Role of water as a solvent :

The electrical dissymmetry of the water molecule is explained of the electronic structure of this molecule. The displacement of electric charges within its structure accounts for the polar character of the particle.

As a result of the separation of positive and negative charges of the water molecule is an electrostatic field in a manner.

Furthermore the polarity of the $H_2O$ particle enables it to exert an attractive force towards a charged body.

Ionic substances such as NaCl exist as ions not only in solution but also in the crystal.

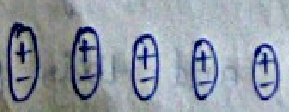
In the process by which a solid of this type enters solution water molecules because of their dipolemoments align their negative centres towards the positive ions and their positive ends in the direction of the negative ions at the surface of the crystal.

The dipole forces exerted by the oriented water molecules weaken the interionic attraction with in the crystal. So that some of the ions are pulled into solution.

Ionic compounds are more soluble in solvents with high dielectric constants. This property sometimes called specific inductive capacity is measure of the ability of a solvent to modify the mutual interaction of electrified bodies immersed in it, or separated by it.

Those solvents which have large dielectric constants also have large separation of charges with in their molecule.

Consequently the magnitude of the dielectric constant ~~also~~ of a solvent is also a measure of its polarity.



The degree of polarity depends upon the distance between charges with a molecule. The degree of polarity is designated as the dipole moment of the molecule.

The dipolemoment is always of the order of $10^{-18}$ esu.

Dipole moments of a number of liquid-liquid compound.

| | |
|---|---|
| $C_6H_5NO_2$ (Nitrobenzene) | $4.18\times10^{-18}$ |
| $H_2O$ (water) | $1.84\times10^{-18}$ |
| $C_2H_5OH$ (ethyl alcohol) | $1.70\times10^{-18}$ |
| $C_6H_5OH$ (phenol) | $1.70\times10^{-18}$ |
| $NH_3$ (ammonia) | $1.46\times10^{-18}$ |
| Benzene | 0 |

The dipole in water are attracted to each other by fairly strong force called Hydrogen bonds.

The dipoles of water are attracted by the electrostatic of hydrogen bonding in the solvent and a penetration by the ion into the intermolecule spaces of the ligands.

On other hand bonding forces between polar molecules of water prevent to the entrance of non-polar molecules into the intermolecular spaces of the solvent.

The might be said that non-polar molecule do not enter into solution in a polar solvent because of a squeezing out effect.

Thus water dissolves an ionic solid such as NaCl but will not dissolve paraffin which is a non-ionic and a non polar solid.

Protonic Solvent : Ammonia ($NH_3$)

Liquid $NH_3$ is one of the most comprehensively studied water like solvent. It is a protonic solvent and is able to dissolve a wide variety of substances.

Physical properties:

M.P = 175.3 K, B.P = 239.6 K

Dielectric constant = 23 at 239.6 K

Specific conductance = $5 \times 10^{-11}$ per ohm per cm.

Solubility of the substances in liq. $NH_3$ : 

i) Inorganic compounds :

Since dielectric constant of $NH_3$ is much less than that of $H_2O$, liq. $NH_3$ is a poor solvent for ionic substances.

The general order of the solubility of halides in liq. $NH_3$ is $I^- > Br^- > F^-$. Most iodide are soluble bromide are less soluble.

ii) Organic compounds :

Alcohols, halogen compounds, ketones, esters, simple ether and phenol and its derivatives are soluble. The aromatic hydrocarbons are in general sparingly soluble.

iii) Non-metals :

The non metals (Eg ; P, S and I) dissolve in liq. $NH_3$ reacting with it.

$$S_{10} + 16NH_3 \longrightarrow N_4S_4 + 6(NH_4)_2S$$

Tetrasulfur tetranitride

Reactions taking place in Liquid Ammonia : ⑥

The Various reactions carried out in liq. $NH_3$ are as follows

i) Auto ionization of Liquid Ammonia

The extent of auto-ionization of Liq. $NH_3$ is less than that of water.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

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

ii) Acid - Base Reactions :

On the basis of Bronsted - Lowry concept, ammonium ions would behave as acids while amide ions as bases in liq. $NH_3$.

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

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

acid (I) base (I) acid (II) base (II)

A typical neutralisation is the reaction of ammonium bromide with potassium amide.

$$NH_4Br + KNH_2 \longrightarrow KBr + 2NH_3$$

acid Base salt Solvent.

iii) precipitation Reactions :

when solutions of silver chloride and

barium nitrate in liquid $NH_3$ are brought together, a white ppt. of $BaCl_2$ is obtained

$$2AgCl + Ba(NO_3)_2 \xrightarrow{liq.NH_3} BaCl_2 + 2AgNO_3$$

iv) Complex formation Reaction:

When KCN is added to silver nitrate soln in liq. $NH_3$ or in water, a ppt of silver cyanide is first formed which dissolves in excess of KCN yielding the complex compound $[KAg(CN)_2]$

$$AgNO_3 + KCN \xrightarrow{liq.NH_3} \underset{ppt}{AgCN} + KNO_3$$

$$AgCN + KCN \longrightarrow \underset{complex}{[KAg(CN)_2]}$$

v) Solvation Reaction:

Solvent gets bonded to a solute species. such reactions taking place in water are called ammonation rxns. Some examples of solvation reactions are,

$$BF_3 + NH_3 \longrightarrow BF_3 \cdot NH_3$$

$$SO_3 + 2NH_3 \longrightarrow SO_3 \cdot 2NH_3$$

Advantages:

i) We have seen that alkali metals, without reacting with liq. $NH_3$, are soluble in this solvent.

The dissolved alkali metals can be recovered by evaporating the alkali metal - liq. $NH_3$ soln.

ii) The alkali metal - liq. $NH_3$ soln contain ammoniated electron and hence these solutions act as strong reducing agents.

iii) The study of pptn/. rxns taking place in liq. $NH_3$ that these rxns can be used to ppt/. metallic halides, sulphides, amides, imides, nitrides.

Disadvantages.

i) Low temp. or high pressure is necessary while working with liq. $NH_3$. This is because of the fact that the liquid range for liq. $NH_3$ is from $-34.0°C$ to $-77.7°C$.

ii) Liq. $NH_3$ is hygroscopic in nature and hence all the reactions must be carried out in the sealed tube.

iii) Liq. $NH_3$ has an offensive odour and hence the use of liq. $NH_3$ as a solvent and as a reaction medium requires special technique.

2) Hydrogen Fluoride (HF):



HF is miscible with water. The other hydrogen halides exhibit limiting solubilities in water. Hydrogen Fluoride form a monohydride $HF \cdot H_2O$. Aqueous solutions of HF are called Hydrofluoric acid.

physical properties:

M.P = -83.6°C

B.P = 19.5°C

Dipole moment = 1.86 D.

Molecular shape = linear.

Uses:

* HF is widely used in the petrochemical industry as a component of superacids.
* Removal of silica from graphite.
* Estimation of silica.

Reaction takes place in HF:

i) Self ionization reactions.

In liquid anhydrous HF, self-ionization occurs.

$$3\,HF \rightleftharpoons H_2F^+ + HF_2^-$$

acid base

ii) Action of HF on silica :

A conc. soln of hydrofluoric acid reacts with silica to form $SiF_4$. But in presence of excess of HF, hydrofluorosilicic acid is formed.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow H_2SiF_6 \text{ (hydrofluorosilicic acid)}$$

iii) Hydrofluoric acid - weak acid :

HF is the only hydrohalic acid (such as HCl, HI) that it is not a strong acid. HF ionizes in an aqueous solution like other acids.

$$HF + H_2O \rightleftarrows H_3O^+ + F^-$$

iv) Action of HF on glass :

HF attacks glass and decomposes it. Hydrofluorosilicic acid and metal silicofluoride are formed which are soluble in $H_2O$. Therefore, glass is slowly eaten up by HF.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O.$$

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O.$$

Non - protonic solvents ::



① Liquid Sulphur dioxide ($SO_2$) :

Liquid $SO_2$ is a water - like solvent and as such is used extensively for carrying out a number of chemical reactions.

physical properties :

B.P = -10°C

F.P = -75.5°C

Dielectric constant = 17.27.

Dipole moment of $SO_2$ = 1.61 D.

Solubility of the substance in liq. $SO_2$.

i) Inorganic materials :

In general iodides are most soluble followed by thiocyanates. The solubilities of alkali metal halides decreases in the order.

MI > MBr > MCl > MF

Alkali metal sulphites and acetates are soluble. The substances such as IBr, $PBr_3$, $CCl_4$, $SiCl_4$, $GeCl_4$ are soluble in liq. $SO_2$.

(ii) Organic materials :

Covalent organic compounds are more soluble in liq. $SO_2$ than the ionic compounds. Aromatic hydrocarbons and alkenes are more soluble than the alkanes. (12)

Uses :

The liq. $SO_2$ has been used as medium for conducting number of organic reactions such as Friedel - Crafts sulphonation and Bromination rxns.

Chemical rxns taking place in liq. $SO_2$ :

i) Acid - base rxns :

Auto - ionisation of liquid $SO_2$ is in accordance with following eqn.

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

ii) Solvolytic Rxn :

Solvolytic rxn of salts in liquid $SO_2$ are more complex than these solvolytic processes in many protonic solvents. For example,

$$PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$$

$$PBr_5 + SO_2 \longrightarrow POBr_3 + SOBr_2$$

iii) precipitation Rxn :

There are a large number of neutra - lization or acid - base reactions which may better be described as precipitation reactions.

$$2KI + SOCl_2 \xrightarrow{liq.\ SO_2} 2KCl + SOI_2$$

iv) Complex Formation Rxns :

A large number of complex ion formation in liq. $SO_2$ has been reported.

For example : The solubility of iodine in liq. $SO_2$ is greatly increased by the addition of K or RbI. This is due to the formation of complexes like $RbI_3$ or $KI_3$.

$$KI + I_2 \longrightarrow KI_3$$

$$RbI + I_2 \longrightarrow RbI_3.$$

v) Rxn with Organic compounds :

Because many organic compounds are soluble in liquid $SO_2$ and because it is itself inert to many of them ∴ a large number of organic reactions have been ~~them~~, a ~~large number of Organic reactions~~ carried out in this solvent.

$$C_6H_6 + SO_3 \xrightarrow{liq.\ SO_2} C_6H_5SO_2OH.$$

② Bromine Trifluoride ($BrF_3$) : 

liq. $BrF_3$ is a water like solvent and as such is used extensively for carrying out a number of ~~chemical~~ chemical reactions.

physical properties :

M.P = 8.8°C

B.P = 127°C

Dipolemoment = 1.19 D

Molecular shape = T- shaped.

Solubility :

It is soluble in $H_2SO_4$ but explodes on contact with water and organic compounds. It is a powerful fluorinating agent and an ionizing inorganic solvent.

Uses :

It is used to produce uranium hexafluoride ($UF_6$) in the processing and reprocessing of nuclear fuels.

chemical Rxns :

i) Autoionisation rxn :

The auto-ionization of $BrF_3$ may be written as

$$2\,BrF_3 \rightleftharpoons \underset{\text{acid}}{BrF_2^{+}} + \underset{\text{Base}}{BrF_4^{-}}$$

ii) Fluorination rxn :

$BrF_3$ is a very reactive solvent and will readily fluorinate the metal and non-metal halides, oxides and carbonates, iodates giving the fluoro complexes.

$$3SiO_2 + 4BrF_3 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$$

$$3GeO_2 + 4BrF_3 \longrightarrow 3GeF_4 + 2Br_2 + 3O_2$$

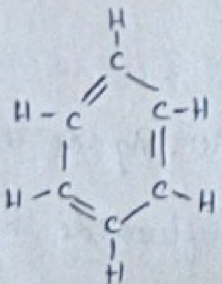
iii) Redox rxns :

Metals like Nb, Au, Ag or the alkali metals dissolve in bromine trifluoride with the evolution of bromine.

$$3K + 4BrF_3 \longrightarrow 3KBrF_4 + \frac{1}{2}Br_2 .$$

## Organic Solvents :

Organic solvents are known as carbon based solvents. A solvent simply refers to a substance that is capable of dissolving other substances by being carbon based these solvents have carbon atoms present in the structure of their compound. For example, benzene.




OH

properties of organic solvents :

* Volatility.
* boiling point
* size and colour

Ethanol :

* Ethanol is very polar molecule due to its hydroxyl group (OH) with higher electronegativity of oxygen allowing hydrogen bonding to take place with other molecules.

* Ethanol therefore attracts polar and ionic molecules. The ethyl group in ethanol is non-polar.

Thus ethanol can dissolve both polar substances. (17)

* In industrial and consumer products ethanol is the second most important solvent after water. Ethanol is the least toxic of the alcohols.

Ethanol is the common solvent in

* Cosmetics (such as perfumes).
* Food colourings and flavouring (such as vanilla essence), medical preparation (such as antiseptics)
* Some cleaning agents, industry.

Reactions :

i) Ester formation :

In presence of acid catalysts, ethanol reacts with COOH to produce ethyl ester and $H_2O$.

$$RCOOH + HOH_5C_2 \longrightarrow RCOOC_2H_5 + H_2O.$$

ii) Dehydration :

In the presence of acid catalysts, ethanol converts to ethylene.

$$CH_3CH_2OH \longrightarrow H_2C=CH_2 + H_2O.$$

iii) Combustion :

Complete combustion of ethanol forms $CO_2$ and $H_2O$

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O.$$

iv) Halogenation :

Ethanol reacts with HCl to produce ethyl chloride

$$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$$

$$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$$

Ether :

$$R-\ddot{\underset{..}{O}}-R'$$

* Ether is a class of organic compounds. It is an oxygen atom bonded to two alkyl or aryl groups.

* Ethers are pleasant smelling colourless liquids less soluble in water and lower boiling points.

* Ethers are also important in medicine and pharmacology, especially for use as anaesthetics. For example ; diethyl ether.

* Ethyl ether is an excellent solvent for extractions and for a wide variety of chemical reactions. It is also used as a volatile starting fluid for diesel engines and gasoline engines.

Reactions :

i) Ethers are relatively unreactive compounds. The ether linkage is quite stable towards bases, oxidizing agents, reducing agents.



$$R-O-R' + HX \longrightarrow R-X + R'-OH$$

Reactivity of HX, HI > HBr > HCl.

combustion :

Ethers are highly inflammable and they form extremely explosive mixtures with air giving $CO_2$ and $H_2O$.

$$C_2H_5OC_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O.$$

Action of $PCl_5$ :

In the presence of heat, we get the following rxn.

$$R-O-R' + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

Action of acetyl chloride :

$$R-O-R + CH_3COCl \xrightarrow[AlCl_3]{ZnCl_2/} RCl + CH_3COOR.$$

Dehydration of ethers :

$$C_2H_5OC_2H_5 \xrightarrow{Al_2O_3} 2CH_2=CH_2 + H_2O$$

Action of HI :

$$R-O-R + HI \xrightarrow{cold} R-OH + RI.$$

Physical properties of solvents and their role in chemical reactions : 

Every liquid cannot be used as a solvent in a chemical rxn. Here we, therefore concentrate on the properties of a solvent which makes the solvent suitable for using it as a good solvent. Here we shall also compare the properties of some non-aqueous solvents with the properties of $H_2O$.

Some important properties of a solvent which make the solvent a useful solvent in chemical rxns are discussed below.

1. Melting point and boiling point :

Most of the chemical rxns are carried out in liquid phase. Hence the melting point and B.p of a solvent indicates the range of temperature within which the solvent can be used. M.p and B.p of some solvents are given below.

$H_2O$ - 0.0, 100; $NH_3$ = -77.7, -33.4;

$SO_2$ = -75.5, -10.2; HF = -89.3, 19.5 and

$CH_3COOH$ - 16.16, 118.1

These values show that $H_2O$ has very convenient

liquid temperature range b/w 0 and 100°c.
$CH_3COOH$ can act as a solvent at ordinary temp range.
$NH_3$ and $SO_2$ exist as gases at ordinary temperature and pressures and hence act as solvents only at low temp.

2) Heat of fusion ($\Delta H_{fus}$) and Heat of vapourisation ($\Delta H_{vap}$):

The heat absorbed by one mole of a substances to change from solid to liquid state is called its molar heat of fusion.

Solid (one mole) → Liquid ; $\Delta H$ = Heat of fusion, $\Delta H_{fus}$.

Similarly, the heat absorbed by one mole of a substance to change from liquid to vapour state is called its molar heat of vapourisation.

Liquid (one mole) → Vapour, $\Delta H$ = Heat of vapourisation, $\Delta H_{vap}$

The heats of fusion and vapourisation of a solvent indicate the nature and strength of forces with which the molecules of the solvent are held together in the solid or in the liquid state. A high value of $\Delta H_{vap}$ of a liquid state. The ratio of $\Delta H_{vap}$ (in J) and boiling point, $T_b$ (in K) of a liquid is a constant which is known as Trouton's constant.

$$\frac{\Delta H_{vap}\ (Joules)}{T_b\ (K)} = \text{Trouton's constant}$$

3) Dielectric constant :

Dielectric constant of a solvent determines the ability of the solvent to dissolve polar and non-polar substances in it. We know that the coulombic force b/w a cation and an anion of an ionic compound is given by the expression.

$$F = \frac{q_1 q_2}{(r_1+r_2)^2}$$

In this expression, $q_1$ and $q_2$ are the charges on cation and anion respectively, $r_1$ and $r_2$ are the radii of the two ions and is the dielectric constant of the solvent. The value of F depends on the nature of the solvent in which the ionic compound is dissolved. The value of dielectric constant of some solvents are given below.

$H_2O$ = 78.5 (25°c), $NH_3$ = 22.0 (−33.5°c),

$SO_2$ = 17.3 (−16°c), $CH_3COOH$ = 9.7 (18°c),

HF = 83.6 (0°c), $N_2O_4$ = 2.42 (0°c).

4) Dipole moment :

Greater is the polarity of the bond in a solvent molecule, greater is the charge separation

and higher will be the value for dipole moment. 
Substances having high dipole moment values are good solvents for polar solutes. This is because of the fact that greater is the polarity of a solvent molecule, greater is the solvation energy released on dissolution of a solute. Dipole moment value of a solvent also gives an idea about the extent of association of the molecules of a liquid and hence its liquid range. Dipole moment values of $H_2O$, $NH_3$ and $SO_2$ are

$H_2O = 1.85$, $NH_3 = 1.47$, $SO_2 = 1.61$

5) Viscosity :

Viscosity gives a measure of the fluidity of the solvent. Solvents like water, $CCl_4$ have low viscosities and flow rapidly under ordinary temp. In solvents of low viscosities, the operations such as precipitation, crystallization, filteration, etc., can be easily carried out without any difficulty. With increasing viscosity of a liquid, the difficulty of such operations ↑. Solvents like anhydrous sulphuric acid have higher viscosities and this reduces their usefulness as solvent. Viscosity of $H_2O$,

$NH_3$ and $SO_2$ is 1.00, 0.241 and 0.009 respectively.

b) proton affinity:

It is applicable for protonic solvents only. It greatly affects the behaviour of a solute in a given solvent. $NH_3$ has greater proton affinity than $H_2O$. Hence acetamide ($CH_3CONH_3$) which behaves as a very weak base in aqueous soln shows acidic properties in liq. $NH_3$.

$$CH_3CONH_3 + H_2O \rightleftharpoons CH_3CONH_3^+ + OH^-$$

$$CH_3CONH_3 + NH_3 \rightleftharpoons CH_3CONH^- + NH_3^+$$

## Classification of Solvents :

Solvents have been classified in a number of ways, depending on the properties of the solvents. The most convenient classification of solvent is based on the electrolytic characteristics of the solvents

**Solvents**

- ① Non-ionising solvents (non-polar liquids) (Aprotic solvents)
  - Ex : benzene, carbon tetrachloride, chloroform
- ② Ionising solvents (polar liquids)
  - i) protonic
    - (a) protogenic (acidic solvents) strong tendency to donate protons
      - Ex : $H_2SO_4$, $H_2F_2$, $CH_3COOH$.
    - (b) protophilic (basic solvents) strong affinity to accept proton
      - Ex : liq. $NH_3$, pyridine, Ethylene diamine
    - (c) Amphiprotic (amphoteric solvents) can act both as acids or bases.
      - Ex : $H_2O$, $CH_3OH$.
  - (ii) Non-protonic
    - Ex : liq $SO_2$, $BrF_3$, $HgBr_2$

(1) Non-ionising solvents (Non-polar solvents) : 

These solvents are also called aprotic solvents (or non-protonic or non-protic solvents). These solvents have no hydrogen in their structure.

Ex : $C_6H_6$, $CCl_4$. These solvents have very little dielectric constant. They dissolve non-polar substance

(2) Ionising solvents (polar solvents) :

Ex of such solvents are $H_2SO_4$, $H_2F_2$, $CH_3COOH$, $H_2O$, liq. $NH_3$, liq. $SO_2$, pyridine, $BrF_3$, $HgBr_2$, $CH_3OH$, etc., Because of their polar nature; these solvents have associated structures. Non-polar substance do not dissolve in these solvents because of the squeezing effect produced by their associated structure. However ionic and covalent polar substance dissolve in them. The dissolution of ionic substance is due to their greater solvation energy than the lattice energy of the salts. Several covalent substance dissolve forming H-bonds.

Classification of ionising solvents.

1) protonic solvents.

These structure have hydrogen in their structure. These may be of the following types.

a) proto-genic solvents (Acidic solvents):

These solvents have a tendency to donate protons. Ex: $H_2SO_4$, $H_2F_2$, $CH_3COOH$. These solvents are also called acidic solvents.

b) proto-philic solvents (Basic solvents):

These solvents have a tendency to accept proton Ex: liq. $NH_3$, pyridine, ethylenediamine. These solvents are also called Basic solvents.

c) Amphi-protic or amphoteric solvents:

These show dual character i.e, they can loose as well as accept protons, depending on the nature of the reacting species. Ex: $H_2O$, alcohol, liq. $NH_3$, $CH_3COOH$. Amphoteric solvents undergo self-ionisation in which a proton transfer between two similar natural molecules takes place and a cation-anion pair of the solvents is obtained.

Ex :

| Acid | Base | | Acid | Base |
|---|---|---|---|---|

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

$$NH_{3(l)} + NH_{3(l)} \rightleftharpoons NH_4^+ + NH_2^-$$

$$CH_3COOH + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$$

ii) Non-protonic solvents :

These solvents have nothing to do with protons. Ex : liq. $SO_2$, $BrF_3$, $HgBr_2$.

Due to self-ionisation they also furnish cations and anions, similar to protonic solvents.

## Types of reactions in Non-aqueous solvents. 

### i) precipitation reactions :

The reactions in which precipitate is formed by mixing two solutions of two compounds are called precipitation reaction. Thus the precipitation reactions are normally double decomposition.

**Ex:** The precipitate of AgCl is obtained by mixing $BaCl_2$ and $AgNO_3$ in aqueous medium.

$$BaCl_2 + 2AgNO_3 \xrightarrow{H_2O} 2AgCl \downarrow + Ba(NO_3)_2 .$$

In liq. $NH_3$, the above reaction is reversed.

$$2AgCl + Ba(NO_3)_2 \xrightarrow{liq.NH_3} BaCl_2 \downarrow + 2AgNO_3 .$$

### ii) Acid - Base reactions :

The ionic solvents are polar compounds and undergo self-ionization. Self-ionization of some important solvents is given below.

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

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

An acid-base reaction in a non-aqueous solvent can be explained on the basis of solvent system concept of acids and bases

According to this concept, an acid is a substance which contains the solvent cation and a base is a substance which contains the solvent anion.

Ex:

$NH_4Cl$ (acid) + $KNH_2$ (base) $\rightleftharpoons$ KCl (salt) + 2 $NH_3$ (solvent)

Some example of acid-base rxn in diff. solvents.

i) $2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$

(acid ion) (Base ion)

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

Acid Base.

iii) Solvation Reactions : Formation of solvates.

In which a solute reacts with one or more molecules of a solvent.

(Ex: $H_2O$, liq. $NH_3$, liq. $SO_2$, etc) to form a product in which the solute and solvent species are attached to each other by a H-bond or by a coordinate bond.

The product formed is called solvate.

Solvate is an addition compound and hence is also called an adduct. The addition [31] compound contains solvent of crystallization.

$BF_3 + NH_3 \longrightarrow BF_3 \cdot NH_3$

iv) Solvolytic reactions : Solvolysis.

In which the solvent molecules react with the solute molecule or in the way which consists of the following steps :

(a) Solvent molecule undergoes auto ionisation to given solvent cations and solvent anions.

(b) The solute (salt) splits into solute cations and solute anions. The solute cations or anions interact with the solvent cations or anions. Due to this interaction the conc. of the solvent cations or anions is increased.

When $H_2O$ and $NH_3$ are used as solvents in the solvolytic reactions these reactions are called hydrolysis and ammonolysis respectively

## chemical structure and Solubility: 

'Like dissolve like' is a familiar rule in organic chemistry and is also applicable to inorganic chemistry.

This rule refers to similarity in reaction not only to diplomoment but also to chemical composition.

It is generally true that a substance tends to dissolve in a solvent which is chemically related is composition to the substance.

For ex;

paraffin readily dissolves in gasoline or water is good solvent of cane sugar.

Gasoline and paraffin are both hydrocarbons compounds containing only carbon and hydrogen. Cane sugar is a carbohydrate and as the name carbohydrates implies the composition of carbon, hydrogen and oxygen in which the ratio of Hydrogen and oxygen is the same as in water.

When the solvent is a liquid whose molecules are associated as a result of H-bonding. Among solvents of this type are water, liquid $NH_3$ and liq.HF.

The H-bond is produced where the H-atom serves as a bridge between two strongly electronegative atoms.

Consequently molecules which contain hydrogen attached to the more electronegative atoms tend to group into clusters which are held together by hydrogen bridges.

Liq. $NH_3$, liq. HF and solvent of this type because of their associated structures will not dissolve polar molecules unless the solute molecules can form hydrogen bonds with the solvent molecules.

For ex:

Nitrobenzene has a dipolemoment of $4.18 \times 10^{-18}$ which is large as compared with the dipolemoment of water but nitrobenzene molecules are insoluble in water because they cannot from hydrogen linkages with the water molecules.

On the other hand, phenol is more than 40 times as soluble in water as nitrobenzene.

Phenol which is similar to nitrobenzene in that has monosubstituted benzene product has a dipole moment of $1.7 \times 10^{-18}$ and should be less solub than nitrobenzene. It relatively solubility were entirely dependent upon the magnitude of the dipolemoment.

This unexpected solubility must be due to the formation of H-bonds between the hydroxyl groups of the phenol and the oxygen atoms in the water molecules.