

## LIQUID AMMONIA AS NON-AQUEOUS SOLVENT

### Physical properties of Ammonia:

Melting Point	-77.74 <sup>0</sup> C
Boiling Point	-33.35 <sup>0</sup> C
Density	0.690 g cm <sup>-3</sup> at -40 <sup>0</sup> C
Dielectric Constant	22.0 at -33.5 <sup>0</sup> C

H-Bonding exists between the molecules of Ammonia but extent is very less as compare to the H-Bonding of water molecules. This is responsible for the lower values of melting and boiling point.

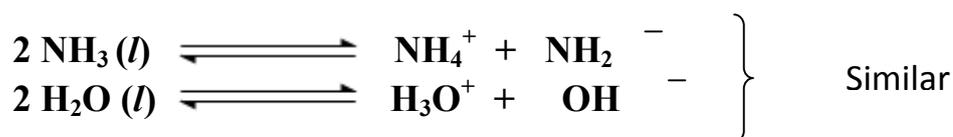
It is also observed that the dielectric constant of Ammonia is also less than the dielectric constant of water. As a result liquid ammonia has the ability to dissolve compounds which are non polar in nature such as organic compounds. But it acts as poor solvent for the ionic compounds as compare with water. Due to difference in the solubility of various compounds, there are some syntheses which are restricted in water but can be easily carried out in ammonia.

Ammonia is also very basic solvent. As a result it functions as the useful solvent for a variety of acidic substances.

**Reactions in Liquid Ammonia:** Chemical Reactions which occur in Liquid Ammonia can be classified as follows:

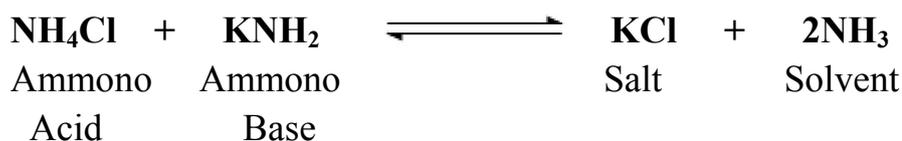
1. Acid-Base Reactions
2. Precipitation Reactions
3. Ammonolysis Reactions
4. Ammoniation Reactions
5. Redox Reactions
6. Complex formation Reaction

#### (1) Acid Base Reactions:

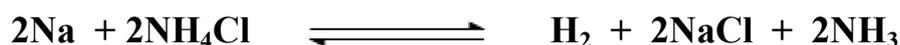


Auto ionisation of ammonia generates ammonium ion and amide ion. Ammonium ion is counterpart of hydronium ion in aqueous medium. Similarly

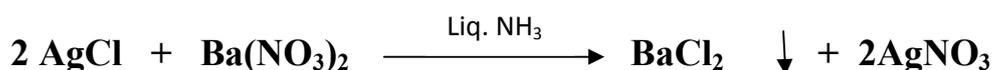
amide ion is counterpart of hydroxyl ion in aqueous medium. On the basis of similarity, it can be said that the ammonium salts which yield ammonium ions in liquid ammonia will act as acids whereas metal amides which yield amide ions will act as base. Such acids are known as “Ammono Acids” and bases are known as “Ammono Base”. When these two are mixed with each other then the resultant reaction is known as Neutralization Reaction results in formation of salt and solvent.



The acidic nature of ammonium salts in liquid ammonia is further confirmed from the release of hydrogen from reactions of these solutions with some active metals such as Na, K and Ca.

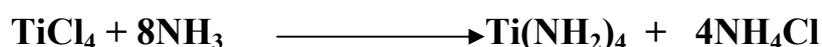


- (2) **Precipitation Reaction:** Precipitation reaction depends upon the solubility of reaction product in given solvent. Due to this the nature of precipitation reaction depends upon the nature of solvent. Because of the differences of solubilities of various substances in liquid ammonia and water, a number of reactions which do not take place in water, can be carried out in Liquid Ammonia.



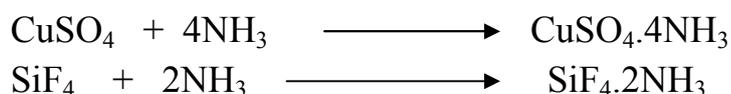
The above reaction proceeds in forward direction due to insolubility of Barium chloride in Liquid Ammonia.

- (3) **Ammonolysis Reactions:** As we know that water hydrolyses certain metal halides to basic salts, similarly Liquid ammonia ammonolyses some salts to Ammono basic salts.



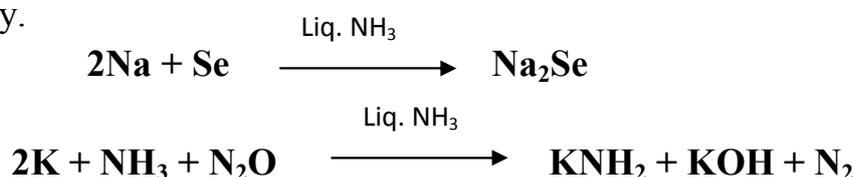
- (4) **Ammoniation Reactions:** When a solute is dissolved in liquid ammonia and the resultant solid product contains a number of molecules of

ammonia, then such reaction is known as Ammoniation reaction. It is an example of solvation reaction. In this case the solvent is ammonia.

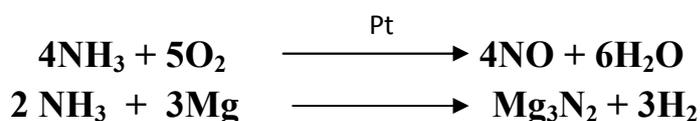


(5) **Redox Reaction:** Redox Reactions can be classified in three categories:

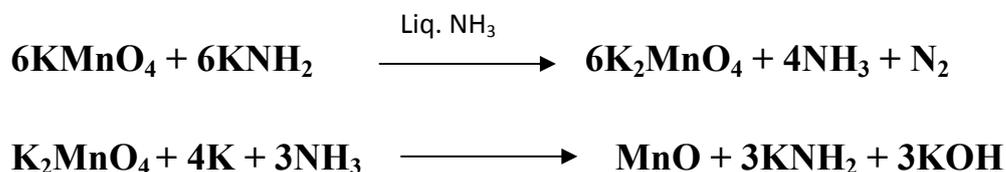
**a. When alkali metals act as reducing agent in liquid ammonia:** Dilute solutions of alkali metal in liquid ammonia have a deep blue colour. These are good conductor of electricity, paramagnetic and show strong reducing property.



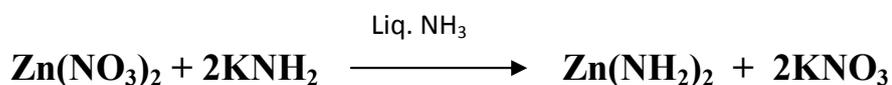
**b. Where liquid ammonia acts as reducing agent:** There are some reactions in which liquid ammonia itself act as reducing agent.

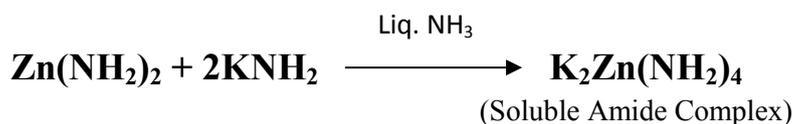


**c. Where liquid ammonia acts as solvent:** There are number of reactions in which Liquid Ammonia acts only as solvent. Potassium permanganate which act as strong oxidising agent in water, behaves as weak oxidising agents in Liquid Ammonia.



(6) **Complex formation reaction:** Numerous Complex formation reactions also take place in Liquid Ammonia. These reactions are akin to the reactions occurring in aqueous system.





***Solution of Alkali Metals in liquid Ammonia:***

Liquid Ammonia has a unique ability to dissolve alkali metals. These alkali metal solutions in liquid ammonia are blue in colour. Characteristic Properties of these solutions are as follows:

- (1) Colour of the solutions is independent of alkali metal involved.
- (2) Paramagnetic character of solutions shows the presence of number of unpaired electrons.
- (3) Density of the solution is similar to that of pure liquid ammonia.
- (4) Alkali metal solutions dissociate to form alkali metal cations and ammoniated electrons.

***Advantages of liquid ammonia as a solvent:***

Advantages of liquid ammonia as a solvent are as follows:

- (1) Ability to dissolve alkali metal is a great advantage of liquid ammonia.
- (2) These alkali metal solutions are strong reducing agent.
- (3) Ammonium salts dissolved in liquid ammonia has very important application in preparative chemistry. Sulphides, halides and sulphates can be precipitated by using these solutions.
- (4) Solvolysis is lesser as compare with water.

***Disadvantages of liquid ammonia as a solvent:***

Disadvantages of liquid ammonia as a solvent are as follows:

- (1) In order to work with liquid ammonia, low temperature and high pressure is required, which require special equipment and technique.
- (2) Ammonia is hygroscopic in nature. So special care needs to be taken to exclude moisture from reaction mixture.
- (3) It has very obnoxious smell.

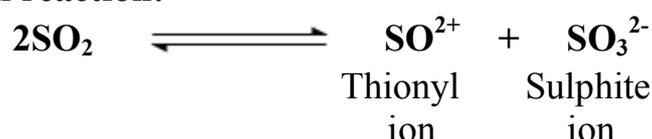
## LIQUID SULPHUR DIOXIDE AS NON-AQUEOUS SOLVENT

### Physical properties of Sulphur Dioxide:

Melting Point	-75.46 <sup>0</sup> C
Boiling Point	-10.02 <sup>0</sup> C
Density	1.46 g ml <sup>-1</sup> at -10 <sup>0</sup> C
Dielectric Constant	15.4 at 0 <sup>0</sup> C

Sulphur Dioxide is one of the most important non-protonic solvent. It is very weakly associated molecule due to lack of hydrogen bonding in the compound. It also has very low dielectric constant which makes it suitable solvent for covalent compounds.

### **Auto-Ionisation reaction:**



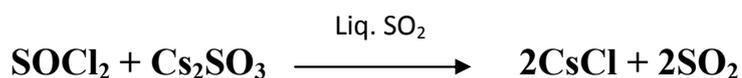
Compounds which release Thionyl ion, will behave as acids while compounds which release sulphite ion, will behave as bases.

**Reactions in Liquid Sulphur Dioxide:** Chemical Reactions which occur in Liquid Sulphur Dioxide can be classified as follows:

1. Acid-Base Reactions
2. Solvolytic Reactions
3. Precipitation Reactions
4. Solvation Reactions
5. Complex Formation Reactions
6. Redox Reactions

(1) **Acid-Base Reactions:** In Auto-Ionisation reaction, we have seen that the compounds which make available Thionyl ion, will behave as acids whereas compounds which make available sulphite ion will behave as bases. Reaction between such compounds are known as Acid-Base Reaction or neutralization reaction



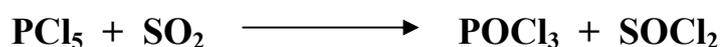


- (2) **Solvolytic reactions:** Solvolytic reactions are not very common in liquid Sulphur Dioxide. A limited number of solvent undergo Solvolytic reaction in liquid sulphur dioxide.

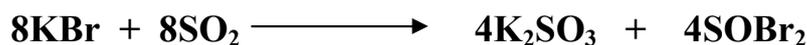
Ammonium Acetate is solvolysed in sulphur dioxide as follows:



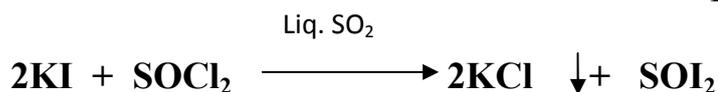
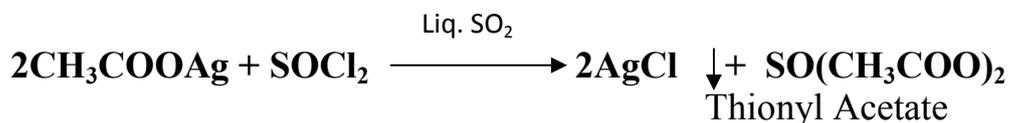
Solvolysis of Binary Halides:



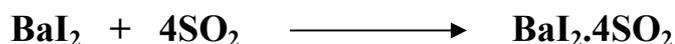
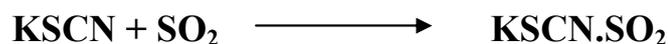
Solvolysis of Alkali Metal Halides



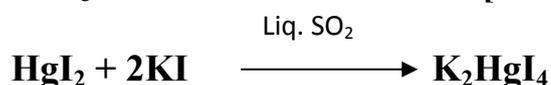
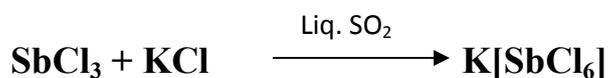
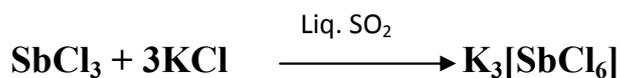
- (3) **Precipitation Reactions:** Several Precipitation reactions can be easily carried out in liquid sulphur dioxide. Precipitation reactions depend upon the relative solubility of reaction products in given solvent. Some reactions are as follows:



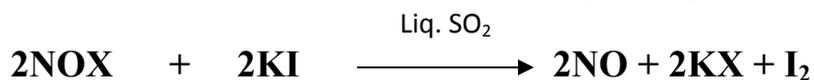
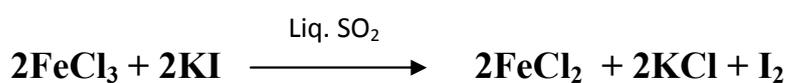
- (4) **Solvation Reactions:** In this reaction a particular number of solvent molecules are attached with solute and form solid product. Some examples of solvates in the sulphur Dioxide are as follows:



- (5) **Complex Formation Reactions:** Examples of complex formation reaction in liquid  $\text{SO}_2$  are as follows:



- (6) **Redox Reactions:** Although liquid Sulphur Dioxide does not behave as oxidising agent or reducing agent itself, but it act as medium to carry out redox reaction. Examples of redox reactions are as follows:



Nitrosyl  
Compound

Where  $\text{X}=\text{Cl}^-$ ,  $\text{BF}_4^-$

Nitrosyl Compounds acts as oxidising agent in liquid sulphur dioxide in above example.