Name of the Teacher- Sutapa Chakrabarty

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PART 1

Comments: Go through the whole lesson thoroughly.

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ACIDS & Bases

Following are the important modern concepts of acids and bases.

1. The Arrhenius concept:-

Arrhenius defined an acid as "any H-containing compound which gives H^+ ions in aquous solution." A base was similarly defined as "any compound which gives hydroxyl ions in aquous solⁿ."
Thus HCl is an acid and NaOH is a base in aquous solution.

$$\underset{\text{acid}}{HCl} \xrightleftharpoons{\text{water}} H^+ + Cl^-$$

$$\underset{\text{base}}{NaOH} \xrightleftharpoons{\text{water}} Na^+ + OH^-$$

⇒ Advantages of Arrhenius concept:-

With the help of this concept, we can explain the following;

i) Aquous solution of non-metallic oxides (CO_2, SO_2 etc) is acidic, since it gives H^+ ions in water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{=}$$

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{=}$$

ii) Aquous solution of metallic oxides (CaO, Na_2O etc) and the compounds like NH_3, N_2H_4, NH_2OH etc are basic, since these substances give OH^- ions in water.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$Na_2O + H_2O \rightleftharpoons 2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$N_2H_4 + H_2O \rightleftharpoons [N_2H_5]^+[OH]^- \rightleftharpoons N_2H_5^+ + OH^-$$

hydrazinium ion

$$NH_2OH + H_2O \rightleftharpoons [NH_3OH]^+ OH^- \rightleftharpoons NH_3OH^+ + OH^-$$

hydroxyl ammonium ion

iii) This concept can explain the acid-base neutralisation reaction taking place in water.

iv) The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the dissociation constant of the acid and base in aquous solution.

$$\underset{acid}{HA} \rightleftharpoons H^+ + A^- \qquad K_a = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}}$$

$$\underset{base}{BOH} \rightleftharpoons B^+ + OH^- \qquad K_b = \frac{C_{B^+} \cdot C_{OH^-}}{C_{BOH}}$$

v) The catalytic proparties of acids in many reactions can be explained by saying that H^+ ions are available from the acid.

⇨ **Limitations of Arrhenius concept :-**

Inspite of its qui wide applications in aquous solution, the Arrhenius theory has certain limitations. These are —

(i) According to this concept, HCl is regarded as an acid only when it is dissolved in H_2O and not in some other solvent such as C_6H_6 or when it exists in the gaseous form.

(ii) It can not account for the acidic and basic character of the materials in non aqu solvants. e.g;

NH_4Cl in liquid amonia acts as an acid, though it does not give H^+ ions.

(iii) It can not explain the acidic character of certain salts such as $AlCl_3$ in aqu. solm.

iv) The formation of NH_4Cl (s) by the combination of NH_3 (g) and HCl (g) can not be explained by Arrhenius concept.

v) According to this concept, acids and bases undergo dissociation only in water. Thus, it can not explain the dissociation of acids and bases in non aquous solvants like liquid amonia, liq SO_2 etc.

2. The Solvent system concept :-

According to this concept the solvents undergo auto-ionisation and give cations and anions which are called solvent cations and solvent anions respectively.

The definition of acids and bases given by this concept is based on the nature of the cations and anions which are the acid or base produces, either by its auto-ionisation or when it is dissolved in this solvent. Thus according to this concept, the substances which give solvent cations when dissolved in that solvent are called acids while the substances which give solvant anions when dissolved in that solvent are called bases. The solvent system concept would be clear, if we consider the auto-ionisation of some solvents like H_2O, liq. NH_3, liq. SO_2, liq. HF etc.

⇒ Auto-ionisation of water :-

Water undergoes self ionisation in the following three ways.

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

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

$H^+ + H_2O \rightleftharpoons H_3O^+$

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

c) $3H_2O \rightleftharpoons 2H_3O^+ + O^{2-}$ (oxide ion)

Therefore according to this concept, the compounds that give H^+ or H_3O^+ ions in H_2O acts as acids while the compounds which give OH^- or O^{2-} ions in H_2O, behave as bases. Since HCl gives H^+ or H_3O^+ ions in water it behaves as an acid in aqu. sol^n.

$HCl \xrightleftharpoons{water} H^+ + Cl^-$

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

Similarly, NaOH, which gives OH^- ions in its aqu. sol^n acts as a base.

$NaOH \xrightleftharpoons{water} Na^+ + OH^-$

⇒ Auto-ionisation of liq. NH_3 :-

Liq. NH_3 ionises in the following

three ways; – a) $NH_3 \rightleftharpoons H^+ + NH_2^-$

$H^+ + NH_3 \rightleftharpoons NH_4^+$

$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (amide ion)

b) $3NH_3 \rightleftharpoons 2NH_4^+ + NH^{2-}$ (imide ion)

c) $4NH_3 \rightleftharpoons 3NH_4^+ + N^{3-}$ (~~nitd~~ nitride)

Therefore in liq. NH_3, any substance that gives NH_4^+ ions will acts as an acid in liq. NH_3, while which produces NH_2^- or NH^{2-} or N^{3-} ions will behave as a base in liq. NH_3. The compounds which give NH_4^+ ions in liq. NH_3 are called ammono-acids while those which give NH_2^- or NH^{2-} or N^{3-} in this solvent are called ammono bases.

Q. Examples of Ammono Acids :-

Ammonium salts (NH_4Cl, NH_4Br, NH_4I etc), organic amides (urea, acitamide etc), accetic acids, sulphamic acid etc all act as ammono acids in liq. NH_3, since they produce NH_4^+ ions in this solvant.

$$NH_4X \xrightleftharpoons{liq\ NH_3} NH_4^+ + X^-$$

$$NH_2-\underset{\underset{O}{\|}}{C}-NH_2 \xrightleftharpoons{liq\ NH_3} NH_4^+ + NH_2-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{NH}$$

$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightleftharpoons{liq.\ NH_3} NH_4^+ + CH_3-\underset{\underset{O}{\|}}{C}-NH^{\ominus}$$

$$CH_3-\underset{\underset{O}{\|}}{C}-OH \xrightleftharpoons{liq\ NH_3} CH_3COO^- + NH_4^+$$

$$NH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH \xrightleftharpoons[\ ]{2\,mole\ liq\ NH_3} \bar{N}H-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^- + 2NH_4^+$$

Q. Examples of Ammono Bases :-

KNH_2, $PbNH$ and BiN are the examples of ammono bases, since these compounds give NH_2^-, NH^{2-} and N^{3-} ions respectively in liq. NH_3.

$$KNH_2 \xrightarrow{liq\ NH_3} K^+ + NH_2^-$$

$$PbNH \xrightarrow{liq.\ NH_3} Pb^{2+} + NH^{2-}$$

$$BiN \xrightarrow{liq.\ NH_3} Bi^{3+} + N^{3-}$$

2nd Reaction Between an Ammono Acid and Ammono Base in liq. NH_3 :-

When an ammono acid reacts with an ammono base in liq NH_3 salts and the solvent are produced.

e.g; $NH_4Cl + KNH_2 \xrightarrow{liq. NH_3} KCl + 2NH_3$
acid base salt solvant

Q. Auto Ionisation of liq SO_2 :-

Autoionisation of liq SO_2 takes place as follows; -

$$SO_2 \rightleftharpoons SO^{2+} + O^{2-}$$
$$SO_2 + O^{2-} \rightleftharpoons SO_3^{=}$$
$$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{=}$$
thionyl ion

Thus all the compounds which contain or make available SO^{2+} ions will act as acids in liq. SO_2. Similarly all the compounds which contained or make available SO_3^{2-} ions, will behave as bases in liq. SO_2.

In liq. SO_2, $SOCl_2$, $SOBr_2$ etc. are the acids and K_2SO_3, Na_2SO_3 are the bases.

Q. Auto-Ionisation of liq. HF :-

The high specific conductance of liq. HF suggests the auto-ionisation of liq HF shown below.

$$HF \rightleftharpoons H^+ + F^-$$
$$HF + H^+ \rightleftharpoons H_2F^+$$
$$HF + F^- \rightleftharpoons HF_2^-$$
$$3HF \rightleftharpoons H_2F^+ + HF_2^-$$

Thus any substance that can give H_2F^+ ions would behave as an acid in liq. HF and any substance that can give HF_2^- ions or F^- ions would act as a base in this solvent.

(2) Examples — (i) CH_3COOH (weak acid in water) acts

as a base in liq. HF, Because it gives F^- ions when dissolved in liq. HF.

$$CH_3COOH + 2HF \longrightarrow CH_3COOH_2^+ + HF_2^-$$

(ii) H_2SO_4 and HNO_3, both act as strong acids in aqueous medium but show basic character in liq. HF, due to the production of F^- ions which are solvent anions.

$$HNO_3 + 2HF \longrightarrow H_2NO_3^+ + HF_2^-$$
$$H_2SO_4 + 2HF \longrightarrow H_3SO_4^+ + HF_2^-$$

Q. Utility of this concept :-

This concept can be used to explain the acid-base reactions occuring in aqu. and non-aqueous solvents.

Q. Limitations or Disadvantages :-

(i) According to this concept the definition of acids and bases is based on the nature of the solvent cation and solvent anion obtained by the auto-ionisation of the solvant.

(ii) It does not explain the acid-base reaction which may occur in the absence of solvant.

(iii) This concept can not explain the acid base reactions occuring in non-ionising solvants like C_6H_6, $CHCl_3$ etc.

Q. Protonic concept :- (Bronsted-Lowry concept) :-

This theory defined acid as substances or species capable of donating one or more protons. Base was defined as substances or species capable of accepting of one or more protons, with no refference to the presence of a solvant. In short, an acid is a proton donor and a base is a proton acceptor.

Substances exibiting stronger tendency of donating protons are strong acids while weak acid exibite weaker tendency of realising proton. Similarly strong bases exibit stronger tendency of accepting protons while weak bases exibit weaker tendency of accepting protons.

⇒ Examples :-

Bronsted acid { Molecular :- HCl, H_2SO_4 etc
Cationic :- NH_4^+, H_3O^+, $[Al(H_2O)_6]^{3+}$ etc
Anionic :- HCO_3^-, HSO_4^-, HS^- etc.

Bronsted base { Molecular :- NH_3, H_2O, Pyridine, etc.
cationic :- $[Al(H_2O)_5(OH)]^{2+}$
Anionic :- HCO_3^-, HSO_4^-, HS^- etc

In this concept, acid-base behavior is applicable in protonic non-aqueous solvants (NH_3, CH_3COOH etc) and in gaseous phase.

⇒ In liq. NH_3 :- $NH_2-\underset{\underset{O}{\|}}{C}-NH_2 + NH_3 \rightleftharpoons NH_4^+ + NH_2-\underset{\underset{O}{\|}}{C}-\bar{N}H$
acid base

⇒ In CH_3COOH :- $HCl + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + Cl^-$
acid base

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

Q. Conjugate acid-base pairs :-

When an acid realeases a proton, the specis formed exibit tendency of accepting proton i.e; basic proparty. These are called conjugate bases of the acids. Similarly when a base accepts a proton the specis formed ~~exibit~~ exhibit acidic proparty and is called conjugate acid of the base. Thus chemical species that are related to each other in termes of protion release - proton acceptors, are called conjugate to each other.

Strong acids have weak conjugate bases while weak acids have strong conjugate bases. Similarly strong bases have weak conjugate acids. while weak bases have strong conjugate acids.

Eg. $HCl \rightleftharpoons H^+ + Cl^-$
(S.A) (W.B)

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
(W.A) (S.B)

~~$NaOH \rightleftharpoons Na^+ + OH^-$~~
~~(S.B)~~ ~~(W.A)~~

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
(W.B) (S.A)

According to this theory, neutralysation reaction between a pair of acid-base produces a pair of conjugate acid-base.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$acid_1$ $base_2$ $acid_2$ $base_1$

Q. Amphoteric behavior of H_2O :-

According to protonic concept water is amphiprotic or amphoteric. Because it can acts both as an acid and a base. When it acts as an acid its conjugate base is OH^- ion.

H_2O (acid) $\rightleftharpoons H^+ + OH^-$ (base), $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$
acid base

When water acts as a base, its conjugate acid is H_3O^+ ion.

H_3O^+ (acid) $\rightleftharpoons H_2O + H^+$; $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
(base) acid base

Q. Some important conjugate acid-base pair :-

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

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

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$ ---- (i)

$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ ---- (ii)

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons H_3O^+ + [Fe(H_2O)_5OH]^{2+}$

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

$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

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

$H_2O + HS^- \rightleftharpoons H_2S + OH^-$ ---- (iii)

$HF + HNO_3 \rightleftharpoons H_2NO_3^+ + F^-$ ---- (iv)

$HClO_4 + HF \rightleftharpoons H_2F^+ + ClO_4^-$ ---- (v)

$HClO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + ClO_4^-$ ---- (vi)