As equilibrium constants for the dissociation of H_2O are in the same ratio as ionic products of water, we can apply the relation

$$\log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{2\cdot303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \log \frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2\cdot303 \times 8\cdot314\ JK^{-1}\ mol^{-1}}\left(\frac{1}{298\ K} - \frac{1}{308\ K}\right)$$

or $\Delta H = 52898\ J\ mol^{-1} = 52\cdot898\ kJ\ mol^{-1}$.

Problem 2. **Calculate the approximate pH of a $0\cdot100$ M aqueous H_2S solution. K_1 and K_2 for H_2S are $1\cdot00 \times 10^{-7}$ and $1\cdot30 \times 10^{-13}$ respectively at 25°C.** **(Roorkee 1986)**

Solution. $K_2 << K_1$. Hence H^+ ions are mainly from 1st dissociation $\quad H_2S \rightleftharpoons H^+ + HS^-$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = \frac{[H^+]^2}{[H_2S]}$$

or $\quad [H^+] = \sqrt{K_1[H_2S]}$

$\therefore \quad [H^+] = \sqrt{10^{-7} \times 10^{-1}} = 10^{-4}$.

Hence $\quad$ pH = 4

Problem 3. **What volume of $0\cdot10$ M sodium formate solution should be added to 50 ml of $0\cdot05$ M formic acid to produce a buffer solution of pH $4\cdot0$? pK_a for formic acid is $3\cdot80$.** **(Roorkee 1990)**

Solution. The pH value of an acid buffer is given by

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} \quad \therefore 4 = 3\cdot8 + \log\frac{[Salt]}{[Acid]}$$

or $\log\frac{[Salt]}{[Acid]} = 0\cdot2$ or $\frac{[Salt]}{[Acid]} = 1\cdot5849$

or $\frac{\text{No. of moles of salt}}{\text{No. of moles of acid}} = 1\cdot5849$

($\because$ Volume is same for both)

No. of moles of acid present $= \frac{0\cdot05}{1000} \times 50$

$= 2\cdot5 \times 10^{-3}$

$\therefore$ No. of moles of salt $= 1\cdot5849 \times 2\cdot5 \times 10^{-3}$

$= 3\cdot962 \times 10^{-3}$

Hence volume of $0\cdot1$ M sodium formate required

$= \frac{1000}{0\cdot1} \times 3\cdot962 \times 10^{-3}$

$= 39\cdot62$ ml

Problem 4. **Calculate the pH at equivalence point when a solution of $0\cdot10$ M acetic acid is titrated with a solution of $0\cdot10$ M NaOH solution. K_a for acetic acid $= 1\cdot9 \times 10^{-5}$** **(Roorkee 1990)**

Solution. At the equivalent point, CH_3COONa is formed and its concentration $= \frac{0\cdot1}{2}$ M $= 0\cdot05$ M.

It is a salt of weak acid and strong base. The formula for finding the pH of such a salt is

$$pH = -\frac{1}{2}\left[\log K_w + \log K_a - \log c\right]$$

$\therefore \quad pH =$

$$-\frac{1}{2}[\log 10^{-14} + \log(1{\cdot}9 \times 10^{-5}) - \log(5 \times 10^{-2})]$$

$$= -\frac{1}{2}[-14 + (-5 + 0{\cdot}2788) - (-2 + 0{\cdot}6990)]$$

$$= \frac{1}{2}(14 + 5 - 0{\cdot}2788 - 2 + 0{\cdot}6990) = \frac{17{\cdot}42}{2} = 8{\cdot}71$$

Problem 5. **Calcium lactate is a salt of a weak organic acid and represented as Ca (Lac)$_2$. A saturated solution of Ca(Lac)$_2$ contains 0·13 mole of this salt in 0·50 litre solution. The pOH of this solution is 5·60. Assuming complete dissociation of the salt, calculate K$_a$ of lactic acid.** *(Roorkee 1991)*

Solution. In solution, Ca (Lac)$_2$ is hydrolysed as follows :

$$Ca(Lac)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + \underset{\text{lactic acid (weak)}}{2HLac}$$

$$Ca^{2+} + 2Lac^- + 2H_2O \rightleftharpoons Ca^{2+} + 2OH^- + 2HLac$$

or $\quad 2Lac^- + 2H_2O \rightleftharpoons 2OH^- + 2HLac$

or $\quad Lac^- + H_2O \rightleftharpoons OH^- + HLac$

Hydrolysis constant,

$$K_h = \frac{[OH^-][HLac]}{[Lac^-]} \qquad ...(i)$$

But $\quad [Ca(Lac)_2] = 0{\cdot}26 \text{ mol L}^{-1}$ so that

$$[Lac^-] = 0{\cdot}52 \text{ mol L}^{-1}$$

and $\quad pOH = 5{\cdot}60$ so that

$$-\log[OH^-] = 5{\cdot}60$$

or $\quad [OH^-] = \text{antilog}(-5{\cdot}6)$

$$= 2{\cdot}51 \times 10^{-6} \text{ M}$$

$$\therefore \quad K_h = \frac{(2{\cdot}51 \times 10^{-6})^2}{0{\cdot}52}$$

$$= 1{\cdot}21 \times 10^{-11}$$

Further $\quad HLac \rightleftharpoons H^+ + Lac^-$

$$\therefore \quad K_a = \frac{[H^+][Lac^-]}{[HLac]} \qquad ....(ii)$$

Also $\quad K_w = [H^+][OH^-] \qquad ...(iii)$

From (*i*), (*ii*) and (*iii*),

$$K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{1{\cdot}21 \times 10^{-11}}$$

$$= 8{\cdot}26 \times 10^{-4}$$

Problem 6. **A 40 mL solution of a weak base BOH is titrated with 0·1 N HCl solution. The pH of the solution is found to be 10·04 and 9·14 after the addition of 5·0 mL and 20·0 mL of acid respectively. Find out K$_b$ for the weak base.** *(I.I.T. 1991)*

Solution. Suppose initially 40 mL of weak base BOH contains *x* milli moles of the base.

Case I. After adding 5·0 mL of 0·1 N HCl,

$$pH = 10{\cdot}04$$

$$\therefore \quad pOH = 14 - 10{\cdot}04 = 3{\cdot}96$$

5 mL of 0·1 N HCl ≡ 5 × 0·1 milli moles = 0·5 milli mole

$$BOH + HCl \longrightarrow BCl + H_2O$$

	BOH	HCl	BCl	H$_2$O
Initial milli moles	x	0·5		
Milli moles after reaction	$x - 0{\cdot}5$	0	0·5	0·5

$$pOH = pK_b + \log\frac{[BCl]}{[BOH]}$$

$$\therefore \quad 3{\cdot}96 = -\log K_b + \log\frac{0{\cdot}5}{x - 0{\cdot}5} \qquad ...(i)$$

Case II. After adding 20·0 mL of 0·1 N HCl,

$$pH = 9{\cdot}14$$

$$\therefore \quad pOH = 10 - 9{\cdot}14 = 4{\cdot}86$$

20 mL of 0·1 N HCl ≡ 20 × 0·1 milli moles = 2 milli moles

$$BOH + HCl \longrightarrow BCl + H_2O$$

	BOH	HCl	BCl	H$_2$O
Initial milli moles	x	2	0	0
Milli moles after reaction	$x - 2$	0	2	2

$$\therefore \quad 4{\cdot}86 = -\log K_b + \log\frac{2}{x-2} \qquad (...ii)$$

Subtracting eqn. (*i*) from eqn. (*ii*), we get

$$4{\cdot}86 - 3{\cdot}96 = \log\frac{2}{x-2} - \log\frac{0{\cdot}5}{x - 0{\cdot}5}$$

or $\quad 0{\cdot}9 = \log 2 - \log(x-2)$

$$- \log 0{\cdot}5 + \log(x - 0{\cdot}5)$$

or $\log\dfrac{x - 0{\cdot}5}{x - 2} = 0{\cdot}9 - \log 2 + \log 0{\cdot}5$

$$= 0{\cdot}9 - 0{\cdot}3010 - 0{\cdot}3010$$

$$= 0{\cdot}298$$

or $\quad \dfrac{x - 0{\cdot}5}{x - 2} = 1{\cdot}986$

or $\quad x - 0{\cdot}5 = 1{\cdot}986x - 3{\cdot}972$

or $\quad 0{\cdot}986x = 3{\cdot}472 \quad$ or $\quad x = 3{\cdot}52$

Substituting in eqn. (*ii*), we get

$$4{\cdot}86 = -\log K_b + \log\frac{2}{3{\cdot}52 - 2}$$

or $\log K_b = -4\cdot86 + 0\cdot301 - 0\cdot1818$

$= -4\cdot7408 = 5\cdot2592$

$\therefore \quad K_b = 1\cdot817 \times 10^{-5}$.

Problem 7. **A certain weak acid has $K_a = 1\cdot0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.** ***(I.I.T. 1991)***

Solution. $\underset{\text{weak}}{HA} + \underset{\text{strong}}{BOH} \rightleftharpoons BA + H_2O$

or $HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$

or $HA + OH^- \rightleftharpoons A^- + H_2O$

$$K = \frac{[A^-]}{[HA][OH^-]} \quad ...(i)$$

Further for the weak acid,

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

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ...(ii)$$

Also $K_w = [H^+][OH^-] \quad ...(iii)$

From eqns. (*i*), (*ii*) and (*iii*),

$$K = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

Problem 8. **The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is $4\cdot42 \times 10^{-5}$. A 500 ml of a saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0·4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated ?** ***(I.I.T. 1992)***

Solution. Step I. *Calculation of amount of $Ca(OH)_2$ in 500 ml of saturated solution.* Suppose solubility of $Ca(OH)_2 = x$ *mol* L^{-1}

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$$

$\therefore \quad K_{sp} = [Ca^{2+}]\ [OH^-]^2$

$= x \times (2x)^2 = 4x^3$

$\therefore \quad 4x^3 = 4\cdot42 \times 10^{-5}$

or $\quad x^3 = 1.105 \times 10^{-5}$

$3 \log x = \log(1\cdot105 \times 10^{-5})$

$= 0\cdot0434 - 5 = -4\cdot9566$

$\log x = -1\cdot6522 = \bar{2}\cdot3478$

or $\quad x = 2\cdot227 \times 10^{-2}\ \text{mol L}^{-1}$

$\therefore$ Amount of $Ca(OH)_2$ present in 500 ml

$$= \frac{2\cdot227 \times 10^{-2}}{2} \times 74\ g$$

$$= 82\cdot39 \times 10^{-2}\ g = 823\cdot9\ mg$$

Step II. *Calculation of the amount of $Ca(OH)_2$ in solution after mixing.* As equal volumes of $Ca(OH)_2$ solution and 0·4M NaOH solution have been mixed

Conc. of NaOH in the mixture $= \dfrac{0\cdot4}{2} = 0\cdot2$ M

$$[OH^-] = [NaOH] = 0\cdot2\ M$$

K_{sp} for $Ca(OH)_2 = [Ca^{2+}][OH^-]^2$

$\therefore \quad [Ca^{2+}] = \dfrac{4\cdot42 \times 10^{-5}}{(0\cdot2)^2}$

$= 1\cdot105 \times 10^{-3}\ \text{mol L}^{-1}$

Total volume of the solution after mixing

$= 500 + 500 = 1000$ ml

$\therefore$ Amount of $Ca(OH)_2$ in the mixture solution

$= 1\cdot105 \times 10^{-3} \times 74\ g = 0\cdot0818\ g = 81\cdot8$ mg

$\therefore$ Amount of $Ca(OH)_2$ precipitated

$= 823\cdot9 - 81\cdot8 = 742\cdot1$ mg

Problem 9. **Calculate the pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0·10 M Mg^{2+} ions. K_{sp} of $Mg(OH)_2 = 1 \times 10^{-11}$.**

Solution. Minimum $[OH^-]$ after which $Mg(OH)_2$ begins to precipitate can be calculated from

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

$(0\cdot10)[OH^-]^2 = 10^{-11}$

or $\quad [OH^-]^2 = 10^{-10}$ or $[OH^-] = 10^{-5}$

or $\quad [H^+] = 10^{-9}$

or $\quad pH = 9$

Problem 10. **The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5M $NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7·4 ? K_a for H_2CO_3 in blood is $7\cdot8 \times 10^{-7}$.** ***(I.I.T. 1993)***

Solution. $pH = pK_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$7\cdot4 = -\log(7\cdot8 \times 10^{-7}) + \log \frac{[NaHCO_3]}{[H_2CO_3]}$$

$$\log \frac{[NaHCO_3]}{[H_2CO_3]} = 7\cdot4 + (-7 + 0\cdot8921)$$

$$= 1\cdot2921$$

or $\quad \dfrac{[NaHCO_3]}{[H_2CO_3]} = \text{Antilog } 1\cdot2921 = 19\cdot59$

H_2CO_3 present in 10 ml of blood ($2M\ H_2CO_3$)

$$= \frac{2}{1000} \times 10 = 0\cdot02 \text{ mole}$$

$\therefore$ $NaHCO_3$ that should be present

$$= 19\cdot59 \times 0\cdot02 = 0\cdot3918 \text{ mole}$$

Volume of 5 M $NaHCO_3$ required

$$= \frac{1000}{5} \times 0\cdot3918 = \mathbf{78\cdot36\ ml}$$

Problem 11. **An aqueous solution of a metal bromide MBr_2 (0·05 M) is saturated with H_2S. What is the minimum pH at which MS will be precipitated ? (K_{sp} for MS = $6\cdot0 \times 10^{-21}$, concentration of saturated H_2S = 0·1 M, $K_1 = 10^{-7}$ and $K_2 = 1\cdot3 \times 10^{-13}$ for H_2S)**

(I.I.T. 1993)

Solution. $[M^{2+}] = [MBr_2] = 0\cdot05$ M

For the precipitation of MS, minimum $[S^{2-}]$ can be calculated from

$$[S^{2-}][M^{2+}] = K_{sp} \quad i.e. \quad [0\cdot05][S^{2-}] = 6\cdot0 \times 10^{-21}$$

$$\text{or } [S^{2-}] = 1\cdot2 \times 10^{-19}$$

S^{2-} ions are obtained from the following dissociations

$$H_2S \overset{K_1}{\rightleftharpoons} H^+ + HS^-$$

$$HS^- \overset{K_2}{\rightleftharpoons} H^+ + S^{2-}$$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]}, \quad K_2 = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$\therefore \quad K_1 K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$10^{-7} \times 1\cdot3 \times 10^{-13} = \frac{[H^+]^2[1\cdot2 \times 10^{-19}]}{(0\cdot1)}$$

or

$$[H^+]^2 = \frac{1\cdot3 \times 10^{-20} \times 10^{-1}}{1\cdot2 \times 10^{-19}} = 1\cdot083 \times 10^{-2}$$

$$\text{or} \quad [H^+] = 1\cdot041 \times 10^{-1} = 0\cdot1041 \text{ M}$$

$$\therefore \quad pH = -\log(0\cdot1041) = \mathbf{0\cdot9826}.$$

Problem 12. **Nicotinic acid ($K_a = 1\cdot4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its percentage dissociation in a solution which contains 0·10 mole of nicotinic acid per 2·0 litre of solution.**

(Roorkee 1993)

Solution. Suppose degree of dissociation of nicotinic acid = α

	$HNiC \rightleftharpoons$	H^+ +	NiC^-
Initial amount	0·1 mole		
Amount at eqm	$0\cdot1 - 0\cdot1\,\alpha$ $= 0\cdot1\,(1-\alpha)$	$0\cdot1\,\alpha$	$0\cdot1\,\alpha$
Molar conc. at eqm.	$= 0\cdot1\,(1-\alpha)/2$	$0\cdot1\,\alpha/2$	$0\cdot1\,\alpha/2$

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

$$\text{or} \quad 1\cdot4 \times 10^{-5} = \frac{(0\cdot1\,\alpha/2)(0\cdot1\,\alpha/2)}{0\cdot1\,(1-\alpha)/2}$$

If $\alpha << 1$, then

$$1\cdot4 \times 10^{-5} = \frac{(0\cdot05\,\alpha)^2}{0\cdot05} = 0\cdot05\,\alpha^2$$

$$\text{or} \quad \alpha^2 = 2\cdot8 \times 10^{-4}$$

$$\text{or} \quad \alpha = 5\cdot29 \times 10^{-2} = 0\cdot053$$

$$\% \text{ dissociation} = 0\cdot053 \times 100 = \mathbf{5\cdot3\%}$$

Problem 13. **The pH of 0·05 M aqueous solution of diethylamine is 12·0. Calculate its K_b.**

(Roorkee 1993)

Solution. $(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

As $\quad pH = 12, \therefore [H^+] = 10^{-12}$

or $\quad [OH^-] = 10^{-2}, (C_2H_5)_2NH = 0\cdot05 - 0\cdot01 = 0\cdot04$

$$K_b = \frac{[(C_2H_5)_2NH_2^+][OH^-]}{[(C_2H_5)_2NH]} = \frac{10^{-2} \times 10^{-2}}{0\cdot04}$$

$$= \mathbf{2\cdot5 \times 10^{-3}}$$

Problem 14. **0·15 mole of pyridinium chloride has been added into 500 cm³ of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume (K_b for pyridine = $1\cdot5 \times 10^{-19}$ M)** ***(Roorkee 1995)***

Solution. For basic buffer,

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

Here base is pyridine and salt is pyridinium chloride.

Conc. of pyridine = 0·2 M

Conc. of pyridinium chloride

$$= 0\cdot15 \text{ mol in } 500 \text{ cm}^3 = 0\cdot30 \text{ M}$$

$$pK_b = -\log(1\cdot5 \times 10^{-9})$$

$$= -[0\cdot1761 - 9] = 8\cdot8239$$

$$\therefore \quad pOH = 8\cdot8239 + \log\frac{0\cdot30}{0\cdot20}$$

$$= 8{\cdot}8239 + \log 1{\cdot}5$$

$$= 8{\cdot}8239 + 0{\cdot}1761 = 9{\cdot}0$$

i.e. $-\log [OH^-] = 9{\cdot}0$

or $\log [OH^-] = -9$

$\therefore [OH^-] = 10^{-9}$

$[OH^-]$ from $H_2O = 10^{-7}$ M

$\therefore$ Total $[OH^-] = 10^{-7} + 10^{-9}$ M

$$= 10^{-9}(10^2 + 1)$$

$$= 1{\cdot}01 \times 10^{-7}\text{ M}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1{\cdot}01 \times 10^{-7}}$$

$$= 9{\cdot}90 \times 10^{-8}\text{ M}$$

$$\therefore pH = -\log [H^+] = -\log (9{\cdot}90 \times 10^{-8})$$

$$= -[0{\cdot}9956 - 8] = 7{\cdot}0044$$

Problem 15. **An aqueous solution contains 10% ammonia by mass and has a density of 0·99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for $NH_4^+ = 5{\cdot}0 \times 10^{-10}$ M**

(Roorkee 1995)

Solution. 10% ammonia by mass means 10 *g* NH_3 are present in 100 *g* of the solution.

$\therefore$ Molarity of the solution

$$= \frac{10}{17} \times \frac{1}{100/0{\cdot}99} \times 1000 = 5{\cdot}82\text{ M}$$

$$NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Initial conc. $\quad C$ mol L^{-1}

Aftr dissociation $\quad C - C\alpha \quad C\alpha \quad C\alpha$

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

$$\therefore [OH^-] = C\alpha = C\cdot\sqrt{K_b/C} = \sqrt{K_bC}$$

$$= \sqrt{(K_w/K_a)\,C}$$

$$= \sqrt{\frac{10^{-14}}{5{\cdot}0 \times 10^{-10}} \times 5{\cdot}82} = 1{\cdot}079 \times 10^{-2}\,M$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1{\cdot}079 \times 10^{-2}}$$

$$= 0{\cdot}9268 \times 10^{-12}\text{ M} = 9{\cdot}268 \times 10^{-13}\text{ M}$$

Problem 16. **Calculate the pH of an aqueous solution of 1·0 M ammonium formate assuming complete dissociation (pK_a of formic acid = 3·8 and pK_b of ammonia = 4·8)** ***(I.I.T. 1995)***

Solution. For the salt of weak acid and weak base,

$$[H^+] = \sqrt{\frac{K_w K_a}{K_b}}$$

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

$$= \frac{1}{2}[pK_a + pK_w - pK_b]$$

$$= \frac{1}{2}[3{\cdot}8 + 14 - 4{\cdot}8] = 6{\cdot}5$$

Problem 17. **What is the pH of a 0·50 M aqueous NaCN solution ? pK_b of CN^- is 4·70.** ***(I.I.T. 1996)***

Solution. $NaCN + H_2O \rightleftharpoons NaOH + HCN$

or $CN^- + H_2O \rightleftharpoons OH^- + HCN$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{[OH^-]^2}{[CN^-]}$$

$$\therefore pK_b = -\log K_b = -2\log [OH^-] + \log [CN^-]$$

or $4{\cdot}70 = -2\log [OH^-] + \log (0{\cdot}5)$

$[\because [CN^-] = [NaCN]]$

or $2\log [OH^-] = -5{\cdot}00$

or $\log [OH^-] = -2{\cdot}5$

$$-\log [OH^-] = 2{\cdot}5$$

$$p_{OH} = 2{\cdot}5$$

$$pH = 14 - 25 = 11{\cdot}5$$

Problem 18. **The ionization constant of NH_4^+ in water is $5{\cdot}6 \times 10^{-10}$ at 25°C. The rate constant for reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is $3{\cdot}4 \times 10^{10}$ litre mol^{-1} sec^{-1}. Calculate the rate constant for proton transfer from water to NH_3.** ***(I.I.T. 1996)***

Solution. $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$,

$$K_a = 5{\cdot}6 \times 10^{-10}$$

$$NH_3 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_4^+ + OH^-,$$

$$k_b = 3{\cdot}4 \times 10^{10}$$

Aim. To find k_f

We know that for a conjugate acid-base pair

$K_{acid} \times K_{base} = K_w$ *i.e.* $K_a \times K_b = K_w$

$$\therefore K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5{\cdot}6 \times 10^{-10}}$$

But $K_b = \dfrac{k_f}{k_b}$

$$\therefore k_f = K_b \times k_b = \frac{10^{-14}}{5{\cdot}6 \times 10^{-10}} \times 3{\cdot}4 \times 10^{10}$$

$$= 0{\cdot}607 \times 10^6 = 6{\cdot}07 \times 10^5$$

Problem 19. **Calculate the percentage of hydrolysis in 0·003 M aqueous solution of NaOCN (K_a for HOCN = $3{\cdot}33 \times 10^{-4}$ M)** ***(Roorkee 1996)***

Solution. $NaOCN + H_2O \rightleftharpoons NaOH + HOCN$

$$\text{or} \quad OCN^- + H_2O \rightleftharpoons OH^- + HOCN$$

Initial conc. c

Conc. at eqm. $c(1-h) \simeq c$ $\quad ch \quad ch$

where h is the degree of hydrolysis

∴ Hydrolysis constant,

$$K_h = \frac{ch \cdot ch}{c} = ch^2 \quad \text{or} \quad h = \sqrt{K_h / c}$$

$$\text{But} \quad K_h = \frac{[OH^-][HOCN]}{[OCN^-]}$$

$$K_a = \frac{[H^+][OCN^-]}{[HOCN]} \quad [HOCN \rightleftharpoons H^+ + OCN^-]$$

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

Combining these equations,

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{3{\cdot}33 \times 10^{-4}}$$

$$\therefore \quad h = \sqrt{\frac{10^{-10}}{3{\cdot}33} \times \frac{1}{3 \times 10^{-3}}} = \sqrt{10^{-8}} = 10^{-4}$$

∴ %age hydrolysis = $10^{-4} \times 100 = 0{\cdot}01$

Problem 20. **An aqueous solution of aniline of concentration 0·24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M ? (K_a for $C_6H_5\overset{+}{N}H_3$ = $2{\cdot}4 \times 10^{-6}$ M)** ***(Roorkee 1996)***

Solution. In aqueous solution, aniline is hydrolysed as

$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5\overset{+}{N}H_3 + OH^-$$

When NaOH is added, hydrolysis will be suppressed so that in the final solutoin,

$$[C_6H_5\overset{+}{N}H_3] = 10^{-8}\,M \; (\textit{Given})$$

If conc. of NaOH added is x mol L^{-1}, then at equilibrium

$$[C_6H_5NH_2] = 0{\cdot}24 - 10^{-8} \simeq 0{\cdot}24$$

$$[C_6H_5\overset{+}{N}H_3] = 10^{-8}\,M \; (\textit{Given})$$

$$[OH^-] = 10^{-8} + x \simeq x\,M$$

∴ Hydrolysis constant,

$$K_h = \frac{[C_6H_5\overset{+}{N}H_3][OH^-]}{[C_6H_5NH_2]} \quad ...(i)$$

Further, we are given

$$C_6H_5\overset{+}{N}H_3 \rightleftharpoons C_6H_5NH_2 + H^+$$

$$K_a = \frac{[C_6H_5NH_2][H^+]}{[C_6H_5\overset{+}{N}H_3]} \quad ...(ii)$$

$$\text{Also} \quad [H^+][OH^-] = K_w \quad ...(iii)$$

Combining eqns. (*i*), (*ii*) and (*iii*)

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{2{\cdot}4 \times 10^{-6}} = \frac{10^{-8}}{2{\cdot}4}$$

Substituting the values in eqn. (*i*), we get,

$$\frac{10^{-8}}{2{\cdot}4} = \frac{10^{-8} \times x}{0{\cdot}24} \quad \text{which gives } x = 10^{-2}\,M$$

Problem 21. **A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^- with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water ? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions ? (Assume $CaCO_3$ to be completely insoluble in water). If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH ? (One ppm means one part of the substance in one million parts of water, weight/weight).** ***(I.I.T. 1997)***

Solution. SO_4^{2-} present in 1000 kg of water

$$= \frac{96}{10^6} \times 1000\text{ kg} = 96\text{ g} = \frac{96}{96} = 1\text{ mole.}$$

HCO_3^- present in 1000 kg of water

$$= \frac{183}{10^6} \times 1000\text{ kg} = 183\text{ g} = \frac{183}{61} = 3\text{ moles}$$

Ca^{2+} present alongwith SO_4^{2-} ions = 1 mole

Ca^{2+} present alongwith HCO_3^- as $Ca(HCO_3)_2$

$$= \frac{3}{2}\text{ mole}$$

∴ Total Ca^{2+} present in 1000 kg of water

$$= 1 + \frac{3}{2} = 2{\cdot}5\text{ moles}$$

CaO added will react with $Ca(HCO_3)_2$ as follows :

$$Ca(HCO_3)_2 + CaO \longrightarrow 2\,CaCO_3 \downarrow + H_2O$$

But $Ca(HCO_3)_2$ present = $\frac{3}{2}$ mole (*calculated above*)

$\therefore$ CaO required = $\frac{3}{2}$ mole = 1·5 moles

After treatment with CaO *i.e.* removal of $Ca(HCO_3)_2$, amount of Ca^{2+} left (due to $CaSO_4$ only) in 1000 kg of water = 1 mole = 40 g

$\therefore$ Concentration of residual Ca^{2+} (in ppm)

$$= 40 \text{ ppm}$$

Now 1000 kg of water contain Ca^{2+} = 1 mole

$\therefore$ 1000 g of water will contain $Ca^{2+} = 10^{-3}$ mole

No. of moles of H^+ exchanged = 2×10^{-3} mole

$$\therefore \quad pH = -\log(2 \times 10^{-3}) = 2{\cdot}7.$$

Problem 22. **A sample of AgCl was treated with 5·00 ml of 1·5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0·0026 g of Cl^- per litre. Calculate the solubility product of AgCl (K_{sp} for $Ag_2CO_3 = 8{\cdot}2 \times 10^{-2}$)** *(I.I.T. 1997)*

Solution. 1·5 M Na_2CO_3 gives $[CO_3^{2-}] = 1{\cdot}5$ M

$$K_{sp} \text{ for } Ag_2CO_3 = [Ag^+]^2[CO_3^{2-}]$$

$$\therefore \quad [Ag^+] = \sqrt{\frac{K_{sp} \text{ for } Ag_2CO_3}{[CO_3^{2-}]}} = \sqrt{\frac{8{\cdot}2 \times 10^{-12}}{1{\cdot}5}}$$

$$= 2{\cdot}34 \times 10^{-6} \text{ M}$$

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

$$= (2{\cdot}34 \times 10^{-6})\left(\frac{0{\cdot}0026}{35{\cdot}5}\right)$$

$$= 1{\cdot}71 \times 10^{-10}$$

Problem 23. **An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0·1. What should be the minimum change in the pH of the solution to observe a complete colour change. ($K_a = 1{\cdot}0 \times 10^{-5}$) ?** *(I.I.T. 1997)*

Solution. $HIn \rightleftharpoons H^+ + In^-$,

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

$$\text{or} \quad [H^+] = K_a \frac{[HIn]}{[In^-]}$$

When $[In^-]/[HIn] = 10$,

$$[H^+] = 10^{-5} \times \frac{1}{10} = 10^{-6}, \quad pH = 6$$

When $[In^-]/[HIn] = 0{\cdot}1$,

$$[H^+] = 10^{-5} \times 10 = 10^{-4}, \; pH = 4$$

$\therefore$ Minimum change in pH = 2

Problem 24. **Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9·0 when total concentration of buffering reagents is 0·6 mol L^{-1}. pK_b for $NH_3 = 4{\cdot}7$, log 2 = 0·30.** *(Roorkee 1997)*

Solution. pH = 9·0. Hence pOH = 14 – 9 = 5

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

$$5 = 4{\cdot}7 + \log\frac{[Salt]}{[Base]} \quad \text{or} \quad \log\frac{[Salt]}{[Base]} = 0{\cdot}3$$

$$\text{or} \quad \frac{[Salt]}{[Base]} = \text{Antilog } 0{\cdot}3 = 2$$

i.e. $[Salt] = 2 \times [Base]$

Also we are given :

$$[Salt] + [Base] = 0{\cdot}6 \text{ mol } L^{-1}$$

This on solving gives **[Base] = 0·2 mol L^{-1}**

and **[Salt] = 0·4 mol L^{-1}**

Problem 25. **K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in an aqueous solution in which the concentration of Asc^- ions is 0·02 M.** *(Roorkee 1997)*

Solution. As ascorbic acid is a weak acid, aqueous solution of Asc^- means the solution of a salt of weak acid with strong base. For such a salt, degree of hydrolysis is given by

$$h = \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-5} \times 2 \times 10^{-2}}}$$

$$= 10^{-4} = 10^{-4} \times 100\% = 0{\cdot}01\%$$

$$\begin{array}{lccc} & Asc^- + H_2O & \rightleftharpoons HAsc & + \; OH^- \\ & c \text{ mol } L^{-1} & & \\ & c - ch & ch & ch \end{array}$$

$$[OH^-] = ch = 0{\cdot}02 \times 10^{-4} = 2 \times 10^{-6} \text{ mol } L^{-1}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2 \times 10^{-6}}$$

$$= 5 \times 10^{-9} \text{ mol } L^{-1}$$

Problem 26. **The solubility product of SrF_2 in water is 8×10^{-10}. Calculate its solubility in 0·1 M NaF aqueous solution.** *(Roorkee 1997)*

Solution. As NaF is a strong electrolyte, it ionizes completely. Hence $[F^-] = 0{\cdot}1$ M

$$K_{sp} \text{ for } SrF_2 = [Sr^{2+}][F^-]^2$$

$$\therefore \; 8 \times 10^{-10} = [Sr^{2+}](0{\cdot}1)^2$$

or $[Sr^{2+}] = 8 \times 10^{-8}\ \text{mol L}^{-1}$

$\therefore$ Solubility of SrF_2 in 0·1 M NaF sol.

$$= 8 \times 10^{-8}\ \text{mol L}^{-1}$$

Problem 27. **What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2·0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12·0) ?** ***(I.I.T. 1998)***

Solution. pH = 2 means $[H^+] = 10^{-2}$ M

pH = 12 means $[H^+] = 10^{-12}$

or $[OH^-] = 10^{-2}$ M

Thus, 200 ml of 10^{-2} M HCl are mixed with 300 ml of 10^{-2} M NaOH. After neutralisation NaOH left = 100 ml of 10^{-2} M

Total volume after mixing = 500 ml

$\therefore$ In the final solution, after mixing

$$[OH^-] = \frac{10^{-2}}{5} = 2 \times 10^{-3}\ \text{M}$$

or $[H^+] = \dfrac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$

$\therefore$ $\text{pH} = -\log [H^+] = -\log (5 \times 10^{-12})$

$= 12 - 0{\cdot}69 = 11{\cdot}39$

Problem 28. **Determine the number of moles of AgI which may be dissolved in 1·0 litre of 1·0 M CN^- solution. K_{sp} for AgI and K_c for $Ag(CN)_2^-$ are $1{\cdot}2 \times 10^{-7}\ M^2$ and $7{\cdot}1 \times 10^{19}\ M^{-2}$ respectively.** ***(Roorkee 1998)***

Solution. Suppose number or moles of AgI which may be dissolved in 1·0 litre of 1·0 M CN^- solution = *x*. Then

	$AgI(s)$ +	$2CN^-(aq)$ $\rightleftharpoons$	$[Ag(CN)_2]^-$ +	I^-
Intial moles	x	1	0	0
Moles after reaction	0	$1-2x$	x	x

$$K_{eq} = \frac{[Ag(CN)_2]^-\,[I^-]}{[CN^-]^2} = \frac{x^2}{(1-2x)^2} \quad ...(i)$$

Further, $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

$K_{sp} = [Ag^+][I^-] = 1{\cdot}2 \times 10^{-17}$ *(Given)* ...(*ii*)

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

$$K_c = \frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2} = 7{\cdot}1 \times 10^{19}\ \textit{(Given)} \quad ...(iii)$$

From eqn. (*i*), (*ii*) and (*iii*)

$$K_{eq} = K_{sp} \times K_c$$

$= (1{\cdot}2 \times 10^{-17}) \times (7{\cdot}1 \times 10^{19})$

$= 8{\cdot}52 \times 10^2$

$\therefore$ $\dfrac{x^2}{(1-2x)} = 8{\cdot}52 \times 10^2$

or $\dfrac{x}{1-2x} = 29{\cdot}2$

or $x = 29{\cdot}2 - 58{\cdot}4x$

or $x = 0{\cdot}49$ **mole**

Problem 29. **0·16 g of N_2H_4 are dissolved in water and the total volume made upto 500 ml. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_b for N_2H_4 is $4{\cdot}0 \times 10^{-6}$ M.** ***(Roorkee 1998)***

Solution. $N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$

Conc. of N_2H_4 = 0·16 g in 500 ml.

$= 0{\cdot}32\ \text{g L}^{-1} = \dfrac{0{\cdot}32}{32}\ \text{mol L}^{-1}$

$= 0{\cdot}01\ \text{M} = 10^{-2}\ \text{M}$

K_b for $N_2H_4 = 4{\cdot}0 \times 10^{-6}$ M (Given)

$$\therefore\ h = \sqrt{\frac{K_w}{K_b c}} = \sqrt{\frac{10^{-14}}{4 \times 10^{-6} \times 10^{-2}}}$$

$= \dfrac{1}{2} \times 10^{-3} = 0{\cdot}5 \times 10^{-3} = 0{\cdot}05\%$

Problem 30. **The solubility of $Pb(OH)_2$ in water is $6{\cdot}7 \times 10^{-6}$ M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.** ***(I.I.T. 1999)***

Solution. $Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

$\therefore$ $K_{sp} = [Pb^{2+}][OH^-]^2$

$= s \times (2s)^2 = 4s^3 = 4 \times (6{\cdot}7 \times 10^{-6})^3$

$= 1{\cdot}20 \times 10^{-15}$

In a solution with pH = 8, $[H^+] = 10^{-8}$

and $[OH]^- = 10^{-6}$

$\therefore$ $1{\cdot}2 \times 10^{-15} = [Pb^{2+}] \times (10^{-6})^2$

or $[Pb^{2+}] = \dfrac{1{\cdot}2 \times 10^{-15}}{(10^{-6})^2} = 1{\cdot}2 \times 10^{-3}$ M

Problem 31. **Two buffers (X) and (Y) of pH 4·0 and 6·0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0·50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers ? ($K_{HA} = 1{\cdot}0 \times 10^{-5}$)** ***(Roorkee 1999)***

Solution. *For buffer* X,

$$\text{pH} = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}\ \textit{i.e.}\ 4 = 5 + \log\frac{[\text{Salt}]}{0{\cdot}5}$$

or $\quad \log \frac{[\text{Salt}]}{0.5} = -1$

or $\quad \frac{[\text{Salt}]}{0.5} = 10^{-1}$

or $\quad [\text{Salt}] = 0.05\ \text{M}$

For buffer Y

$$\text{pH} = p\,\text{K}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

i.e. $\quad 6 = 5 + \log \frac{[\text{Salt}]}{0.5}$

or $\quad \log \frac{[\text{Salt}]}{0.5} = 1$

or $\quad \frac{[\text{Salt}]}{0.5} = 10$

or $\quad [\text{Salt}] = 5\ \text{M}$

When equal volumes of both the buffers are mixed,

$$[\text{Acid}] = 0.5,$$

$$[\text{Salt}] = \frac{5 + 0.05}{2} = 2.5025$$

$$\text{pH} = p\,\text{K}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 5 + \log \frac{2.5025}{0.5}$$

$$= 5 + \log 5.05 = 5.7$$

Problem 32. **Determine the concentration of NH_3 solution whose one litre can dissolve 0·10 mole AgCl. K_{sp} of AgCl and K_f of $Ag(NH_3)_2^+$ are $1.0 \times 10^{-10}\ M^2$ and $1.6 \times 10^7\ M^{-2}$ respectively.** ***(Roorkee 1999)***

Solution. $AgCl \longrightarrow Ag^+ + Cl^-$

$\therefore$ 0·1 mole AgCl on dissolution will give 0·1 mole Ag^+ and 0·1 mole Cl^- ions. Ag^+ ions will combine with NH_3 as follows :

$$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

Hence $[Ag^+] + [Ag(NH_3)_2^+] = 0.1$ mole ...(*i*)

Also for the above formation reaction, we are given

$$K_f = 1.6 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+]\,[NH_3]^2} \quad ...(ii)$$

Further $[Ag^+]\,[Cl^-] = K_{sp} = 10^{-10}$

or $\quad [Ag^+]\,(0.1) = 10^{-10}$

or $\quad [Ag^+] = 10^{-9}$.

Neglecting this conc. in eqn. (*i*), we get

$$[Ag(NH_3)_2^+] = 0.1.$$

Putting these values in eqn. (*ii*), we get

$$\frac{0.1}{10^{-9} \times [NH_3]^2} = 1.6 \times 10^7$$

$$\text{or } [NH_3]^2 = \frac{0.1}{10^{-9} \times 1.6 \times 10^7}$$

$$= \frac{1}{16 \times 10^{-2}}$$

$$\text{or } [NH_3] = \frac{1}{4 \times 10^{-1}} = 2.5\ \text{M}$$

Also 0·2 M NH_3 is needed to dissolve 0·01 M Ag^+ ions. Thus

$$[NH_3] = 2.5 + 0.2 = 2.7\ \text{M}.$$

Problem 33. **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 moles litre^{-1} and the pK_a of H_2SO_3 is 1·92, estimate the pH of rain on that day.** ***(I.I.T. 2000)***

Solution. $SO_2 + H_2O \longrightarrow H_2SO_3$

$$[H_2SO_3] = [SO_2] = 1.3653 \text{ moles litre}^{-1}$$

$$H_2SO_3 \rightleftharpoons 2\,H^+ + SO_3^{2-}$$

Suppose at equilibrium, $[H^+] = x$ mol L^{-1}

Then $[H_2SO_3] = \left(1.3653 - \frac{x}{2}\right)$,

$$[SO_3^{2-}] = \frac{x}{2} \text{ mol L}^{-1}$$

$$K_a = \frac{[H^+]^2\,[SO_3^{2-}]}{[H_2SO_3]}$$

$$= \frac{x^2 \times x/2}{(1.3653 - x/2)} = 10^{-1.92}$$

($\because pK_a = 1.92$ means $-\log K_a = 1.92$

or $\log K_a = -1.92$ or $K_a = 10^{-1.92}$)

Neglecting $x/2$ in comparison to 1·3653, we get

$$\frac{x^3}{2 \times 1.3653} = 10^{-1.92}$$

or $\quad x^3 = 2.7306 \times 10^{-1.92}$

or $3 \log x = \log 2\cdot7306 - 1\cdot92$

$= 0\cdot4348 - 1\cdot92 = -1\cdot4852$

or $-\log x = 0\cdot485$

i.e. $pH = 0\cdot485$.

Problem 34. **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 0·01 M ?**
$[K_{sp}\ H_2S = 1\cdot1 \times 10^{-22}$ and $K_{sp}\ ZnS = 1\cdot0 \times 10^{-21}]$

(Roorkee 2000)

Solution. K_{sp} for $ZnS = 10^{-21}$

and $[Zn^{2+}] = 0\cdot01\ M = 10^{-2}\ M$

But $K_{sp}\ (ZnS) = [Zn^{2+}]\,[S^{-2}]$

i.e. $10^{-21} = [10^{-2}]\,[S^{2-}]$

or $[S^{2-}] = 10^{-19}\ M$

Thus to prevent precipitation of Zn^{2+} ions, $[S^{2-}]$ must be less than 10^{-19} M. Further

$$H_2S \xrightarrow{2\,H_2O} 2\,H_3O^+ + S^{2-}$$

$\therefore$ $K_{sp}\ (H_2S) = [H_3O^+]^2\,[S^{2-}]$

$1\cdot1 \times 10^{-22} = [H_3O^+]^2 \times 10^{-19}$

or $[H_3O^+]^2 = 1\cdot1 \times 10^{-3} = 11 \times 10^{-4}$

or $[H_3O^+] = 3\cdot32 \times 10^{-2}$ M.

Problem 35. **0·01 mol of $AgNO_3$ is added to one litre of a solution which is 0·1 M in Na_2CrO_4 and 0·005 M in $NaIO_3$. Calculate the mol of precipitate formed at equilibrium and the concentration 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).** *(Roorkee 2001)*

Solution. $2\,AgNO_3 + \underset{0\cdot1\ \text{mol}}{Na_2CrO_4} \longrightarrow Ag_2CrO_4 + 2\,NaNO_3$

$AgNO_3 + \underset{0\cdot005\ \text{mol}}{NaIO_3} \longrightarrow AgIO_3 + NaNO_3$

$AgNO_3$ that will react with $NaIO_3 = 0\cdot005$ mol

$AgIO_3$ (ppt.) formed $= 0\cdot005$ mol

$AgNO_3$ left $= 0\cdot01 - 0\cdot005 = 0\cdot005$ mol. Whole of it will react completely with Na_2CrO_4 (as it is present in larger amount). Na_2CrO_4 reacted $= 0\cdot005/2 = 0\cdot0025$ mol. Hence Na_2CrO_4 left $= 0\cdot1 - 0\cdot0025 = 0\cdot0975$ mol

Ag_2CrO_4 (ppt.) formed $= 0\cdot0025$ mol.

Total $[CrO_4^{2-}] = 0\cdot0975$ mol + CrO_4^{2-} obtained from Ag_2CrO_4 (negligible)

$= 0\cdot0975$ mol $= 9\cdot75 \times 10^{-2}$ M

$$Ag_2CrO_4 \longrightarrow 2\,Ag^+ + CrO_4^{2-}$$

$K_{sp}\ (Ag_2CrO_4) = [Ag^+]^2\,[CrO_4^{2-}]$

$[Ag^+]^2 \times (9\cdot75 \times 10^{-2}) = 10^{-8}$

or $[Ag^+]^2 = 0\cdot1 \times 10^{-6}$

or $[Ag^+] = 0\cdot32 \times 10^{-3}$ M

$= 3\cdot2 \times 10^{-4}$ M

Total precipitate formed $= 0\cdot005 + 0\cdot0025$

$= 0\cdot0075$ mol

This is the total $[Ag^+]$ present in the solution (obtained from Ag_2CrO_4 and $AgIO_3$).

$$AgIO_3 \longrightarrow Ag^+ + IO_3^-$$

$K_{sp}\ (AgIO_3) = [Ag^+]\,[IO_3^-]$

$10^{-13} = (3\cdot2 \times 10^{-4})\,[IO_3^-]$

or $[IO_3^-] = 0\cdot3125 \times 10^{-9}$

$= 3\cdot125 \times 10^{-10}$ M

Problem 36. **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 on mixing : K_a of acetic acid is $1\cdot75 \times 10^{-5}$ mol L^{-1}] *(I.I.T. 2002)*

Solution. (*i*) Millimoles of CH_3COOH

$= 500 \times 0\cdot2 = 100$

Millimoles of $HCl = 500 \times 0\cdot2 = 100$

Final volume after mixing $= 500 + 500$

$= 1000$ mL

$$\therefore\ [CH_3COOH] = \frac{100}{1000} = 0\cdot1\ M,$$

$$[HCl] = \frac{100}{1000} = 0\cdot1\ M$$

$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons\ CH_3COO^- & +\ H^+ \\ \text{Before dissociation} & 0\cdot1\ M & 0 & 0\cdot1\ M \\ & & & \text{(from HCl)} \\ \text{After dissociation} & (0\cdot1 - x) & x & (0\cdot1 + x) \end{array}$$

$$K_a = \frac{x\,(0\cdot1 + x)}{(0\cdot1 - x)}$$

As in the presence of HCl, dissociation of CH_3COOH will be very small (due to common ion effect), x is very very small. Hence

$$K_a = \frac{x\,(0\cdot1)}{0\cdot1} = x$$

$$= 1\cdot75 \times 10^{-5}\ \text{mol L}^{-1}\ (\textit{Given})$$

$$\therefore\ \text{Degree of dissociation} = \frac{x}{0\cdot1} = \frac{1\cdot75 \times 10^{-5}}{0\cdot1}$$

$$= 1\cdot75 \times 10^{-4}$$

$$= 0\cdot00175\%$$

Further $[H^+] = 0\cdot1 + x \approx 0\cdot1$

$$\therefore\ pH = -\log 0\cdot1 = 1$$

(*ii*) 6 *g* of NaOH $= \frac{6}{40}$ mole

$$= 0\cdot15\ \text{mole}$$

Hence now the equilbrium will be

$$\begin{array}{llll} & CH_3COOH & +\ HCl & +\ NaOH \ \rightleftharpoons \\ \text{Initial} & 0\cdot1 & 0\cdot1 & 0\cdot15 \\ \text{At eqm.} & 0\cdot05 & 0 & 0 \end{array}$$

$$\begin{array}{lll} CH_3COONa & +\ NaCl & +\ H_2O \\ 0 & 0 & 0 \\ 0\cdot05 & 0 & 0 \end{array}$$

Thus the solution will now be 0·05 M in CH_3COOH and 0·05 M in CH_3COONa *i.e.* it is acidic buffer.

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

$$= -\log(1\cdot75 \times 10^{-5}) + \log\frac{0\cdot05}{0\cdot05}$$

$$= 4\cdot757$$

Problem 37. **The ionization constant of benzoic acid is $6\cdot46 \times 10^{-5}$ and K_{sp} for silver benzoate is $2\cdot5 \times 10^{-13}$. How many times is silver benzoate more soluble in a buffer of *p*H 3·19 compared to its solubility in pure water?** *(N.C.E.R.T.)*

Solution. $C_6H_5COOAg \longrightarrow C_6H_5COO^- + Ag^+$

Solubility in water. Suppose solubility in water $= x$ mol L^{-1}. Then

$$[C_6H_5COO^-] = [Ag^+] = x\ \text{mol L}^{-1}.$$

$$\therefore\ x^2 = K_{sp} \text{ or } x = \sqrt{K_{sp}} = \sqrt{2\cdot5 \times 10^{-13}}$$

$$= 5 \times 10^{-7}\ \text{mol L}^{-1}$$

Solubility in buffer of pH = 3·19

$$pH = 3\cdot19 \text{ means} \quad -\log[H^+] = 3\cdot19$$

$$\text{or} \quad \log[H^+] = -3\cdot19 = \bar{4}\cdot81$$

$$\text{or} \quad [H^+] = 6\cdot457 \times 10^{-4}$$

$C_6H_5COO^-$ ions now combine with the H^+ ions to form benzoic acid but $[H^+]$ remains almost constant because we have buffer solution. Now

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$$

$$\therefore\ K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$$

$$\text{or} \quad \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{[H^+]}{K_a} = \frac{6\cdot457 \times 10^{-4}}{6\cdot46 \times 10^{-5}} = 10 \quad ...(i)$$

Suppose solubility in the buffer solution is y mol L^{-1}. Then as most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionized), we have

$$y = [Ag^+] = [C_6H_5COO^-] + [C_6H_5COOH]$$

$$= [C_6H_5COO^-] + 10\,[C_6H_5COO^-]$$

$$= 11\,[C_6H_5COO^-] \qquad \text{(using eqn. } (i))$$

$$\therefore\ [C_6H_5COO^-] = \frac{y}{11}$$

$$\therefore\ K_{sp} = [C_6H_5COO^-][Ag^+]$$

$$\textit{i.e.}\ 2\cdot5 \times 10^{-3} = \frac{y}{11} \times y$$

$$\text{or} \quad y^2 = 2\cdot75 \times 10^{-12} \quad \text{or} \quad y = 1\cdot66 \times 10^{-6}$$

$$\therefore\ \frac{y}{x} = \frac{1\cdot66 \times 10^{-6}}{5 \times 10^{-7}} = 3\cdot32.$$

Note that in case of salt of weak acids, the solubility is more in the acidic solution than in water. The reason, in general, may be explained as follows :

Taking example of C_6H_5COOAg, we have

$$C_6H_5COOAg \rightleftharpoons C_6H_5COO^- + Ag^+$$

In acidic solution, the anions ($C_6H_5COO^-$ in the present case) undergo protonation in presence of acid. Thus, $C_6H_5COO^-$ ions are removed. Hence equilibrium shifts forward producing more Ag^+ ions. Alternatively, as $C_6H_5COO^-$ ions are removed, Q_{sp} decreases. In order to maintain solubility product equilibrium ($Q_{sp} = K_{sp}$), Ag^+ ion concentration must increase. Hence solubility is more.

Problem 38. **Calculate the solubility of AgCN in a buffer solution of pH 3·00. K_{sp} for AgCN is $2{\cdot}2 \times 10^{-16}$ and K_a for HCN is $6{\cdot}2 \times 10^{-12}$.**

Solution. Similar to Problem 37. We shall get

$$\frac{[HCN]}{[CN^-]} = \frac{[H^+]}{K_a} = \frac{10^{-3}}{6{\cdot}2 \times 10^{-10}} = 1{\cdot}6 \times 10^6$$

Solubility, $x = [Ag^+] = [CN^-] + [HCN] \simeq [HCN]$

(as $[CN^-] = [HCN]/(1{\cdot}6 \times 10^6)$ is negligible in comparison to HCN)

$$\therefore [CN^-] = \frac{[HCN]}{1{\cdot}6 \times 10^6} = \frac{x}{1{\cdot}6 \times 10^6}$$

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

$$= x \times \frac{x}{1{\cdot}6 \times 10^6} = 2{\cdot}2 \times 10^{-16}$$

or $\quad x = 1{\cdot}9 \times 10^{-5}\ \text{mol L}^{-1}$.

Problem 39. **0·1 M HA is titrated against 0·1 M NaOH. Find the pH at the end point. Dissociation constant for the acid HA is 5×10^{-6} and the degree of hydrolysis, $h < 1$.** ***(I.I.T. 2004)***

Solution. $\quad \underset{\text{(weak)}}{HA} + NaOH \longrightarrow NaA + H_2O$

At the end point, their equivalent amounts react together

$$\therefore \text{In the final solution, } [NaA] = \frac{0{\cdot}1}{2} = 0{\cdot}05\ M$$

As NaA is a salt of weak acid and strong base, it hydrolyses as

$$A^- + H_2O \rightleftharpoons HA + OH$$

For such a salt,

$$pH = 7 + \frac{1}{2}[pK_a + \log c]$$

$$= 7 + \frac{1}{2}[-\log(5 \times 10^{-6}) + \log 0{\cdot}05]$$

$$= 7 + \frac{1}{2}[6 - 0{\cdot}6990 + 0{\cdot}6990 - 2]$$

$$= 9$$

Problem 40. **A sample of mixed alkalis containing NaOH and Na_2CO_3 is titrated in the following two schemes :**

(*i*) 10 ml of above mixture requires 8 ml of 0·1 N HCl by using phenolphthalein.

(*ii*) 10 ml of above mixture requires 10 ml of 0·1 N HCl by using methyl orange.

Calculate the ratio of the weight of NaOH and Na_2CO_3 in the sample mixture.

(West Bengal J.E.E. 2004)

Solution. Basic principle involved is as follows :

Acid used with phenolphthalein as indicator

= Complete neutralization of NaOH

$+ \frac{1}{2}$ neutralization of Na_2CO_3

Acid used with methyl orange as indicator

= Complete neutralization of NaOH

+ Complete neutralization of Na_2CO_3

M eq of HCl used for 10 ml of mixture using phenolphthalein

$$= 8 \times 0{\cdot}1 = 0{\cdot}8$$

$$\therefore \text{M eq of NaOH} + \frac{1}{2}\text{ M eq of } Na_2CO_3 = 0{\cdot}8 \qquad ...(i)$$

$\therefore$ M eq of HCl used for 10 ml of mixture using methyl orange

$$= 10 \times 0{\cdot}1 = 1$$

$$\therefore \text{M eq of NaOH} + \text{M eq of } Na_2CO_3 = 1 \qquad ...(ii)$$

From eqns (*i*) and (*ii*),

M eq of $Na_2CO_3 = (1 - 0{\cdot}8) \times 2 = 0{\cdot}4$

M eq of NaOH $= 1 - 0{\cdot}4 = 0{\cdot}6$

Eq. wt of $Na_2CO_3 = 106/2 = 53$

Eq. wt of NaOH = 40

$$\therefore 0{\cdot}4 \text{ M eq of } Na_2CO_3 = \frac{53}{1000} \times 0{\cdot}4 = 0{\cdot}0212\,g$$

$$0{\cdot}6 \text{ M eq of NaOH} = \frac{40}{1000} \times 0{\cdot}6 = 0{\cdot}024\,g$$

Ratio of weight of NaOH and Na_2CO_3

$$= 0{\cdot}024/0{\cdot}0212 = 1{\cdot}132$$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Metal ions like Ag^+, Cu^{2+} etc. act as
   (a) Bronsted acid (b) Bronsted bases
   [✓ (c) Lewis acids] (d) Lewis bases.

2. With increase in temperature, ionic product of water
   [✓ (a) increases] (b) decreases
   (c) remains unaffected
   (d) may increase or decrease

3. In the titration of a weak acid against a strong base, at the half-equivalence point (half-neutralisation)
   (a) $pH = \frac{1}{2} pK_a$ [✓ (b) $pH = pK_a$]
   (c) $pH = 2pK_a$ (d) None is correct.

4. The pH of a 10^{-8} M solution of HCl in water is
   (a) 8 (b) —8
   (c) between 7 and 8 [✓ (d) between 6 and 7.]
   (M.L.N.R. Allahabad 1990, M.P. P.M.T. 1998, Haryana C.E.E.T. 2000)

5. At 90°C pure water has $[H_3O^+] = 10^{-6}$ M. What is the value of K_w at this temperature ?
   (a) 10^{-6} [✓ (b) 10^{-12}]
   (c) 10^{-13} (d) 10^{-14}
   (M.L.N.R. Allahabad 1990)

6. Given that the dissociation constant for H_2O is $K_w = 1 \times 10^{-14}$ mol² litre^{-2}, what is the pH of a 0·001 M KOH solution ?
   (a) 10^{-11} (b) 10^{-3}
   (c) 3 [✓ (d) 11.]
   (M.L.N.R. Allahabad 1990)

7. Among the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is
   (a) $Mg(OH)_2$ (b) $Ca(OH)_2$
   (c) $Ba(OH)_2$ [✓ (d) $Be(OH)_2$.]
   (I.I.T. 1990)

8. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.
   $$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$
   The set that characterises the conjugate acid base pair is
   (a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-)
   (b) (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)
   (c) ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
   [✓ (d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH).]
   (I.I.T. 1992)

9. Which of the following solutions will have pH close to 1·0 ?
   (a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH
   (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) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH
   (I.I.T. 1992)

10. Which of the following will occur if a 0·1 M solution of a weak acid is diluted to 0·01 M at constant temperature ?
    (a) $[H^+]$ will decrease to 0.01 M
    (b) pH will decrease
    [✓ (c) percentage ionization will increase]
    (d) K_a will increase.
    (M.L.N.R. Allahabad 1992)

11. The pH of a 10^{-10} M NaOH solution is nearest to
    (a) 10 [✓ (b) 7]
    [✓ (c) 4] (d) —10.
    (M.L.N.R. Allahabad 1992)

12. The precipitate of CaF_2 ($K_{sp} = 1 \cdot 7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed :
    (a) 10^{-4} M Ca^{2+} + 10^{-4} M F^-
    [✓ (b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-]

ANSWERS

1. c 2. a 3. b 4. d 5. b 6. d 7. d 8. d 9. d 10. c
11. b

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

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

(M.L.N.R. Allahabad 1992)

13. A certain buffer solution contains equal concentration of X^- and HX. The K_a for HX is 10^{-8}. The pH of the buffer is

(a) 3 [✓ (b) 8]
(c) 11 (d) 14.

(M.L.N.R. Allahabad 1992)

14. Which of the following is not a Lewis base ?

[✓ (a) Ag^+] (b) H_2O
(c) CN^- (d) NH_3.

(B.I.T. Ranchi 1992)

15. Which anion is the weakest base ?

(a) $C_2H_5O^-$ [✓ (b) NO_3^-]
(c) F^- (d) CH_3COO^-

(B.I.T. Ranchi 1992)

16. The correct order of increasing $[H_3O^+]$ in the following aqueous solutions is

(a) 0·01 M H_2S < 0·01 M H_2SO_4 < 0·01 M NaCl < 0·01 M $NaNO_2$

(b) 0·01 M NaCl < 0·01 M $NaNO_2$ < 0·01 M H_2S < 0·01 M H_2SO_4

(c) 0·01 M $NaNO_2$ < 0·01 M NaCl < 0·01 M H_2S < 0·01 M H_2SO_4

(d) 0·01 M H_2S < 0·01 M $NaNO_2$ < 0·01 M NaCl < 0·01 M H_2SO_4.

(M.L.N.R. Allahabad 1993)

17. The best explanation for the solubility of MnS in dil HCl is that

(a) solubility product of $MnCl_2$ is less than that of MnS

(b) concentration of Mn^{2+} is lowered by the formation of complex ions with chloride ions

(c) concentration of sulphide ions is lowered by oxidation to free sulphur

(d) concentration of sulphide ions is lowered by the formation of the weak H_2S.

(M.L.N.R. Allahabad 1993)

18. The pK_a of HCN is 9·30. The pH of a solution prepared by mixing 2·5 moles of KCN and 2·5 moles of HCN in water and making upto total volume to 500 ml is

[✓ (a) 9·30] (b) 7·30
(c) 10·30 (d) 8·30.

(I.I.T. 1993)

19. The solubility of AgI in NaI solution is less than that in pure water because :

(a) AgI forms complex with NaI

[✓ (b) of common ion effect]

(c) solubility product of AgI is less than that of NaI

(d) the temperature of the solution decreases.

(M.L.N.R. Allahabad, 1994)

20. What is the percentage hydrolysis of NaCN in N/80 slution when the dissociation constant for HCN is $1·3 \times 10^{-9}$ and $K_w = 1·0 \times 10^{-14}$

[✓ (a) 2·48] (b) 5·26
(c) 8·2 (d) 9·6

(U.P. C.E.E.T. 1998)

21. The pH indicators are

(a) salts of strong acids and strong bases

(b) salts of weak acids and weak bases

[✓ (c) either weak acids or weak bases]

(d) either strong acids or strong bases

(Haryana C.E.E.T. 1996)

22. The solubility product of AgCl is $4·0 \times 10^{-10}$ at 298 K. The solubility of AgCl in 0·04 m $CaCl_2$ will be ?

(a) $2·0 \times 10^{-5}$ m (b) $1·0 \times 10^{-4}$ m
(c) $5·0 \times 10^{-9}$ m (d) $2·2 \times 10^{-4}$ m.

(Haryana C.E.E.T. 1996)

23. How much sodium acetate should be added to 0·1 m solution of CH_3COOH to give a solution of pH 5·5 (pK_a of CH_3COOH=4·5).

(a) 0·1 m (b) 0·2 m
[✓ (c) 1·0 m] (d) 10·0 m

(Haryana C.E.E.T. 1996)

24. The strongest base of the following species is

(a) NH^{2-} (b) OH^-
(c) O^{2-} (d) S^{2-}

(Haryana C.E.E.T. 1996)

25. Which of the following sulphides has the lowest solubility product ?

? (a) FeS (b) MnS
(c) PbS (d) ZnS.

(Haryana C.E.E.T. 1996)

ANSWERS

12. b 13. b 14. a 15. b 16. c 17. d 18. a 19. b 20. a 21. c
22. c 23. c 24. a 25. c

26. The pH of a solution obtained by mixing 50 ml of 0·4 N HCl and 50 ml of 0·2 N NaOH is

(*a*) —log 2 (*b*) —log 0·2
[✓ (*c*) 1·0] (*d*) 2·0.

(Haryana C.E.E.T. 1996)

27. In a mixture of a weak acid and its salt, the ratio of the concentration of acid to salt is increased ten-fold. The pH of the solution

[✓ (*a*) decreases by one] (*b*) decreases by one tenth
(*c*) increases by one (*d*) increases ten-fold.

(Haryana C.E.E.T. 1996)

28. If a neutral solution has $pK_w = 13 \cdot 36$ at 50°C, then pH of the solution is

[✓ (*a*) 6·68] (*b*) 7
(*c*) 7·63 (*d*) None of these

(A.F.M.C. Pune 1997, Kerala E.E.E. 2001)

29. The solubility product of CuS, Ag_2S and HgS and 10^{-31}, 10^{-44} and 10^{-54} respectively. The solubilities of these sulphides are is the order

(*a*) $Ag_2S > CuS > HgS$ (*b*) $Ag_2S > HgS > CuS$
(*c*) $HgS > Ag_2S > CuS$ (*d*) $CuS > Ag_2S > HgS$.

(C.B.S.E. P.M.T. 1997)

30. If pK_b for flouride ion at 25°C is 10·83, the ionisation constant of hydrofluoric acid at this temperature is

(*a*) $1 \cdot 74 \times 10^{-5}$ (*b*) $3 \cdot 52 \times 10^{-3}$
(*c*) $6 \cdot 75 \times 10^{-4}$ (*d*) $5 \cdot 38 \times 10^{-2}$.

(I.I.T. 1997)

31. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is

(*a*) $6\,y^4$ (*b*) $64\,y^4$
(*c*) $36\,y^5$ [✓ (*d*) $108\,y^5$.] *(I.I.T. 1997)*

32. Which of the following can act both as Bronsted acid and Bronsted base ?

(*a*) Na_2CO_3 (*b*) OH^-
(*c*) HCO_3^- (*d*) NH_3

(M.P. P.M.T. 1998)

33. Which of the following statement(s) is (are) correct ?

(*a*) The pH of $1 \cdot 0 \times 10^{-8}$ 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 against a strong base at half neutralization point, pH = $(1/2)\,pK_a$. *(I.I.T. 1998)*

34. The concentration of $[H^+]$ and $[OH^-]$ of 0·1 M aqueous solution of 2% ionized weak acid is (ionic product of water = 1×10^{-14})

(*a*) $0 \cdot 02 \times 10^{-3}$ M and 5×10^{-11} M
(*b*) 1×10^{-3} M and 3×10^{-11} M
(*c*) 2×10^{-3} M and 5×10^{-12} M
(*d*) 3×10^{-2} M and 4×10^{-13} M.

(C.B.S.E. P.M.T. 1999)

35. The strongest conjugate base is

(*a*) NO_3^- (*b*) Cl^-
(*c*) SO_4^{2-} [✓ (*d*) CH_3COO^-.]

(C.B.S.E. P.M.T. 1999)

36. The solubility of a saturated solution of calcium fluoride is 2×10^{-4} moles per litre. Its solubility product is

(*a*) 12×10^{-2} (*b*) 14×10^{-4}
(*c*) 22×10^{-11} [✓ (*d*) 32×10^{-12}.]

(C.B.S.E. P.M.T. 1999)

37. A monoprotic acid in a 0·01 M solution ionises to 0·001%. Its ionization constant is

(*a*) $1 \cdot 0 \times 10^{-3}$ (*b*) $1 \cdot 0 \times 10^{-6}$
(*c*) $1 \cdot 0 \times 10^{-8}$ [✓ (*d*) $1 \cdot 0 \times 10^{-12}$.]

(M.P. C.E.E. 1999)

38. What is the correct representation for the solubility product of SnS_2 ?

(*a*) $[Sn^{2+}]\,[S^{2-}]^2$ [✓ (*b*) $[Sn^{4+}]\,[S^{2-}]^2$]
(*c*) $[Sn^{2+}]\,[2\,S^{2-}]^2$ [✓ (*d*) $[Sn^{4+}]\,[2\,S^{2-}]^2$.]

(M.P. C.E.E. 1999)

39. The solubility of $CaCO_3$ in water is $3 \cdot 05 \times 10^{-4}$ moles/litre. Its solubility product will be

(*a*) $6 \cdot 1 \times 10^{-4}$ (*b*) 9·3
(*c*) $3 \cdot 05 \times 10^{-4}$ (*d*) $9 \cdot 3 \times 10^{-8}$.

(D.C.E.E.E. 1999)

40. pH of water is 7. When a substance Y is dissolved in water, the pH becomes 13. The substance Y is a salt of

A N S W E R S

26. *c* **27.** *a* **28.** *a* **29.** *a* **30.** *c* **31.** *d* **32.** *c* **33.** *b, c* **34.** *c* **35.** *d*
36. *d* **37.** *d* **38.** *b* **39.** *d*

(*a*) weak acid and weak base

(*b*) strong acid and strong base

(*c*) strong acid and weak base

(*d*) weak acid and strong base. (*D.C.E.E.E. 1999*)

41. The pH 0·1 M solution of the following salts increases in the order

(*a*) NaCl < NH_4Cl < NaCN < HCl

[✓ (*b*)] HCl < NH_4Cl < NaCl < NaCN

[✓ (*c*)] NaCN < NH_4Cl < NaCl < HCl

(*d*) HCl < NaCl < NaCN < NH_4Cl. (*I.I.T. 1999*)

42. Which one of the following is true for any diprotic acid, H_2X ?

(*a*) $K_{a_2} > K_{a_1}$ [✓ (*b*)] $K_{a_1} > K_{a_2}$

(*c*) $K_{a_2} = \frac{1}{K_{a_1}}$ (*d*) $K_{a_2} = K_{a_1}$. (*C.B.S.E. P.M.T. 2000*)

43. The conjugate acid of NH_2^- is

(*a*) NH_4^+ (*b*) NH_2OH

[✓ (*c*)] NH_3 (*d*) N_2H_4. (*C.B.S.E. P.M.T. 2000*)

44. Which of the following statements about *p*H and H^+ ion concentration is incorrect ?

[✓ (*a*)] A solution of the mixture of one equivalent each of CH_3COOH and NaOH has a *p*H of 7

(*b*) *p*H of pure neutral water is not zero

(*c*) A cold and concentrated H_2SO_4 has lower H^+ ion concentration than a dilute solution of H_2SO_4

(*d*) Addition of one drop of concentrated HCl in NH_4OH solution decreases *p*H of the solution. (*C.B.S.E. P.M.T. 2000*)

45. Which of the following has lowest *p*H value ?

(*a*) 1 M HCl (*b*) 1 M NaOH

[✓ (*c*)] 1 M H_2SO_4 (*d*) 1 M C_2H_5OH. (*A.F.M.C. 2000*)

46. Which solutions are mixed to form a buffer solution ?

(*a*) Strong acid and its salt with strong base

(*b*) Strong acid and its salt with weak base

[✓ (*c*)] Weak acid and its salt with strong base

(*d*) Weak acid and its salt with weak base. (*B.H.U. 2000*)

47. Which solution will be strongly acidic ?

(*a*) When pOH=4·5 (*b*) When *p*H = 0

(*c*) When pOH = 14 [✓ (*d*)] Both (*b*) and (*c*). (*C.P.M.T. 2000*)

48. The *p*H of an aqueous solution of CH_3COONa will be

(*a*) 7 (*b*) 3

[✓ (*c*)] 9 (*d*) 14. (*C.P.M.T. 2000*)

49. Which of the following is *not* a buffer ?

(*a*) H_2CO_3/HCO_3^-

(*b*) CH_3COOH/CH_3COONa

(*c*) NH_4OH/NH_4Cl

[✓ (*d*)] NH_4OH/CH_3COOH. (*J.I.P.M.E.R. 2000*)

50. For a buffer with equal amounts of the salt and the acid with $K_a = 10^{-8}$, the *p*H is

(*a*) 0 (*b*) 13

[✓ (*c*)] 8 (*d*) 8 — log 2. (*Haryana C.E.E.T. 2000*)

51. Ionisation constant of CH_3COOH is $1{\cdot}7 \times 10^{-5}$ and concentration of H^+ ions is $3{\cdot}4 \times 10^{-4}$. Then initial concentration of CH_3COOH molecules is

(*a*) $3{\cdot}4 \times 10^{-4}$ (*b*) $3{\cdot}4 \times 10^{-3}$

[✓ (*c*)] $6{\cdot}8 \times 10^{-3}$ (*d*) $1{\cdot}7 \times 10^{-3}$ (*C.B.S.E. P.M.T. 2001*)

52. In HS^-, I^-, R—NH_2, NH_3, order of proton accepting tendency will be

(*a*) $I^- > NH_3 >$ R$-NH_2 > HS^-$

(*b*) $NH_3 >$ R—$NH_2 > HS^- > I^-$

(*c*) R—$NH_2 > NH_3 > HS^- > I^-$

(*d*) $HS^- >$ R—$NH_2 > NH_3 > I^-$ (*C.B.S.E. P.M.T. 2001*)

53. Hydrogen ion concentration of an aqueous solution is 1×10^{-4} M. The solution is diluted with equal volume of water. Hydroxyl ion concentration of the resultant solution in terms of mol dm^{-3} is

(*a*) $0{\cdot}5 \times 10^{-10}$ [✓ (*b*)] 2×10^{-10}

ANSWERS

40. ***d*** **41.** ***b*** **42.** ***b*** **43.** ***c*** **44.** ***a*** **45.** ***c*** **46.** ***c*** **47.** ***d*** **48.** ***c*** **49.** ***d***
50. ***c*** **51.** ***c*** **52.** ***c***

(*c*) 1×10^{-6} (*d*) 1×10^{-8}

(K.C.E.T. 2001)

54. *p*H of a solution produced when an aqueous solution of *p*H 6 is mixed with an equal volume of an aqueous solution of *p*H 3 is about

(*a*) 4·5 (*b*) 4·0

(*c*) 4·3 (*d*) 3·3 *(K.C.E.T. 2001)*

55. The pK_a of a weak acid is 4·8. What should be the ratio of [Acid]/[Salt] of a buffer if *p*H = 5·8 is required ?

(*a*) 0·1 (*b*) 10

(*c*) 1 (*d*) 2

(E.A.M.C.E.T. 2001)

56. Which of the following would produce a buffer solution when mixed in equal volumes ?

(*a*) 1 M CH_3COOH and 0·5 M NaOH

(*b*) 1 M CH_3COOH and 0·5 M HCl

(*c*) 1 M NH_4OH and 0·5 M NaOH

(*d*) 1 M NH_4Cl and 0·5 M HCl

(E.A.M.C.E.T. 2001)

57. The *p*H of a 0·1 M aqueous solution of a weak acid (HA) is 3. What is its degree of dissociation ?

(*a*) 1% (*b*) 10%

(*c*) 50% (*d*) 25%

(E.A.M.C.E.T. 2001)

58. The *p*H range of methyl red indicator is

(*a*) 4·2 to 6·3 (*b*) 8·3 and 10·0

(*c*) 8·0 to 9·6 (*d*) 6·8 to 8·4

(E.A.M.C.E.T. 2001)

59. For a sparingly soluble salt $A_p\, B_q$, the relationship of its solubility product (L_S) with its solubility (S) is

(*a*) $L_S = S^{p+q} . p^p . q^q$

(*b*) $L_S = S^{p+q} . p^q . q^p$

(*c*) $L_S = S^{pq} . p^p . q^q$

(*d*) $L_S = S^{pq} (pq)^{p+q}$. *(I.I.T. 2001)*

60. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium

(*a*) CuS > ZnS > Na_2S

(*b*) ZnS > Na_2S > CuS

(*c*) Na_2S > CuS > ZnS

(*d*) Na_2S > ZnS > CuS *(I.I.T. 2002)*

61. Which of the following has highest *p*H ?

(*a*) CH_3COOK (*b*) Na_2CO_3

(*c*) NH_4Cl (*d*) $NaNO_3$

(C.B.S.E. P.M.T. 2002)

62. Which of the following is the buffer solution of strong acidic nature ?

(*a*) $HCOOH + HCOO^-$

(*b*) $CH_3COOH + CH_3COO^-$

(*c*) $H_2C_2O_4 + C_2O_4^{2-}$

(*d*) $H_3BO_3 + BO_3^{3-}$ *(M.P. P.E.T. 2002)*

63. Water is a

(*a*) protophobic solvent (*b*) protophilic solvent

(*c*) amphiprotic solvent (*d*) aprotic solvent

(K.C.E.T. 2002)

64. Among the following, the weakest base is

(*a*) H^- (*b*) CH_3^-

(*c*) CH_3O^- (*d*) Cl^- *(M.P. P.M.T. 2002)*

65. In the reaction $I_2 + I^- \longrightarrow I_3^-$, which is the Lewis base ?

(*a*) I_2 (*b*) I^-

(*c*) I_3^- (*d*) None of these

(Rajasthan P.M.T. 2002)

66. How do you differentiate between Fe^{3+} and Cr^{3+} in group III ?

(*a*) By taking excess of NH_4OH

(*b*) By increasing NH_4^+ ion concentration

(*c*) By decreasing OH^- ion concentration

(*d*) Both (*b*) and (*c*) *(A.I.E.E.E. 2002)*

67. Solubility of an MX_2 type electrolyte is $0 \cdot 5 \times 10^{-4}$ mol L^{-1}, then K_{sp} of the electrolyte is

(*a*) 5×10^{-12} (*b*) 25×10^{-10}

(*c*) 1×10^{-13} (*d*) 5×10^{-13}

(C.B.S.E. P.M.T. 2002)

68. In which of the following acid-base titration, pH is greater than 8 at the equivalence point ?

(*a*) Acetic acid versus ammonia

ANSWERS

53. *b* **54.** *d* **55.** *a* **56.** *a* **57.** *a* **58.** *a* **59.** *a* **60.** *d* **61.** *b* **62.** *a*

63. *c* **64.** *d* **65.** *b* **66.** *d* **67.** *d* (*b*) Acetic acid versus sodium hydroxide

(*c*) Hydrochloric acid versus ammonia

(*d*) Hydrochloric acid versus sodium hydroxide

(A.I.I.M.S. 2003)

69. When rain is accompanied by a thunderstorm, the collected rain water will have pH value

(*a*) slightly higher than that when the thunder storm is not there

(*b*) uninfluenced by the thunder storm

(*c*) which depends on the amount of dust in air

(*d*) slightly lower than that of rain water without thunder storm *(A.I.E.E.E. 2003)*

70. In the hydrolysis of a salt of weak acid and weak base, the hydrolysis constant K_h is equal to

(*a*) K_w/K_b (*b*) K_w/K_a

(*c*) $K_w/K_a \cdot K_b$ (*d*) $K_a \cdot K_b$

(Orissa J.E.E. 2003)

71. The solubility product of AgI at 25°C is $1{\cdot}0 \times 10^{-16}$ mol^2 L^{-2}. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately (in mol L^{-1})

(*a*) $1{\cdot}0 \times 10^{-16}$ (*b*) $1{\cdot}0 \times 10^{-12}$

(*c*) $1{\cdot}0 \times 10^{-10}$ (*d*) $1{\cdot}0 \times 10^{-8}$

(C.B.S.E. P.M.T. 2003)

72. Solubility of PbI_2 is 0·0013 M. Then solubility product of PbI_2 is

(*a*) $2{\cdot}2 \times 10^{-9}$ (*b*) $8{\cdot}8 \times 10^{-9}$

(*c*) $6{\cdot}8 \times 10^{-6}$ (*d*) $8{\cdot}8 \times 10^{-6}$

(D.P.M.T. 2003)

73. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first ?

(*a*) FeS (*b*) MgS

(*c*) HgS (*d*) ZnS *(I.I.T. 2003)*

74. What is the *p*H of 0·01 M glycine solution ? For glycine

$K_{a_1} = 4{\cdot}5 \times 10^{-3}$ and $K_{a_2} = 1{\cdot}7 \times 10^{-10}$ at 298 K

(*a*) 3·0 (*b*) 10·0

(*c*) 6·1 (*d*) 7·2 *(A.I.I.M.S. 2004)*

75. The rapid change of *p*H near the stoichiometric point of an acid-base titration is the basis of indicator detection. *p*H of the solution is related to ratio of concentration of conjugate acid. (H*In*) and the base [*In*$^-$) forms of the indicator by the expression

(*a*) $\log \dfrac{[In^-]}{[HIn]} = pK_{In} - pH$

(*b*) $\log \dfrac{[HIn^-]}{[In^-]} = pK_{In} - pH$

(*c*) $\log \dfrac{[HIn]}{[In^-]} = pH - pK_{In}$

(*d*) $\log \dfrac{[In^-]}{[HIn]} = pH - pK_{In}$

(C.B.S.E. P.M.T. 2004)

76. 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

(*a*) 0·0001% (*b*) 0·01%

(*c*) 0·1% (*d*) 0·15% *(I.I.T. 2004)*

77. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is *s*. The corresponding solubility product is given by K_{sp}. *s* is given in terms of K_{sp} by the relation

(*a*) $s = (K_{sp}/128)^{1/4}$ (*b*) $s = (128\,K_{sp})^{1/4}$

(*c*) $s = (256\,K_{sp})^{1/5}$ (*d*) $s = (K_{sp}/256)^{1/5}$

(A.I.E.E.E. 2004)

78. Which one of the following is not an amphoteric substance ?

(*a*) HNO_3 (*b*) HCO_3^-

(*c*) H_2O (*d*) NH_3

(Karnataka C.E.T. 2004)

79. The mixture of acetic acid and sodium acetate, the ratio of concentrations of the salt to the acid is increased ten times. Then *p*H of the solution

(*a*) increases by one (*b*) decreases by one

(*c*) decreases ten fold (*d*) increases ten fold

(Karnataka C.E.T. 2004)

80. Select the pK_a value of the strongest acid from the following :

(*a*) 1·0 (*b*) 3·0

ANSWERS

68. *b* **69.** *d* **70.** *c* **71.** *b* **72.** *b* **73.** *c* **74.** *c* **75.** *d* **76.** *b* **77.** *d*

78. *a* **79.** *a*

(c) 2·0 (d) 4·5

(Karnataka C.E.T. 2004)

81. The pK_a of acetic acid is 4·74. The concentration of CH_3COOH is 0·01 M. The pH of CH_3COOH is

(a) 3·37 (b) 4·37

(c) 4·74 (d) 0·474

(Orissa J.E.E. 2004)

82. 50 ml of 0·1 M HCl and 50 ml of 0·2 M NaOH are mixed. The pH of the resulting solution is

(a) 1·30 (b) 4·2

(c) 12·70 (d) 11·70

(J & K C.E.T. 2004)

83. 0·365 g of HCl gas was passed through 100 cm^3 of 0·2 M NaOH solution. The pH of the resulting solution would be

(a) 1 (b) 5

(c) 8 (d) 9

(e) 13

(Kerala C.E.E. 2004)

84. The principal buffer present in human blood is

(a) $NaH_2PO_4 + Na_2HPO_4$

(b) $H_3PO_4 + NaH_2PO_4$

(c) $CH_3COOH + CH_3COONa$

(d) $Na_2HPO_4 + Na_3PO_4$

(e) $H_2CO_3 + HCO_3^-$

(Kerala P.M.T. 2004)

85. Degree of dissociation of NH_4OH in water is $1·8 \times 10^{-4}$, then hydrolysis constant of NH_4Cl is

(a) $1·8 \times 10^{-5}$ (b) $1·8 \times 10^{-10}$

(c) $5·55 \times 10^{-5}$ (d) $5·55 \times 10^{-10}$

(Bihar C.E.C.E. 2004)

HINTS/EXPLANATIONS to Multiple Choice Questions

3. At half-equivalence point,

$$pH = pK_a.$$

4. See solved example on page 8/26.

5. $K_w = [H^+][OH^-] = (10^{-6})(10^{-6}) = 10^{-12}$

6. 0·001 M KOH means $[OH^-] = 10^{-3}$.

Hence $[H_3O^+] = 10^{-11}$ ∴ $pH = 11$.

7. The solubility increases down the group due to increase in size of the ion and decrease in lattice energy. Lower the solubility, lower is the K_{sp}.

9. (a) $pH = 7$.

(b) M/10 HCl left unneutralized = 10 ml of M/10

Total volume = 100 ml.

$$\therefore \quad 10 \times \frac{M}{10} = 100 \times ?\ M$$

$$\therefore \quad [HCl] = \frac{1}{100} = 10^{-2}\ M.\ pH = 2$$

(c) solution is basic, pH will be > 7.

(d) 75 ml M/5 HCl = 15 millimoles, 25 ml of M/5 NaOH = 5 millimoles. HCl left unneutralised = 10 millimoles. Volume = 100 ml.

$$\therefore \quad [HCl] = \frac{10}{100} = 0·1\ M$$

$$pH = -\log(0·1) = 1.$$

10. On dilution of a weak acid solution, percentage ionisation increases.

11. See solved example on page 8/26.

12. In (b), ionic product = $[Ca^+][F^-]^2$

$= 1·25 \times 10^{-9}$ which is greater than K_{sp}.

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

$$= -\log 10^{-8} + \log 1 = 8.$$

14. Ag^+ ion is a Lewis acid. CH_4 is neither Lewis acid nor Lewis base.

15. Weak base has a strong conjugate acid. NO_3^- has the strongest conjugate acid HNO_3.

16. H_2S = weak acid, H_2SO_4 = strong acid, NaCl = neutral, $NaNO_2$ = basic. Hence $[H_3O^+]$ will be in the order : $NaNO_2 < NaCl < H_2S < H_2SO_4$.

17. $MnS + 2HCl \longrightarrow MnCl_2 + H_2S$. As H_2S is a weak electrolyte, it ionises very less. Hence concentration of S^{2-} ions is lowered.

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

$$= 9·30 + \log\frac{5·0}{5·0} = 9·30$$

19. $AgI(s) + aq \rightleftharpoons Ag^+(aq) + I^-(aq)$,

$NaI \longrightarrow Na^+ + I^-$. Due to common ion effect, equilibrium shifts backward.

ANSWERS

80. a **81.** a **82.** c **83.** e **84.** e **85.** d

20. NaCN is a salt of weak acid (HCN) and strong base (NaOH).

Hence

$$h = \sqrt{\frac{K_w}{K_a c}} = \sqrt{\frac{10^{-14}}{(1{\cdot}3 \times 10^{-9}) \times 1/80}}$$

$= 2{\cdot}48 \times 10^{-2}$

$\therefore$ %age hydrolysis

$= (2{\cdot}48 \times 10^{-2}) \times 100 = 2{\cdot}48.$

22. If x is the solubility of AgCl in $0{\cdot}04\ m$ $CaCl_2$, then

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

$[Cl^-] = (0{\cdot}04 \times 2) + x \approx 0{\cdot}08\ m$

$\therefore\ x\,(0{\cdot}08) = 4 \times 10^{-10}$

or $\quad x = 5{\cdot}0 \times 10^{-9}\ m$

23. $pH = pK_a + \log \dfrac{[CH_3COONa]}{[CH_3COOH]}$

$5{\cdot}5 = 4{\cdot}5 + \log \dfrac{[CH_3COONa]}{0{\cdot}1}$

$= 4{\cdot}5 + \log [CH_3COONa] + 1$

or $\log [CH_3COONa] = 0$

$\therefore\ [CH_3COONa] = 1\ m$

24. Due to highest electron density on N in NH^{2-}, it can accept protons most easily and hence is the strongest base.

25. Sulphides of Group II (PbS) have low solubility product.

26. 50 ml of 0·4 N HCl $= \dfrac{0{\cdot}4}{1000} \times 50 = 0{\cdot}02$ g eq.

50 ml of 0·2 N NaOH $= \dfrac{0{\cdot}2}{1000} \times 50 = 0{\cdot}01$ g eq.

0·01 g eq. of NaOH will neutralise 0·01 g eq. of HCl

$\therefore$ HCl left unneutralised = 0·01 g eq.

Volume of solution = 50 + 50 = 100 ml

$\therefore\ [HCl] = \dfrac{0{\cdot}01}{100} \times 1000\ N = 0{\cdot}1\ N$

or $\ [H^+] = 0{\cdot}1\ M$

$\therefore\ pH = \log (0{\cdot}1) = 1{\cdot}0.$

27. $pH = pK_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

$= pK_a + \log \dfrac{1}{10} = pK_a - 1.$

28. $pK_w = pH + pOH.$

As $[H^+] = [OH^-],$

$pK_w = 2 \times pH$

or $\quad pH = 13{\cdot}36 / 2 = 6{\cdot}68$

29. $s\,(CuS) = \sqrt{K_{sp}} = \sqrt{10^{-31}} = 10^{-15{\cdot}5},$

$Ag_2S \longrightarrow 2\,Ag^+ + S^{2-},$

$K_{sp} = (2\,s)^2 \times s = 4\,s^3$

or $\quad s = \left(\dfrac{1}{4} K_{sp}\right)^{1/3}$

$= \left(\dfrac{10^{-44}}{4}\right)^{1/3} = (2{\cdot}5)^{1/3} \times 10^{-15},$

$s\,(HgS) = \sqrt{K_{sp}} = \sqrt{10^{-54}} = 10^{-27}$

30. The dissociation constants of a weak acid and its conjugate base are related as

$pK_a + pK_b = pK_w$

$\therefore\ pK_a + 10{\cdot}83 = 14$

or $\quad pK_a = 3{\cdot}17$

$-\log K_a = 3{\cdot}17$

or $\quad \log K_a = -3{\cdot}17 = \bar{4}{\cdot}83$

or $\quad K_a = 6{\cdot}76 \times 10^{-4}.$

31. $A_2X_3 \longrightarrow 2\,A^{3+} + 3\,X^{-2},$

$K_{sp} = (2\,y)^2 \times (3\,y)^3 = 108\,y^5.$

32. HCO_3^- can accept a proton as well as give a proton.

34.

$$\begin{array}{lccc} & HA & \rightleftharpoons & H^+ \quad + \quad A^- \\ & c & & \\ & c\,(1-\alpha) & & c\,\alpha \qquad c\,\alpha, \end{array}$$

$\therefore\ [H^+] = C\,\alpha = 0{\cdot}1 \times 0{\cdot}02 = 2 \times 10^{-3}.$

Hence $[OH^-] = \dfrac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$

35. Strong conjugate base has a weak conjugate acid. Weakest conjugate acid is CH_3COOH.

36. $CaF_2 \longrightarrow Ca^{2+} + 2\,F^-,$

$K_{sp} = s\,(2\,s)^2$

$= 4\,s^3 = 4 \times (2 \times 10^{-4})^3$

$= 32 \times 10^{-12}$

37.

$$\begin{array}{lccc} & HA & \rightleftharpoons & H^+ + A^- \\ & c & & \\ & c\,(1-\alpha) & & c\,\alpha \qquad c\,\alpha \end{array}$$

$K = \dfrac{c\,\alpha \times c\,\alpha}{c\,(1-\alpha)} \approx c\,\alpha^2$

$c = 10^{-2}$ M,

$\alpha = \dfrac{0{\cdot}001}{100} = 10^{-5},$

$\therefore\ K = 10^{-2} \times (10^{-5})^2 = 10^{-12}$

40. $pH = 13$ means the solution is basic.

41. NaCl = neutral ($pH = 7$) ; NH_4Cl = Slightly acidic ($pH < 7$); NaCN = basic ($pH > 7$) ; HCl = strongly acidic ($pH << 7$).

$\therefore$ Order will be $HCl < NH_4Cl < NaCl < NaCN$.

42. For diprotic acid $K_{a_2} < K_{a_1}$.

43. $NH_2^- + H^+ = NH_3$.

44. $pH = 7$ at the end point is only for strong acid with strong base.

45. Higher the $[H^+]$, lower is the pH.

1 M H_2SO_4 has highest $[H^+]$.

47. $p_{OH} = 14$ means $pH = 0$. Less the pH, more acidic is the solution.

48. As the solution is basic (not very strongly basic), $pH = 9$.

50. See Q. 13.

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

Initial $\quad a$

At. eqm. $(a - 3{\cdot}4 \times 10^{-4}) \quad 3{\cdot}4 \times 10^{-4} \quad 3{\cdot}4 \times 10^{-4}$

$$\frac{(3{\cdot}4 \times 10^{-4})(3{\cdot}4 \times 10^{-4})}{(a - 3{\cdot}4 \times 10^{-4})} = 1{\cdot}7 \times 10^{-5} \text{ (Given)}$$

$$\text{or } (a - 3{\cdot}4 \times 10^{-4}) = \frac{(3{\cdot}4 \times 10^{-4})^2}{1{\cdot}7 \times 10^{-5}}$$

$$= 6{\cdot}8 \times 10^{-3}$$

$$\text{or } a = 6{\cdot}8 \times 10^{-3} + 3{\cdot}4 \times 10^{-4} \approx 6{\cdot}8 \times 10^{-3}$$

52. In R—NH_2, electron pair on N is most easily available for protonation because R is electron releasing group.

53. After dilution, $[H^+] = 10^{-4}/2$.

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

$$= \frac{10^{-14} \times 2}{10^{-4}} = 2 \times 10^{-10} \text{ M}$$

54. In the final solution,

$$[H^+] = (10^{-6} + 10^{-3})/2$$

$$= \frac{10^{-3}(10^{-3} + 1)}{2} = \frac{1{\cdot}001 \times 10^{-3}}{2}$$

$$\approx 0{\cdot}5005 \times 10^{-3} \approx 5{\cdot}005 \times 10^{-4}$$

$$pH = -\log[H^+] = -\log(5{\cdot}005 \times 10^{-4})$$

$$\approx 4 - 0{\cdot}6994 \approx 3{\cdot}3$$

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

$$\text{or} \quad \log \frac{[Salt]}{[Acid]} = 5{\cdot}8 - 4{\cdot}8 = 1{\cdot}0$$

$\therefore$ $[Salt]/[Acid] = 10$

or $[Acid]/[Salt] = 1/10 = 0{\cdot}1$

56. Vc.c. of 0·5 M NaOH will neutralise V/2 c.c. of 1 M CH_3COOH to form sodium acetate. V/2 c.c. of 1 M acetic acid will be present alongwith sodium acetate.

57. $HA \rightleftharpoons H^+ + A^-$,

$[H^+] = c\,\alpha = 10^{-3} \qquad (\because pH = 3)$

i.e. $0{\cdot}1 \times \alpha = 10^{-3}$

or $\qquad \alpha = 10^{-2} = 1\%$

59. $A_pB_q \;=\; pA^+ \;+\; qB^-$

$\quad S \qquad pS \qquad qS$

K_{sp} *i.e.* $L_s = (pS)^p\,(qS)^q = S^{p+q}\,p^p\,q^q$

60. Sulphides of alkali metals are soluble in water. Sulphides of group II have lower solubility than those of group IV radicals.

61. NH_4Cl solution is acidic, its $pH < 7$. $NaNO_3$ solution is neutral, its $pH = 7$. CH_3COOK and Na_2CO_3 solutions are basic, their $pH > 7$. But Na_2CO_3 solution is more basic, its $pH > pH$ of CH_3COOK solution.

62. Out of the given acids, HCOOH is the strongest.

63. Water is an amphiprotic solvent as it can accept protons as well as given protons.

64. Cl^- is the weakest base because it has the strongest conjugate acid viz. HCl.

65. In the reaction $I_2 + I^- \longrightarrow I_3^-$, I^- is the electron pair donor and hence is a Lewis base.

66. In group III of analysis, addition of NH_4Cl increases NH_4^+ ion concentration and decreases OH^- ion concentration produced from NH_4OH due to common ion effect.

67. $MX_2 \rightleftharpoons M^{2+} + 2X^-$

$\quad s \qquad\quad s \qquad 2s$

$$K_{sp} = (s)\,(2s)^2 = 4s^3$$

$$= 4 \times (0{\cdot}5 \times 10^{-4})^3$$

$$= 5 \times 10^{-13}.$$

68. $pH > 8$ at the equivalence point means that the salt formed on hydrolysis should give basic solution *i.e.* when acetic acid reacts with NaOH.

69. Due to thunder storm, temperature increases *i.e.* $[H^+]$ increases which means pH decreases.

70. For salts of weak acid and weak base,

$$K_h = K_w / K_a\,K_b.$$

71. Total $[I^-] = 10^{-4} + 10^{-6} - 10^{-4}$ M

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

$$\therefore \; [Ag^+][10^{-4}] = 1\cdot0 \times 10^{-16}$$

or $\qquad [Ag^+] = 10^{-12}$.

72. $PbI_2 \longrightarrow Pb^{2+} + 2\,I^-$

$$\therefore \; [Pb^{2+}] = 1\cdot3 \times 10^{-3}\ M$$

$$[I^-] = 2 \times 1\cdot3 \times 10^{-3}\ M = 2\cdot6 \times 10^{-3}\ M$$

$$K_{sp} = [Pb^{2+}][I^-]^2$$

$$= (1\cdot3 \times 10^{-3})(2\cdot6 \times 10^{-3})^2$$

$$= 8\cdot8 \times 10^{-9}.$$

73. The one with lowest value of K_{sp} *i.e.* HgS will precipitate out first.

74. Glycine $H_3N^+CH_2COO^-$ is more acidic than basic. Instead of K_b value, the second given K_a value is corresponding to the K_b value ($\because K_a \times K_b = 10^{-14}$). Hence overall ionization constant,

$$K_{a_1} \times K_{a_2} = 4\cdot5 \times 10^{-3}$$

$$\times 1\cdot7 \times 10^{-10} = 7\cdot65 \times 10^{-13}$$

$$H^+ = \sqrt{KC} = \sqrt{7\cdot65 \times 10^{-13} \times 0\cdot01}$$

$$= \sqrt{0\cdot765 \times 10^{-14}} = 0\cdot87 \times 10^{-7}\ M$$

$$pH = -\log(0\cdot87 \times 10^{-7}) = 7 - 0\cdot93 = 6\cdot07$$

75. $pH = pK_a + \log \dfrac{[\text{Conjugate base}]}{[\text{Acid}]}$ (see page 8/51)

$$\therefore pH - pK_{In} = \log \frac{[In^-]}{[H\,In]}$$

76. Hydrolysis reaction is $X^- + H_2O \rightleftharpoons HX + OH^-$ For a salt of weak acid with strong base,

$$K_b = \frac{K_w}{K_a} = c\alpha^2$$

$$\therefore \; \frac{10^{-14}}{10^{-5}} = 0\cdot1 \times \alpha^2 \text{ or } \alpha^2 = 10^{-8} \text{ or } \alpha = 10^{-4}$$

% hydrolysis $= 10^{-4} \times 100 = 10^{-2} = 0\cdot01$

77.

$$\begin{array}{ccc} MX_4\,(s) & \rightleftharpoons & M^{4+}\,(aq) + 4X^-\,(aq) \\ & & s \qquad\quad 4\,s \end{array}$$

$$K_{sp} = s \times (4\,s)^4 = 256\,s^5 \text{ or } s = (K_{sp}/256)^{1/5}$$

79. **Ist case.** $pH = pK_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]} = pK_a + \log \dfrac{a}{b}$

2nd case. $pH = pK_a + \log \dfrac{10\,a}{b}$

$$= pK_a + \log\frac{a}{b} + \log 10 = pK_a + \log\frac{a}{b} + 1$$

80. Higher the K_a value or lower the pK_a value, stronger is the acid.

81.

$$\begin{array}{ccc} CH_3COOH & \rightleftharpoons & CH_3CrO^- + H^+ \\ c & & 0 \qquad\quad 0 \\ c - c\,\alpha & & c\,\alpha \qquad c\,\alpha \end{array}$$

$$K_a = \frac{c\,\alpha \, . \, c\,\alpha}{c\,(1-\alpha)} = \frac{c\,\alpha^2}{1-\alpha} = c\,\alpha^2, \alpha = \sqrt{K_a/c}$$

$$[H^+] = c\alpha = c \,.\, \sqrt{K_a/c} = \sqrt{K_a \,.\, c}$$

$$pH - \log[H^+] = -\log(K_a c)^{1/2}$$

$$= \frac{1}{2}[-\log K_a - \log c]$$

$$= \frac{1}{2}[pK_a - \log c] = \frac{1}{2}[4\cdot74 - \log 10^{-2}]$$

$$= \frac{1}{2} \times 6\cdot74 = 3\cdot37$$

82. 50 ml of $0\cdot1$ MHCl $= 50 \times 0\cdot1$ millimoles $= 5$ millimoles. 50 ml of $0\cdot2$ NaOH $= 50 \times 0\cdot2$ millimoles $= 10$ millimoles Millimoles of NaOH left after neutralization $= 5$. Volume of solution $= 100$ ml.

$$\therefore \text{Molar conc. of NaOH} = \frac{5}{100} = 5 \times 10^{-2}\ M$$

$$pOH = -\log(5 \times 10^{-2})$$

$$= \log \frac{1}{5 \times 10^{-2}} = \log 20 = 1\cdot301$$

$$pH = 14 - 1\cdot301 = 12\cdot699 = 12\cdot70.$$

83. $0\cdot365$ g HCl $= \dfrac{0\cdot365}{36\cdot5}$ mole $= 0\cdot01$ mole

$100\ cm^3$ of $0\cdot2$ M NaOH $= \dfrac{0\cdot2}{1000} \times 100 = 0\cdot02$ mole

NaOH left unneutralized $= 0\cdot01$ mole

Volume of solution $= 100$ ml

$\therefore$ Molarity of NaOH in the solution

$$= \frac{0\cdot01}{100} \times 1000 = 0\cdot1\ M = 10^{-1}\ M$$

$$\therefore \quad [H^+] = \frac{10^{-14}}{10^{-1}M} = 10^{-13}\ M$$

$$\therefore \quad pH = 13$$

85. $K_h = \dfrac{K_w}{K_b} = \dfrac{10^{-14}}{1\cdot8 \times 10^{-5}}$

$$= 5\cdot55 \times 10^{-10}$$

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) If both Assertion and Reason are true and the Reason is the correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true but reason is not a correct explanation of the 'Assertion'.

(*c*) If Assertion is true but Reason is false.

(*d*) If Assertion is false but Reason is true.

(*e*) If both Assertion and Reason are false.

	Assertion	Reason
1.	Water is specially effective in screening the electrostatic interactions between the dissolved ions.	The force of ionic interaction depends upon the dielectric constant of the solvent.
2.	The degree of ionization of water is small at 25°C, only about one of every 10^7 molecules in pure water is ionized at any instant.	In pure water at 25°C the molar concentration of water is essentially constant.
3.	The pK_a of a weak acid becomes equal to pH of the solution at the mid-point of its titration.	The molar concentrations of proton acceptor and proton donor become equal at mid point of a weak acid.
4.	pH of HCl solution is less than that of acetic acid of the same concentration.	In equimolar solutions, the number of titrable protons present in HCl is less than that present in acetic acid.
5.	Acetic acid is a weak acid.	It has a weak conjugate base.
6.	pH value of HCN solution decreases when NaCN is added to it.	NaCN provides a common ion CN^- to HCN.
7.	pH of water increases with increase in temperature.	K_w of water increases with increase in temperature.
8.	When a small amount of strong acid is added to a buffer solution, its pH value does not change significantly.	Buffer action of the buffer solution resists the change in pH when some acid is added to it.
9.	A buffer solutions has a capacity to resist the change in pH value on addition of a small amount of acid or base to it.	An aqueous solution of ammonium acetate can act as buffer.
10.	Sb (III) is not precipitated as sulphide when in its alkaline solution, H_2S is passed.	The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation. *(A.I.I.M.S. 2004)*
11.	Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate AgBr rather than AgCl.	K_{sp} of AgCl < K_{sp} of AgBr. *(A.I.I.M.S. 2004)*

True/False Statements

Which of the following statements are false ? Rewrite them correctly.

1. The degree of ionization of a salt is directly proportional to its molar concentration
2. A Lewis base is a substance which can donate a pair of electrons.
3. CO_2 is a Lewis base.
4. The ionic product of water changes if a few drops of acid or base are added to it.
5. A solution with pH less than zero or greater than 14 cannot be prepared.
6. More acidic is the solution, greater is its pH.
7. The pH of 10^{-8} M HCl solution is 8.
8. Ionic product of water is always equal to 10^{-14}.
9. Phenolphthalein is not a suitale indicator for titration of HCl solution with Na_2CO_3 solution.
10. The solubility of PbI_2 in water decreases if KI is added to it.

Fill In The Blanks

1. A compound whose aqueous solution or melt conducts electricity is called ..... .
2. The degree of dissociation of a salt is ..... proportional to ..... .
3. According to Bronsted-Lowry concept, an acid is a substance which can ..... whereas a base is a substance which can ..... .
4. A strong acid has a weak ..... base.
5. The sum of pH and ..... is equal to 14.
6. The lower the pH, more ..... is the solution.
7. Solubility product is the product of the concentration of ions in a ..... solution.
8. In the reaction $I^- + I_2 \longrightarrow I_3^-$, the Lewis acid is ...... *(I.I.T. 1997 ; A.I.I.M.S. 1997)*

Matching Type Questions

1. Match the entries of column A with appropriate entries of column B.

Column A	**Column B**
(*a*) Titration of acetic acid with NaOH solution	(*a*) No suitable indicator
(*b*) Titration of Na_2CO_3 solution with HCl	(*b*) Phenolphthalein
(*c*) Titration of NH_4OH with acetic acid	(*c*) Methyl orange

2. Match the entries of column A with appropriate entries of columns B.

Column A	**Column B**
(*a*) Copper sulphate solution	(*a*) $p\text{H} > 7$
(*b*) Sodium acetate solution	(*b*) $p\text{H} < 7$
(*c*) Potassium nitrate solution	(*c*) $p\text{H} = 0$

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*b*) **3.** (*a*) **4.** (*c*) **5.** (*c*) **6.** (*d*) **7.** (*d*) **8.** (*a*) **9.** (*b*) **10.** (*c*) **11.** (*c*).

TRUE/FALSE STATEMENTS

1, 3, 4, 6, 7, 8.

FILL IN THE BLANKS

1. an electrolyte **2.** inversely, square root of molar concentration **3.** donate a proton, accept a proton **4.** conjugate **5.** pOH **6.** acidic **7.** saturated. **8.** I_2

MATCHING TYPE QUESTIONS

1. (*a*) — (*b*), (*b*)—(*c*), (*c*)—(*a*) **2.** (*a*) — (*b*), (*b*) — (*a*), (*c*) — (*c*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

2. Degree of ionization of H_2O is small because H_2O is a very weak electrolyte.

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

   At mid point [Salt] = [Acid].

4. Number of titratable protons in HCl is greater than present in acetic acid.

5. Weak acid has a strong conjugate base.

6. $HCN \rightleftharpoons H^+ + CN^-$. NaCN gives common CN^- ions. Equilibrium shifts backward, $[H^+]$ decreases so that pH increases.

7. pH of water decreases with increase in temperature.

10. Sb (III) is precipitated (in Group IIB) by H_2S in acidic medium (dil. HCl). In acidic medium, S^{2-} concentration decreases so that radicals of Group IV are not precipitated. In alkaline medium, S^{2-} ion concentration increases and not decreases.

11. K_{sp} of AgCl > K_{sp} of AgBr. For precipitation to occur, ionic product should exceed solubility product.