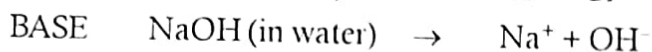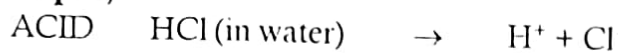# THEORIES OF ACIDS AND BASES

INTRODUCTION—ARRHENIUS THEORY

It is the most important theory among the earlier theories of acids and bases. According to Arrhenius theory, an acid is a substance which dissociate in an aqueous solution to give hydrogen ions (H^+) while a base gives hydroxyl ions (OH^-).

Examples,

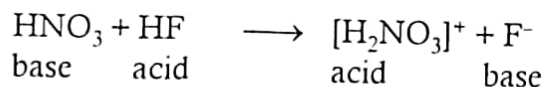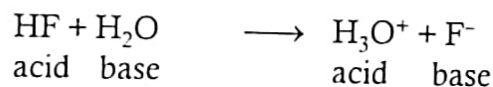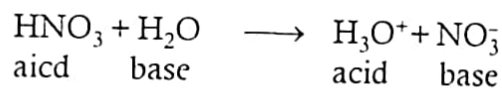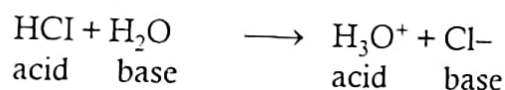| ACID | HCl (in water) | $\rightarrow$ | $H^+ + Cl^-$ |
| BASE | NaOH (in water) | $\rightarrow$ | $Na^+ + OH^-$ |

Bronsted-Lowry Theory of Acids and Bases

Arrhenius theory has several limitations in conforming a substance as acid on base under different conditions. As for example, it considers HCl as an acid in water (as it dissociates to provide a H^+ ion) but not in benzene. Thus the role of solvent is not considered in Arrhenius theory.

Again according to this theory HF and HNO_3 are independently acidic in water but when taken together, HNO_3 does not act as an acid anymore rather in Liquid HF it accepts a H^+ ion. Thus the term acids and bases are relative to each other.

Bronsted and Lowry rectified the above discrepencies in Arrhenius theory and suggested that an acid is a proton donor and a base is a proton acceptor. Here the role of solvent is taken into account for deciding the acidic or basic character of a substance by considering the acid and base simultaneously in the solution as without one of these the other becomes insignificant. Hence the relativeness of a substance showing acidic or basic character under different environments is also considered.
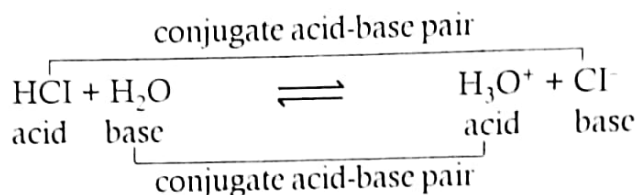
For example,

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$\text{acid} \quad \text{base} \qquad\quad \text{acid} \quad \text{base}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$\text{base} + \text{acid} \qquad\quad \text{acid} \quad \text{base}$$

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$
$$\text{aicd} \quad \text{base} \qquad\quad \text{acid} \quad \text{base}$$

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$
$$\text{acid} \quad \text{base} \qquad\quad \text{acid} \quad \text{base}$$

$$HNO_3 + HF \longrightarrow [H_2NO_3]^+ + F^-$$
$$\text{base} \quad \text{acid} \qquad\quad \text{acid} \qquad \text{base}$$

Conjugate Acid-Base Pair

When a Bronsted acid looses a proton, a negatively charged species is generated which has a general tendency to accept a proton back and consequently behaves as a base. Similarly the relative Bronsted base of the above Bronsted acid would accept a proton to generate a positively charged species and have a general tendency to loose a proton reversibly and consequently behave as an acid. The above pairs of acids and bases are called conjugate acid-base pair.

For example,

$$\underbrace{\underbrace{HCl}_{acid} + \underbrace{H_2O}_{base} \rightleftharpoons \underbrace{H_3O^+}_{acid} + \underbrace{Cl^-}_{base}}_{}$$

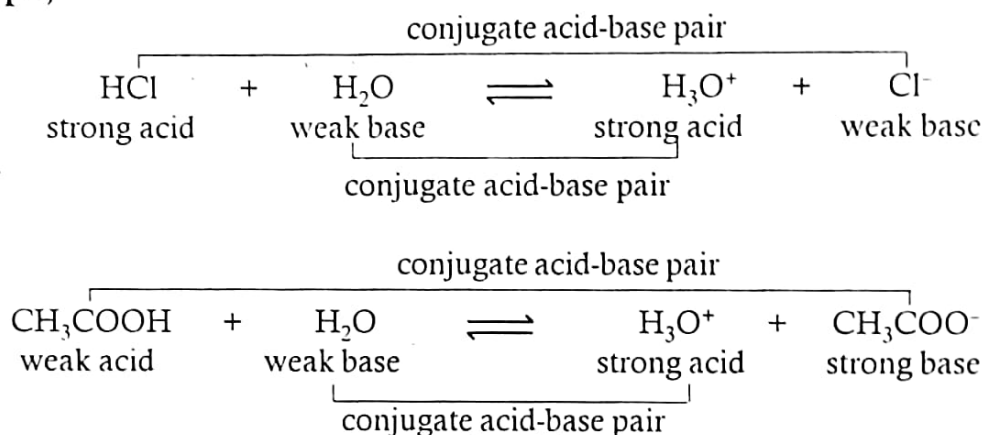conjugate acid-base pair

conjugate acid-base pair

Thus the species generated after a Bronsted acid looses a proton is called the conjugate base of the acid and the species generated after a Bronsted base accepts a proton is called the conjugate acid of the base.

Relative Acidity-Basicity of Conjugate Pair

Since the above pairs of conjugate acids and bases are in equilibrium, a strong Bronsted acid would have a greater tendency to loose its proton and thus the equilibrium would shift to the right. This suggests that the conjugate base would be weak in nature to facilitate the equilibrium to shift in forward direction. Hence a strong acid would generate a weak-conjugate-base and a strong base would generate a weak-conjugate-acid.

For example,

conjugate acid-base pair

$$\underset{\text{strong acid}}{HCl} + \underset{\text{weak base}}{H_2O} \rightleftharpoons \underset{\text{strong acid}}{H_3O^+} + \underset{\text{weak base}}{Cl^-}$$

conjugate acid-base pair

conjugate acid-base pair

$$\underset{\text{weak acid}}{CH_3COOH} + \underset{\text{weak base}}{H_2O} \rightleftharpoons \underset{\text{strong acid}}{H_3O^+} + \underset{\text{strong base}}{CH_3COO^-}$$
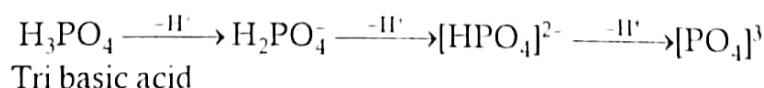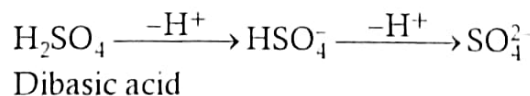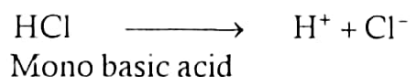
conjugate acid-base pair

Amphiprotic Solvent

A solvent which can behave both as an acid as well as a base under different set of conditions is called an amphiprotic solvent. An excellent example is H_2O and its acidic and basic characters are discussed earlier.

Acidity and Basicity

The number of H^+ ions furnished by a single molecule of an acid is called its basicity and the number of H^+ ions accepted by a single molecule of base is called its acidity.

For example,

$$HCl \longrightarrow H^+ + Cl^-$$
Mono basic acid

$$H_2SO_4 \xrightarrow{-H^+} HSO_4^- \xrightarrow{-H^+} SO_4^{2-}$$
Dibasic acid

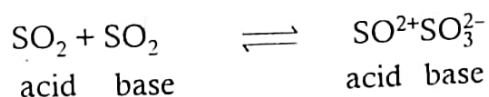$$H_3PO_4 \xrightarrow{-H^+} H_2PO_4^- \xrightarrow{-H^+} [HPO_4]^{2-} \xrightarrow{-H^+} [PO_4]^{3-}$$
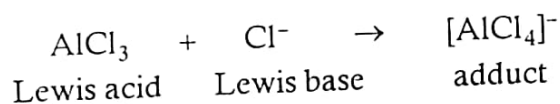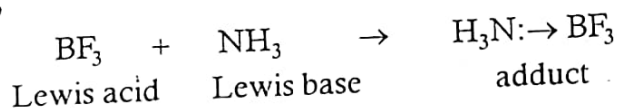Tri basic acid

LEWIS THEORY OF ACIDS AND BASES

There are also a number of acid-base reactions which occurs without any transfer of protons.

For example,

$$SO_2 + SO_2 \rightleftharpoons SO^{2+}SO_3^{2-}$$

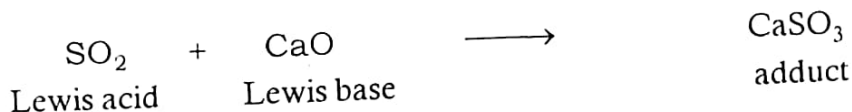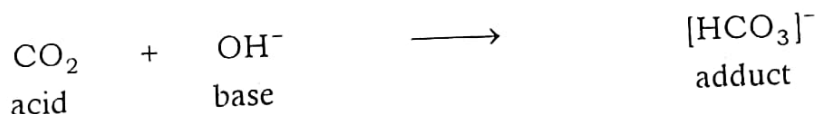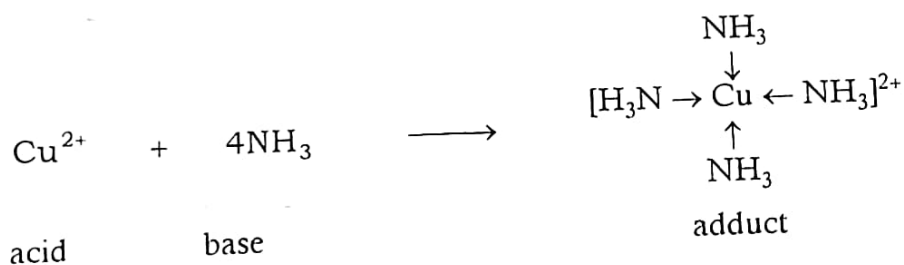$$\text{acid} \quad \text{base} \qquad\qquad \text{acid} \quad \text{base}$$

The acidic and basic character of these non protonic species are difficult to explain by Bronsted theory of acids and bases. Hence a more simplified generalisation of the concept of acids and bases is suggested by Lewis according to which an acid is a substance which can accept a pair of electrons and a base is one which can donate a pair of electrons (to form a coordinate bond in case of no transfer of atoms)

For example,

$$BF_3 \quad + \quad NH_3 \quad \rightarrow \quad H_3N:\rightarrow BF_3$$

$$\text{Lewis acid} \quad \text{Lewis base} \qquad\qquad \text{adduct}$$

$$AlCl_3 \quad + \quad Cl^- \quad \rightarrow \quad [AlCl_4]^-$$

$$\text{Lewis acid} \quad \text{Lewis base} \qquad \text{adduct}$$

Hence in a non protonic acid-base reaction Lewis acid is an electron deficient species which must have at least one empty orbital in valence shell to accept an electron pair from a Lewis-base which has a lone pair of electrons.

For example,

$$Ag^+ \quad + \quad 2NH_3 \quad \longrightarrow \quad [H_3N:\rightarrow Ag \leftarrow:NH_3]^+$$

$$\text{acid} \qquad\qquad \text{base} \qquad\qquad\qquad\qquad \text{adduct}$$

$$Cu^{2+} \quad + \quad 4NH_3 \quad \longrightarrow \quad \begin{array}{c} NH_3 \\ \downarrow \\ [H_3N \rightarrow Cu \leftarrow NH_3]^{2+} \\ \uparrow \\ NH_3 \end{array}$$

$$\text{acid} \qquad\qquad \text{base} \qquad\qquad\qquad\qquad\qquad \text{adduct}$$

$$CO_2 \quad + \quad OH^- \quad \longrightarrow \quad [HCO_3]^-$$

$$\text{acid} \qquad \text{base} \qquad\qquad\qquad\qquad \text{adduct}$$

$$SO_2 \quad + \quad CaO \quad \longrightarrow \quad CaSO_3$$

$$\text{Lewis acid} \quad \text{Lewis base} \qquad\qquad\qquad \text{adduct}$$

HARD AND SOFT ACIDS AND BASES—"HSAB" CONCEPT

In HSAB concept, the Lewis theory of acids and bases is comprehensively elaborated for a comparative estimation of relative stability/reactivity towards different counter species. This reactivity relativeness brought about the classification of acids and bases into two sub-groups namely "HARD" and "SOFT".

HARD ACIDS have the electron pair acceptor atom smaller in size with high positive charge on it and contains unpaired electrons in the valence shell. In other words, hard acids have high electronegativity and low polarisibility.

SOFT ACIDS contrarily have large electron pair acceptor atoms of low positive charge on them and contain unpaired electrons in the valence shell leading to the general property of low electronegatirvity and high polarisibility.

Similarly, HARD BASES have high electronegativity an low polarisibility of the donor atoms leading to a strong hold on the electron-pair and thus can not be oxidised easily.

On the other hand, SOFT BASES have low electronegativity and high polarisibility of the electron pair donor atoms and thus can be easily oxidised.

In the above classification of HARD and SOFT acids and bases there is no sharp line demarcation and thus an intermediate borderline-species having dual properties are present.

ACIDS
Hard acids
H^+, Li^+, Na^+, K^+ (Rb^+, Cs^+) Be^{2+}, $Be(CH_3)_2$, Mg^{2+}, Ca^{2+}, Sr^{2+} (Ba^{2+}) Sc^{3+}, La^{3+}, Ce^{4+}, Gd^{3+}, Lu^{3+}, Th^{4+}, U^{4+}, UO_2^{2+}, Pu^{4+} Ti^{4+}, Zr^{4+}, HF^{4+}, Cr^{3+}, Cr^{6+}, MoO^{3+}, WO^{4+}, Mn^{2+}, Mn^{7+}, Fe^{3+}, Co^{3+} BF_3, BCl_3, $B(OR)_3$, Al^{3+}, $AI(CH_3)_3$, $AlCl_3$, AlH_3, Ga^{3+}, In^{3+} CO_2, RCO^+, NC^+, Si^{4+}, Sn^{4+}, CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$ N^{3+}, RPO_2^+, $ROPO_2^+$, As^{3+} SO_3, RSO_2^+, $ROSO_2^+$ Cl^{3+}, Cl^{7+}, I^{5+}, I^{7+} HX (hydrogen bonding molecules)
Borderline acids
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+} $B(CH_3)_3$, GaH_3 R_3C^+, $C_6H_5^+$, Sn^{2+}, Pb^{2+} NO^+, Sb^{3+}, Bi^{3+} SO_2
Soft acids
$Co(CN)_5^{3-}$, Pd^{2+}, Pt^{2+}, Pt^{4+} Cu^+, Ag^+, Au^+, Cd^{2+}, Hg_2^{2+}, Hg^{2+} CH_3Hg^+ BH_3, $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3, Tl^+, $Tl(CH_3)_3$ CH_2, carbenes π-acceptors: trinitrobenzene, chloroanil. quinones, tetracyanoethylen, etc. HO^+, HO^+, RS^+, RSe^+, $Te4^+$ RTe^+ Br_2, Br^+, I_2, I^+, ICN, etc.   O, Cl, Br, I, N, RO, RO_2. M^0 (metal atoms) and bulk metals

BASES
Hard bases
NH_3, RNH_2, N_2H_4 H_2O, OH^-, O^{2-}, ROH, RO^-, R_2O CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^- F^-, (Cl^-)
Borderline bases
$C_6H_5NH_2$, C_5H_5N, N_3^-, N_2 NO_2^-, SO_3^{2-} Br^-
Soft bases
H^- R^-, C_2H_4, C_6H_6, CN^-, RNC, CO SCN^-, R_3P, $(RO)_3P$, R_3As R_2S, RSH, RS^-, $S_2O_3^{2-}$ I^-

'HSAB' PRINCIPLE

According to this generalised principle, due to similar properties (electronegativity and polarisibility) of the acid-base complex species, stable comlexes are formed by the combination of hard acids with hard bases and soft acids with soft bases preferably.
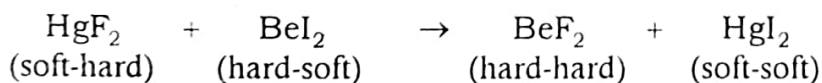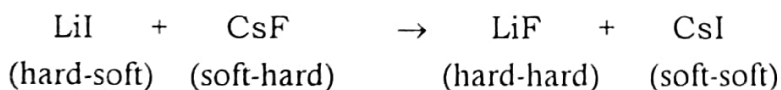
APPLICATIONS OF 'HSAB' PRINCIPLE

1. Stability of Complexes

Ag^+ (a soft acid) forms a stable complex with $I^\ominus$ (a soft base) as $[AgI_2]^-$ (soft acid + soft base) but with $F^\ominus$ (a hard base) it forms unstable complex $[AgF_2]^-$ (soft acid + hard base) and thus AgF_2^- does not exist. Contrarily, Co^{3+} (a hard acid) forms stable $[CoF_6]^{3-}$ complexes (hard acid + hard base) and relatively unstable $[CoI_6]^{3-}$ (hard acid + soft base].

2. Predicting Feasibility of a Reaction

Due to the hard-hard and soft-soft stability factor, the feasibility of the following reactions can be understood.

$$\begin{array}{ccccccc}
LiI & + & CsF & \rightarrow & LiF & + & CsI \\
\text{(hard-soft)} & & \text{(soft-hard)} & & \text{(hard-hard)} & & \text{(soft-soft)}
\end{array}$$

$$\begin{array}{ccccccc}
HgF_2 & + & BeI_2 & \rightarrow & BeF_2 & + & HgI_2 \\
\text{(soft-hard)} & & \text{(hard-soft)} & & \text{(hard-hard)} & & \text{(soft-soft)}
\end{array}$$

Due to smaller sizes and high electronegativites, the hard acid-hard base stable complex forms predominantly ionic bonding whereas the soft acid-soft base stable complexes are of predo ninantly covalent bondings due to their large sizes and high polarisibility.

pH OF SOLUTIONS

The pH of solution is defined as the negative logarithm of H^+ ion activity and can be mathematically expressed as.
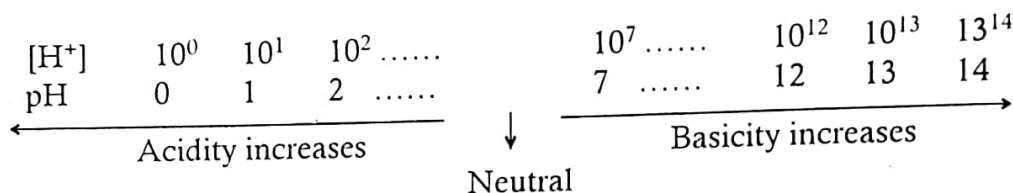
$$pH = -\log a_{H^+}$$

activity (a_H) is the effective concentration of H^+ ion in solution, when the solution is dilute.

$$a_H = [H^+]$$

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

Hence pH decreases with the increase of $[H^+]$. In other words, lower the pH value higher is the acidity. Thus the pH scale corresponding to H^+ ion concentration in a given solution can be represented as

| $[H^+]$ | 10^0 | 10^1 | 10^2 ...... | 10^7 ...... | 10^{12} | 10^{13} | 13^{14} |
| pH | 0 | 1 | 2 ...... | 7 ...... | 12 | 13 | 14 |

$\longleftarrow$ Acidity increases

$\downarrow$ Neutral

Basicity increases $\longrightarrow$

From the above pH scale, it can also be concluded that with decrease in one unit of pH value, the acidity of a solution increases ten times of the initial.

pK$_a$ OF A SOLUTION

Acids get dissociated in solution to form the following equilibrium
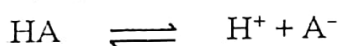
$$HA \rightleftharpoons H^+ + A^-$$

and the dissociation constant of acids (k_a) is expressed in terms of the concentrations (for dilute solution) as,

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

Since the dissociation constant of acids is directly proportional to the dissociated species, stronger the strength of the acid larger would be the $[H^+]$ leading to a higher value of k_a. Since numerically k_a is a extremely small value, it is more convenient to express the strength of an acid as pk$_a$ which is defined as the negative logarithm of the k_a and can be denoted as

$$pk_a = -\log_{10} k_a$$

Dissociation constants and the respective pk$_a$ values of some acids are given below (at 25°C)

Acid	K_a	pK_a
HCOOH	1.77×10^{-4}	3.75
CH$_3$COOH	1.8×10^{-5}	4.75
C$_6$H$_5$COOH	6.4×10^{-5}	4.2
HCN	7.2×10^{-10}	9.14

ACID-BASE CONCEPT IN NON-AQUEOUS MEDIA

As stated earlier, the acidic and basic character of a species alongwith its strength is a relative property which is dependent on the nature of solvent used. Apart from water, a large number of acid-base reactions take place in non-aqueous solvents showing different properties and characteristics than that in water. Some of the non-aqueous solvents alongwith their effect on the acid-base reactions are discussed below: