Chapter - 2
ACIDS, BASES & SALTS

ACIDS AND BASES

1. Different workers gave different definitions for acids and bases from time to time.

(i) **Arrhenius Theory :** Arrhenius defined acids as those compounds which give hydrogen ions in aqueous solution, and bases as those compounds which give hydroxide ions in solutions.

e.g.,

$$H_2SO_4\,(aq) \rightleftharpoons 2H^+\,(aq) + SO_4^{2-}\,(aq)$$

The strength of an acid or base depends upon its tendency to furnish H^+ or OH^- ions in solution.

This definition can be applied only for those reactions which take place in aqueous solutions. Further this theory does not include substances that do not contain H^+ and OH^- ions but still can neutralize acids and bases.

Basicity or protonicity of acids : - It is the number of H^+ ions furnished by a molecule of an acid.

***Monobasic acid* :** An acid furnishing one H^+ ions e.g.HCl, HNO_3 etc.

***Dibasic acid* :** An acid furnishing two H^+ ions e.g. H_2SO_4, H_3PO_3 etc.

***Tribasic acid* :** An acid furnishing three H^+ ions e.g. H_3PO_4.

Acidity or Hydroxicity of base : It may be defined as the number of OH^- ions furnished by a molecule of a base.

***Monoacidic base* :** NaOH, KOH

***Diacidic base* :** $Ca(OH)_2$, $Ba(OH)_2$

(ii) **Bronsted Lowry Theory :** According to this theory acids are defined as substances which give up proton and bases as a substance which accepts proton.

e.g.,

$$\underset{A_1}{HCl} + \underset{B_2}{H_2O} \rightleftharpoons \underset{A_2}{H_3O^+} + \underset{B_1}{Cl^-} \qquad \text{Equation .....1}$$

$$\underset{B_1}{NH_3} + \underset{A_2}{H_2O} \rightleftharpoons \underset{A_1}{NH_4^+} + \underset{B_2}{OH^-} \qquad \text{Equation .....2}$$

From the above observations we may conclude that every acid has a conjugate base and every base has a conjugate acid.

In above equation 1 the conjugate base of acid HCl is Cl^- The conjugate acid of water is H_3O^+ (hydroxonium ion)

In the above equation 2 the conjugate acid of base NH_3 is NH_4^+ and the conjugate base of H_2O is OH^-.

Thus according to this theory the following conclusions can be drawn.

(a) A substance can act as an acid/base when another substance capable of accepting a proton/ capable of donating a proton exists.

(b) In aqueous solutions $H^{\oplus}$ ions exist as hydrated ions or H_3O^+ (H^+. H_2O) ions.

(c) Even ions may act as acids or bases.

(d) Water, can act both as an acid or base because it can give off a proton as well as can accept a proton.

$$\underset{B_1}{H_2O} + \underset{A_2}{H_2O} \rightleftharpoons \underset{A_1}{H_3O^+} + \underset{B_2}{OH^-}$$

(e) The strength of acids (or bases) depends on the medium which acts as base (or acids)

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

$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$

HCl + Benzene $\rightarrow$ No reaction

Acidic nature of HCl is greatest in ammonia and least in benzene.

Classification of Solvents :

(i) Aprotic - Solvents which can neither accept nor donate a proton.e.g. CCl_4, CS_2, Benzene.

(ii) Amphiprotic - Solvents which can both accept and donate a proton, e.g. H_2O, liquor Ammonia.

(iii) Protophillic - Solvents which have a greater tendency to accept proton e.g. H_2O, R-OH, liquor NH_3.

Levelling Effect :

Water acts as a very strong base because it has a great tendency to accept proton from mineral acids. The ionization of strong acids in water may be represented as below :

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

$H_2SO_4 + H_2O \rightarrow H_3O^{\oplus} + HSO_4^-$

Thus all strong acids (e.g. HNO_3, HCl, H_2SO_4, $HClO_4$) react almost completely to form H_3O^+ ion.

Therefore all strong acids in aqueous solution appear equally strong. i.e. Acidic levels for all acids are same. This is called **levelling effect** and water is the levelling solvent. Thus the relative acidic strengths or basic strengths in aqueous solutions cannot be compared.

When acetic acid is used as solvent instead of water it is found that the acidic strength of the acid lowers and now the given acid in acetic acid becomes weak and thereby different acids will dissociate to different extent in glacial acetic acid. (This is because of poor proton accepting character of acetic acid).

$$HA + CHCOOH \rightleftharpoons CH_3COOCH_2^+ + A^-$$

In this reaction the equalibrium does not lie very much to the right and hence strong acids are feebly dissociated.

The degree of dissociations of a number of acids dissolved in glacial acetic acid has been determined and it is found that the acidic strength order is

$HClO_4 > HI > HBr > H_2SO_4 > HCl > HNO_3 > H_3O^+ > HSO_4^- > H_3PO_4 > HF > CH_3COOH > H_2CO_3 > H_2S > NH_4^+ > HCN$

Lewis Concept of Acids And Bases

According to Lewis, an acid is any species which is capable of accepting a pair of electrons and a base is a species that is having a lone pair of electrons for donations.

This statement covers a wide range of acids and bases.

Thus all Bronsted-Lowry bases are Lewis bases while all Bronsted-Lowry acids are not Lewis acids.

Hence this theory includes acids which do not donate proton or liberate H^+ (aprotic)

$$NH_3 + BF_3 \longrightarrow H_3\overset{\delta+}{N} \rightarrow \overset{\delta-}{BF_3}$$

$$R\text{-}Cl + AlCl_3 \longrightarrow R^+ — AlCl_4^-$$

Lewis acids :

(i) Compounds where the central atom has incomplete octet. This means all electron deficient molecules can act as Lewis acids e.g.

BF_3, BBr_3, $AlCl_3$, $FeCl_3$, $GaCl_3$ etc.

(ii) Compounds in which the central atom has available vacant orbitals. e.g. SnF_4, $SnCl_2$, $SnCl_4$, PF_3, PF_4, SF_4, $TiCl_4$ etc.

(iii) Simple cations like Ag^+, Cu^{2+}, Al^{3+} etc. e.g. $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$.

Lewis Bases :

(i) All simple anions are Lewis bases e.g. Cl^-, NO_3^-, OH^-.

(ii) Molecules containing one or more unshaired pairs of electrons (Lone pairs) e.g. H_2O, NH_3, ROH, NX_3, R_2S, etc. are Lewis bases.

(iii) Multiple bonded compounds which can donate the pair of electrons. e.g. C = O, N = O, $CH_2 = CH_2$, CH ≡ CH.

SALT

A substance which ionizes in water to produce ions other than H^+ and OH^- is called a salt.

Types of Salts

Neutral Salts : Those salts whose aqueous solutions neither turn blue litmus red nor red litmus blue are called neutral salts. These are prepared by the neutralization of strong acid and strong base. e.g. NaCl, K_2SO_4, KNO_3 etc.

Acidic Salts : Those salts whose aqueous solutions turn blue litmus red are called Acidic salts. These are prepared by neutralisation of strong acid with weak base, e.g., NH_4NO_3, NH_4Cl.

Basic Salts : Those salts whose aqueous solutions turn red litmus blue are called basic salts. These are formed by the neutralization of strong bases with weak acids. e.g. Na_2CO_3, CH_3COONa

Mixed salts : Salts formed by the neutralization of one acid by two bases or one base by two acids are called mixed salts. e.g. $CaOCl_2$

Double Salts : A compound of two salts whose aqueous solution shows the tests for all constituent ions is called double salt e.g.

Mohr Salt $FeSO_4.(NH_4)_2SO_4.6H_2O$

Potash Alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$

Complex Salts : A compound whose solutions does not give tests for the constituent ions is called a complex salt. e.g.

$K_4[Fe(CN)_6]$

$Li(AlH_4)$

pH :

It may be defined in number of ways.

(i) The pH value of a solution is equal to the negative power to which 10 must be raised in order to express $[H^+]$ concentration

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

(ii) It can also be defined as the negative logrithm of its $[H^+]$ ion concentrations

$pH = -\log[H^+]$

pH values do not give instantaneous idea above the relative strengths of the solution

pOH :

It may be defined as the negative logrithms of hydroxyl ions concentration

$pOH = -\log (OH^-)$.

Ionic product of water

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

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

$\Rightarrow$ $pH + pOH = pK_w = 14$.

SOME IMPORTANT CHEMICALS

Bleaching Powder ($CaOCl_2$)

Preparation

In Hasen-Clever Plant

$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$

Properties

(1) It is yellowish white solid having chlorine like smell

(2) Bleaching powder decomposes to form O_2

$$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$$

(3) When reacted with H_2O liberates Cl_2.

$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

(4) Bleaching powder is decomposed to Cl_2 by dilute H_2SO_4.

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

(5) It reacts with carbondioxide to form calcium carbonate and Cl_2.

$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

(6) The chlorine liberated in above reaction can be used to oxidise I^- to I_2 thereby liberating I_2. This I_2 can be estimated by $Na_2S_2O_3$ thus we can measure the available chlorine in bleaching powder.

$2KI + Cl_2 \rightarrow 2KCl + I_2$

Uses

Bleaching powder is used for the disinfection of drinking water or swimming pool water. For use in outdoor swimming pools, it can be used as a sanitizer in combination with a cyanuric acid stabilizer. The stabilizer will reduce the loss of chlorine because of UV radiation. Calcium does make the water 'hard' and tends to clog up some filters, for this reason Sodium hypochlorite is preferred.

Bleaching powder is also used for bleaching cotton and linen and used in the manufacture of chloroform.

Sodium Hydroxide (NaOH)

Preparation

(1) Soda lime process, causticisation process or Gossage process

$$Na_2CO_3 + Ca(OH)_2 \xrightarrow{80 - 90^oC} 2NaOH + CaCO_3$$

(2) Castner kellner proces - Electrolytic process

Electrolyte → Brine (NaCl Solution in water)

Anode → Graphite

Cathode → Iron rods and Mercury acts as intermediate cathode by induction.

Reaction

$NaCl \rightarrow Na^+ + Cl^-$

At anode – $Cl^- \rightarrow Cl + e$

$Cl + Cl \rightarrow Cl_2$

At cathode – $Na^+ + e^- + Hg \rightarrow Na - Hg$

$2Na - Hg + 2H_2O \rightarrow 2NaOH + H_2 + 2Hg$

(sodium amalgam)

Properties

(1) White hygroscopic solid.

(2) Sodium hydroxide decomposes on heating to form sodium, hydrogen and oxygen.

$$2NaOH \xrightarrow{1300^oC} 2Na + H_2 + O_2$$

(3) It reacts with acids to form salt and water

(a) $NaOH + HCl \rightarrow NaCl + H_2O$

(b) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

(4) It reacts with acidic oxides to form salt and water.

(a) $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$
(Sodium carbonate)

(b) $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$
(Sodium sulphite)

(c) $2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$

(5) Metals like Zn, Al, Sn, Pb etc. displace hydrogen from sodium hydroxide. Even silicon displaces hydrogen from NaOH.

(a) $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
(Sodium zincate)

(b) $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
(Sodium meta-aluminate)

(c) $2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$
(Sodium aluminate)

(d) $Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$
(Sodium silicate)

(6) Non metals like P, S, Cl_2, Br_2 disproportionate in sodium hydroxide.

(a) $4S + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$
(Sodium thiosulphate)

(b) $4P + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$
(Sodium hypophosphite)

(c) $Cl_2 + 2NaOH$ (cold and dilute) $\rightarrow NaCl + NaClO + H_2O$
(Sodium hypochloride)

(d) $3Cl_2 + 6NaOH$ (hot and conc.) $\rightarrow 5\ NaCl + NaClO_3 + 3H_2O$
(Sodium chlorate)

(7) It precipitates Fe^{3+}, Cu^{2+}, Cd^{2+} etc. as metal hydroxides.

(a) $FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 \downarrow + 3NaCl$
(Brown)

(b) $CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 \downarrow + Na_2SO_4$
(Green)

(c) $CdCl_2 + 2NaOH \rightarrow Cd(OH)_2 \downarrow + 2NaCl$

(8) Metallic salts of Al^{3+} and Zn^{2+} are precipitated as $Al(OH)_3$ and $Zn(OH)_2$ but in excess of NaOH these precipitation dissolve to form aluminates and zincates respectively.

(a) $AlCl_3 + 3NaOH \rightarrow Al(OH)_3 \downarrow + 3NaCl$
$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$

(b) $Zn\ SO_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4$
$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

Uses

Used as strong base in chemical industry. Also used in detection of elements in chemical analysis, soap making and in making of biodiesel as catalyst.

Plaster of Paris

Quick-setting gypsum plaster consisting of a fine, white powder, calcium sulfate hemihydrate, which hardens when moistened and allowed to dry. Plaster of paris is prepared by heating calcium sulfate dihydrate, or gypsum, to 120°–180° C (248°–356° F). With an additive to retard the set, it is called wall, or hard-wall, plaster.

$$CaSO_4.2H_2O \xrightarrow{\Delta} CaSO_4.\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$$

Gypsum Plaster of paris

Uses

Used since ancient times, plaster of paris is so called because gypsum was early used near Paris to make plaster and cement. Plaster of paris is also used to precast and hold parts of ornamental plasterwork placed on ceilings and cornices and is used in medicine to make plaster casts to immobilize broken bones while they heal. Some modern sculptors work directly in plaster of paris. The speed at which the plaster sets gives the work a sense of immediacy and enables the sculptor to achieve the original idea quickly.

Water of crystallisation

Water chemically bonded to a salt in its crystalline state is called water of crystallisation. For example, in copper (II) sulphate, there are five moles of water per mole of copper sulphate: hence its formula is $CuSO_4.5H_2O$. This water is responsible for the colour and shape of the crystalline form. When the crystals are heated gently, the water is driven off as steam and a white powder of the anhydrous salt is formed.

$$CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(g)$$

Baking Soda

Sodium bicarbonate is the chemical compound with the formula $NaHCO_3$. Because it has long been known and is widely used, the salt has many other names including sodium hydrogencarbonate, sodium bicarb, baking soda, bread soda, cooking soda, bicarb soda, saleratus or bicarbonate of soda. It is soluble in water. Sodium bicarbonate is a white solid that is crystalline but often appears as a fine powder. It has a slight alkaline taste resembling that of sodium carbonate. It is a component of the mineral natron and is found dissolved in many mineral springs. The natural mineral form is known as nahcolite. It is also produced artificially by passing CO_2 through aqueous sodium carbonate solution.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Uses

It is primarily used in cooking. Also used as antacid in medicines and as an absorbant for moisture and odour. In toothpaste it is used as whitener.

Washing Soda

Sodium carbonate (also known as washing soda or soda ash), Na_2CO_3, is a sodium salt of carbonic acid. It most commonly occurs as a crystalline heptahydrate which readily effloresces to form a white powder, the monohydrate. It has a cooling alkaline taste, and can be extracted from the ashes of many plants. It is synthetically produced in large quantities from table salt in a process known as the Solvay process.

Solvay's ammonia process : In this process Brine (NaCl) solutions is saturated with ammonia and carbon dioxide to get the precipitate of $NaHCO_3$ which on heating gives Na_2CO_3. The various reactions taking place are given below :

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$NH_3 + H^+ \rightarrow NH_4^+$$

$$NH_4^+HCO_3^- + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{250^oC} Na_2CO_3 + H_2O + CO_2 \text{ (recycled)}$$

$$2NH_4Cl + CaO \rightarrow CaCl_2 + H_2O + 2NH_3 \text{ (recycled)}$$

Uses

Sodium carbonate's most important use is in the chemical make-up of glass. In chemistry, sodium carbonate is often used as an electrolyte. Domestically it is used as a water softener during laundry. It competes with the ions magnesium and calcium in hard water and prevents them from bonding with the detergent being used. Without using washing soda, additional detergent is needed to soak up the magnesium and calcium ions. Called Washing Soda or Sal Soda in the detergent section of stores, it effectively removes oil, grease, and alcohol stains. Sodium Carbonate is also used as a descaling agent in boilers such as found in coffee pots, espresso machines, etc. Sodium carbonate is widely used in photographic processes as a pH regulator to maintain stable alkaline conditions necessary for the action of the majority of developing agents.
It is also used for making fusion mixture ($Na_2CO_3 + K_2CO_3$) and black ash ($Na_2CO_3 + CaS$).

ASSIGNMENT

I. Multiple Choice Questions

1. H_3PO_2 is a

(a) monobasic acid (b) dibasic acid

(c) tribasic acid (d) tetrabasic acid

2. $AlCl_3$ is

(a) Arrhenius acid (b) Bronsted acid

(c) Lewis acid (d) None of these

3. Aqeous solution of C_6H_5COONa is

(a) Acidic (b) Basic

(c) Neutral (d) Amphoteric

4. Bleaching powder acts as

(a) oxidising agent (b) reducing agent

(c) both of these (d) none of these

5. Soaps are sodium salts of

(a) carbonic acid (b) benzoic acid

(c) lower fatty acids (d) higher fatty acids

6. Which of the following is a weak electrolyte ?

(a) NH_4Cl (b) NH_4OH (c) NaOH (d) HCl

7. Which of the following is the best conductor of electricity ?

(a) 1 MHCl (b) 1 M H_2CO_3 (c) $1MH_3SO_4$ (d) $1MH_2SO_4$

8. The reaction of water with ammonia is given by the following equation

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^{\ddot{O}}$$

In this reaction water behave as -

(a) neutral (b) base (c) acid (d) both acid and base

9. The compound that is not a Lewis acid is

(a) BF_3 (b) $BaCl_2$ (c) $AlCl_3$ (d) $SnCl_4$

10. Which of the following will not change red litmus blue ?

(a) $B(OH)_3$ (b) NaOH (c) $Ca(OH)_2$ (d) $Ba(OH)_2$

II. Fill in the blanks

(i) Washing soda solution has pH _____ than 7.

(ii) When Equal amounts of strong acid and base are mixed, the solution will be _____.

(iii) Famous "Dandi March" is related to chemical compound _____.

(iv) Sodium bicarbonate is also called _____.

(v) HSO_4^- is a conjugate acid of _____.

III. True / False

(i) The pH of neutral water at 90ºC is 7.

(ii) BF_3 is strong lewis acid than BBr_3.

(iii) $NaBH_4$ is a complex salt.

(iv) Organic acids are weak acids generally.

(v) The blood is slightly alkaline.

IV. Subjective Type Questions

1. Calculate the pH of 0.1 M NaOH.

2. What will be the nature of solution obtained by mixing 200 ml of 0.1 M NaOH with 100 ml of 0.2 M H_2SO_4 ?

3. Out of SO_3 and SO_2 which is stronger and why ?

4. Write the reaction for formation of sodium hypophosphite.

5. Which of the following is a Bronsted-Base ?

I^-, H_3O^+, HCl, NH_4^+

6. Complete the reaction :

(i) $Ca(OH)_2 + Cl_2 \longrightarrow$

(ii) $CaSO_4 \cdot 2H_2O \xrightarrow{\Delta 373K}$

(iii) $NaCl + NH_3 + H_2O + CO_2 \longrightarrow$

(iv) $NaHCO_3 \xrightarrow{\Delta}$

(v) $CuSO_4 \cdot 5H_2O \xrightarrow{\Delta}$

ANSWERS

I. Multiple Choice Questions :

1. (a) **2.** (c) **3.** (b) **4.** (a) **5.** (d)

6. (b) **7.** (d) **8.** (c) **9.** (b) **10.** (a)

II. Fill in the blanks :

(i) higher (ii) neutral

(iii) NaCl (iv) sodium hydrogen carboante or baking soda

(v) SO_4^{2-}

III. True / False

(i) False (ii) False

(iii) True (iv) True

(v) True

IV. Subjective Type Questions

(i) 13.

(ii) acidic.

(iii) SO_3.

(iv) $4P + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$.

(v) I^-.

6. (i) $Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$

(ii) $2CaSO_4 . 2H_2O \xrightarrow{\Delta 373K} 2CaSO_4 . H_2O + 3H_2O$

(iii) $NaCl + NH_3 + H_2O + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$

(iv) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

(v) $CuSO_4 . 5H_2O \xrightarrow{\Delta} CuSO_4 + 5H_2O$