Acids, Bases& Salts
Concepts of Acids and Bases

Arrhenius Theory:

This concept was presented in 1884.

According to this theory all substances which give H^+ ions when dissolved in water are called acids, while those which ionise to give OH^- ions are called bases.

The H^+ ions do not exist as such and exist in combination with molecules of H_2O as H_3O^+ ions (Known as hydronium ion).

$$H^+ + H_2O \;\; H_3O^+$$

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

e.g.

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

Acid

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

Acid

$$BOH + H2O \; B^+ + OH^-$$

Base

$$NaOH + H_2O \;\; Na^+ + OH^-$$

Base

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

Base

A) Limitations of Arrhenius theory:

The concept does not explain the acidic or basic properties of acids or bases in nonaqueous solvents. It fails to explain acidic nature of non - protic compounds like SO_2, P_2O_5, CO_2, NO_2 etc. Which do not have hydrogen in their molecules to furnish H^+ ions.

It fails to explain acidic nature of certain salts like $AlCl_3$ etc., in aqueous solutions.

Example:

Which of the following is not the characteristics of an acid–

(a) Turns blue litmus to red

(b) Turns phenolphthalein pink from colourless

(c) Decompose carbonates

(d) Oxy compounds of non–metals

Solution :

Correct answer is (B) Refer (1.1) preliminary classification of acid & bases.

Option (b) indicates characteristic of bases.

Example :

Arrhenius theory of acid–base is not applicable in

(a) aqueous solution

(b) In presence of water

(c) Non–aqueous solutions

(d) None of the above

Solution :

Correct answer is (C), since Arrhenius theory is only applicable to aqueous media.

B) Acid Base Concept of Bronsted and Lowry :

The theory was given by Bronsted, a Danish chemist and Lowry, an English chemist independently in 1923. According to it an acid is a substance, molecule or ion which has a tendency to release the proton (protogenic) and similarly a base has a tendency to accept the proton (protogenic).

e.g.

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

In the reaction, HCl acts an as acid because it donates a proton to the water molecule. Water, on the other hand, behaves as a base by accepting a proton.

Bronsted and lowry theory is also known as proton donor and proton acceptor theory.

Other examples:

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

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

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

In the reaction (i) and (ii) water is acting as a base, while in reaction (iii) it is acting as an acid. Thus water can donate as well as accept H^+ and can act as both acid and base.

Example :

Suitable reason (s) for higher strength of an acid or base will be –

(a) Higher value of K_a or K_b

(b) Higher extent of ionisation

(c) (a) and (b) both

(d) Larger number of replaceable H atoms.

Solution :

Correct answer is (C), both K_a or K_b and degree of ionisation are the measure of strength of an acid or base.

Example :

The basicity of phosphorous acid is –

(a) 1 (b) 2 (c) 3 (d) 4

Solution :

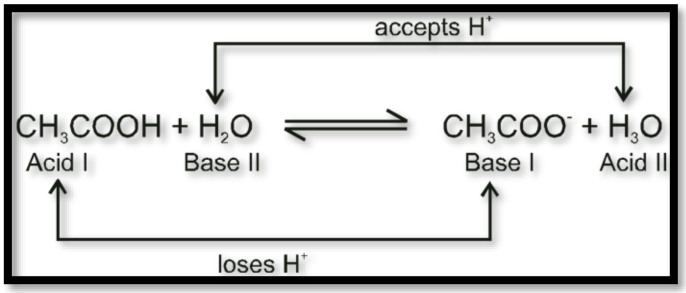
Correct answer is (B) since Phosphorous acid is H_3PO_3 which has two replaceable H^+ ions.

The species like H_2O, NH_3, CH_3COOH which can act as both acid and base are called amphiprotic.

Moreover according to theory, an acid on losing a proton becomes a base, called **conjugate base**, while the base by accepting proton changes to acid called **conjugate acid.**

Here CH_3COO^- ion is conjugate base of CH_3COOH^-, while H_3O^+ ion is conjugate acid of H_2O.

¬ **List of some common conjugate Acid–Base pairs:**



Acid = Base + H^+	**Base = Acid $-H^+$**
$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)
HI (hydriodic acid)	I (Iodine ion)
HBr (hydrobromic acid)	Br (bromine ion)
HCl (hydrochloric acid)	Cl (chloride ion)
H_2SO_4 (sulphuric acid)	HSO_4^- (hydrogensulphate ion)
NHO_3 (Nitric acid)	NO_3^- (nitrate ion)
H_3O^+ (hydronium ion)	H_2O (water)
HSO_4^- (hydrogen sulphate ion)	SO_4^{-2} (sulphate ion)
HF (hydro fluoric acid)	F (fluorine ion)

Acid = Base + H^+	Base = Acid $-H^+$
HNO_2 (nitrous acid)	NO_2^- (nitrite ion)
HCOOH (formic acid)	HCOO (formate ion)
CH_3COOH (acetic acid)	CH_3COO (acetate ion)
NH_4^- (ammonium ion)	NH_3 (ammonia)
H_2O (water)	OH (hydroxide ion)
NH_3 (ammonia)	NH_2^- (amide ion)

Classification of Bronsted Lowry Acid & Bases:

Type	Acid	Base
Molecular	HCl, HNO_3, $HClO_4$, H_2SO_4, H_3PO_4, CH_3COOH, HBr, H_2O etc.	NH_3, N_2H_4, Amines, H_2O, Alcohol, Ethers
Cationic	NH_4^+, $N_2H_5^+$, PH_4^+, Na^+, Ba^{+2} (All cations) $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{+3}$, $[Al(H_2O)_6]^{3+}$,	$[Fe(H_2O)_5OH]^{2+}$ $[Al(H_2O)_5OH]^{2+}$
Anionic	HS^-, HSO_3^-, $H_2SO_4^-$, HSO_4^-, HCO_3^-, HPO_4^{2-}, all amphiprotic anions	Cl^-, Br^-, OH^-, HSO_4^- CH^-, CO_3^{2-}, SO_4^{2-}, NH_2^-, CH_3COOH^-

Reactions in Non–aqueous solvents:

(i) Solvents like C_6H_6, CCl_4, THF (Tetrahydrofuran), DMF (N, N - dimethyl formamide) etc. are used in organic chemistry. In Inorganic chemistry reactions are generally studied in water. However a large number of nonaqueous solvents (such as Glacial acetic acid, Hydrogen halides, SO_2 etc.) have been introduced in Inorganic chemistry.

(ii) The physical properties of a solvent such as M.P., B.P., Dipole moment and Dielectric constant are important in deciding its be haviour.

Lux – Flood Concept (1939 & 1947) :

(i) The proton plays an important role in explaining the acid–base behaviour in the Bronsted–Lowery Concept. Lux observed that acid – base reactions are also feasible in oxide systems without the aid of protons.

(ii) Above approach was extended by Flood and applied to non–protonic systems, which were not covered by the Bronsted Lowery Concept.

(iii) According to this concept a base (like CaO, BaO, Na_2O) is an oxide ion (O^{2-}) donor and an acid (like SiO_2, CO_2 or P_4O_{10}) is an oxide ion (O^{2-}) acceptor.

e.g. Base Acid

(a) $CaO + SiO_2 \quad CaSiO_3$

(b) $CaO + P_4O_{10} \quad 4Na_3PO_4$

(iv) Substances are termed amphoteric if they show a tendency of losing as well as accepting an oxide ion.

e.g. ZnO, Al_2O_3

Example :

The aprotic solvent is –

(a) H_2O (b) C_6H_6 (c) HF (d) NH_3

Solution :

Correct Answer is (b)

Example :

Which of the following is the strongest conjugate base

(a) Cl^- (b) CH_3COO^- (c) kk (d) kl+

Solution :

Correct answer is (b), since CH_3COOH is weakest acid among HCl, CH_3COOH, and HNO_2

Example :

The strongest Bronsted base in the following anions is

(a) ClO^- (b) (c) (d)

Solution :

Correct answer is (a), since HClO is weakest acid among HClO, $HClO_2$, $HClO_3$ and $HClO_4$.

Example :

Urea can show weak acidic nature in liquid NH_3 solution . Write appropriate equation and label as acid & base.

Solution :

$NH_2CONH_2 + NH_3 \quad + NH_2CONH^-$

Urea Acid base

(c) Lewis theory :

The theory was given by G.N.Lewis in 1938. According to it, an acid is a species which can accept a pair of electrons, while the base is one which can donate a pair of electrons.

It is also known as electron pair donor and electron pair acceptor theory.

e.g.

(i) $FeCl_3$ and $AlCl_3$ are Lewis acids, because the central atoms have only six electrons after sharing and need to have more electrons.

(ii) NH_3 is a Lewis base as it has a pair of electrons which can be easily donated.

Lewis acids:- CH_3^+, H^+, BF_3, $AlCl_3$, $FeCl_3$, etc.

Lewis bases :- NH_3, H_2O, R-O-R, R - OH, CN^-, OH^- etc.

(i) Characteristics of species which can act as Lewis acid :

❖ **Molecules with vacant orbitals :**

Lewis acids are electron deficient molecules such as BF_3, $AlCl_3$, $GaCl_3$ etc.

❖ **Molecules in which the central atom has incomplete octet :**

The central atom of the halides such as $TiCl_4$, $SnCl_4$, PCl_3, PF_5, SF_4, $TeCl_4$. etc., have vacant d-orbitals. These can, therefore, accept an electron pair and act as Lewis acids.

$$\underset{\text{Lewis acid}}{SiF_4} + \underset{\text{Lewis base}}{2\,:\ddot{F}:} \longrightarrow \underset{\text{complex}}{[SiF_6]^{2-}}$$

❖ **Simple cation :**

All cations are expected to act as Lewis acid, since they are electron deficient in nature.

$$Ag^+ + 2\ddot{N}H_3 \rightarrow [H_3N \rightarrow Ag \leftarrow NH_3]^+$$
$$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-}$$

❖ **Molecules having a multiple bond between atoms of dissimilar electronegativity :**

Typical examples of molecules belonging to this class of acids are CO_2, SO_2, and SO_3.

(ii) Characteristics of species which can act as Lewis bases :

- **Netural species having at least one lone pair of electrons :**

  For example, ammonia amines, alcohols etc., act as Lewis bases as they contain a pair of electrons.

$$:NH_3, R-\ddot{N}H_2, R--H, H--H, R--R$$

- **Negatively charged species or simple anions:** For example chloride (Cl^-),cyanide (CN^-)

hydroxide (OH^-) ions etc. act as Lewis bases.

- **Multiple bonded compounds:** The compounds such as CO, NO, Ethylene, acetylene etc. can act as Lewis bases.