B.Sc. (Honours) Part-I

Paper-IA

Topic: Solvent System Definition (Acid &Base)

UG

Subject-Chemistry

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Solvent system (auto-ionization) concept

The concept was introduced by Franklin in 1905 and was extended by Cady- Esley in 1928. The definition of acids and bases given by this concept can be applied for protonic as well as for non-protonic solvents. According to this concept, the solvents usually undergo self ionization (auto-ionization) and give rise to cations and anions which are called solvent cations and solvent anions, respectively. The substances which form solvent cations when dissolved in that solvent are called acids while the substances which give solvent anions when dissolved in that solvent are called bases. We can now also conclude that solvent cations can also be called acid cations and solvent anions can also be called base anions.

Auto-ionization of water –

Water (H_2O) undergoes self-ionization in the following three ways:

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

(b) $H^+ + H_2O \rightleftharpoons H_3O^+$

$2H_2O \rightleftharpoons H_3O^+$ (Hydronium ions) + OH^- (Hydroxyl ions)
(Solvent cations : acid ions) (Solvent anions)
$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

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

These three different modes of ionization suggest that, according to the solvent system concept, the substance that gives H^+ or H_3O^+ ions in water, act as acid in aqueous solution, while the substances which furnish OH^- or O^{2-} ions in water, behave as bases.

HCl gives H^+ or H_3O^+ ions in water, hence; it behaves as an acid in aqueous solution.

$$HCl \overset{Water}{\rightleftharpoons} H^+ + Cl^-$$

$$Or\ Hcl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

Similarly, NaOH, which furnish OH^- ions in its aqueous solution, acts as a base.

$$NaOH \overset{Water}{\rightleftharpoons} Na^+ + OH^-$$

Likewise, for a solvent system of BrF_3, the autoionization reaction is-

$$2BrF_3 \rightleftharpoons \underset{\text{acidic}}{BrF_2^+} + \underset{\text{base}}{BrF_4^-}$$

Hence, according to solvent system concept, the substance which can give BrF_2^+ in BrF_3 is acid and the substance which can form BrF_4^- is base.

$SbF_5 + BrF_3 \rightarrow BrF_2^+ + SbF_6^-$
Acid

$KF + BrF_3 \rightarrow BrF_4^- + K^+$
Base

Advantages of solvent system concept:

1. The definition of acids and bases given by solvent system concept can be used for both protonic (e.g. H_2O, NH_3 etc.) as well as non-protonic (e.g. SO_2, $SOCl_2$ etc.) solvents.
2. The definition is applicable for aqueous (H_2O) as well as non-aqueous solvents (NH_3, HF, H_2SO_4 etc).

Limitations solvent system concept:

1. The definition of acids and bases is based on the nature of the solvent cation and solvent anion obtained by auto-ionization of the solvent.
2. Acid base reaction taking place in the absence of a solvent can't be explained, i.e., acid-base reaction takes place only in presence of solvent.
3. The concept can't account for the acid-base reaction occurring in non- ionizing solvents like C_6H_6, $CHCl_3$ etc.