Chapter 8
Acids, Bases And Salts

Acids turn blue litmus paper red and react with carbonates to evolve CO_2.

Bases turn red litmus paper blue.

There are certain substances which are not acids or bases themselves but show acidic or basic nature when dissolved in water.

e.g There are certain oxides of metals, like Na_2O and CaO which react with water to furnish bases.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

These oxides are basic in nature.

Certain non-metal oxides like CO_2, SO_2 and N_2O_5 when react with water yield carbonic acid (H_2CO_3), H_2SO_4 and HNO_3. Such oxides are acidic in nature

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Certain oxides are on the borderline of being acidic or basic. These oxides which tend to be insoluble in water, ~~and~~ are soluble in both acids and bases. They are said to be amphoteric in nature. e.g Al_2O_3, Cr_2O_3.

In addition to oxides, certain salts are also acidic and basic in nature e.g NH_4Cl is acidic bcz when dissolved in water it furnishes an acidic solution. Potassium carbonate (K_2CO_3) is basic since it yields a basic solution in water.

BASES:

Bases form a class of chemical substances including metal oxides and hydroxides.

ALKALI:

A soluble base is called an alkali and forms OH^- ions when dissolved in H_2O. In general the bases on hydrolysis produce alkali.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

ARHENIOUS THEORY

ACID

A substance which contains hydrogen and produce H^+ ions in aqueous solution.

The presence of water is essential for the formation of H^+ ions. e.g HCl is covalent in nature and doesnot form H^+ ions. However it forms H_3O^+ ions in the presence of H_2O

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

BASE

A substance that contains hydroxyl groups and produces hydroxyl ions, OH^- in aqueous solution.

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

NEUTRALIZATION

The process of neutralization of an acid by a base is represented by the reaction of H^+ with OH^- to form water.

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

AMPHOTERIC SUBSTANCE

The substance which behaves as an acid in basic solution and acts as a base in acidic solution.

IDENTIFYING AMPHOTERIC SUBSTANCES

To identify amphoteric substances, we have to see if it can accept as well as donate a proton. e.g H_2O is amphoteric in nature.

MCQ: Which one is amphoteric.

a) CO_3^{-2} ✓c) HPO_4^{-2}

b) H_3O^+ d) NH_4^+

Explanation:

a) CO_3^{-2}

It does not have any proton so it cannot act as an acid.

b) HPO_4^{-2}

It is conjugate base of $H_2PO_4^{-2}$

It can accept a proton to go back to $H_2PO_4^-$

It can donate a proton to become PO_4^{-3}

Thus, it is amphoteric.

c) H_3O^+

It can donate a proton to go back to H_2O

But it cannot accept any other proton.

d) NH_4^+

It can donate a proton to go back to NH_3

It cannot accept any proton.

BRONSTED - LOWERY CONCEPT

A Bronsted Acid is a proton donor.
A Bronsted base is a proton acceptor.

e.g

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

CONJUGATE ACIDS AND CONJUGATE BASES

Conjugate acid is a species which is formed as a result of acceptance of proton by a base. Every bronsted acid has a conjugate base.

Conjugate base is a species which is left behind after donation of a proton from the acid.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightarrow \underset{\text{conj. Acid}}{H_3O^+} + \underset{\text{conjugate base}}{Cl^-}$$

A strong acid produces a relatively weak conjugate base. Likewise a strong base produces a relatively weak conjugate acid. Similarly, a weaker acid have a strong conjugate base and vice versa.

A reactant and product that differ by a proton (H^+) is called conjugate acid - base pair.

STRENGTH OF ACIDS AND BASE

An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid.

A base which can accept proton to higher degree than another base is a relatively stronger base.

Acids and bases when dissolved in water dissociate into electrically charged ions. The degree of ionization is characteristic of the acids and bases.

Acid-base Reactions are reversible.

AUTO IONIZATION OF WATER

In auto ionization of water, water act both as a weak acid and a weak base, as it is amphoteric.

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

IONIC PRODUCT OF WATER (K_w)

Pure water feebly ionizes into hydrogen and hydroxyl ions.

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

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

Water is in large excess and its concentration remains constant, so equation becomes

$$K_c[H_2O] = [H^+][OH^-]$$

$$K_w = [H^+][OH^-]$$

K_w is called Ionic product of water which is equal to 10^{-14} at 25°C.

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

$[H^+] = [OH^-] = 10^{-7}$ mol/dm^3 in neutral/pure water

If $[H^+] = 10^{-7}$ M → Solution is neutral, pH = 7

$[H^+] > 10^{-7}$ M → Solution is Acidic, pH < 7

$[H^+] < 10^{-7}$ M → Solution is Basic, pH > 7

As K_w is an equilibrium constant, it is temperature dependant.

K_w remains constant on addition of acid or base

pH, pOH and pKw

$$pH = -\log[H^+]$$
$$pOH = -\log[OH^-]$$
$$pK_w = -\log K_w = -\log 10^{-14}$$
$$pK_w = 14 \text{ at } 25^\circ C$$

The value of pK_w decrease with increase in temperature.

$$pH + pOH = pK_w = 14$$

The value of K_a, K_w, K_b increase with increase in temperature.

→ When pH decreases by 1, acidity increase 10 times
→ When pH decreases by 2, acidity increase 100 times and so on.

$$pK_w = pK_a + pK_b$$

MCQ: What is the pH and pOH of 0.001M HCl solution?

Solution:

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

$$pH = -\log [H^+]$$
$$= -\log 10^{-3}$$
$$pH = 3$$
$$pOH = 14 - pH$$
$$pOH = 14 - 3 = 11$$

MCQ: What is $[H^+]$ and $[OH^-]$ ions concentration of a solution which has a pH = 4

Solution:

$$pH = -\log [H^+]$$
$$[H^+] = 10^{-pH}$$
$$[H^+] = 10^{-4}$$

$$[H^+][OH^-] = 10^{-14}$$
$$[OH^-] = 10^{-14} / 10^{-4}$$
$$= 10^{-14+4}$$
$$[OH^-] = 10^{-10}$$

MCQ: A solution with pH = 0, indicate $[H^+]$ concentration

Sol:

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

ACID IONIZATION CONSTANT (Ka, pKa)

The extent of ionization and the acid dissociation constant Ka can be used to distinguish between strong and weak acid.

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

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

Ka is called dissociation constant of acid. It is the ratio of product of concentrations of dissociated ions to the undissociated acid molecules in aqueous solution. It represent the extento to which an acid is dissociated.

Greater the value of ka, stronger is the acid.

$$pK_a = -\log K_a$$

Smaller pKa value corresponds to greater Ka value. Hence greater the value of pKa weaker would be the acid.

Ka of H_2O at 25°C → 1.8×10^{-5}

pKa of H_2O at 25°C → 15.7

When $K_a < 10^{-3}$, acid is weak

When $K_a = 1$ to 10^{-3}, acid is moderately strong

When $K_a > 1$, acid is strong

Base Ionization Constant

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

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Greater the value of K_b greater will be strength of base.

$$pK_b = -\log K_b$$

Relationship of Ka and Kb

$$K_w = K_a \times K_b = 10^{14}$$

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

K_w being constant

$$K_a \propto \frac{1}{K_b}$$

A stronger acid would have a larger value of K_a and its conjugate base would be weak with a smaller K_b value and vice versa.

$$pK_a + pK_b = 14$$

Knowing the pK_a value of an acid we can find pK_b of its conjugate base. and vice versa.

MCQ: Acetic Acid, CH_3COOH has a pKa value of 4.7 at 25°C. What is the pKb of its conjugate base CH_3COO^-

Sol:

$$pK_a + pK_b = 14$$
$$pK_b = 14 - 4.7$$
$$pK_b = 9.3$$

MCQ: Calculate concentration of H^+ ions of a solution that contains 1.0M HF ($K_a = 7.2 \times 10^{-4}$)

Sol:

	HF	$\rightleftharpoons$	H^+	$+ F^-$
Initial conc.	1.0M		0	0
Eq. conc. ($mol \cdot dm^{-3}$)	1.0		x	x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$7.2 \times 10^{-4} = \frac{x \cdot x}{1.0 - x}$$

Since x is very small as compared to 1.0, the term in denominator can be approximated as

$$1.0 - x = 1.0$$
$$7.2 \times 10^{-4} = x^2$$
$$x = 0.268 M$$
$$[H^+] = 0.268 M$$

* Ammonia is stronger base than pyridine and aniline but weaker than methylamine and ethylamine.

MCQ: The pK_b of pyridine at 25°C is 8.25. Calculate the pK_a of conjugate acid of pyridine.

Sol:

$$pK_a + pK_b = 14$$

$$pK_a = 14 - 8.25$$

$$pK_a = +5.75$$

FINDING PERCENTAGE IONIZATION

$$\% \text{ Ionization} = \frac{\text{Concentration of ionized acid}}{\text{Original concentration}} \times 100$$

or

$$\% \text{ Ionization} = \frac{[H^+]}{[HA]} \times 100$$

We find % ionization for weak acids.

LEWIS ACID AND BASE

A base is a substance that donates a pair of electrons, and an acid is a substance which accept a pair of electrons.

FORMATION OF $Al(H_2O)_6$

Al^{+3} ions form bonds to six water molecules to give a complex ion

$$Al^{+3} + 6H_2O \rightleftharpoons [Al(H_2O)_6]^{+3}$$

The Lewis structure of water suggests that this molecule has non bonding pairs of valence electrons and can therefore act as a Lewis base.

The electronic configuration of the Al^{+3} ion suggests that this ion has empty 3s, 3p and 3d orbitals that can be used to hold pairs of non bonding electrons donated by neighbouring water molecules.

$$Al^{+3} = [Ne]\ 3s^0\ 3p^0\ 3d^0$$

Thus, the $Al(H_2O)_6^{+3}$ ion is formed when an Al^{+3} ion acting as a Lewis acid picks up six pairs of electrons from neighbouring water molecules acting as Lewis bases to give an acid-base complex, or complex ion.

Lewis Acid and base react with each other such that a covalent bond forms, with both electrons provided by the Lewis base.

LEWIS ACIDS

1. Atoms, ions or molecules with incomplete octet of electrons.
2. Cations (Positive ions)
3. All Group III Halides
4. Pentahalides of phosphorus, Arsenic and Antimony

EXAMPLES:

H^+, BF_3, $AlCl_3$, Ag^+, CO_2, K^+, Mg^{+2}, SO_3, $RMgX$, Br_2

LEWIS BASES

1. Molecules containing an atom with lone pair of electrons.
2. Negative ions (anions) are bases.

EXAMPLES:

OH^-, NH_3, CO, H_2O, Cyanide ion (CN^-), H_2O, ROH, F^-, SO_4^{-2}, C_6H_6

BUFFER SOLUTIONS

A solution which resists changes in pH when a small amount of a strong acid or a strong base is added to it, is called buffer solution.

PREPARATION

A buffer solution can be made by mixing a weak acid with one of its salts OR mixing a weak base with one of its salts.

In other words, a buffer solutions consists of a mixture of a weak acid and its conjugate base OR a weak base and its conjugate acid.

PROPERTIES

1. A buffer solution resists change in pH even if a small amount of strong acid or a base is added to it.
2. A buffer solution maintains the stability of its pH by shifting their equilibrium to consume added H^+ ions or to replace H_3O^+ ions which have reacted with the added OH^- ions.
3. An aqueous solution of a strong acid and its conjugate base cannot act as a buffer solution. Similarly a solution of strong base and its conjugate acid donot form a buffer solution.

EXAMPLES

1. Blood is a buffer and maintain a pH of 7.4.
2. Acetic Acid / Sodium acetate
3. Phosphoric acid / potassium dihydrogen phosphate

ACIDIC BUFFERS

A weak acid and its Salt with a strong conjugate base is considered acidic with pH less than 7.
e.g CH_3COOH / CH_3COONa

BASIC BUFFERS

A weak base and its salt with a strong conjugate base is considered basic with pH greater than 7.
e.g NH_4OH / NH_4Cl

BUFFER ACTION

Consider an acidic buffer solution consisting of acetic acid and sodium acetate.

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

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

When a strong acid is added, H^+ ion of the acid reacts with acetate ion (CH_3COO^-) of the buffer.

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

When a strong base is added, the added OH^- ions are removed by the reaction with acetic acid molecules.

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

CALCULATING pH OF BUFFER SOLUTION

Henderson - Hesselbalch Equation:

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

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

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

If [salt] = [acid] then $pH = pK_a$
If [salt] > [acid] then $pH > pK_a$
If [salt] < [acid] then $pH < pK_a$

LEVELING EFFECT

One way to compare the strength of acids is to select a refrence base (usually the solvent) and determine the extent of proton donation from the acids to the reference base.

The strongest acid that can exist in a given solvent is acid characteristic of that solvent e.g H_3O^+ in water.

Strong acids like perchloric acid, HCl, HNO_3 and H_2SO_4 in water appear to be of equal strength bcz all of them dissociate completely. Thus, water as a base, is unable to differentiate among the relative acid strength of acids stronger than hydroxonium ion. Such inability of any solvent to differentiate among the relative strength of all acids is termed as the levelling effect.

The Leveling effect of water can be compensated for, if a more weakly basic solvent like acetic acid is employed in place of water. Since acetic acid is much weaker base than water, it is not easily protonated. In acetic acid they are partially ionized so we can find the strength of acids.

The more basic the solvent the more will acid donate hydrogen ions and the more it will dissociate.

Relative Strength of Certain Acids:

$HClO_4 > HI > HBr > HCl > H_2SO_4 > HNO_3 > HClO_3$

SALT HYDROLYSIS

"The reaction of cations and anions of salt with water is called hydrolysis"

Hydrolysis is different from hydration. In hydrolysis H-OH bond is broken whereas in hydration water molecule adds up to a substance without bond breakage.

In salt hydrolysis, salt completely dissociates in water and its anion and cation reacts with water to produce hydroxide ions or hydronium ions that affect the pH of the solution.

FOUR TYPES OF SALTS

1. Salts that are from strong bases and strong acids donot hydrolyze. The pH will remain neutral at 7. e.g

   $NaCl$; Na_2SO_4 , KNO_3 etc

2. Salts of weak acids and strong bases hydrolyze producing basic solutions ($pH > 7$)

   e.g CH_3COONa , $NaCN$, Na_2S etc

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

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

3. Salts of strong acids and weak bases hydrolyze producing acidic solutions ($pH < 7$)

e.g $CuSO_4$, NH_4Cl, NH_4NO_3 etc

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$

4. Salts of weak acids and weak bases hydrolyze, but the resulting solution is either neutral, acidic or basic. This depends on the relative values of K_a and K_b of cations of the salt. Whichever is the stronger acid or base will be the dominant factor in determining whether it is acidic or basic. The cation will be the acid and the anion will be the base, and will either form a hydronium ion or a hydroxide ion depending on which ion reacts more readily with water.

e.g NH_4CN, NH_4NO_2, $FeCO_3$, CH_3COONH_4

OXYACID

An oxyacid, or oxoacid, is an acid that contains oxygen.

RELATIVE STRENGTH OF ACIDS:

The relative strength of oxyacids can be predicted on the basis of the E.N difference and oxidation number of the central non metal atom.

The acidic strength increases as the E.N of the central atom increases. e.g As E.N of chlorine is greater than Sulphur, which in turn is greater than that of phosphorus it can be predicted that $HClO_4 > H_3PO_4$.

For a given non-metal, the acid strength increases as the oxidation number of the central atom increases e.g Nitric Acid → HNO_3 in which N has oxidation number of +5 is a stronger acid than nitrous acid HNO_2 where the nitrogen oxidation state is +3.

→ Cl_2O_7 is strongly acid in nature bcz Cl possess +7 oxidation state.

IMPORTANT POINTS

1. Monochloro acetic acid is stronger acid than acetic acid due to the presence of electron attracting group, Chlorine.

* Acidic Strength of Halogen Acids:

$$HI > HBr > HCl > HF$$

HF bond is strongest hence it is weakest acid among all halogen acids.

* POLYPROTIC ACIDS:

Polyprotic acids are specific acids that are capable of losing more than a single proton per molecule in acid-base reaction.

* MONOPROTIC ACIDS:

A monoprotic acid is an acid that donates only one proton or hydrogen atom per molecule to an aqueous Solution.

* HYDROLYSIS CONSTANT

$$K_h = \frac{K_w}{K_b} \quad \text{or} \quad K_h = \frac{K_w}{K_a}$$

Smaller value of K_a or K_b, more will the salt hydrolyze