US03CCHE21 (SEM-3)

Unit-1 [B]: NON-AQUEOUS SOLVENTS

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Introduction:

Most of the chemical reactions familiar to us take place in aqueous solution since water, due to the high value of its dielectric constant, has an increased ability to dissolve the ionic compounds and many other substances. However there are many chemical reactions which cannot be carried out in aqueous solution but can be studied in a non-aqueous medium. A large number of non-aqueous solvents have been discovered in the last few years. These solvents have a sizable value of their dielectric constant and hence can dissolve many substances. Examples of such solvents are anhydrous liq. NH_3, liq.SO_2, anhydrous HF, liq. N_20_4, etc.

Classification of Solvents :

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

1. **Non-ionising solvents** or Nonpolar liquids or Aprotic solvents: e.g. benzene, carbon tetrachloride.
2. **Ionising solvent or Polar liquids:**
   - a. **Protonic:**
     - i. Protogenic (acidic solvents) Strong tendency to donate protons. e.g.H_2SO_4,H_2F_2,CH_3COOH
     - ii. Protophilic (basic solvents) Strong affinity to accept protons. e.g. Liq. NH_3, Pyridine, Ethylene diamine
     - iii. Amphiprotic (amphoteric solvents) Can act both as acids or bases. e.g. H_2O, CH_3OH
   - b. **Non-protonic:** e.g. liq. SO_2, BrF_3, $HgBr_2$

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

These solvents are also called aprotic solvents or non-protic or non-protic solvents. These solvent have no hydrogen in their structure. e.g. C_6H_6, CCl_4, etc.These solvents have very little dielectric constant. They dissolve non substances.

2. Ionising solvents (Polar solvents):

Examples 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. Polar solvents have associated structures. Non-polar substances do not dissolve in these solvents because of the squeezing effect produced by their associated structure. However ionic and covalent polar substances dissolve in them. The dissolution of ionic substances is due to their greater solvation energy than the lattice energy of the salts. Several covalent substances dissolve forming H-bonds.

Classification of Ionising Solvents:

I. Protonic Solvents:

These solvents 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. e.g. H_2SO_4, H_2F_2,CH_3COOH.

B. Protophilic solvents (Basic solvents):

These solvents have a tendency to accept protons. E.g. liq. NH_3, pyridine, ethylenediamine etc.

C. Amphi-protic or amphoteric solvents:

These show dual character i.e. they can lose as well as accept protons, depending on the nature of the reacting species, e.g. H_2O, alcohols, liq.NH_3, CH_3COOH, etc. Amphoteric solvents undergo auto-ionisation (self-ionisation) in which a proton transfer between two similar neutral molecules takes place and a cation-anion pair of the solvent is obtained e.g.

Acid		**Base**		**Acid**		**Base**
H_2O	+	H_2O	=	H_30^+	+	OH^-
$NH_3(l)$	+	$NH_3(l)$	=	NH_4^+	+	NH_2^-

$$CH_3COOH + CH_3COOH = CH_3COOH_2^+ + CH_3COO^-$$

II. Non-Protonic Solvents:

These solvents have nothing to do with protons.e.g. liq. SO_2, BrF_3, $HgBr_2$. Due to self-ionisation they also furnish cations and anions, similar to protonic solvents.

In this chapter we shall restrict our study on ionising solvents only. i.e. in which inorganic substances ionise and give ionic reactions as in H_2O. Non-ionising solvents are of great interest in organic chemistry.

Physical Properties of Solvents and their Role in Chemical Reactions:

Every liquid cannot be used as a solvent in a chemical reaction.Here we compare the properties of some non-aqueous solvents with the properties of H_20.

1. Melting point and boiling point:

Most of the chemical reactions are carried out in the liquid phase. Hence the melting point and boiling point of a solvent indicates the range of temperature within which the solvent can be used. Melting points and boiling points(^{0}C) of some solvents are given below:

Solvent	Melting point	Boiling point	Characteristics
H_2O	0.0	100	Very convenient liquid
CH_3COOH	16.16	118.1	Can act at ordinary temperature
NH_3	-77.7	-33.4	Can act at low temperature
SO_2	-75.5	-10.2	Can act at low temperature
HF	-89.3	19.5	----

2. Dielectric constant (ε):

Dielectric constant (ε) of a solvent determine ability of the solvent to dissolve polar and non-polar substances in it.The coulombic force (F) between a cation and an anion of an ionic compound is given by the expression:

$$F = q_1q_2 / \varepsilon(r_1+r_2)^2$$

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 ε is the dielectric constant of the solvent. The value of ε 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.

Solvent	Value of ε	Solvent	Value of ε
H_2O	78.5 (25°C)	CH_3COOH	9.7 (18°C)
NH_3	22.0 (- 33. 5°C)	HF	83.6 (0°C)
SO_2	17.3(-16°C)	N_2O_4	2.42 (0°C)

It may be clear from the above expression that if ε of a solvent is large, F would be small i.e. if ε is large, small amount of energy would be required to separate the ions and hence it would be easy for a solvent having a high value of ε to dissolve an ionic compound in it. For example, since anhydrous HF and H_2O have high values of ε, these are the best solvents for ionic compounds.

On the other hand, since liq.NH_3 and liq.SO_2 has low values of ε , these solvents show smaller ability to dissolve ionic compounds especially those containing multi-charged ions. Thus carbonates, sulphates and phosphates which contain multi-charged ions are insoluble in liq.NH_3 and liq.SO_2.

3. 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 solvent 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 (in D) of H_2O, NH_3 and SO_2 are given below.

Solvent	H_2O	NH_3	SO_2
Dipole moment	1.85	1.47	1.61

4. Viscosity:

Viscosity gives a measure of the fluidity of the solvent. Solvents like water, carbon tetrachloride have low viscosity and flow rapidly under ordinary temperature. In solvent of low viscosity, the operations such as precipitation, crystallization, filtration, etc. can be easily carried out without any difficulty. With increasing viscosity of a liquid, the difficulty of such operations increases. 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.

5. 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 ($CH_3\ CO\ NH_2$) which behaves as a very weak base in aqueous solution shows acidic properties in liq.NH_3.

$$CH_3\ CO\ NH_2 \quad + \quad H_2O \quad \rightleftarrows \quad CH_3\ CO\ NH_3^+ \quad + \quad OH^-$$

$$CH_3\ CO\ NH_2 \quad + \quad NH_3 \quad \rightleftarrows \quad CH_3\ CO\ NH^- \quad + \quad NH_4^+$$

Proton affinity (in kJ mol^{-}) for H_2O and NH_3 are 760 and 865 respectively. The properties of H_2O, NH_3 and SO_2 other than those mentioned above are given below:

Property	**H_2O**	**NH_3**	**SO_2**
Equivalent conductance (ohm^{-1})	6×10^{-8} (25°C)	5×10^{-8} (133.4°C)	1×10^{-7}
Critical temperature (°C)	374	132.4	157.5
Critical pressure	217.7	112.0	77.8
Density (g/cc)	0.96	0.68	1.46

Types of Chemical Reactions Taking Place in Non-aqueous Solvents:

1. Metathetical (Precipitation) Reactions

The reactions in which precipitate is formed by mixing two solutions of two compounds are called metathetical or precipitation reactions. Thus precipitation reactions are normally double decomposition. The formation of a precipitate in different solvents depends on the solubilities of the products in those solvents. For example the precipitate of AgCl is obtained by mixing $BaCl_2$ and $AGNO_3$ in aqueous medium.

$$BaCl_2 + 2AgNO_3 \xrightarrow{\text{water}} AgCl\downarrow + Ba(NO_3)_2 \quad \text{--------------------(i)}$$

In liq.NH_3 the above reaction is reversed, i.e., in liq.NH_3 ppt. of $BaCl_2$ is obtained by combining AgCl with Ba $(NO_3)_2$.

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

Thus we see that reaction (i) is reversed on changing the solvent.

2. Acid-Base Reactions

We have already said that the ionic solvents are polar compounds and undergo self-ionisation, Self-ionisation of some important solvents is given below:

Solvent		**Solvent cation** **(Acid ion)**		**Solvent anion** **(Base ion)**
$2H_2O$	$\rightleftarrows$	H_3O^+	+	OH^-
$2NH_3$	$\rightleftarrows$	NH_4^+	+	NH_2^-
$2BrF_3$	$\rightleftarrows$	BrF_2^+	+	BrF_4^-
$2HgBr_2$	$\rightleftarrows$	$HgBr^+$	+	$HgBr_3^-$
$2SO_2$	$\rightleftarrows$	SO^{2+}	+	SO_3^{2-}
$2H_2SO_4$	$\rightleftarrows$	$H_3SO_4^+$	+	HSO_4^-
CH_3COOH	$\rightleftarrows$	$CH_3COOH_2^+$	+	CH_3COO^-
$2HClO_4$	$\rightleftarrows$	H_2ClO_4	+	ClO_4^-
$3HF$	$\rightleftarrows$	H_2F^+	+	HF_2^-
N_2O_4	$\rightleftarrows$	NO^+	+	NO_3^-

An acid-base reaction in a non-aqueous solvent can be explained on the basis of the 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. For example since self-ionisation of liq.NH_3.

$$NH_4Cl(\text{acid}) + KNH_2\,(\text{base}) \rightleftarrows KCl(\text{salt}) + 2NH_3(\text{solvent})$$

Acidic character of CH_3COOH in H_2O and liq. NH_3:

When CH_3COOH reacts with H_2O and liq.NH_3 (solvents), H_2O and liq,NH_3 both accept a proton from CH_3COOH to produce H_2O^+ and NH_4^+ ions. Due to the production of these ions, CH_3COOH behaves as an acid in both the solvents.

↷

$$CH_3COOH \quad + \quad H_2O \rightleftarrows H_3O^+ \quad + \quad CH_3CO0^-$$

Acid (weak acid)	Base	Acid	Base

↷

$$CH_3COOH \quad + \quad NH_3 \rightleftarrows NH_4^+ \quad + \quad CH_3CO0^-$$

Acid (weak acid)	Base	Acid	Base

Now since the proton accepting ability of H_2O is less than that of liq.NH_3, CH_3COOH behaves as weak acid in aqueous solution and acts as a strong acid in liq.NH_3.

3. Solvation Reactions: Formation of Solvates

Solvation reaction is a general reaction in which a solute (a cation, an anion or a neutral molecule) reacts with one or more molecules of a solvent (e.g.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 compound contains **solvent of crystallisation**.

In the formation of a solvate, the solvent acts as a Lewis base while the solute species behaves as a Lewis acid. When the solvent used is water, the solvation reaction is called **hydration** and the addition compound formed is called **hydrate**. Hydrate contains one or more molecules of water as water of crystallisation. Similarly when the solvent is liq. NH, the reaction is called **ammoniation** and the addition compound formed is called **ammoniate**.Ammoniate contains one or more molecules of ammonia as **ammonia of crystallisation**.

4. Solvolytic Reactions: Solvolysis

Solvolytic reactions are the reactions in which the solvent molecules react with the solute molecule (salt) or ion in the way which consists of the following steps:

(a) The solvent molecule undergoes auto-ionisation (self-ionisation) to give solvent cations and solvent anions.

(b) The solute (salt) splits into solute cations and solute anions. The solute cations or solute anions interact with the solvent cations or solvent anions. Due to this interaction the concentration of the solvent cations or solvent anions is increased.When H_2O and NH_3 are used as solvents in the solvolytic reactions, the reactions are called **hydrolysis and ammonolysis (or ammonolysis reactions)** respectively.

Liquid Ammonia (Liq. NH_3)

Solubility of Various Substances in Liq.NH_3 :

A. Solubility of ionic compounds (inorganic salts):

We know that ammonia has a low value of its dielectric constant (= 22 at -34°C). This low value suggests that liq.NH_3 has a poor ability to dissolve ionic compounds. Ammonium salts (e.g. NH_4NO, NH_4SCN, CH_3COONH_4 etc.) and most of the nitrites, nitrates, cyanide, thiocyanate, perchlorates, are soluble in liq.NH_3. Salts containing highly charged ions (e.g., oxides, sulphides, sulphates, phosphates and carbonates) are insoluble. Fluorides and chlorides (except Be^{2+} and Na^+ chlorides) are practically insoluble, bromides are less soluble while iodides are freely soluble. Thus the solubility of the halides of a given metal increases in going from fluoride to iodide (MF <MCL < MBr <MI).

Most of the metal amides (except those of alkali metals) are insoluble. The salts of some metals (e.g. Ni^{2+}, Cu^{2+}, Zn^{2+} etc.) react with liq.NH_3 and form ammine complexes.

B. Solubility of non-ionic compounds (organic compounds):

Halogen compounds, alcohols, ketones, esters, simple ethers, amines, phenol and its derivatives etc. are soluble. Alkanes are insoluble and alkenes and alkynes are slightly soluble. In this sense, liq.NH_3 is a better solvent for non ionic and nonpolar compounds (organic compounds).

C. Solubility of non-metals:

The non-metals like S, P, I_2, Se etc. are soluble and they react with the solvent.

D. Solubility of alkali metals and alkaline earth metals:

All the alkali metals and alkaline earth metals (excepting Be) are soluble in liq.NH_3.100g of liq.NH_3 dissolves 10.9g of Li, 24.8g of Na, 46.8g of K (all at-33°C) and 334g of Cs (at -50°C). Thus we see that the solubility of alkali metals in liq. NH_3 increases as we pass from Li to Cs (Li < Na < K< Cs).

Chemical Reactions Taking Place in Liq. NH_3

1. Metathetical (Precipitation) Reactions

Examples of some precipitation reactions taking place in liq. NH_3 are given below.

a. Chlorides are precipitated:

$$2NH_4Cl(\text{Ammono acid}) + Sr(NO_3)_2 \rightarrow SrCl_2\downarrow + 2NH_4N0_3$$

$$Ba(NO_3)_2 + 2AgCl \rightarrow BaCl_2\downarrow + 2AgNO_3$$

b. Bromides and iodides are precipitated:

$$Sr(NO)_2 + 2NH_4Br\ (\text{Ammono acid}) \rightarrow SrBr_2\downarrow + 2NH_4N0_3$$

$$Zn(NO)_2 + 2NH_4I\ (\text{Ammono acid}) \rightarrow ZnI_2\downarrow + 2NH_4N0_3$$

c. Amides (NH_2^-), imides (NH^{2-}) and nitrides (N^{3-})can be precipitated:

$$KNH_2(\text{Ammono base}) + AgNO_3 \rightarrow KNO_3 + AgNH_2\downarrow\ (\text{Amide})$$

$$KNH_2 + 3HgI_2 \rightarrow 2KI + 4HI + Hg_3N_2\downarrow(\text{Nitride})$$

d. Sulphides are precipitated:

$$(NH_4)_2S(\text{ammono acid}) + 2AgNO_3 \rightarrow Ag_2S\downarrow + 2NH_4NO_3$$

$(NH_4)_2S$(ammono acid) + $M(NO_3)_2$(M=Ba,Cu,Cd) → MS↓ + $2NH_4NO_3$

e. Barium alcoholate can be precipitated:

$$K(OC_2H_5) + Ba(NO_3)_2 \rightarrow Ba(OC_2H_5)_2\downarrow + 2KNO_3$$

2. Acid-base Neutralisation reaction(salt formation) reactions

A compound containing or making available NH_4^+ or NH^{2-} or N^{3-} ion(ammono base)to form the salt and the solvent NH_3.

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$KNH_2 \rightarrow K^+ + NH_2^-$

On adding: $NH_4Cl + KNH_2 \rightarrow K^+ + Cl^- + NH_4^+ + NH_2^-$

or NH_4Cl(ammono acid) + KNH_2(ammono base) → KCl(salt) + $2NH_3$(solvent)

or NH_4^+(solvent cation) + NH_2^-(solvent anion) → $2NH_3$(solvent)

Above equation indicates that neutralisation reaction in liq.NH_3can also be defined as the combination of solvent cation(NH_4^+) and solvent anion(NH_2^-) to form the un-ionised solvent(liq.NH_3). Other examples in liq.NH_3 are:

Ammono acid	Ammono base	Ammono salt	Solvent
NH_4X (Cl,NO_3) +	$NaNH_2$ →	NaX	+ $2NH_3$
$2NH_4X$ (Cl,I) +	PbNH →	PbX_2	+ $2NH_3$
$3NH_4X$ (Cl,I) +	BiN →	BiX_3	+ $4NH_3$
$2CH_3COONH_4$ +	$Zn(NH_2)_2$ →	$Zn(CH_3COO)_2$	+ $4NH_3$

3. Amphoteric Behaviour of $Zn(NH_2)_2$ in Liq.NH_3:

$Zn(NH_2)_2$ dissolves in ammono acid as well as in ammono base in liq. NH_3 and hence is said to show amphoteric character in liq. NH_3.

$$Zn(NH_2)_2 + 2NH_4Cl \text{ (Ammono acid)} \rightarrow$$

$$ZnCl_2\text{(Salt)} + 4NH_3\text{(Solvent)}$$

$$Zn(NH_2)_2 + 2NaNH_2 \text{ (Ammono base)} \rightarrow Na_2[Zn(NH_2)] + 2NH_3$$

Above reactions can be compared with the following reactions in aqueous solution. In these reactions $Zn(OH)_2$ shows amphoteric character since it dissolves in HCL (acid) as well as in NaOH (base).

$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$$

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2[ZnO_2] + 2H_2O$$

4. Ammonation Reaction : Formation of Ammoniates (Solvation Reactions - Formation of Solvates):

Solvation reaction in which liq, NH_3 is used as solvent is called **ammonation reaction** and the solvate formed is called **ammoniate.** In the formation of ammoniate liq. NH_3 (solvent) acts as a Lewis base and the solute behaves as a Lewis acid. The formation of some ammoniates in liq. NH_3 has been shown below. These ammoniates may be 1 : 2 or 1 : 1 adducts.

Solute (Lewis acid)	**Solvent (Lewis base)**	**Ammoniates**

$$SO_3 + 2NH_3 \rightarrow SO_3.2NH_3 \text{ (1:2 adduct)}$$

$$SiF_4 + 2NH_3 \rightarrow SiF_4.2NH_3 \text{ (1:2 adduct)}$$

$$BF_3 + NH_3 \rightarrow BF_3.NH_3 \text{ (1:1 adduct)}$$

The formation of $NH_4^+$by action of liq.NH_3 on H_2O is also an example of ammoniation.More examples of ammoniates formed by liq. NH_3 with inorganic salts are MgI_2. $6NH_3$, NiI_2. $6NH_3$, NaI. $4NH_3$ etc. In the formation of these ammoniates, NH_3 molecules (solvent molecules) are coordinated to the metal ions of the inorganic salt (solute).

5. Ammonolysis or Ammonolytic Reaction :(Solvolysis or Solvolytic Reactions)

The solvolytic reactions taking place in aqueous medium (H_2O) and liq. NH_3 are called hydrolysis and ammonolysis (or ammonolytic reactions) respectively. In hydrolysis H_2O is used as a solvent while in ammonolysis liq. NH_3 is used as a solvent.

Examples of ammonolysis:

a. Ammonolysis of $SnCl_4$, $SiCl_4$ and SO_2Cl_2 :

In the ammonolysis of $SnCl_4$ and SO_2Cl_2 (solute) the concentration of NH_4^+ (solvent cations) is increased as shown below:

$$8NH_3 \text{ (Solvent)} \rightleftharpoons 4NH_4^+\text{(Solvent cations)} + 4NH_2^-\text{(Solvent anions)}$$

$$SnCl_4\text{(Solute)} \rightarrow Sn^{4+} \text{ (Solute cations)} + 4Cl^-$$

$$Sn^{4+} \text{ (Solute cations)} + 4NH_2^-\text{(Solvent anions)} \rightarrow Sn(NH_2)_4$$

On adding: $SnCl_4$(Solute) + $8\ NH_3$ (Solvent) $\rightarrow Sn(NH_2)_4 + 4Cl^- + 4NH_4^+$

b. Ammonolysis of alkali metal hydrides and oxides:

The ammonolysis of alkali metal hydrides and oxides gives alkali metal amides (MNH_2). In these reactions the concentration of NH_2^- ions (solvent anions) is increased..

NaH (Solute) + NH_3(Solvent) → $NaNH_2 + H_2$

or $H^- + NH_3 \rightarrow NH_2^- + H_2$ (In water: $H^- + H_2O \rightarrow OH^- + H_2$

Na_2O (Solute) + $2NH_3$ (Solvent) → $2NaNH_2 + H_2O$

c. Ammonolysis of $TiCl_4$:

Ammonolysis of $TiCl_4$ (salt) in presence of excess of liq. NH_3 produces $Ti(NH_2)_4$. In each step Cl-atom of the salt undergoing ammonolysis is replaced by $-NH_2$ group.

$TiCl_4 + NH_3 \rightarrow TiCl_3(NH_2) + HCl$

$TiCl_3(NH_2) + NH_3 \rightarrow TiCl_2(NH_2)_2 + HCl$

$TiCl_2(NH_2)_2 + NH_3 \rightarrow TiCl(NH_2)_3 + HCl$

$TiCl(NH_2)_3 + NH_3 \rightarrow Ti(NH_2)_4 + HCl$

On adding: $TiCl_4 + 4NH_3 \rightarrow Ti(NH_2)_4 + 4HCl$

d. Ammonolysis of alkyl and aryl halides:

The ammonolysis of alkyl halides RX(R = alkyl group. X = Cl, Br, I) takes place slowly at the boiling point of lig.NH_3. In this reaction mixture of primary (RNH_2) secondary (R_2NH) and tertiary (R_3N) amines is obtained.

$RX + 2NH_3 \rightarrow R(NH_2) + NH_4^+ + X^-$

$2RX + 3NH_3 \rightarrow R_2(NH) + 2NH_4^+ + 2X^-$

$3RX + 4NH_3 \rightarrow R_3N + 3NH_4^+ + 3X^-$

$C_6H_5Cl + 2NH_3 \rightarrow C_6H_5NH_2 + NH_4^+ + Cl^-$

e. Ammonolysis reactions:

In all these reactions the concentration of NH_4^+ is increased.

$Hg_2Cl_2 + 2NH_3 \rightarrow Hg(NH_2)Cl + Hg + NH_4^+ + Cl^-$

$BX_3 + 6NH_3 \rightarrow B(NH_2)_3 + 3NH_4^+ + 3X^-$

$AlCl_3 + 2NH_3 \rightarrow AlCl_2(NH_2) + NH_4^+ + Cl^-$ (In water : $AlCl_3 + 2H_2O \rightarrow AlCl_2(OH) + H_3O^+ + Cl^-$)

$Cl_2 + 2NH_3 \rightarrow Ci(NH_2) + NH_4^+ + 3Cl^-$ (In water :$Cl_2 + 2H_2O \rightarrow Cl(OH) + H_3O^+ + Cl^-$)

$POCl_3 + 6NH_3 \rightarrow PO(NH_2)_3 + 3NH_4^+ + 3Cl^-$(In water:$POCl_3 + 6H_2O \rightarrow PO(OH)_3 + 3H_3O^+ + 3Cl^-$)

$PCl_3 + 6NH_3 \rightarrow P(NH_2)_3 + 3NH_4^+ + 3Cl^-$

$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$

6. Complex Formation Reactions:

a. Many metal salts (e.g. $Zn(NO_3)_2$, $AlCi_3$, etc.) react with excess of KNH_2 solution in liq NH_3 to form soluble amido complexes. For example:

i. $Zn^{2+} + 4NH_2^-(\text{excess}) \rightarrow [Zn(NH_2)_4]^{2-}$

$Zn(NO_3)_2 + 2KNH_2 \rightarrow K_2[Zn(NH_2)_2]$ (insoluble) $+ 2KNO_3$

$Zn(NH_2)_2 + 2KNH_2$(excess) $\rightarrow K_2[Zn(NH_2)_4]$

On adding: $Zn(NO_3)_2 + 4KNH_2 \rightarrow K_2[Zn(NH_2)_4]$ (soluble) $+ 2KNO_3$

Above reaction that occurs in aqueous(H_2O) medium.

$Zn(NO_3)_2 + NaOH \rightarrow Zn(OH)_2$ (insoluble) $+ 2NaNO_3$

$Zn(OH)_2 + 2NaoH$(excess) $\rightarrow Na_2[Zn(OH)_4]$

On adding: $Zn(NO_3)_2 + 4NaOH \rightarrow Na_2[Zn(OH)_4]$ (soluble amido complex) $+ 2NaNO_3$

ii. $Al^{3+} + 4NH_2^-$(excess) $\rightarrow [Al(NH_2)_4]^-$

$AlCl_3 + 3KNH_2 \rightarrow Al(NH_2)_3$ (insoluble) $+ 3KCl$

$Al(NH_2)_3 + KNH_2$(excess) $\rightarrow K[Al(NH_2)_4]$

On adding: $AlCl_3 + 4KNH_2 \rightarrow K[Al(NH_2)_4]$ (soluble amido complex) $+ 3KCl$

This reaction can be compared with the reaction of $AlCl_3$ with excess of NaOH taking place in aqueous solution.

$Al^{3+} + 4OH^- \rightarrow [Al(OH)_4]^-$(soluble hydroxo complex) or $[AlO_2^- + 2H_2O]$

$AlCl_3 + 3NaOH \rightarrow [Al(OH)_3]$(ppt) $+ 3NaCl$

$[Al(OH)_3]$(ppt) $+ 4NaOH$(excess) $\rightarrow Na[Al(OH)_4]$ (soluble hydroxo complex)

On adding: $AlCl_3 + 4NaOH$(excess) $\rightarrow 3NaCl + Na[Al(OH)_4]$

b. Many metal amides,imides and nitrides dissolve in the excess of KNH_2 in liq. NH_3 to form soluble amido complexes. For example

- **i.** $Zn(NH_2)_2 + 2KNH_2$ (excess) → $K_2[Zn(NH_2)_4]$ (soluble amido complex)
- **ii.** $AgNH_2 + KNH_2$ (excess) → $K[Ag(NH_2)_2]$
- **iii.** $Al(NH_2)_3 + KNH_2$ (excess) → $K[Al(NH_2)_4]$

7. Redox Reactions:

a. Redox reactions in which liq. NH_3 serves as a medium only.

- **i.** KMnO acts as a weak oxidising agent in liq. NH_3. It oxidises KNH_2 to N_2 in liq. NH_3 and is itself reduced to K_2MnO_4.

$$6KMnO_4(Mn=+7) + 6KNH_2(N=-3) \rightarrow 6K_2MnO_4(Mn=+6) + 6NH_3 + N_2(N=0)$$

- **ii.** Iodine also acts as a weak oxidising agent in liq.NH_3.It oxidises potassium ammonostannite, $K_4[Sn(NH_2)_6]$ to potassium ammonostannate, $K_2[Sn(NH_2)_6]$ and is itself reduced to KI.

$$I_2\,(I=0) + K_4[Sn(NH_2)_6]\,(Sn=+2) \rightarrow K_2[Sn(NH_2)_6]\,(Sn=+4) + 2KI\,(I=-1)$$

b. Redox reactions in which liq. NH_3 (N= -3, H = +1) itself acts as a reducing agent:

- **i.** $4NH_3(N=-3) + 5O\,(O=0) \rightarrow 4NO\,(N=+2) + 6H_2O\,(O=-2)$
- **ii.** $2NH_3(N=-3) + 3CuO\,(Cu=+2) \rightarrow N_2\,(N=0) + 3Cu\,(Cu=0) + 3H_2O$

c. Redox reactions in which alkali metals in liq. NH_3 acts as reducing agents:

Liq.NH_3 can dissolve the alkali metals in it. The solution thus obtained contains ammoniated electrons. These electrons reduce various substances. Thus alkali metals in liq. NH_3 are able to reduce a variety of substances and are themselves oxidised to some alkali metal salt.

i. Sodium in liq.NH_3 reduces ammonium salt to H_2

$2Na\ (Na=0) + 2NH_4Br\ (H=1) \rightarrow 2NaBr\ (Na=+1) + H_2\ (H=0)$

ii. Potassium in liq. NH_3 reduces nitrous oxide (N_2O) to N_2

$2K\ (K=0) + NH_3 + N_2O \rightarrow KNH_2\ (K=+1) + KOH + N_2\ (N=0)$

iii. Sodium in liq. NH_3 reduces elemental sulphur to sodium sulphide (Na_2S)

$S\ (S=0) + 2Na\ (Na=0) \rightarrow Na_2S\ (Na=+1, S=-2)$

iv. Li and Na in liq.NH_3 reduce elemental oxygen to their peroxide, while other alkali metals give their peroxide (M_2O_2) as well as superoxide (MO_2).

$2K\ (K=0) + O_2\ (O=0) \rightarrow K_2O_2\ (K=+1, O=+1)$ (peroxide - white)

$K\ (K=0) + O_2\ (O=0) \rightarrow KO_2\ (K=+1, O=-1/2)$ (superoxide-yellow)

v. Na in liq. NH_3 reduces CuI to Cu

$CuI\ (Cu=+1) + Na\ (Na=0) \rightarrow Cu\ (Cu=0) + NaI\ (Na+1)$

vi. K in liq. NH_3 reduces $KMnO_4$ to MnO and is itself oxidised to KNH_2.

$30K(K=0)+20NH_3+6KMnO_4(Mn=+7) \rightarrow 6MnO(Mn=+2)+18KNH_2(K=+1)+18KOH+3H_2+N_2$

vii. Na in liq. NH_3 reduces ZnI_2 to $NaZn_4$ and is itself oxidised to NaI.

$4ZnI_2\ (Zn=+2)+9Na\ (Na=0) \rightarrow NaZn_4\ (Zn=-1/4)+8NaI\ (Na+1)$

viii. Excess of K in liq. NH_3 reduces $K_2[Ni(CN)_4]$ and $[Pt(NH_3)_4]Br_2$ to $K_4[Ni(CN)_4]$ and $[Pt(NH_3)_4]^0$respectively.

$K_2[Ni(CN)_4]\ (Ni=+2)(\text{excess of K in liq. } NH_3\ (-33^0C) \rightarrow K_4[Ni(CN)_4]\ (Ni=0)$

$[Pt(NH_3)_4]Br_2\ (Pt=+2)((\text{excess of K in liq. } NH_3\ (-33^0C) \rightarrow [Pt(NH_3)_4]^0\ (Pt=0)$

8. Dissociation of Weak Acids by Liq. NH_3:

Since liq. NH_3 has strong proton accepting ability, it accepts a proton from weak acids like CH_3COOH.

$NH_3\ (l) + CH_3COOH \rightarrow NH_4^+ + CH_3COO^-$

CH_3COOH is completely ionised in liq. NH_3 and hence acts as a strong acid in liq, NH_3.

9. Reactions in Which NH_3 accepts a Proton : Pyrolysis :

NH_3 is a powerful proton acceptor to form NH_4^+ ion. For example:

a. NH_3 picks up a proton from H_2O to form NH_4^+ and OH^- ions

$NH_3 + HOH \rightarrow NH_4^+ + OH^-$

The high solubility of NH_3 in H_2O is due to the above reaction

b. CH_3COOH is a weak acid in H_2O but shows strong acidic character in liq.NH_3 because NH_3 picks up a proton from CH_3COOH to form NH_4^+ ion.

$NH_3\,(l) + CH_3COOH \rightarrow NH_4^+ + CH_3COO^-$

c. Urea (NH_2CONH_2) and acetamide (CH_3CONH_2) are weakly basic in aqueous solution but show acidic properties in liq. NH_3 since these compounds can donate a proton to NH_3 to produce NH_4^+ ion.

$H_2N\text{-}CO\text{-}NH_2 + NH_3 \rightarrow H_2N\text{-}CO\text{-}NH^- + NH_4^+$

$H_3C\text{-}CO\text{-}NH_2 + NH_3 \rightarrow H_3C\text{-}CO\text{-}NH^- + NH_4^+$

d. Sulphonic acid (NH_2SO_2OH) behaves as a dibasic acid in liq. NH_3

$H_2N\text{-}SO_2\text{-}OH + 2NH_3 \rightarrow HN^-\text{-}SO_2\text{-}O^- + 2NH_4^+$

Here it may be noted that NH_2SO_2OH acts as a monobasic acid in aqueous solution, since only the OH group present in this compound donates a proton to H_2O.

$H_2N\text{-}SO_2\text{-}OH + H_2O \rightarrow H_2N^-\text{-}SO_2\text{-}O^- + H_3O^+$

e. $AgNH_2$ behaves as a weak base in aqueous solution but in liq.NH_3 it behaves as an acid.

$$AgNH_2 + 2NH_3 \rightarrow [Ag(NH_2)_2]^- + NH_4^+$$

In all the above examples concentration of NH_4 increased. Hence,according to Cady and Esley concept of acids and bases, all these substances behave as acids in liq.NH_3.

Advantages of Using Liquid Ammonia as a Solvent:

1. All the alkali metals,without reacting with liq. NH_3, is soluble in this solvent. The dissolved alkali metals can be recovered by evaporating the alkali metal-liq.NH_3 solution.
2. The alkali metal-liq NH_3 solution contains ammoniated electrons and hence these solutions act as strong reducing agents.
3. The study of precipitation reactions taking place in liq.NH_3 these reactions can be used to precipitate metallic halides, sulphides, alcoholates, amide, imide and nitrides.

Disadvantages of Using Liquid Ammonia as a Solvent :

1. Low temperature 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^{0}C.
2. Liq. NH_3 is hygroscopic in nature and hence all the reaction must be carried out in a sealed tube.
3. Liq, NH_3 has an offensive odours and hence the use of liq.NH_3 as a solvent and as a reaction medium requires special technique.

Liquid Sulphur Dioxide (Liq.SO_2)

Introduction: Liq.SO_2 is a non-protonic solvent,because it cannot give a proton on self ionisation. Under normal tempereture and pressure, sulphur dioxide is a gas but can be readily liquefied.It has a wide liquid range from -10.0^{0}C(b.p.) to -75.5^{0}C(m.p.) and hence can be used as a solvent.It's dielectric constant is low (=17.4 at -20^{0}C) and hence it is poor solvent for ionic compounds but acts as a good solvent for covalent compound.

Solubility of various substances in liq.SO_2:

A. Solubility of ionic compounds (inorganic salts):

Iodide and thiocyanates : **Most soluble**

Sulphates,sulphides,oxides and hydroxides : **Partially insoluble**

Ammonium,thallium and mercuric salts : **Soluble**

B. Solubility of non-ionic compounds (covalent compound) :

Covalent halide like IBr,BCl_3,$AlCl_3$,$AsCl_3$,PBr_3,CCl_4,$SiCl_4$ and $SnCl_4$: **Soluble**

Organic compound like amines, ether, alcohols, benzene, alkenes, pyridine,quinoline, Halogen derivatives and acid chlorides : **Soluble**

Alkanes : **Insoluble**

C. Solubility of metals:

Metals are insoluble in liq.SO_2

D. Conductivity of salt solution:

Conductivity of electrolyte solution of salt containing Na^+,NH_4^+,K^+,$(CH_3)_3S^+$ and $(CH_3)_4N^+$ increase with the increase in the size of these cations. Increasing order of conductivity :

$Na^+ < NH_4^+ < K^+ < (CH_3)_3S^+ < (CH_3)_4N^+$

SIze of anions in increasing order of conductivity:

$SCN^- < ClO_4^- < Cl^- < I^-$

Auto-Ionisation of liq.SO_2 :

SO_2 + SO_2 ⇄ SO^{2+}(thionyl ion) + SO_3^{2-}(sulphite ion)
(solvent) (solvent) (solvent cation:acid) (solvent anion:base)

Compare the self ionisation of liq. SO_2 with water and liq.NH_3: SO^{2+} ion analogous to H_3O^+ and NH_4^+ ions while SO_3^{2-} ion is analogous to OH^- and NH_2^- ions produced by the self-ionisation of H_2O and liq. NH_3 respectively.

Chemical reaction taking place in Liq.SO_2 :

1) Metathetical (Precipitation) Reaction:

a) Thionyl chloride (SO_2Cl_2) in liq.SO_2 has helped to prepare many compounds.

$2KBr + SOCl_2 \rightarrow 2KCl\downarrow + SOBr_2$
$2KI + SOCl_2 \rightarrow 2KCl\downarrow + SOI_2$
$NH_4(SCN) + SOCl_2 \rightarrow NH_4Cl\downarrow + SO(SCN)_2$
$2Ag(CH_3COO) + SOCl_2 \rightarrow 2AgCl\downarrow + SO(CH_3COO)_2$

b) Some other reaction precipitation reaction that carried out in liq.SO_2:

$SbCl_3 + 3LiI \rightarrow SbI_3\downarrow + 3LiCl$
$PbF_2 + Li_2SO_4 \rightarrow PbSO_4\downarrow + 2LiF$
$AlCl_3 + 3NaI \rightarrow AlI_3\downarrow + 3NaCl$
$BaI_2 + Zn(CNS)_2 \rightarrow Ba(CNS)_2\downarrow + ZnI_2$

2) Acid-Base neutralisation (salt formation) reaction:

In these reactions compounds contain SO_2^+ ion(acid) combined with compounds containing SO_3 ion(base) to form the salt and the solvent (liq.SO_2).E.g.

a) $SOCl_2$(acid) + Cs_2SO_3(base) $\rightarrow$ 2CsCl(salt) + $2SO_2$(solvent)
Or $SO_2^+ + 2Cl^- + 2Cs^+ + SO_3^{2-} \rightarrow 2Cs^+Cl^- + SO^{2+} + SO_3^{2-}$

b) $SO(SCN)_2 + K_2CO_3 \rightarrow 2K(SCN) + 2SO_2$

c) $SOBr_2 + [N(CH_3)_4]_2SO_3 \rightarrow 2[N(CH_3)_4]Br + 2SO_2$

3) Amphoteric behavior of salts in liq.SO_2 :

a) Acidic and basic character with salts of Zn(II) and Al(III)

$ZnCl_2(acid) + K_2SO_3 \rightarrow ZnSO_3 + 2KCl$
$ZnSO_3(base) + K_2SO_3 \rightarrow K_2[Zn(SO_3)_2]$
$2AlCl_3(acid) + 3K_2SO_3 \rightarrow Al_2(SO_3)_3 + 6KCl$
$Al_2(SO_3)_3(base) + 3K_2SO_3 \rightarrow 3K_3[Al(SO_3)_3]$

b) Acidic and basic behavior with $AlCl_3$ and $GaCl_3$

$AlCl_3(acid) + 3OH^- \rightarrow Al(OH)_3(ppt) + 3Cl^-$
$2AlCl_3(base) + 3SO_3^{2-} \rightarrow Al(SO_3)_3 + 6Cl^-$

4) Solvation Reactions : Formation of Solvates:

Like water and liq. NH_3,liq.SO_2 also form addition compounds(solvates) with solutes.
E.g.$LiI.2SO_2$, $KBr.4SO_2$, $MI.4SO_2$ (M=Na,K,Rb), $MI_2.4SO_2$ (M=Ca,Ba,Sr), $AlCl_32SO_2$

5) Solvolytic or solvolysis reaction:

$PCl_5 + SO_2(l) \rightarrow POCl_3 + SOCl_2$
$NbCl_5 + SO_2(l) \rightarrow NbOCl_3 + SOCl_2$ (at 70^0 C)
$WCl_6 + SO_2(l) \rightarrow WOCl_4 + SOCl_2$ (at 70^0 C)
$UCl_6 + 2SO_2(l) \rightarrow UO_2Cl_2 + 2SOCl_2$

6) Complex formation reaction:

A large number of complex compounds is formed by $SbCl_3$ and $SbCl_5$ in liq.SO_2.
$SbCl_3 + 3KCl \rightarrow K_3[SbCl_6]$ (in liq. SO_2)
$SbCl_5 + KCl \rightarrow K[SbCl_6]$ (in liq. SO_2)
$SbCl_5 + CH_3COCl \rightarrow [CH_3CO][SbCl_6]$ (in liq. SO_2)
$2SbCl_3 + 3SOCl_2 \rightarrow [SO]_3[SbCl_6]_2$ (in liq. SO_2)
$SbCl_5 + NOCl \rightarrow [NO][SbCl_6]$ (in liq. SO_2)

7) Redox reaction:

Liq.SO_2 does not have any strong oxidising or reducing properties, although it may serve as a medium for redox reaction. It reduced iodine but not bromine.

$I_2 + 2RSO_3 \rightarrow RSO_4 + RI_2 + SO_2$

Conversely soluble iodide oxidised to free iodine by $SbCl_5$.

$6KI + 3SbCl_5 \rightleftarrows 3I_2 + SbCl_3 + 2K_3[SbCl_6]$ (in liq.SO_2)

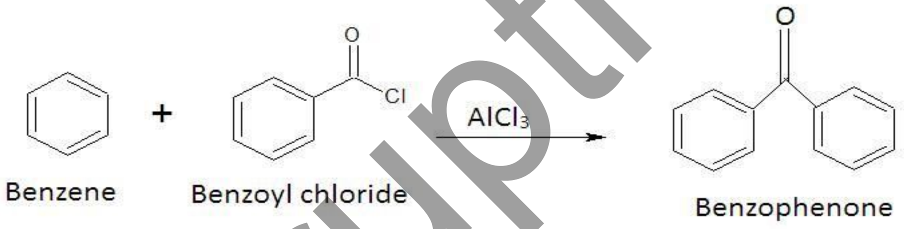
8) Reactions with Organic compounds:

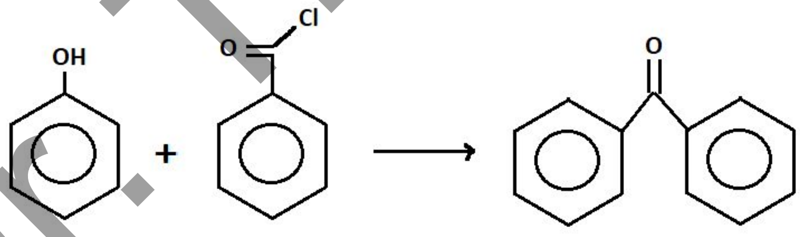
a) Hydrocarbons undergo sulfonation in liq.SO_2 :

$C_6H_6 + ClSO_3H \rightarrow C_6H_5SO_3H + HCl$

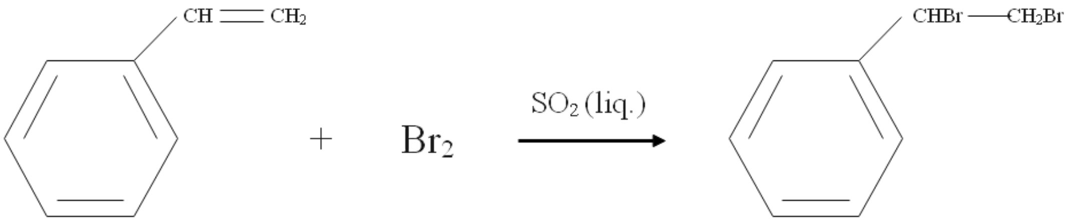
b) Friedel-Craft's reaction :

$AlCl_3$ which is used as a catalyst and reaction carried out in liq.SO_2 medium.

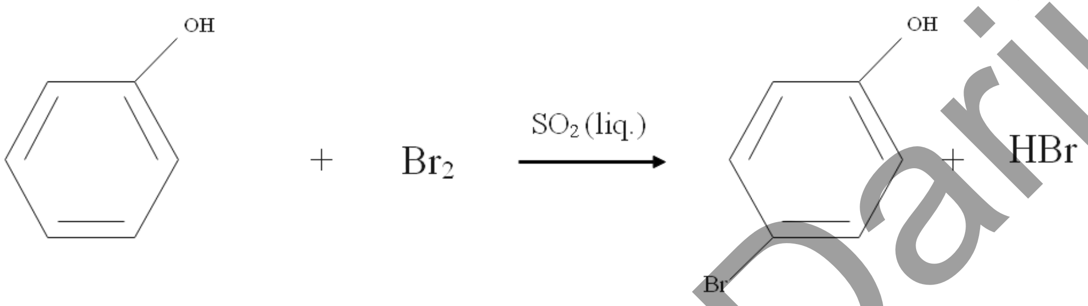




c) Bromination: Liq. SO_2 is also used as a solvent in various Bromination reactions.



Additional Compound



Substitutional
Compound