

# NON-AQUEOUS SOLVENTS

**Solvent.** A solvent is defined as a substance which has the power of dissolving other substances. Water is an excellent solvent. On account of its high dielectric constant, it is capable of reducing forces of electrostatic attraction binding the charged ions in electrolytes in the solid state. Thus, salts and other electrolytes get dissociated into ions when they dissolve in water and the solutions conduct electricity. Water has a long liquid range (0° to 100°C) and hence is liquid at ordinary temperatures. It is most easily available and can be easily purified. It is neutral, odourless, non-toxic and non-poisonous. It can, therefore, be handled safely. Due to all these characteristics, water serves as the most useful solvent.

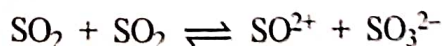
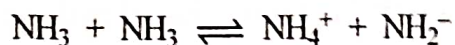
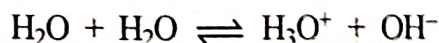
Attempts have been made to find out some other common substances which could serve as good solvents like water and could also have sizeable dielectric constants so that they could have high ionising capacities. Liquid ammonia, liquid sulphur dioxide, anhydrous hydrogen fluoride, anhydrous sulphuric acid and liquid dinitrogen tetroxide are some such solvents.

**Classification of Solvents.** The various solvents are generally classified as follows :

**1. Protonic and aprotic solvents.** Solvents from which protons (*i.e.*,  $H^+$  ions) can be derived are called protonic solvents. Common examples are :  $H_2O$ ,  $NH_3$ ,  $HF$ , etc. Solvents from which protons cannot be ordinarily derived are called aprotic solvents. Examples are :  $CCl_4$ ,  $C_6H_6$ , acetonitrile, etc.

**2. Acid solvents, basic solvents and amphiprotic solvents.** Solvents which have a strong tendency to give protons are called acid solvents, *e.g.*, liquid hydrogen fluoride, sulphuric acid and acetic acid. Solvents which have strong affinity for protons are called basic solvents, *e.g.*, liquid ammonia, pyridine, hydrazine, etc. Amphiprotic solvents are those which neither have a strong tendency to gain nor a strong tendency to lose protons. Examples are : water, methyl alcohol, ethyl alcohol, etc.

**3. Ionising and non-ionising solvents.** Ionising solvents are those which are capable of undergoing auto or self-ionisation. Examples are : water, ammonia, sulphur dioxide, etc. These solvents ionise as follows :



Solvents which do not ionise at all are non-ionising solvents. Ionising solvents have high dielectric constants and are polar. Non-ionising solvents have low dielectric constants and are non-polar.

**Characteristic Properties of a Solvent.** Some characteristic physical and chemical properties of a solvent which govern its usefulness as a solvent are given below.

**1. Melting point and boiling point.** The melting and boiling points of a solvent indicate the range of temperature over which it can exist in the liquid state under atmospheric pressure. The melting and boiling points of various solvents alongwith their critical temperatures and critical pressures are given in Table 1.



Solvent	M.P./F.P. (°C)	B.P. (°C)	Critical temperature (°C)	Critical pressure (atm)
Sulphuric acid	10.4	300.0	—	—
Water	0	100.0	374.0	—
Ammonia	-77.7	-33.5	132.4	217.7
Sulphur dioxide	-75.5	-10.1	157.5	112.0
Hydrogen fluoride	-89.4	19.5	230.2	77.8
Dinitrogen tetroxide	-11.2	21.1	—	—

Because of the above values while water exists as liquid at ordinary temperature and pressure, ammonia and sulphur dioxide exist as gases under these conditions. These gases, therefore, act as solvents only at low temperatures.

**2. Heats of fusion and vaporisation.** The heat absorbed by one mole of a substance to change from solid to liquid state is called its molar heat of fusion. Likewise, the heat absorbed by one mole of a substance to change from liquid to vapour state is called its molar heat of vaporisation. These constants for water, ammonia, sulphur dioxide and hydrogen fluoride are given in Table 2.

TABLE 2

Molar Heats of Fusion and Vaporisation of Some Solvents

Solvents	Molar heat of fusion (kJ mol <sup>-1</sup> )	Molar heat of vaporisation at boiling point (kJ mol <sup>-1</sup> )
Water	6.02	40.65
Ammonia	5.65	23.34
Sulphur dioxide	7.40	24.93
Hydrogen fluoride	4.58	30.28

The heats of fusion and vaporisation indicate the nature and strength of forces with which the molecules of the solvent are held together in the solid or the liquid state. A high heat of vaporisation of a liquid indicates that the intermolecular forces in it are strong. A better idea of the intermolecular forces is obtained by dividing the heat of vaporisation by the boiling point. For normal liquids, the ratio of the heat of vaporisation expressed in joules to the boiling point (K) is a constant known as Trouton constant. This constant is about 90 J K<sup>-1</sup> mol<sup>-1</sup> for normal liquids. Such liquids have single molecules without any bonds between them. A higher value of the constant indicates association of molecules. The molecules of liquids which undergo association are polar. The common solvents like water, ammonia, hydrogen fluoride and alcohols are all associated liquids.

It is evident from Table 2 that heats of fusion for water and ammonia are very nearly the same. This indicates that the forces which hold molecules together in water and ammonia are of the same magnitude. The heat of fusion of sulphur dioxide is comparatively high while that of hydrogen fluoride is comparatively low indicating that while the force holding SO<sub>2</sub> molecules together is stronger, the force holding HF molecules is weaker.

TABLE 3

Dipole Moments and Dielectric Constants of Some Solvents

Solvent	Dipole Moment (Debye Units)	Dielectric Constant
Water	1.85	78.5 (25°C)
Ammonia	1.47	22.0 (-33.5°C)
Sulphur dioxide	1.61	17.4 (-20°C)
Hydrogen fluoride	1.90	83.6 (0°C)
Dinitrogen tetroxide	—	2.42 (0°C)

**3. Dielectric constant.** The coulombic force  $F$  between a cation and an anion is given by the expression  $F = q_1 q_2 / [\epsilon (r_1 + r_2)^2]$  where  $q_1$  and  $q_2$  are the charges for cations and anions, respectively;  $r_1$  and  $r_2$  are the radii of the two ions and  $\epsilon$  is the dielectric constant. A high value of  $\epsilon$  indicates that a small



amount of energy will be required to separate the ions and hence it will be easy to dissolve an ionic solute. Thus, dielectric constant, in general, determines the ability of a solvent to dissolve ionic compounds. For example, solvents such as anhydrous hydrogen fluoride and water, which have high dielectric constants, are the best solvents for ionic and polar compounds. On the other hand, solvents like liquid ammonia and liquid sulphur dioxide with low dielectric constants show decreased ability to dissolve ionic compounds especially those containing multi-charged ions. Thus, carbonates, sulphates and phosphates are practically insoluble in liquid ammonia and liquid sulphur dioxide.

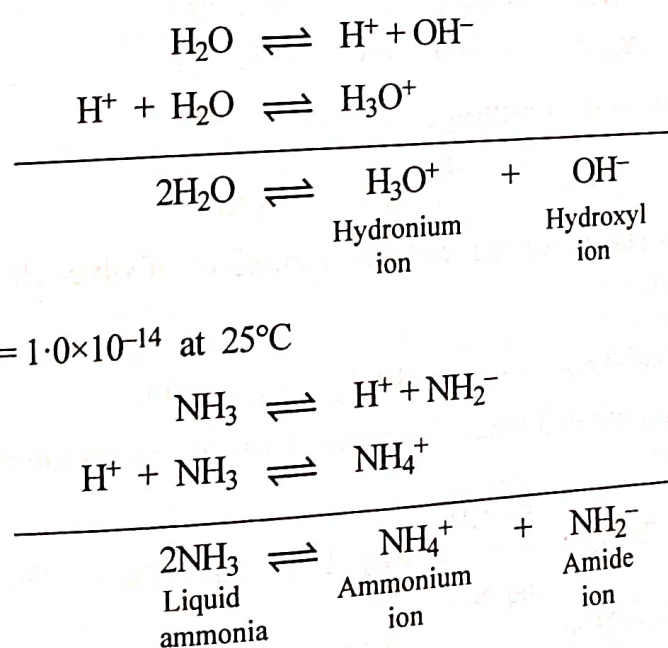
The dielectric constant and the polarity of a solvent are closely related. An ionising solvent not only has a large dipole moment but also has a large dielectric constant. This is evident from the data given in Table 3.

Some important **non-aqueous solvents** are described below.

### LIQUID AMMONIA

Liquid ammonia is one of the most extensively studied non-aqueous solvents. It is a protonic solvent and its water-like properties have made it a highly useful solvent and a reaction medium for carrying out several types of organic and inorganic reactions.

Liquid ammonia shows a striking resemblance with water in its solvent action. Ammonia molecules are, however, less strongly associated through hydrogen bonding in liquid ammonia. Consequently, the freezing and boiling points of liquid ammonia are lower than those of water. Another similarity with water is the polarity of the ammonia molecule. It has a pyramidal structure which makes it polar. A third similarity is autoionisation of liquid ammonia, similar to the autoionisation of water. Both liquid ammonia and water show comparable autoionisation, represented as below :



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$K_b = [\text{NH}_4^+][\text{NH}_2^-] = 1.9 \times 10^{-33} \text{ at } -50^\circ\text{C}.$

However, the extent of autoionisation of liquid ammonia is much less than that of water (compare the values of  $K_w$  and  $K_b$ ).

Ammonia can, therefore, conduct electricity only to a feeble extent. The dielectric constant of liquid ammonia (22.0) is much smaller than that of water (78.5). The lower dielectric constant results in a generally decreased ability of liquid ammonia to dissolve ionic compounds. Liquid ammonia is, therefore, a poor solvent for ionic substances. However, low viscosity of ammonia (0.254 centipoise at  $-33.5^\circ\text{C}$ ) compared to that of water (0.959 centipoise at  $25^\circ\text{C}$ ) is expected to promote greater ionic mobilities and thereby compensate to some extent the effect of the comparatively low dielectric constant. The physical properties of water and liquid ammonia are given in Table 4.

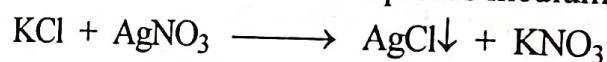
Properties	Water	Ammonia
Boiling point	100°C	-33.5°C
Freezing point	0°C	-77.7°C
Density	1.0 g ml <sup>-1</sup> (4°C)	0.68 g ml <sup>-1</sup> (-33.5°C)
Dielectric constant	78.5 (25°C)	22.0 (-33.5°C)
Specific conductance (ohm <sup>-1</sup> cm <sup>-1</sup> )	6.0 × 10 <sup>-8</sup> (25°C)	1 × 10 <sup>-11</sup> (-33.5°C)
Viscosity (centipoise)	0.959 (25°C)	0.254 (-33.5°C)
Dipole moment (Debye)	1.85	1.47
Trouton constant (J K <sup>-1</sup> mol <sup>-1</sup> )	109	101.2

### Chemical Reactions in Liquid Ammonia

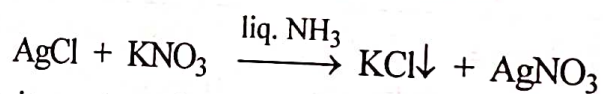
As mentioned above, liquid ammonia has water-like properties and hence the reactions which take place in aqueous solutions can also occur in liquid ammonia solutions. Chemical reactions that take place in liquid ammonia are of the following types.

**1. Precipitation Reactions.** Precipitation reactions normally involve double decomposition. The solubilities of various substances in liquid ammonia and water are different and hence many reactions which are not normally possible in water have been reported to occur in liquid ammonia. Some of these reactions are discussed below.

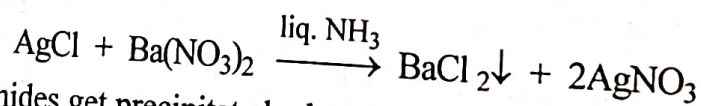
- a. Consider the precipitation of silver chloride in aqueous medium.



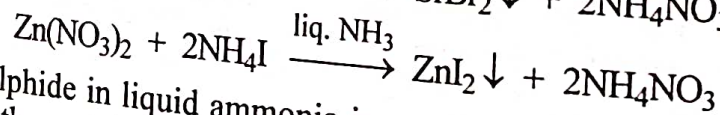
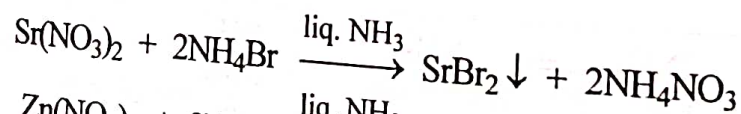
In liquid ammonia, the direction of the reaction is reversed.



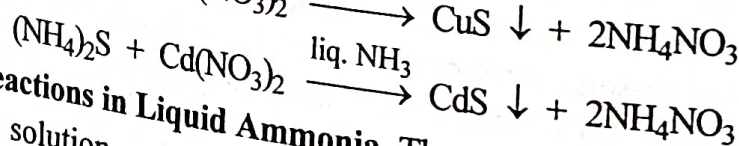
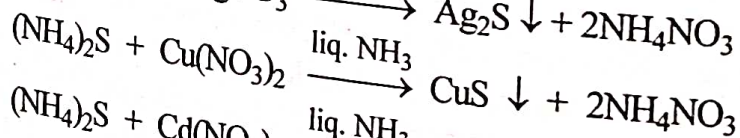
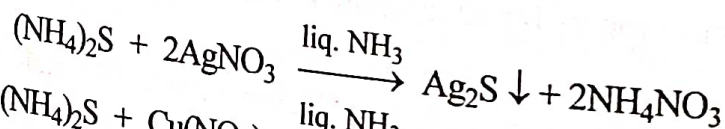
Similarly, a white precipitate of BaCl<sub>2</sub> is produced when solutions of silver chloride and barium nitrate in liquid ammonia are brought together.



- b. Iodides and bromides get precipitated when solutions of various metal nitrates and ammonium halides in liquid ammonia are mixed together.



- c. Ammonium sulphide in liquid ammonia is capable of precipitating many metal sulphides from the solutions of nitrates of the metals.



**2. Acid-Base Reactions in Liquid Ammonia.** There is an interesting comparison between neutralisation reactions in aqueous solution and in liquid ammonia solution. Hydrochloric acid gas dissolves in liquid ammonia giving NH<sub>4</sub><sup>+</sup> ions and Cl<sup>-</sup> ions.

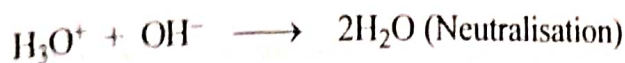
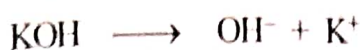




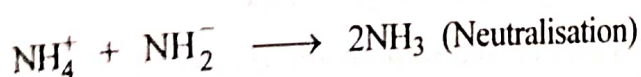
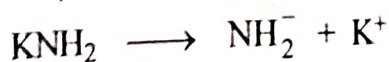
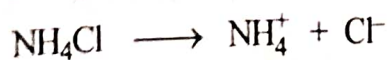
A similar reaction takes place in the case of water.



In aqueous solution, the process of neutralisation of a strong acid by a strong base involves the combination of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions to form practically un-ionised  $\text{H}_2\text{O}$ , the anion of the acid and the cation of the base remaining unchanged. For instance, the neutralisation of hydrochloric acid with potassium hydroxide may be represented as



A similar thing happens in the case of liquid ammonia solution. The process of neutralisation involves combination of  $\text{NH}_4^+$  and  $\text{NH}_2^-$  ions to form un-ionised  $\text{NH}_3$ . For instance, the neutralisation of ammonium chloride with potassium amide may be represented as

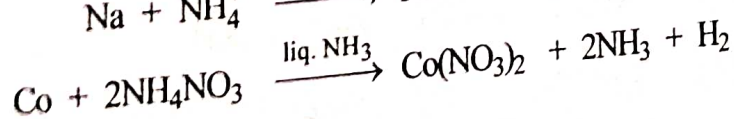
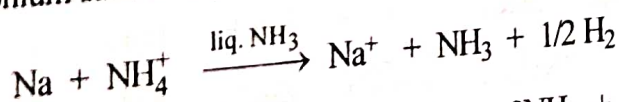


Obviously, the role of  $\text{NH}_4\text{Cl}$  in liquid ammonia solution is the same as that of  $\text{HCl}$  in aqueous solution. Similarly, the role of  $\text{KNH}_2$  in liquid ammonia solution is the same as that of  $\text{KOH}$  in aqueous solution. Thus,  $\text{NH}_4\text{Cl}$  may be regarded as a strong acid and  $\text{KNH}_2$  as a strong base in liquid ammonia solution. They are termed as ammono acids and ammono bases, respectively. Some typical reactions of ammono acids and ammono bases are given below.

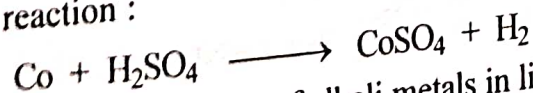
**2. Reactions of Ammono Acids.** Ammono acid is a substance which in liquid ammonia furnishes  $\text{NH}_4^+$  ion. The following reactions show their behaviour to be similar to that of aqua acids.

1. *Neutralisation.* This has already been discussed above.

2. *Replacement of protons by reactive metals.* Acids give out hydrogen with metals in aqueous solutions. Likewise, the solutions of ammonium salts in liquid ammonia react with alkali and other metals to give hydrogen.

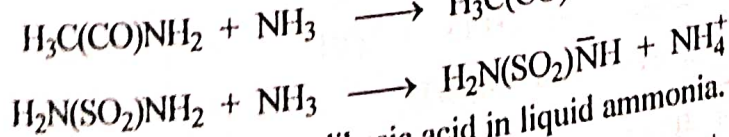
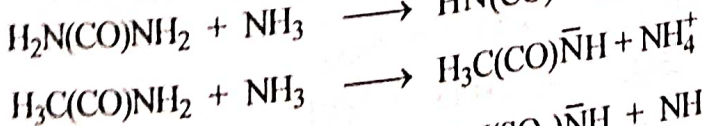
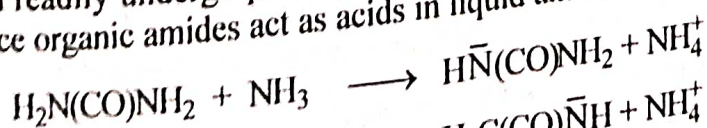


This is analogous to the reaction :

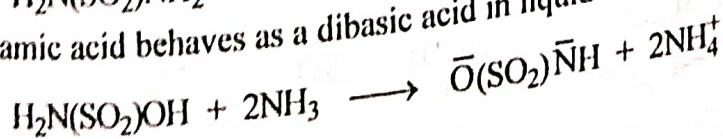


Ammonium salts decolourise blue solutions of alkali metals in liquid ammonia.

3. *Protolysis.* Certain compounds like urea, acetamide, sulphamide, etc., which are incapable of donating protons to water, can readily undergo protolysis in liquid ammonia, i.e., they can donate protons to  $\text{NH}_3$  in liquid ammonia. Hence organic amides act as acids in liquid ammonia, as illustrated by the following reactions:



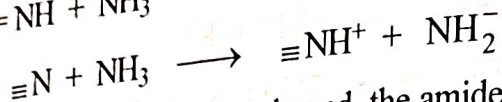
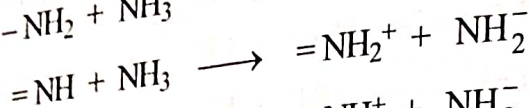
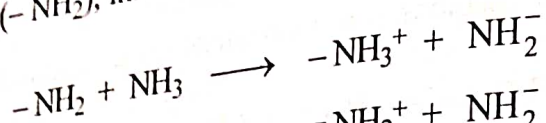
Similarly, sulphamic acid behaves as a dibasic acid in liquid ammonia.





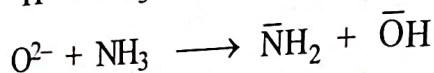
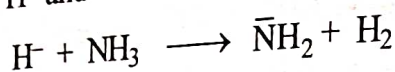
However, it acts as a monobasic acid in aqueous solution. This is because  $\text{NH}_2$  group cannot donate a proton to water.

**h Reactions of Ammono Bases.** Ammono base is a substance which in liquid ammonia furnishes  $\text{NH}_2^-$  ion. Consequently, amides ( $-\text{NH}_2$ ), imides ( $=\text{NH}$ ) and nitrides ( $\equiv\text{N}$ ) behave as bases in liquid ammonia, as shown below :

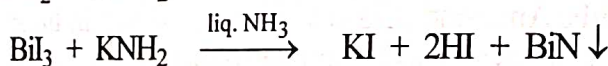
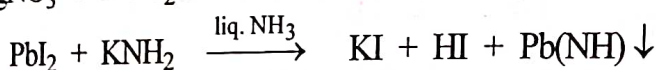
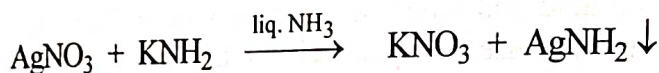


Since in all the above reactions, the  $\text{NH}_2^-$  ion is released, the amide, imide and nitride all behave as ammono bases.

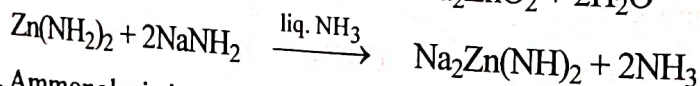
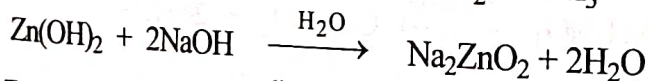
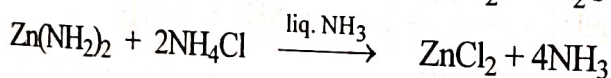
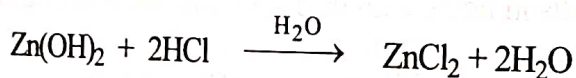
Several species that are considered as strong bases in water, behave as weak bases in liquid ammonia. Extremely strong bases such as  $\text{H}^-$  and  $\text{O}^{2-}$  are levelled to  $\text{NH}_2^-$  ion in liquid ammonia.



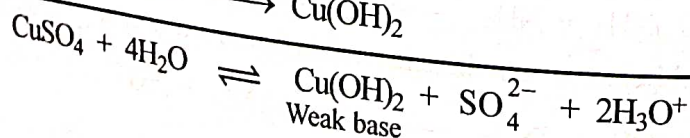
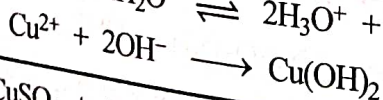
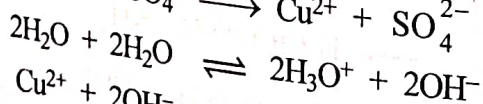
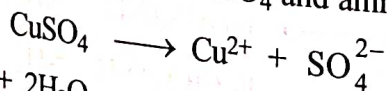
Since alkaline earth amides and lithium and sodium amides have very low solubility, potassium amide ( $\text{KNH}_2$ ), which is much more soluble, is usually employed as an ammono base. Thus, salts of metals in liquid ammonia are precipitated as amides, imides and nitrides by the addition of a solution of  $\text{KNH}_2$ .



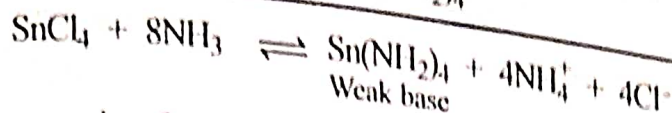
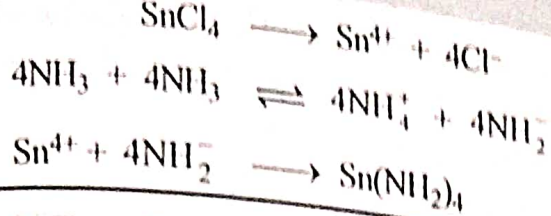
**3. Amphoterism.** A compound that dissolves both in acids and bases is said to be amphoteric in character. In aqueous medium, zinc and aluminium hydroxides are amphoteric. In liquid ammonia, zinc amide shows amphoteric behaviour. This is illustrated by the following reactions :



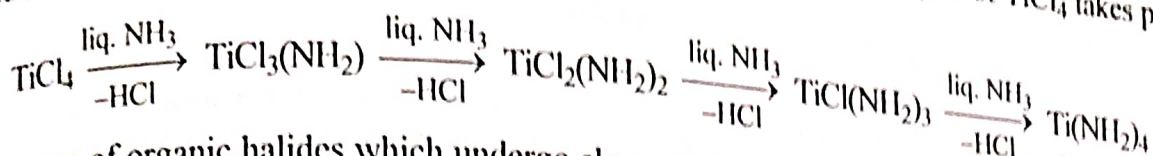
**4. Ammonolysis.** Ammonolysis in liquid ammonia is similar to hydrolysis in aqueous medium. Just as in hydrolysis, the concentration of  $\text{H}^+$  or  $\text{OH}^-$  ions increases due to interaction of cations or anions of a salt with  $\text{H}^+$  or  $\text{OH}^-$  ions furnished by autoionization of  $\text{H}_2\text{O}$ , in ammonolysis, the concentration of either  $\text{NH}_4^+$  or  $\text{NH}_2^-$  ions increases due to interaction of cations or anions of a salt with  $\text{NH}_4^+$  or  $\text{NH}_2^-$  ions furnished by autoionisation of  $\text{NH}_3$ . Consider the hydrolysis of  $\text{CuSO}_4$  and ammonolysis of  $\text{SnCl}_4$  :



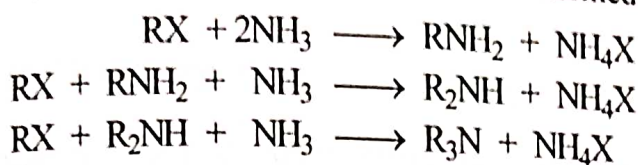




In ammonolysis, the atom or ion from the compound undergoing ammonolysis is replaced by  $-\text{NH}_2$  or  $=\text{NH}$  or  $\equiv\text{N}$  group. For example, in excess of liquid ammonia, the ammonolysis of  $\text{TiCl}_4$  takes place in steps as follows :

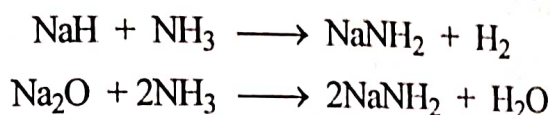


In the case of organic halides which undergo slow ammonolysis at the boiling point of liquid ammonia, mixtures of primary, secondary and tertiary amines are formed.



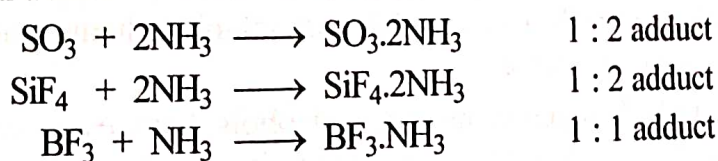
where  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ .

Alkali metal hydrides and oxides also undergo ammonolysis to give amides.



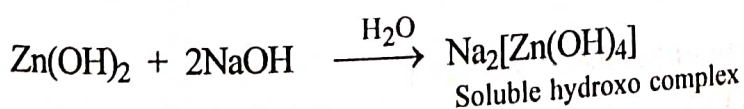
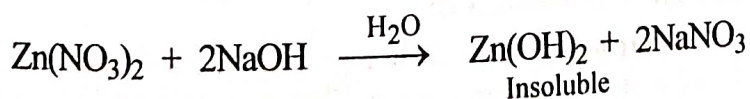
**5. Ammonation and formation of Ammoniates.** Ammonation is a type of solvation reaction in which liquid ammonia is used as a solvent and in which one or more ammonia molecules are attached to a solute species (a cation, an anion or a neutral molecule) by a chemical bond. The products of solvation are called solvates and in the case of ammonation they are known as **ammoniates**. Solvation in water is called hydration and the products are known as hydrates.

Formation of typical ammoniates is shown below :

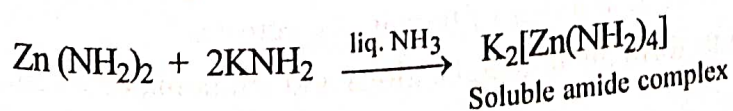
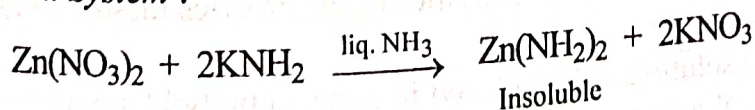


**6. Complex Formation Reactions.** Several complex formation reactions in liquid ammonia are known. These are similar to reactions occurring in aqueous systems. The following reactions are given for illustration:

*Aqueous System :*

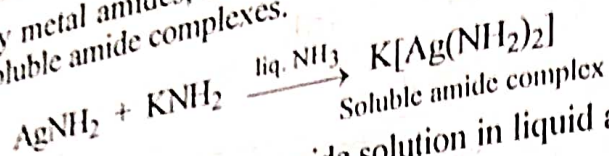


*Liquid Ammonia System :*

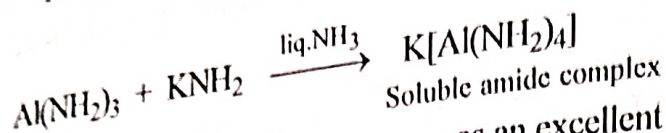
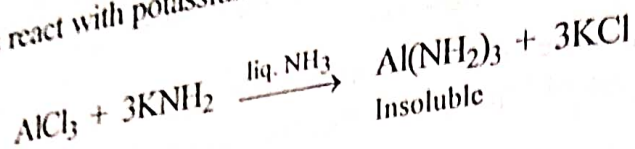




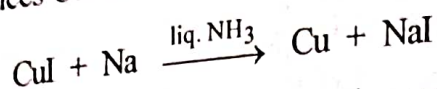
Similarly, many metal amides, imides and nitrides dissolve in ammonia forming soluble amide complexes.



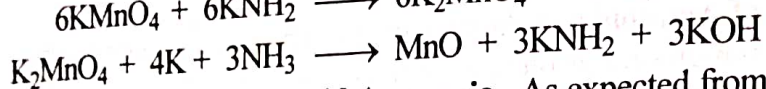
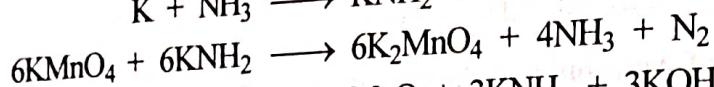
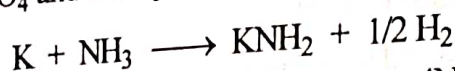
Aluminium salts react with potassium amide solution in liquid ammonia forming soluble amide complexes.



**7. Reduction Reactions.** Liquid ammonia serves as an excellent medium for reduction reactions involving inorganic species. For instance, alkali metals dissolve in liquid ammonia giving blue coloured solutions which are strong reducing agents as they can readily supply electrons for reduction processes. Sodium metal in liquid ammonia, for instance, reduces  $\text{CuI}$  to  $\text{Cu}$ .



**8. Oxidation Reactions.** Oxidising action of various oxidising agents is weaker in liquid ammonia than in aqueous solutions. For instance,  $\text{HNO}_3$  in liquid ammonia does not act as an oxidising agent. Similarly,  $\text{KMnO}_4$  in liquid ammonia acts as a very weak oxidising agent.  $\text{KMnO}_4$  is reduced by a solution of potassium in liquid ammonia to  $\text{K}_2\text{MnO}_4$  and finally to  $\text{MnO}$ .



**9. Solubility of Substances in Liquid Ammonia.** As expected from its very low dielectric constant, liquid ammonia is a poor solvent for ionic substances. Amongst the **inorganic compounds**, nitrates, thiocyanates, perchlorates and most of the cyanides are soluble in liquid ammonia. Oxides, hydroxides, carbonates, phosphates, sulphates and most of the sulphides are insoluble. Most of the iodides are soluble and bromides are less soluble. Fluorides and chlorides (except  $\text{Be}^{2+}$  and  $\text{Na}^+$  chlorides) are practically insoluble. Most of the ammonium salts such as  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{SCN}$ ,  $\text{CH}_3\text{COONH}_4$  are soluble in liquid ammonia. Most of the metal amides, except those of alkali metals, are insoluble.

Amongst the **organic compounds**, halogen compounds, alcohols, ketones, esters, simple ethers, phenol and its derivatives are soluble. Aromatic hydrocarbons are sparingly soluble. Alkanes are insoluble. Alkenes and alkynes are slightly soluble.

Amongst the **elements**, metals like  $\text{Mg}$ ,  $\text{Al}$ ,  $\text{Zn}$ ,  $\text{Ca}$ ,  $\text{La}$ ,  $\text{Ce}$ ,  $\text{Mn}$ , etc., have low solubilities in liquid ammonia. Alkali metals and alkaline earth metals are highly soluble in liquid ammonia. The non-metals like sulphur, phosphorus, iodine are soluble and they react with the solvent.

**Solutions of Alkali Metals in Liquid Ammonia.** The ability to dissolve the alkali metals is one of the striking features of liquid ammonia as a solvent. The alkali metal solutions in liquid ammonia are blue in colour. The blue solution is characterised by

- (i) its colour which is independent of the metal involved.
- (ii) its density which is similar to that of pure liquid ammonia.
- (iii) its conductivity which is in the range of conductivities of electrolytes dissolved in liquid ammonia, and
- (iv) its paramagnetism (i.e., these solutions when placed in a magnetic field are attracted into the field) which indicates the presence of a large number of unpaired electrons.

The alkali metal solutions dissociate to form alkali metal cations and ammoniated electrons.



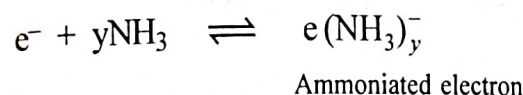
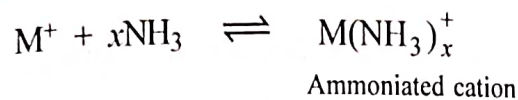
The dissociation into cation and ammoniated electron accounts for the electrolytic conductivity of the blue coloured dilute solutions. As the concentration of the solution is increased,  $M^+$  and  $e^-$  species associate resulting in a decrease of conductivity.

Very dilute solutions of alkali metals in liquid ammonia are metastable and when catalysed they undergo decomposition.



As the concentration of metal increases, the blue colour changes to bronze and finally the colour disappears altogether. On evaporating the alkali metal-ammonia solutions, the alkali metal can be recovered.

The blue colour of dilute metal-ammonia solutions is attributed to the presence of ammoniated cation as well as ammoniated electron.



### Advantages of Liquid Ammonia as a Solvent

1. Dissolution of alkali metals in liquid ammonia without chemical reaction is the greatest advantage of using liquid ammonia as a solvent. The dissolved alkali metals can be recovered from the solution by evaporation.
2. The alkali metal solutions in liquid ammonia are strong reducing agents, even stronger than hydrogen.
3. Ammonium salts dissolved in liquid ammonia find application in preparative chemistry. They can be used to precipitate sulphides, halides, sulphates and alcoholates.
4. The tendency for solvolysis is less in liquid ammonia than in water.

### Limitations of Liquid Ammonia as a Solvent

1. Low temperature or high pressure is necessary while working with liquid ammonia. This is because the liquid range for liquid ammonia is from  $-33.5^\circ C$  to  $-77.7^\circ C$ .
2. Liquid ammonia is hygroscopic in nature. Hence, all the reactions are to be carried out in sealed tubes.
3. The use of liquid ammonia as a solvent and as a reaction medium requires special technique as it has an offensive odour.

## ANHYDROUS HYDROGEN FLUORIDE

Hydrogen fluoride is one of the most water-like solvents since it is **liquid** at temperatures below  $19.4^\circ C$  upto  $-89.4^\circ C$ . Its boiling point ( $+19.5^\circ C$ ) is very high as compared to the boiling points of other non-aqueous solvents. Its dipole moment (1.90 D) and dielectric constant (83.6 at  $0^\circ C$ ) are also quite close to those of water. Because of its high dielectric constant, it serves as an excellent ionising solvent.

However, its use as a non-aqueous solvent has been quite limited because it is poisonous, its specific conductance is low and it can dissolve only a few substances without reacting with them.

The characteristic physical properties of anhydrous hydrogen fluoride are given in Table 5.

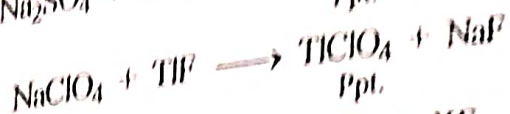
TABLE 5  
Some Characteristic Physical Properties of Anhydrous Hydrogen Fluoride

Property	Values
Freezing point	$-89.4^\circ C$
Boiling point	$19.5^\circ C$
Density	$0.99 \text{ g ml}^{-1}$
Dielectric constant	$83.6 (0^\circ C)$
Dipole moment	$1.90 \text{ D}$
Viscosity	$0.256 \text{ centipoise } (15^\circ C)$
Specific conductance	$1.4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1} (15^\circ C)$

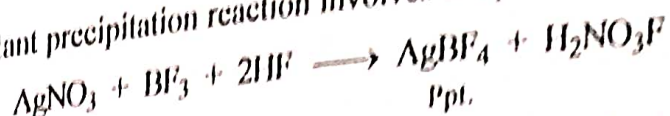


**Chemical Reactions in Anhydrous Hydrogen Fluoride.** Some of the important chemical reactions take place in anhydrous hydrogen fluoride are discussed below briefly.

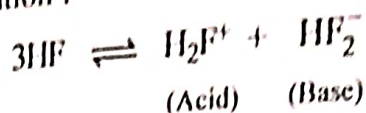
**1. Precipitation Reactions.** Sulphates, perchlorates and periodates of non-alkali metals get precipitated when their fluorides dissolved in anhydrous hydrogen fluoride are treated with solutions of sulphates, perchlorates and periodates of alkali metals.



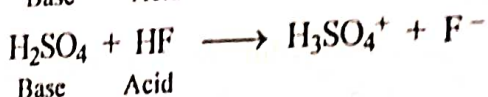
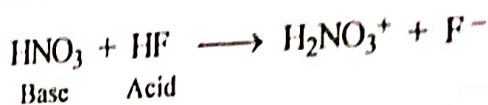
Another important precipitation reaction involves the precipitation of  $\text{AgBF}_4$ .



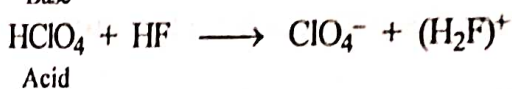
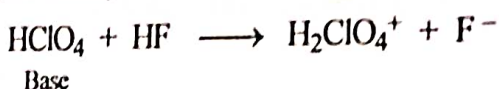
**2. Acid-Base Reactions.** The high specific conductance of anhydrous hydrogen fluoride suggests a relatively large degree of its autoionisation :



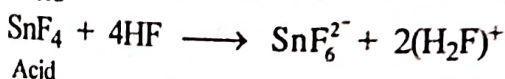
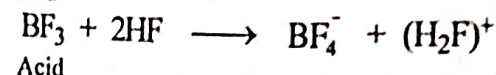
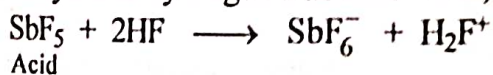
Thus, any substance which can yield  $\text{H}_2\text{F}^+$  ion would behave as an acid and any substance which can yield  $\text{HF}_2^-$  or  $\text{F}^-$  ion would behave as a base. Accordingly, even strong acids such as  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  behave as bases in hydrogen fluoride since they release  $\text{F}^-$  ions.



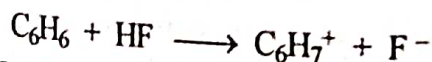
Perchloric acid, which behaves as the strongest acid in aqueous solution, exhibits an amphoteric character in anhydrous hydrogen fluoride. Thus,



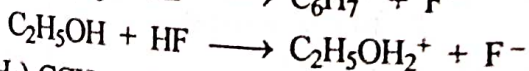
Only a few substances such as  $\text{BF}_3$ ,  $\text{AsF}_5$ ,  $\text{SbF}_5$  and  $\text{SnF}_4$ , which behave as Lewis acids in aqueous solutions, function as acids in anhydrous hydrogen fluoride. Thus,



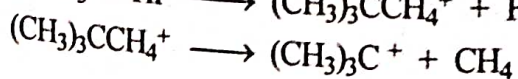
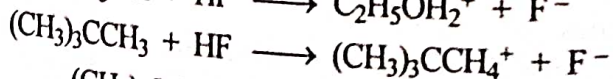
**3. Protonation of Organic Compounds.** Organic compounds such as benzene, ethanol, alkanes get protonated when dissolved in HF. Thus,



(i)



(ii)





Because of the formation of some compounds mentioned above, give conducting solutions in HF. The aromatic hydrocarbons give coloured solutions in HF and their solubilities can be increased further by adding fluoride acceptors such as  $\text{BF}_3$  and  $\text{SbF}_5$ . The protonated species can be isolated as crystalline salts of  $\text{BF}_4^-$  and  $\text{SbF}_6^-$ .

**4. Formation of Addition Compounds.** Metallic fluorides form addition compounds with HF. Examples are:  $\text{KF} \cdot \text{ZHF}$ ,  $\text{KPF}_3 \cdot \text{HF}$ ,  $\text{NH}_4 \cdot \text{P} \cdot \text{HF}$ , etc.

### ANHYDROUS SULPHURIC ACID

The characteristic physical properties of anhydrous sulphuric acid are given in Table 6.

The viscosity of anhydrous  $\text{H}_2\text{SO}_4$  is about 25 times higher than that of water. Therefore, solutes dissolve very slowly in sulphuric acid and are also difficult to crystallise from  $\text{H}_2\text{SO}_4$ .

#### Chemical Reactions of Anhydrous Sulphuric Acid

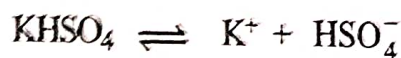
**1. Autoionisation.** Anhydrous sulphuric acid autoionises to give  $\text{H}_3\text{SO}_4^+$  and  $\text{HSO}_4^-$  ions:



Therefore, any chemical species producing  $\text{HSO}_4^-$  ions will act as a base and any chemical species producing  $\text{H}_3\text{SO}_4^+$  ion acts as an acid in anhydrous  $\text{H}_2\text{SO}_4$ .

**2. Acid-Base Reactions.** Some typical acid-base reactions of anhydrous  $\text{H}_2\text{SO}_4$  are given below:

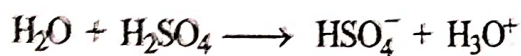
(a)  $\text{KHSO}_4$  acts as a base in anhydrous sulphuric acid.



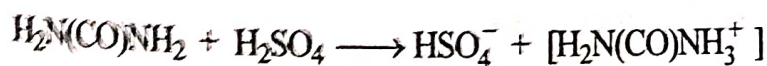
(b) Species that are basic in water are also basic in  $\text{H}_2\text{SO}_4$ .



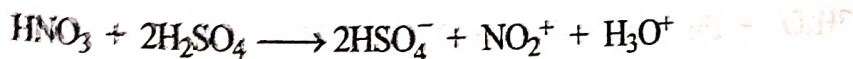
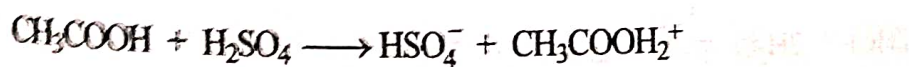
(c) Water behaves as a base in anhydrous sulphuric acid.



(d) Species containing lone pair of electrons easily accept a proton from  $\text{H}_2\text{SO}_4$  and act as bases. Thus, amides (like urea, etc), which act as acids in liquid  $\text{NH}_3$ , are neutral in water and behave as bases in anhydrous  $\text{H}_2\text{SO}_4$ .



(e) Acids which behave as weak acids or even as strong acids in water behave as bases in anhydrous  $\text{H}_2\text{SO}_4$ .



(f) Even very strong acids like perchloric acid behave as weak acids in anhydrous  $\text{H}_2\text{SO}_4$ .

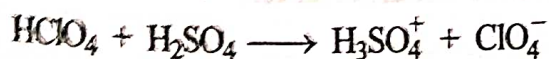
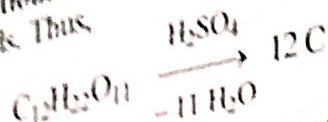


TABLE 6  
Some Characteristic Physical Properties of  
Anhydrous Sulphuric Acid

Properties	Values
Freezing point	10.4°C
Boiling point	300°C
Density	1.84 ml <sup>-1</sup> (25°C)
Dielectric constant	110
Viscosity (centipoise)	24.54 (20°C)



3. **Dehydrating Action.** Anhydrous  $\text{H}_2\text{SO}_4$  acts as a strong dehydrating agent and extracts water even from chemical compounds. Thus,



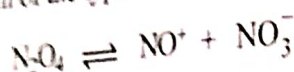
4. **Super Acids.** The acids which behave as *strong acids* in strong acid solvents are termed as *super acids*. For example,  $[\text{HB}(\text{HSO}_4)_4]$ , hydrogen[tetrakis(hydrogen sulphato)borate] whose solutions can be prepared in anhydrous sulphuric acid, behaves as an exceptionally strong acid.

The super acid  $\text{HB}(\text{HSO}_4)_4$  has not been isolated as such. Only its solutions can be prepared. The other super acids are  $\text{H}_2\text{Sn}(\text{HSO}_4)_4$  and  $\text{H}_2\text{Pb}(\text{HSO}_4)_4$  in  $\text{H}_2\text{SO}_4$  solution.

### LIQUID DINITROGEN TETROXIDE

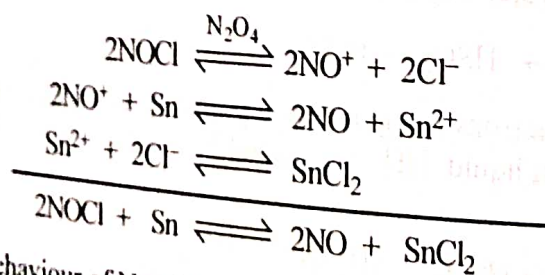
Dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , has been studied extensively as a non-protonic non-aqueous solvent. The physical properties of this solvent are given in Table 7.

Much of the chemistry in this solvent can be rationalised in terms of an autoionisation equilibrium of the type



Although there is no physical evidence for the above type of autoionization occurring in  $\text{N}_2\text{O}_4$ , it has been found that the electrical conductance of  $\text{N}_2\text{O}_4$  increases on adding a donor or a polar solvent to it. This may perhaps be due to increased stabilisation of cations and anions ( $\text{NO}^+$  and  $\text{NO}_3^-$ ) of  $\text{N}_2\text{O}_4$  as a result of the ion-dipole interaction of these ions with the molecules of the added donor or polar solvent.

Thus, assuming that  $\text{N}_2\text{O}_4$  undergoes autoionisation as mentioned above, it can be said that any chemical species which gives the cation  $\text{NO}^+$  in this solvent will behave as an acid and any chemical species which gives the anion  $\text{NO}_3^-$  in this solvent will behave as a base. Thus,  $\text{NOCl}$  behaves as an acid in  $\text{N}_2\text{O}_4$ , as is evident from the following reaction :



Thus, the acid behaviour of  $\text{NOCl}$  in  $\text{N}_2\text{O}_4$ , when it reacts with  $\text{Sn}$ , is parallel to the behaviour of  $\text{HCl}$  in water when it reacts with  $\text{Zn}$  as is apparent from the following reaction :

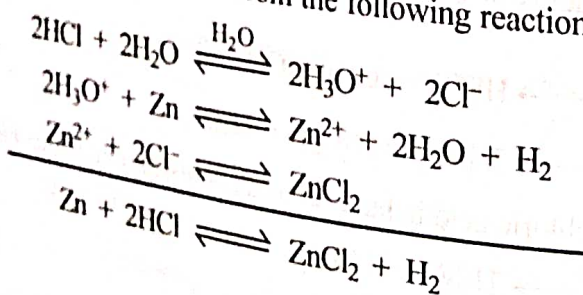


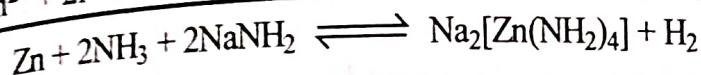
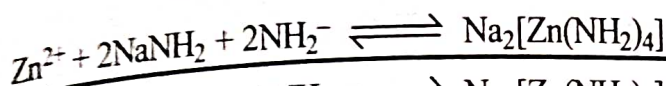
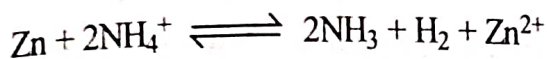
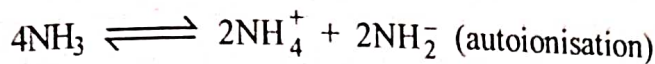
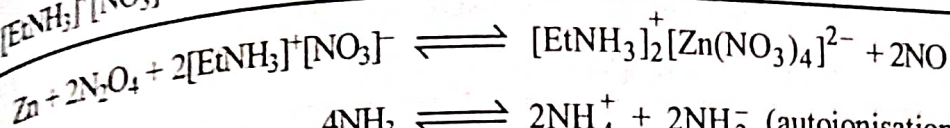
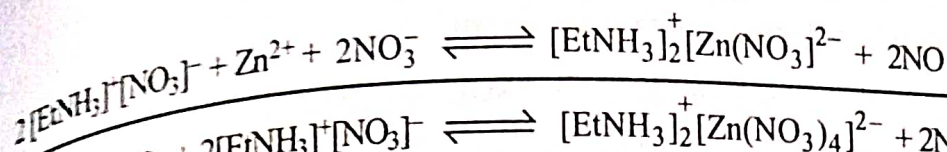
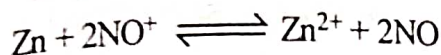
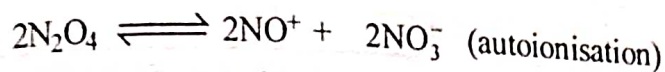
TABLE 7

Some Characteristic Physical Properties of Liquid Dinitrogen tetroxide

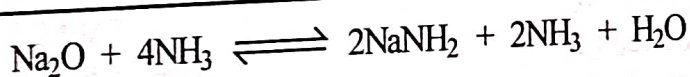
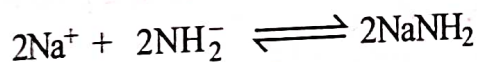
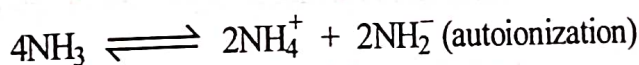
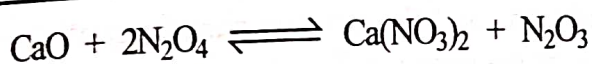
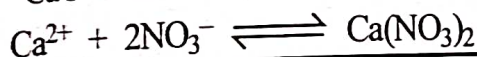
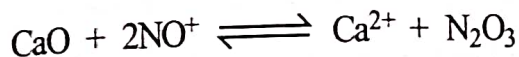
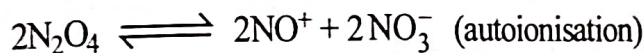
Properties	Values
Freezing point	$-11.2^\circ\text{C}$
Boiling point	$21.1^\circ\text{C}$
Density	$1.493 \text{ g ml}^{-1} (0^\circ\text{C})$
Dielectric constant	2.42
Viscosity	$0.527 \text{ centipoise } (0^\circ\text{C})$
Specific conductance	$1.3 \times 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1} (0^\circ\text{C})$



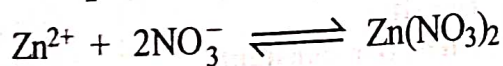
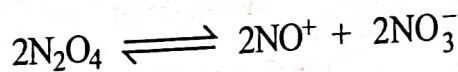
NON-AQUEOUS SOLV. The compound  $[\text{EtNH}_3]^+[\text{NO}_3]^-$  releases  $\text{NO}_3^-$  anion in  $\text{N}_2\text{O}_4$ . It, therefore, acts as a base in  $\text{N}_2\text{O}_4$ . A chemical reaction of  $[\text{EtNH}_3]^+[\text{NO}_3]^-$  with zinc metal in  $\text{N}_2\text{O}_4$  is similar to the reaction of zinc with  $\text{NaNH}_2$  in liquid ammonia, as is evident from the following reactions:



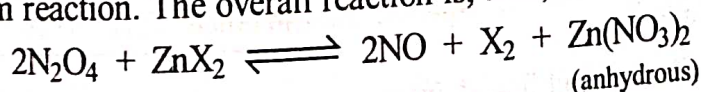
The solvolysis of metal oxides in  $\text{N}_2\text{O}_4$  is similar to their solvolysis in liquid ammonia, as shown below:



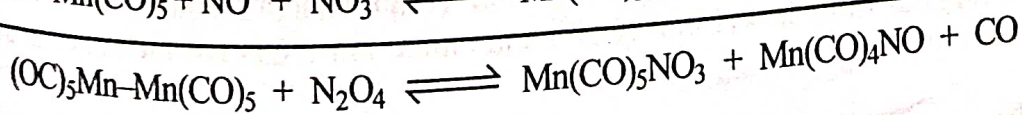
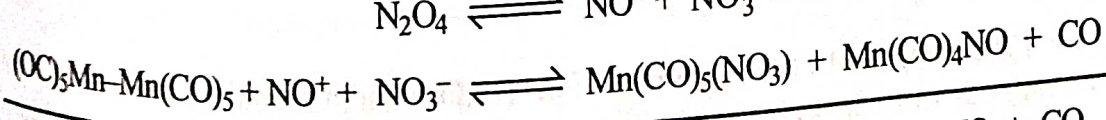
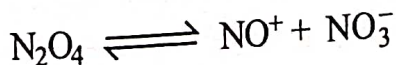
In fact, solvolysis of the halides of metals in  $\text{N}_2\text{O}_4$  provides an excellent method for preparing anhydrous metal nitrates which are otherwise extremely difficult to prepare. Thus,



The  $\text{NOX}$  produced in the reaction decomposes to  $\text{NO}$  and  $\text{X}_2$  and, therefore, it does not participate in the reverse equilibrium reaction. The overall reaction is, thus,

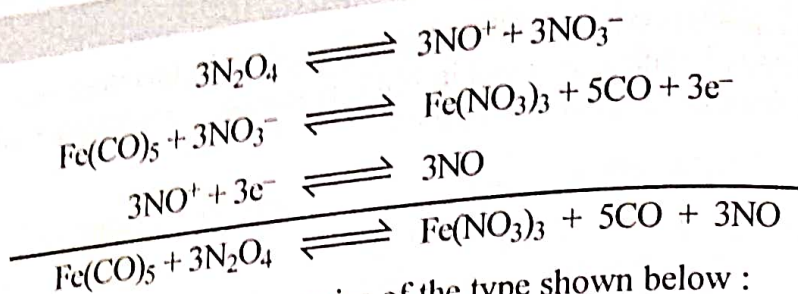


Several metal carbonyls are also solvolysed in a similar manner. Thus,

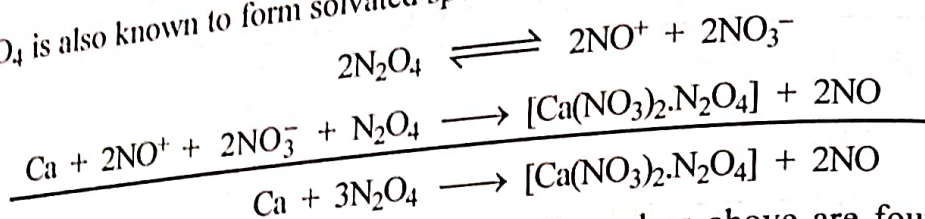




Similarly,

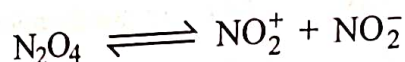


$\text{N}_2\text{O}_4$  is also known to form solvated species of the type shown below :



Quite often, however, the solvated species formed as above are found to be nitrosonium nitrate compounds. For example,  $\text{Sc}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4$  and  $2\text{Fe}(\text{NO}_3)_3 \cdot 3\text{N}_2\text{O}_4$  are actually  $[\text{NO}^+]_2[\text{Sc}(\text{NO}_3)_5]^{2-}$  and  $[\text{NO}^+]_3[\text{Fe}(\text{NO}_3)_4]_2[\text{NO}_3]^-$ , respectively.

There are certain reactions which cannot be explained on the basis of the autoionisation of  $\text{N}_2\text{O}_4$  proposed as above. For instance, the reaction of  $\text{N}_2\text{O}_4$  with  $\text{BF}_3$  yields  $[\text{NO}_2]^+[\text{ONOF}_3]^-$  and  $[\text{NO}_2]^+[\text{F}_3\text{BONOF}_3]^-$ , which can be explained better by assuming the following autoionisation of  $\text{N}_2\text{O}_4$ :



It is worthwhile mentioning here that neither the two proposed ionisations of  $\text{N}_2\text{O}_4$  nor the partial equations written for various chemical reactions occurring in liquid  $\text{N}_2\text{O}_4$  are essentially an experimental reality. Nevertheless, the two proposed auto-ionisations and the various partial equations described as above do explain satisfactorily the chemistry of reactions occurring in liquid dinitrogen tetroxide.

## LIQUID SULPHUR DIOXIDE

Liquid sulphur dioxide is also a non-protonic solvent as it does not yield a proton ( $\text{H}^+$ ) on ionisation. It is widely used for carrying out a number of chemical reactions.

Under normal temperature and pressure, sulphur dioxide is a gas but it can be readily liquefied. It has a wide liquid range ( $-10^\circ\text{C}$  to  $-75.5^\circ\text{C}$ ) and hence can serve as a good solvent. Its use as a non-aqueous solvent is rapidly increasing due to its low cost and ease of its handling. Its dielectric constant is small (17.4 at  $-20.0^\circ\text{C}$ ) which makes it a good solvent for covalent compounds but a poor solvent for electrovalent compounds.

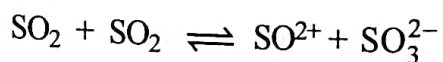
The characteristic physical properties of liquid sulphur dioxide are given in Table 8.

TABLE 8

Some Characteristic  
Physical Properties of Liquid Sulphur Dioxide

Properties	Values
Freezing point	$-75.5^\circ\text{C}$
Boiling point	$-10.1^\circ\text{C}$
Density	$1.46 \text{ g ml}^{-1} (-10^\circ\text{C})$
Dielectric constant	$17.4 (-20^\circ\text{C})$
Dipole moment	$1.61 \text{ Debye}$
Viscosity	$0.428 \text{ centipoise } (-10^\circ\text{C})$
Specific conductance	$4 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1} (-10^\circ\text{C})$

**Autoionisation.** By analogy with water and liquid ammonia, autoionisation of sulphur dioxide takes place as under :



The thionyl ion ( $\text{SO}^{2+}$ ) is analogous to the hydronium ion ( $\text{H}_3\text{O}^+$ ) and ammonium ion ( $\text{NH}_4^+$ ) while sulphite ion ( $\text{SO}_3^{2-}$ ) corresponds to hydroxyl ion ( $\text{OH}^-$ ) and amide ion ( $\text{NH}_2^-$ ) of the aqueous and liquid ammonia systems, respectively.



Sulphur dioxide solutions are not as good electrical conductors as are liquid ammonia solutions or aqueous solutions.

**Solubility of Substances in Liquid Sulphur Dioxide.** Amongst the **inorganic compounds**, iodides and alkylates are the most soluble. Metal sulphates, sulphides, oxides and hydroxides are practically insoluble. Many of the ammonium, thallium and mercuric salts are soluble. Liquid sulphur dioxide is an excellent solvent for covalent compounds. Substances such as  $\text{IBr}$ ,  $\text{PBr}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{SnCl}_4$  are soluble in it. **Metals** are insoluble in liquid sulphur dioxide.

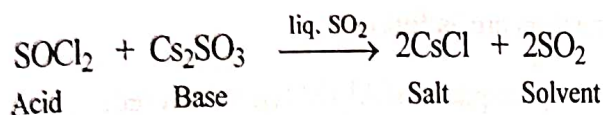
Amongst the **organic compounds**, benzene and alkenes dissolve in it freely. Pyridine, quinoline, ethers, halogen derivatives and acid chlorides also dissolve in liquid sulphur dioxide. Alkanes are insoluble.

**Reactions in Liquid Sulphur Dioxide.** Chemical reactions that occur in liquid sulphur dioxide are of the following types :

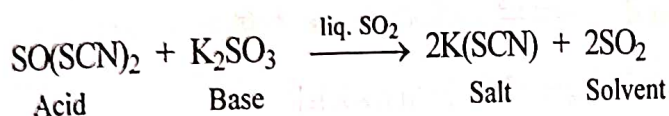
**1. Acid-base Reactions or Neutralisation Reactions.** Comparing the autoionisation of liquid sulphur dioxide with that of water, it can be seen that thionyl ion ( $\text{SO}^{2+}$ ) is analogous to hydronium ion ( $\text{H}_3\text{O}^+$ ) and sulphite ion  $\text{SO}_3^{2-}$  is analogous to hydroxyl ion ( $\text{OH}^-$ ). Hence, all compounds containing or making available  $\text{SO}_3^{2-}$  ions in liquid sulphur dioxide will act as bases in this medium. Similarly, all compounds which make available  $\text{SO}^{2+}$  ions in liquid sulphur dioxide will act as typical acids in liquid sulphur dioxide.

Typical acid-base or neutralisation reactions in liquid sulphur dioxide are given below.

Reaction between thionyl chloride and cesium sulphite :

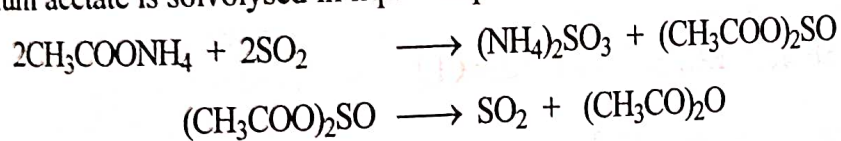


Reaction between thionyl thiocyanate and potassium sulphite.

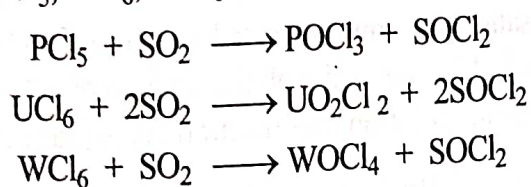


**2. Solvolytic Reactions.** Only a limited number of salts undergo solvolysis in liquid sulphur dioxide. Some common reactions are given below.

Ammonium acetate is solvolysed in liquid sulphur dioxide.

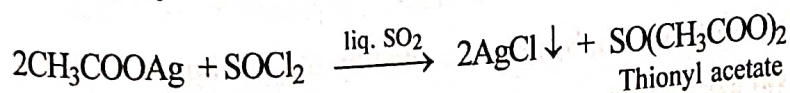


Binary halides such as  $\text{PCl}_5$ ,  $\text{UCl}_6$ ,  $\text{WCl}_6$  undergo solvolysis in liquid sulphur dioxide.

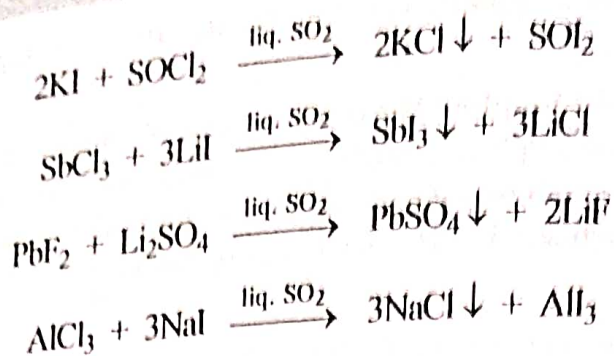


The formation of solvates, *i.e.*, the addition compounds with the solvent, is also known. Typical solvates formed are  $\text{NaI} \cdot 4\text{SO}_2$ ,  $\text{RbI} \cdot 4\text{SO}_2$ ,  $\text{KBr} \cdot 4\text{SO}_2$ ,  $\text{CaI}_2 \cdot 4\text{SO}_2$ ,  $\text{BaI}_2 \cdot 4\text{SO}_2$ ,  $\text{SrI}_2 \cdot 4\text{SO}_2$ ,  $\text{AlCl}_3 \cdot 2\text{SO}_2$ , etc.

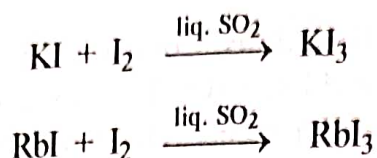
**3. Precipitation Reactions.** A large number of precipitation reactions can be carried out in liquid sulphur dioxide due to specific solubility relationships. Some of these reactions are given below.



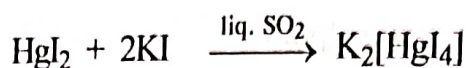




**4. Complex Formation Reactions.** A large number of complex formation reactions of liquid sulphur dioxide have been reported. For instance, the solubility of iodine in liquid sulphur dioxide is greatly increased by the addition of potassium or rubidium iodide. This is due to the formation of the complex  $\text{KI}_3$  or  $\text{RbI}_3$ .

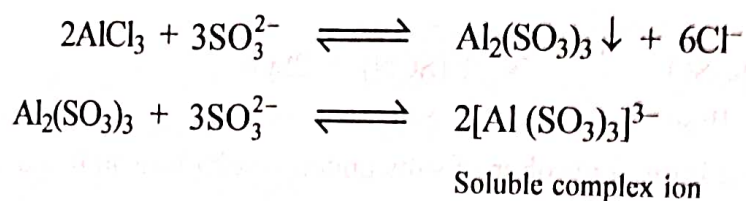


Similarly, the increase in the solubility of cadmium iodide and mercuric iodide in liquid sulphur dioxide is attributed to the formation of complexes.

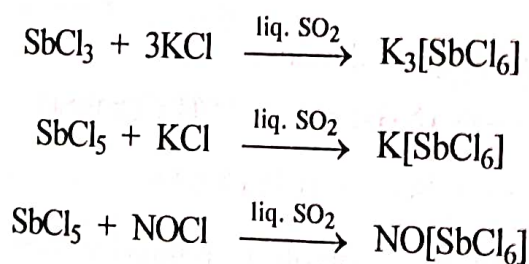


Some other examples of complex formation are as follows :

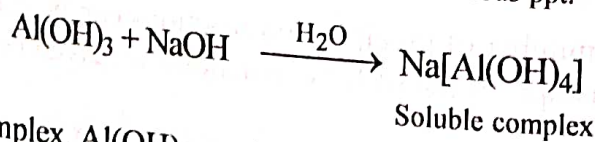
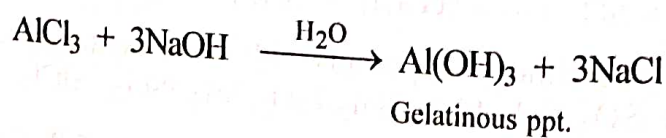
$\text{AlCl}_3$  reacts with  $\text{SO}_3^{2-}$  ions to form a precipitate of  $\text{Al}_2(\text{SO}_3)_3$  which redissolves in excess of  $\text{SO}_3^{2-}$  ions forming the complex ion  $[\text{Al}(\text{SO}_3)_3]^{3-}$ .



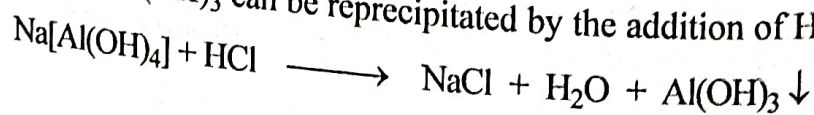
Similarly,



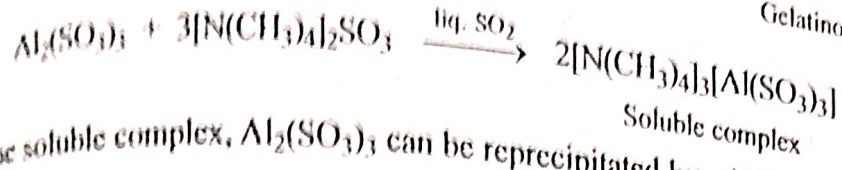
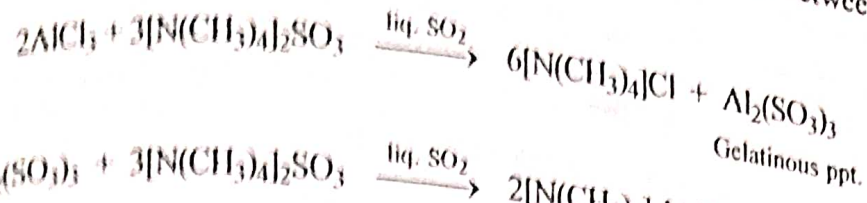
**5. Amphoteric Behaviour.** Various salts show amphoteric behaviour in liquid sulphur dioxide. The reaction of  $\text{AlCl}_3$  with  $\text{NaOH}$  in aqueous medium can be compared with the reaction of  $\text{AlCl}_3$  with tetramethyl ammonium sulphite in liquid sulphur dioxide. In aqueous solution, the reaction takes place as follows.



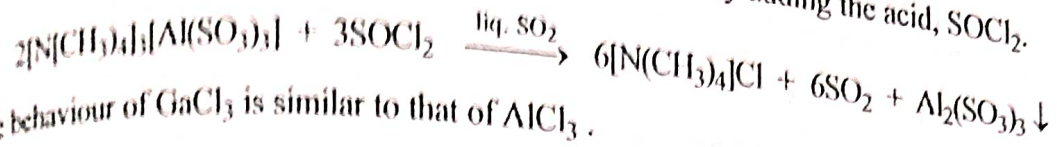
From the soluble complex,  $\text{Al}(\text{OH})_3$  can be reprecipitated by the addition of  $\text{HCl}$ .



In liquid sulphur dioxide medium, an identical reaction takes place between  $\text{AlCl}_3$  and tetramethyl ammonium sulphite :

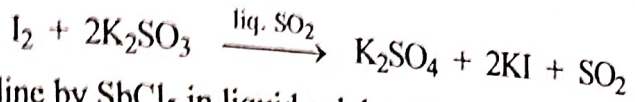


From the soluble complex,  $\text{Al}_2(\text{SO}_3)_3$  can be reprecipitated by adding the acid,  $\text{SOCl}_2$ .

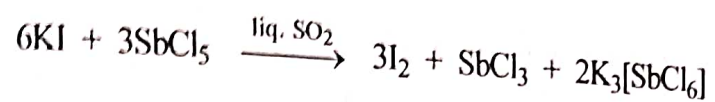


The behaviour of  $\text{GaCl}_3$  is similar to that of  $\text{AlCl}_3$ .

**6. Redox Reactions.** Liquid sulphur dioxide does not have any strong oxidising or reducing properties. It serves only as a medium for redox reactions. For instance, liquid sulphur dioxide cannot reduce iodine. However, a sulphite in liquid sulphur dioxide reduces iodine to iodide. Thus,



KI is oxidised to free iodine by  $\text{SbCl}_5$  in liquid sulphur dioxide.



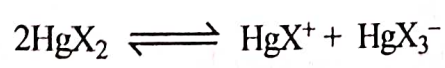
### MOLTEN SALTS AS NON-AQUEOUS SOLVENTS

The molten salts which act as non-aqueous solvents can be divided into two categories, viz.,

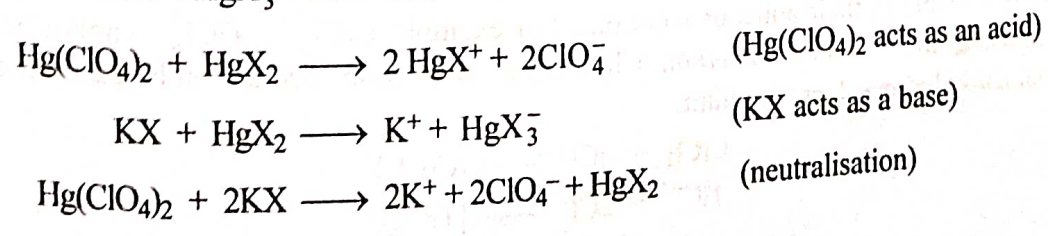
1. High Temperature Molten Salts
2. Room Temperature Molten Salts

**1. High Temperature Molten Salts.** This category contains melts of compounds containing mainly ionic bonds, e.g., alkali halides. The coordination number of the ions drops from 6 in solids to 4 in their melts. The long range lattice symmetry is destroyed in the molten state of such salts but the short range symmetry around the ions still exists. Ionic compounds can be dissolved in such melts giving rise to highly conducting solutions. The cryoscopic technique can be applied to determine the number of ions of the solute. For example, the number of ions of KF in molten sodium chloride is 2 and of  $\text{BaF}_2$  is 3. But the number of ions of NaF in molten NaCl comes out to be 1 by the cryoscopic method because the  $\text{Na}^+$  ion of solute is common with the  $\text{Na}^+$  ion of molten NaCl solvent.

Another type of molten salts are melts of covalently bonded compounds although some autoionisation may occur in such compounds also. The example is the autoionisation of molten  $\text{HgX}_2$  :

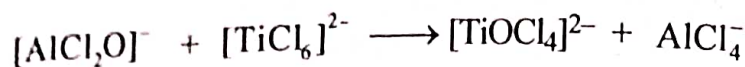
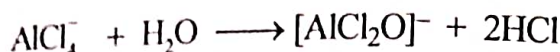


Thus, any substance which increases the concentration of  $\text{HgX}^+$  behaves as an acid and any substance which increases the concentration of  $\text{HgX}_3^-$  behaves as a base. Other examples are :





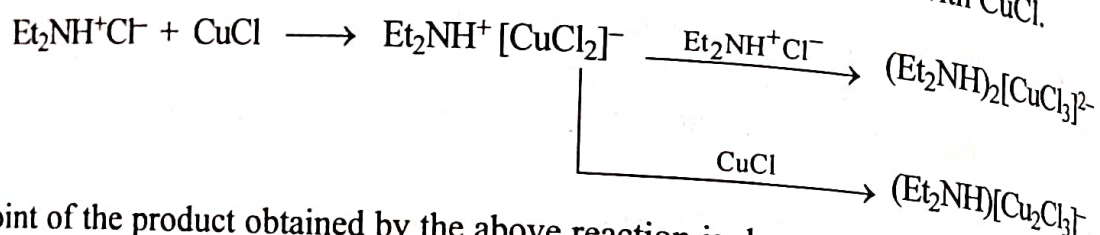
2. Room Temperature Molten Salts. Some chloroaluminates such as  $[R-N\text{C}_6\text{H}_5]^+ [AlCl_4]^-$  are liquids at room temperature and can be used as solvents for many ionic compounds. But a serious limitation of such liquid chloroaluminate solvents is that they are highly hygroscopic and hydrolyse readily. The hydrolysed chloroaluminates may further react with the dissolved salts to produce their oxidised products.



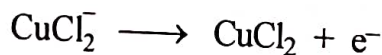
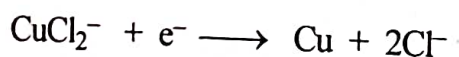
However, the oxygen of the oxidised product can be quantitatively removed by passing phosgene into the solution of the salt in the chloroaluminate melt.



Another salt which is liquid at room temperature is obtained by reacting  $Et_2NH^+Cl^-$  with  $CuCl$ .



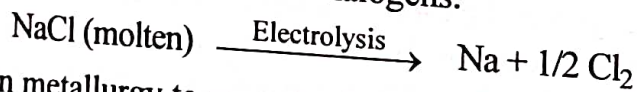
The low melting point of the product obtained by the above reaction is due to the presence of a mixture of salts such as  $Et_2NH^+[CuCl_2]^-$ ,  $(Et_2NH^+)_2[CuCl_3]^{2-}$ , in the product. This solvent can be easily reduced and can also be easily oxidised.



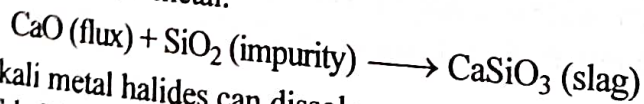
Therefore, the species which are even mildly oxidising or mildly reducing cannot be studied in this solvent. Moreover, all reactions to be studied in this solvent have to be carried out in the absence of air.

### Utility of Molten Salts as Solvents

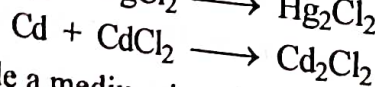
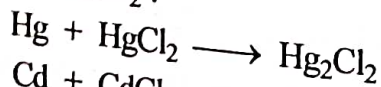
1. The highly reacting solutes which cannot be studied in reactive solvents can be studied in molten salts. For example, the halogens which cannot be studied in water can be conveniently studied in molten halides.
2. Molten halides are used for the production of halogens.



3. Molten salts are used in metallurgy to remove silica as slag which is in molten state at the temperature required for extraction of the metal.



4. Molten alkali metal halides can dissolve any amount of the corresponding alkali metal. However, molten halides of Zn, Cd, Hg dissolve the corresponding metal to a smaller extent. It is assumed that the metal dissolved in metal halides loses electrons so that the solution becomes reducing. That is why Cd and Hg reduce a part of molten  $HgCl_2$  and  $CdCl_2$ .



5. The molten salts provide a medium in which the concentration of anionic ligands can be much more than is possible in their aqueous solutions. For example,  $CrCl_6^{3-}$ ,  $TiCl_6^{3-}$  cannot be isolated from aqueous solutions as these species immediately hydrolyse. But, these species can be easily prepared by using molten metal chlorides as solvent medium.

