

Non-aqueous Solvents

Introduction

Most of the chemical reactions familiar to us take place in aqueous solution, since water, due to 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 sizeable 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_2O_4 etc.

Classification of solvents

Solvents have been classified in a number of ways, depending on the properties of the solvents.

First classification

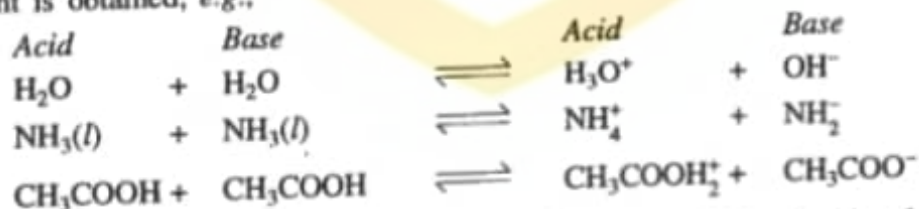
This classification is based on the proton-donating and proton-accepting ability of the solvent. This classification gives the following types of solvents. All these solvents contain hydrogen in their formula.

1. Protic or protonic solvents. These solvents either lose protons or gain them or can show both the tendencies. Thus these solvents are of three types:

(a) *Acidic (proto-genic) solvents.* These can lose protons readily. Examples are HF , H_2SO_4 , HCOOH , HCN , $\text{C}_6\text{H}_5\text{COOH}$, CH_3COOH etc.

(b) *Basic (proto-philic) solvents.* These can accept proton, e.g., NH_3 , N_2H_4 , NH_2OH , amines 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.,



2. Non-protic or non-protonic or aprotic solvents. These can neither lose nor gain the protons, e.g., C_6H_6 , CHCl_3 , CH_2Cl_2 , CCl_4 etc.

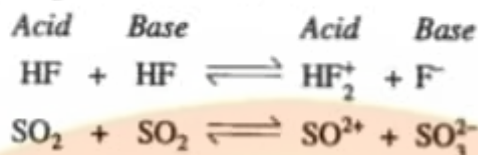
Second classification

This classification is based on the polar and non-polar nature of the solvents. This classification gives the following types of solvents.

1. Ionising, ionic or polar solvents (e.g., H_2O , NH_3 , HF etc.) (a) These have high polarity and high dielectric constants.

(b) They dissolve ionic compounds and initiate ionic reactions.

(c) They can undergo auto-ionisation. Auto-ionisation of H_2O and NH_3 has already been shown while that of HF and SO_2 is shown below:



(d) Polar solvents tend to associate due to the dipole-dipole interactions. The association is more effective in case of protonic solvents (protonic solvents are those which contain hydrogen) due to hydrogen bonding and leads to a higher b.pt. and increases the liquid state range of the solvent.

2. Non-ionising or non polar solvents. (e.g., C_6H_6 , CCl_4 etc.) (a) These have low dipole moment and low dielectric constants.

(b) They dissolve non-ionic (covalent) compounds and cannot initiate ionic reactions.

Third classification

Water is called *aqueous solvent* while all others (e.g., NH_3 , SO_2 , HF , C_6H_6 , CHCl_3 etc.) are called *non-aqueous solvents*.

Relation between the dielectric constant (K) of an ionising solvent and the solubility of an ionic salt (solute) in it

Let us consider an ionic substance (solute) which is composed of cations and anions having their charges equal to c^+ and a^- respectively and separated from each other by a distance equal to r . Obviously r will be equal to the sum of the radii of the cation (r_+) and the anion (r_-). Let the ionic substance be placed in an ionising solvent of dielectric constant equal to K . From Coulomb's law, the force of attraction (F) between the cations and anions is given (in cgs units) by the expression:

$$F = \frac{c^+ \times a^-}{K r^2} = \frac{c^+ \times a^-}{K (r_+ + r_-)}$$

K is a dimensionless number and is a measure of the decrease in the intensity of the electric field between two charges in presence of the dielectric medium than in vacuum.

The above equation shows that F and K are inversely proportional to each other. This means that if the value of K for a solvent is high, the force between the ions of the solute is very low and hence the solvent will dissolve the solute quickly. Thus a solvent with a high value of K (e.g., water and anhydrous HF) has an increased ability to dissolve the ionic or polar compound. On the other hand a solvent with a low value of K (e.g., liq. NH_3 and liq. SO_2) shows almost no ability to dissolve the ionic compounds especially those containing multi-charged ions like oxides, sulphates, carbonates, sulphates and phosphates.

Relation between the dielectric constant (K) and dipole moment (D) of an ionising solvent

These two constants of an ionising solvent are closely related to each other. It has been seen that if an ionising solvent has a large value of its dielectric constant, the value of its dipole moment will also be large. This is evident from the following data:

<i>Solvent</i>	<i>Dipole moment (in Debye units)</i>	<i>Dielectric constant</i>
Hydrogen cyanide	2.93	106.8 (25°C)
Hydrogen fluoride	1.91	83.6 (0°C)
Water	1.84	78.5 (25°C)
Ethyl alcohol	1.69	24.2 (25°C)
Sulphur dioxide	1.63	17.4 (–19°C)
Ammonia	1.46	22.0 (–34°C)

Physical properties of water, ammonia and sulphur dioxide

These are given below :

<i>Properties</i>	<i>Water</i>	<i>Ammonia</i>	<i>Sulphur dioxide</i>
Boiling point (0°C)	100	– 34.00	– 10.0
Freezing point (0°C) (Melting point)	0.0	–77.7	–75.5
Density (g.ml ^{–1})	1.0 (4°C)	0.68 (at b.pt.)	1.46 (–10°C)
Dielectric constant	78.5 (25°C)	22.0 (at b.pt.)	17.4 (–20°C)
Specific conductance (Ohm ^{–1} cm ^{–1})	6.0×10^{-8} (25°C)	0.5×10^{-8} (at b.pt.)	4×10^{-8} (–10°C)
Viscosity (centipoise)	0.959 (25°C)	0.254 (at b.pt.)	0.428
Dipole moment (Debye)	1.85	1.47	1.61 (–10°C)

Introduction

Liq. NH_3 is a protonic solvent, since it gives a proton (H^+) on ionisation ($\text{NH}_3 \rightarrow \text{H}^+ + \text{NH}_2^-$). It is a highly useful solvent and a number of chemical reactions are carried out in this medium. The value of dielectric constant of liq. NH_3 (= 22.0 at –34°C) is much smaller than that of water (= 78.5 at 25°C) and hence liq. NH_3 has decreased ability to dissolve ionic compounds. The liquid range for liq. NH_3 is from –34.0°C to –77.7°C (b.pt. = –34.0°C, m.pt. = –77.7°C).

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_3 , NH_4SCN , $\text{CH}_3\text{COONH}_4$ etc.) and most of the nitrites, nitrates, cyanides, thiocyanates, 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 ($\text{MF} < \text{MCl} < \text{MBr} < \text{MI}$). 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.

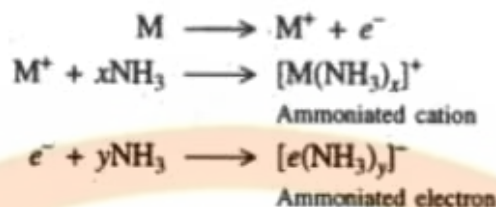
(b) **Solubility of non-ionic compounds (organic compounds).** Halogen compounds, alcohols, ketones, esters, simple ethers, amines, phenol and its derivatives etc. are soluble. Alkanes are insoluble and alkenes and alkynes are slightly soluble. In this sense, liq. NH_3 is a better solvent for non ionic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

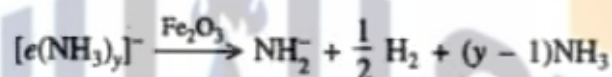
(d) **Solubility of alkali metals and alkaline earth metals.** All the alkali metals and alkaline earth metals (excepting Be) are soluble in liq. NH_3 . 100g. of liq. NH_3 dissolves 10.9g of Li,

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 ($\text{Li} < \text{Na} < \text{K} < \text{Cs}$). The solution obtained by dissolving alkali metals in liq. NH_3 has the following characteristics:

(i) *Colour of the solution.* The colour of the dilute solution is deep blue. As the concentration of the solution increases, the blue colour changes to bronze which disappears on the further increase of the concentration of the solution. The colour of the solution is independent of the metal dissolved in liq. NH_3 . The blue colour of the dilute solution is due to the formation of ammoniated metal cation and ammoniated electron in it.



(ii) *Decomposition of very dilute solution.* Very dilute solution of the alkali metals in liq. NH_3 is meta stable, since in presence of a catalyst like Fe_2O_3 its ammoniated electron undergoes decomposition.



(iii) *Evaporation of the solution.* When alkali metal-ammonia solution is evaporated, alkali metal dissolved in the solution is recovered.

(iv) *Paramagnetic character.* Dilute solution of alkali metals in liq. NH_3 is paramagnetic which is due to the presence of unpaired ammoniated electrons in the solution. The susceptibility of the solution falls down as the concentration of the solution increases and ultimately the solution becomes diamagnetic. Paramagnetism reappears at higher concentration of the solution.

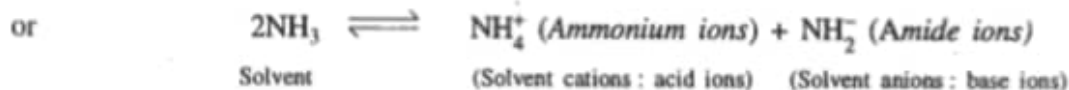
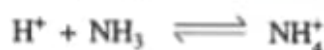
(v) *Electrical conductivity.* The electrical conductivity of very dilute solutions is high and is in the range of fully ionised salts in water. The high conductivity is due to the presence of ammoniated electrons in the solution. It decreases with concentration upto about 0.05M, but then rises sharply. The concentrated bronze solution has conductivities in the range of metals.

(vi) *Density.* Dilute solution has very low density. Low density is due to the fact that ammoniated electrons present in the solution are supposed to occupy the cavities or holes within ammonia molecules.

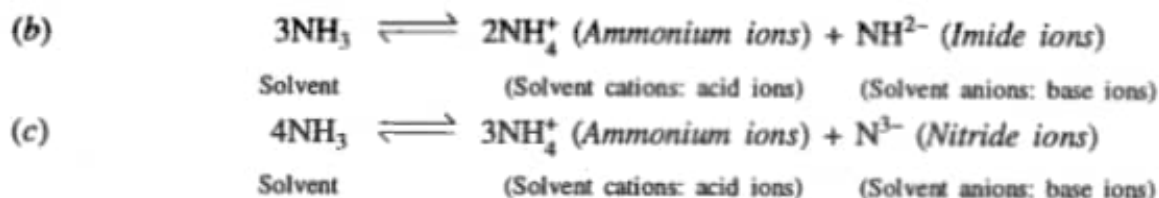
(vii) *Reducing property of dilute solution.* We have said above that the blue solution of alkali metals in liq. NH_3 contains ammoniated electrons. These ammoniated electrons reduce various substances. Thus dilute solutions of alkali metals are reducing agents. The reactions showing the reducing property of alkali metals in liq. NH_3 have been discussed on page 478. In these reactions the alkali metal is oxidised to some alkali metal salt.

Auto-ionisation of liq. NH_3

Liq NH_3 ionises in the following three ways :



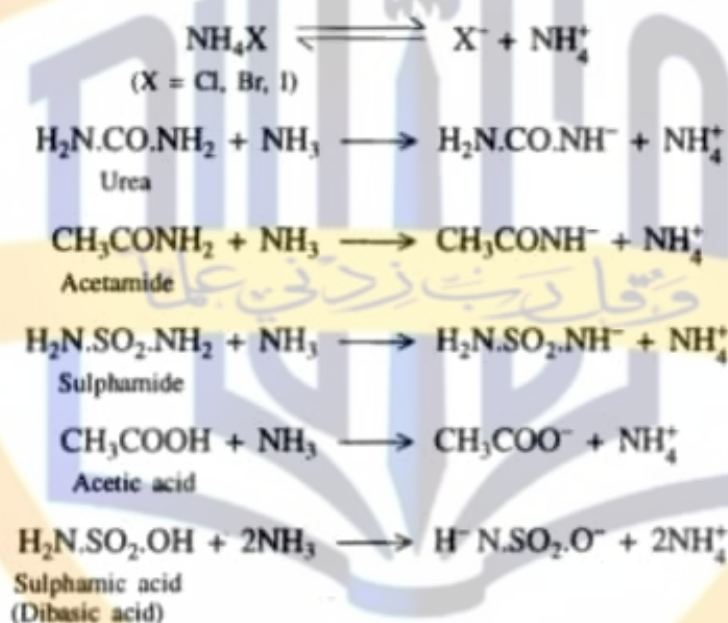
$$K_b = [\text{NH}_4^+][\text{NH}_2^-] = 1.9 \times 10^{-33} \text{ at } -50^{\circ}\text{C}.$$



Different modes of auto-ionisation of liq. NH_3 , given above, indicate that, according to solvent system concept, in liq. NH_3 , any substance that gives NH_4^+ ions (which are solvent cations) will act as an acid in liq. NH_3 , while that which produces NH_2^- or NH^{2-} or N^{3-} ions (which are solvent anions) will behave as a base in liq. NH_3 . The compounds which give NH_4^+ ions in liq. NH_3 are called *ammono acids*, while those which give NH_2^- or NH^{2-} or N^{3-} ions in this solvent are called *ammono bases*.

Examples of ammono acids

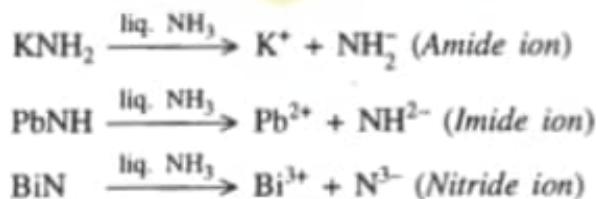
Ammonium salts [e.g., NH_4Cl , NH_4Br , NH_4I , NH_4NO_3 , $(\text{NH}_4)_2\text{S}$ etc.], organic amides (e.g., urea, acetamide, sulphamide etc.), acetic acid, sulphamic acid etc., all act as ammono acids in liq. NH_3 , since they produce NH_4^+ ions in this solvent, as shown below:



It may be noted that since $\text{H}_2\text{N.SO}_2\text{.OH}$ produces two ions, this acid behaves as a dibasic acid in liq. NH_3 .

Examples of ammono bases

KNH_2 , PbNH and BiN are the examples of ammono bases, since these compounds give NH_2^- , NH^{2-} and N^{3-} ions respectively in liq. NH_3 .



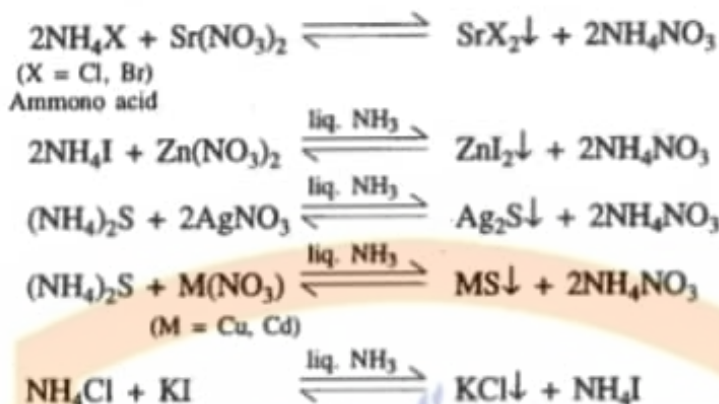
Chemical Reactions Taking Place in Liq. NH_3

Chemical reactions that can take in liq. NH_3 are of the following types :

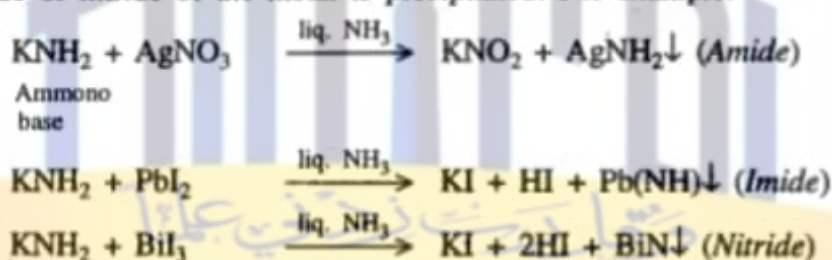
1. Precipitation (metathetical) reactions

Examples of some precipitation reactions that can be carried out in liq. NH_3 are given below:

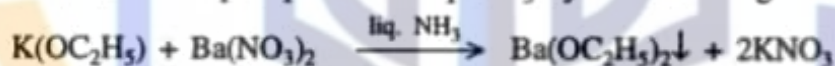
(a) **Precipitation reaction shown by ammono acids in liq. NH_3 .** When an ammono acid like NH_4Cl , NH_4Br , NH_4I , $(\text{NH}_4)_2\text{S}$ etc. is mixed with the liq. NH_3 solution of a metallic salt like $\text{Sr}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, KI etc., the salt of the metal is precipitated. For example :



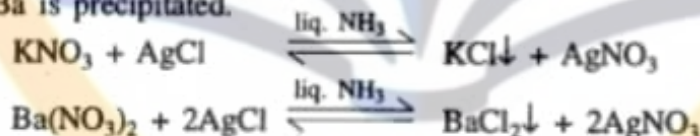
(b) **Precipitation reactions shown by ammono bases in liq. NH_3 .** When an ammono base like KNH_2 is mixed with the liq. NH_3 solution of a metallic salt like AgNO_3 , PbI_2 , BiI_3 etc., the amide, imide or nitride of the metal is precipitated. For example:



Metal alcoholates can be precipitated in liq. NH_3 by the following reaction.

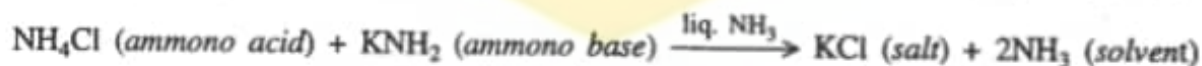


(c) When solutions of the nitrate of K and Ba and of AgCl in liq. NH_3 are mixed together, chloride of K and Ba is precipitated.

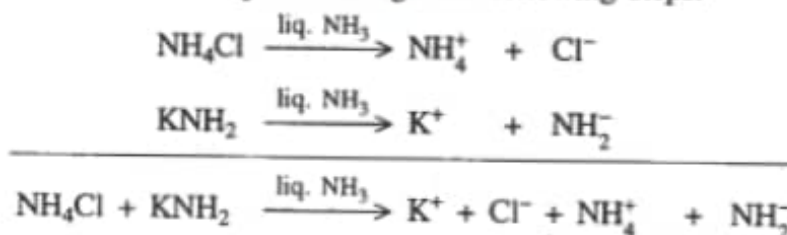


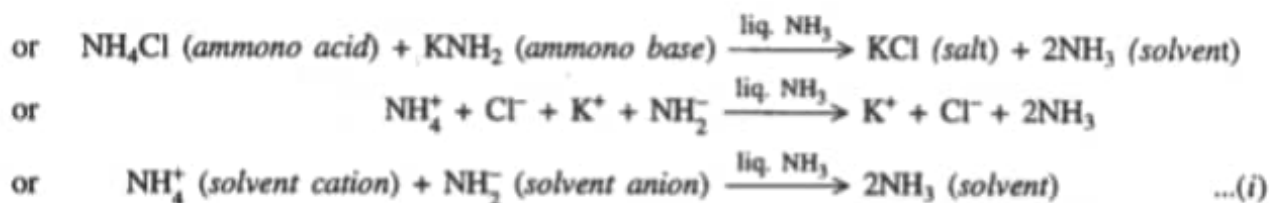
2. Acid-base neutralisation (salt formation) reactions

In liq. NH_3 acid-base neutralisation reaction is that in which a compound containing or making available NH_4^+ ion (*ammono acid*) combines with a compound containing or making available NH_2^- or N_3^{3-} ion (*ammono base*) to form the salt and the solvent (*i.e.*, NH_3), *e.g.*,



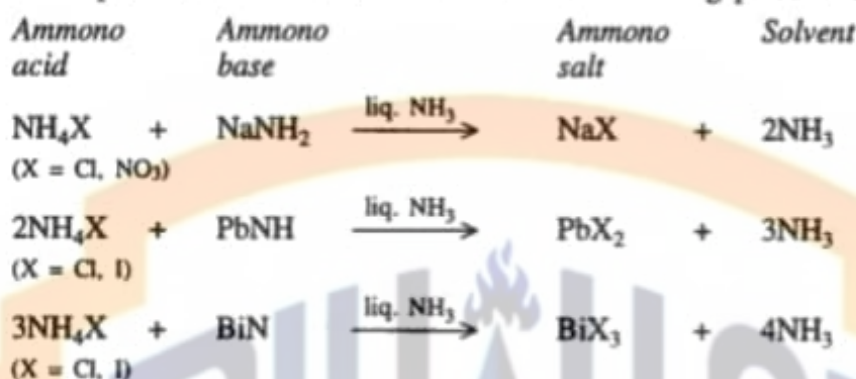
Actually the above reaction takes place through the following steps:





Equation (i) indicates that neutralisation reaction in liq. NH_3 can also be defined as the combination of solvent cation (NH_4^+) and solvent anion (NH_2^-) to form the un-ionised solvent (*i.e.*, liq. NH_3).

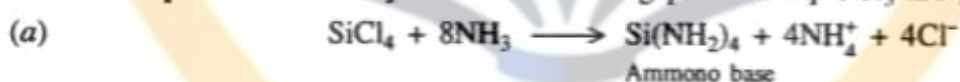
Other examples of acid-base neutralisation reactions taking place in liq. NH_3 are:



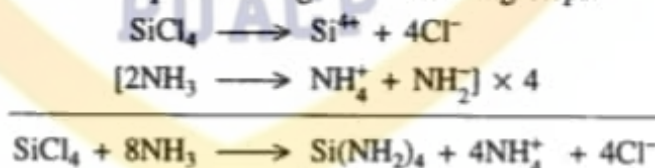
3. Solvolysis (solvolytic) reactions in liq. NH_3 : Ammonolysis or amonolytic reactions

The solvolysis reactions taking place in liq. NH_3 are called ammonolysis reactions. These reactions are analogous to hydrolysis that takes place in aqueous medium. Just as in hydrolysis, the concentration of H_3O^+ or OH^- ions increases due to auto-ionisation of water ($\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$), in ammonolysis the concentration of NH_4^+ or NH_2^- (or NH^{2-} or N^{3-}) ions increases due to the auto-ionisation of liq. NH_3 ($2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$, $3\text{NH}_3 \rightleftharpoons 2\text{NH}_4^+ + \text{NH}^{2-}$, $4\text{NH}_3 \rightleftharpoons 3\text{NH}_4^+ + \text{N}^{3-}$). In these reactions an atom, ion or radical of the compound undergoing ammonolysis is replaced by NH_2^- , NH^{2-} or N^{3-} ion and an ammono base is formed.

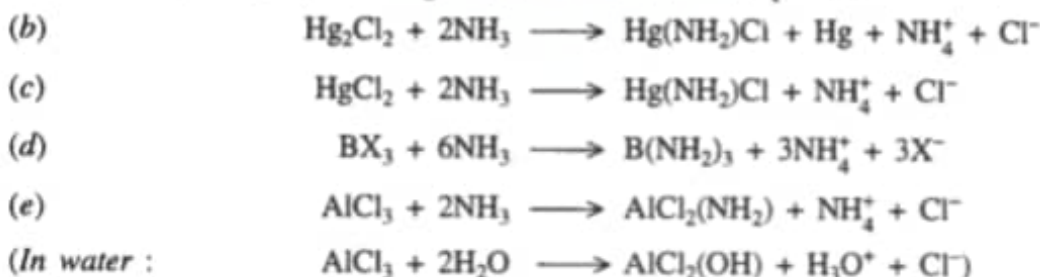
Some examples of ammonolysis reactions taking place in liq. NH_3 are given below:



Actually the above reaction takes place through the following steps:



On the same lines the following reactions can also be explained.





In this reaction Cl-atom of $(\text{SiH}_3)\text{Cl}$ is replaced by N^{3-} ion.

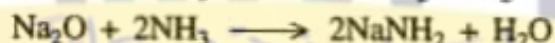
(i) The ammonolysis of TiCl_4 produces $\text{Ti}(\text{NH}_2)_4$ whose formation can be explained as follows :



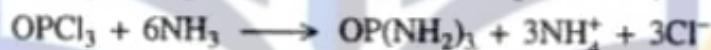
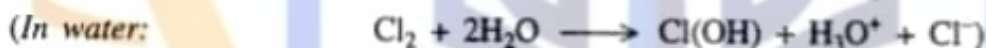
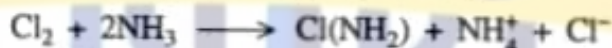
(j) The ammonolysis of alkyl halides, RX (R = alkyl group, $\text{X} = \text{Cl}, \text{Br}, \text{I}$) takes place slowly at the boiling point of liq. NH_3 . In this reaction mixture of primary (RNH_2), secondary (R_2NH) and tertiary (R_3N) amines is obtained.



(k) Alkali metal hydrides (e.g., NaH) and oxides (e.g., Na_2O) undergo ammonolysis to produce alkali metal amides.



(l) Cl_2 and OPCl_3 give $\text{Cl}(\text{NH}_2)$ and $\text{OP}(\text{NH}_2)_3$ respectively.



4. Solvation reactions in liq. NH_3 : Ammoniation reactions and formation of ammoniates

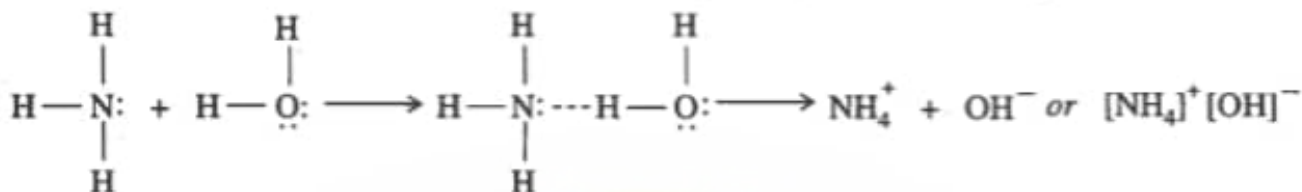
Solvation reaction is a general reaction in which a solute (a cation, an anion or a neutral molecule) reacts with one or more molecules of a solvent (e.g., H_2O , liq. NH_3 , liq. SO_2 etc.) to form a product in which the solute and solvent species are attached to each other by a H-bond or by a coordinate 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_3 , 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*.

In the formation of ammoniates 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.

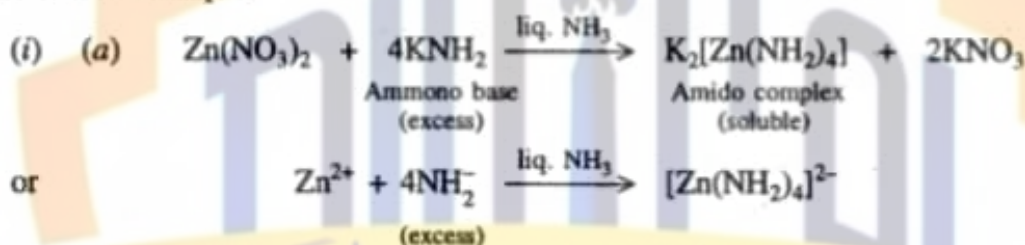
Solute (Lewis acid)	Solvent (Lewis base)	Ammoniates
SO ₃	+ 2NH ₃	→ SO ₃ .2NH ₃ (1 : 2 adduct)
SiF ₄	+ 2NH ₃	→ SiF ₄ .2NH ₃ (1 : 2 adduct)
BF ₃	+ NH ₃	→ BF ₃ .NH ₃ (1 : 1 adduct)

The Formation of NH₄⁺ by the action of liq. NH₃ on H₂O is also an example of ammoniation.

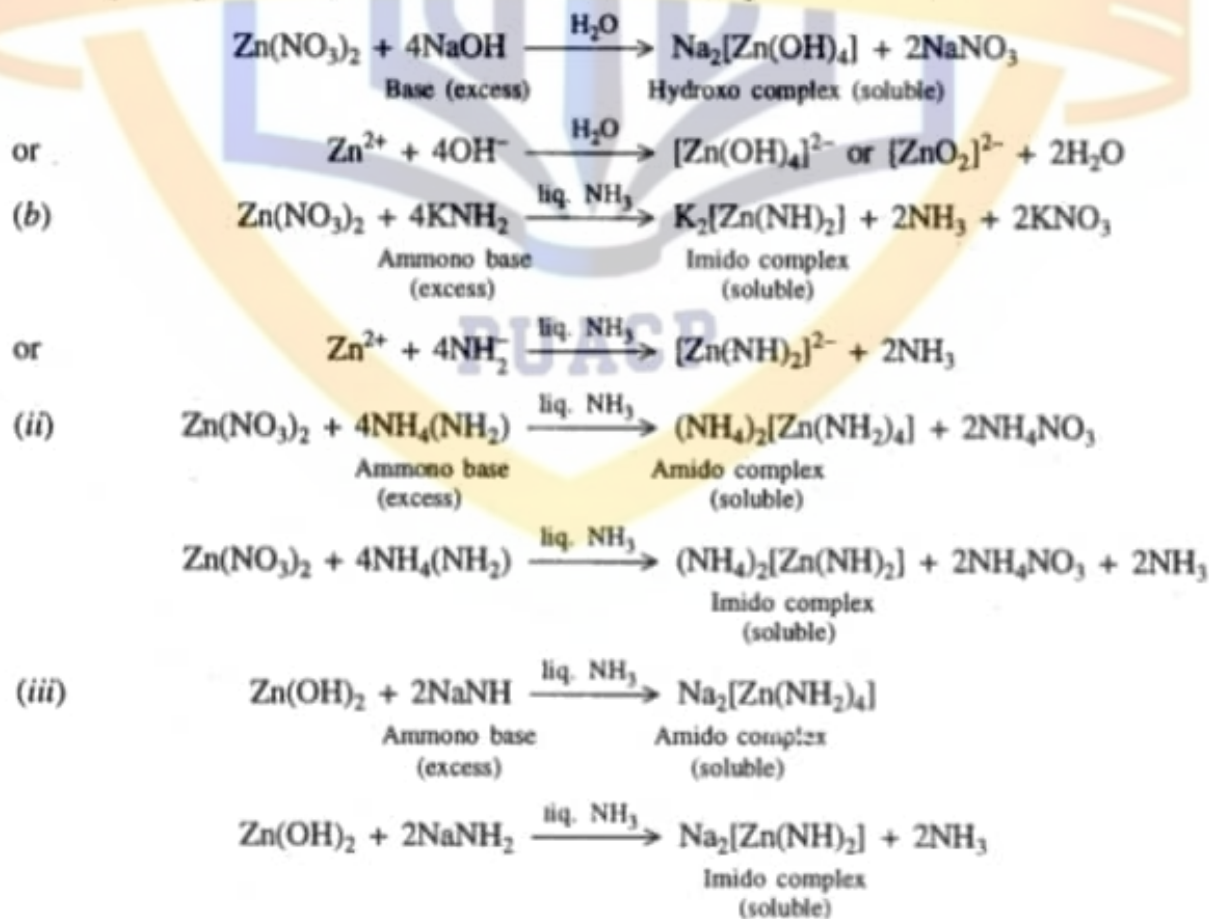


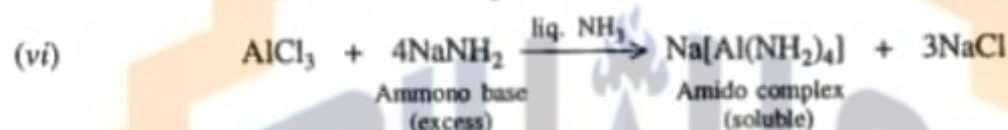
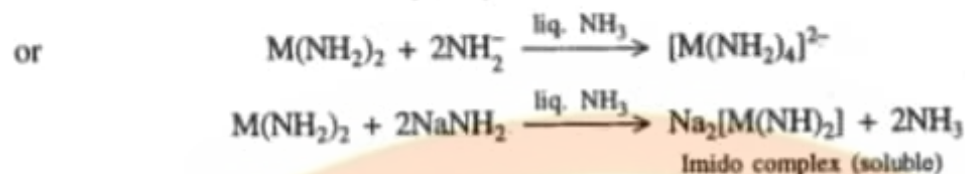
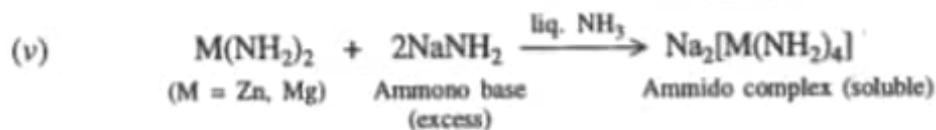
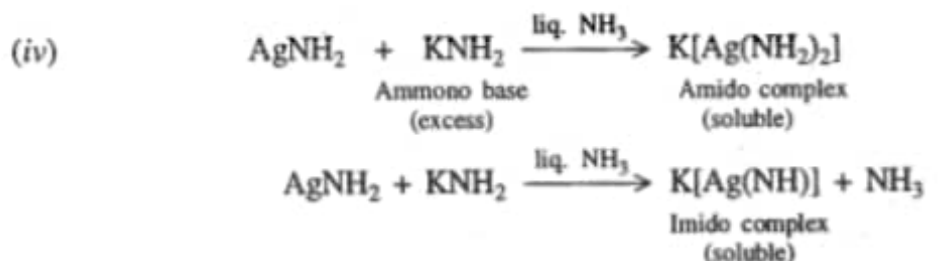
5. Complex formation reactions

When Zn(II), Mg(II), Al(III), Ag(I) compounds [e.g., Zn(NO₃)₂, Zn(OH)₂, Zn(NH₂)₂, Mg(NH₂)₂, AlCl₃, AgNH₂ etc.] react with the excess of an ammonio base [e.g., NH₄(NH₂), KNH₂, NaNH₂ etc.] in liq. NH₃, soluble amido or imido complex compound of the metal is obtained. For example:

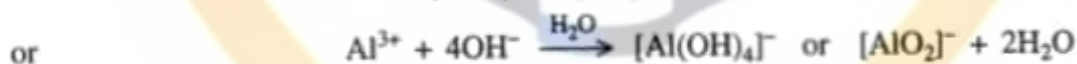
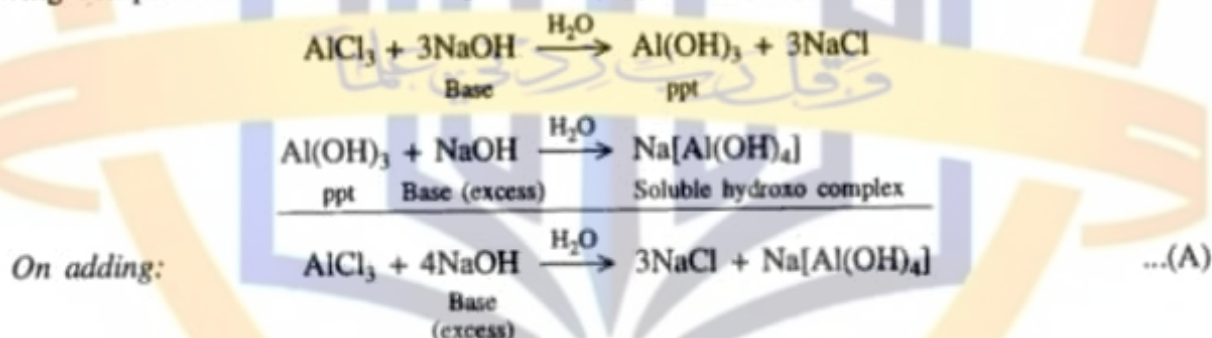


The above complex formation reaction that takes place in liq. NH₃ can be compared with the following complex formation reaction that occurs in aqueous medium.

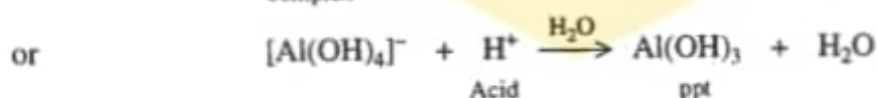
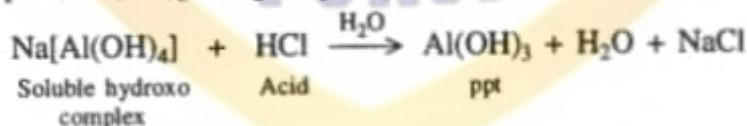




Complex formation reaction (vi) that takes place in liq. NH₃ can be compared with the following complex formation reaction [reaction (A)] that occurs in aqueous medium.



When HCl (which acts as an acid in aqueous medium) is added to the solution containing Al(III) hydroxo complex, Al(OH)₃ is again precipitated.



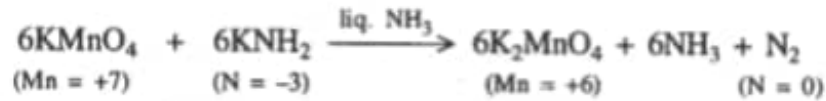
The precipitation of Al(OH)₃ by adding an acid to the soluble Al(III) hydroxo complex indicates that AlCl₃ behaves as an amphoteric substance in aqueous medium.

6. Redox reactions

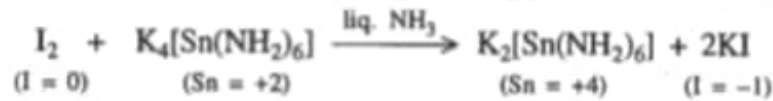
Redox reactions in which liq. NH₃ is involved can be studied under the following heads:

(i) **Redox reactions in which liq. NH₃ serves as a medium only.** Liquid NH₃ provides a medium in which various redox reactions can be carried. For example:

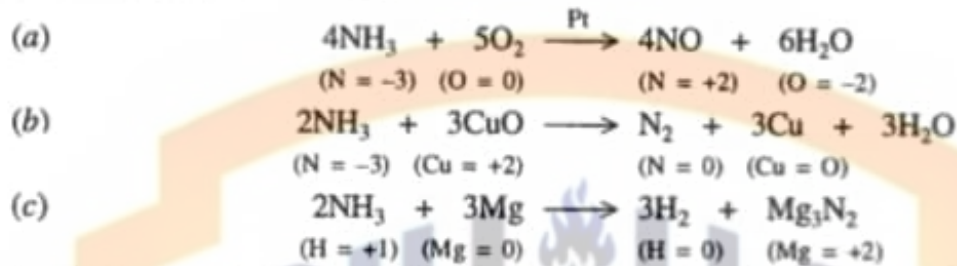
(a) KMnO_4 acts as a weak oxidising agent in liq. NH_3 . It oxidises KNH_2 to N_2 in liq. NH_3 and is itself reduced to K_2MnO_4 .



(b) Iodine also acts as a weak oxidising agent in liq. NH_3 . It oxidises potassium ammonostannite, $\text{K}_4[\text{Sn}(\text{NH}_2)_6]$ to potassium ammonostannate, $\text{K}_2[\text{Sn}(\text{NH}_2)_6]$ and is itself reduced to KI .

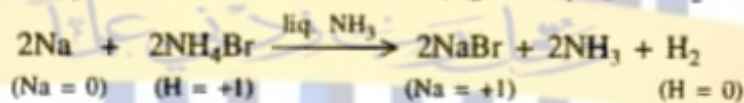


(ii) **Redox reactions in which liq. NH_3 ($\text{N} = -3$, $\text{H} = +1$) itself acts as a reducing agent.** Liq. NH_3 reduces various substances like O_2 , CuO , Mg etc. and is itself oxidised to NO ($\text{N} = +2$), N_2 ($\text{N} = 0$) etc. Examples are:

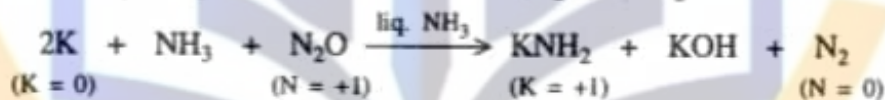


(iii) **Redox reactions in which alkali metals in liq. NH_3 act as reducing agents.** Liq. NH_3 can dissolve the alkali metals in it. The solution thus obtained contains ammoniated electrons. These electrons reduce various substances. Thus alkali metals in liq. NH_3 are able to reduce a variety of substances and are themselves oxidised to some alkali metal salt. Following examples illustrate the reducing property of alkali metals in liq. NH_3 .

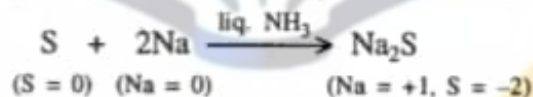
(a) Sodium in liq. NH_3 reduces ammonium salts (e.g., NH_4Br) to H_2 .



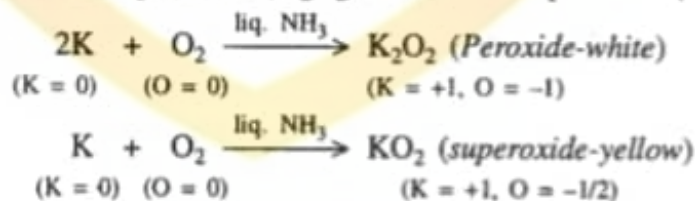
(b) Potassium in liq. NH_3 reduces nitrous oxide (N_2O) to N_2 .



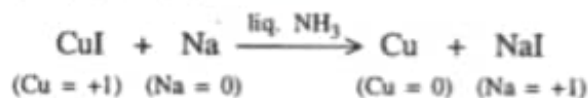
(c) Sodium in liq. NH_3 reduces elemental sulphur to sodium sulphide (Na_2S)



(d) Li and Na in liq. NH_3 reduce elemental oxygen to their peroxide (K_2O_2 or Na_2O_2) while other alkali metals give their peroxide (M_2O_2) as well as superoxide (MO_2).



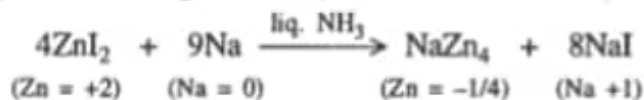
(e) Na in liq. NH_3 reduces CuI to Cu .



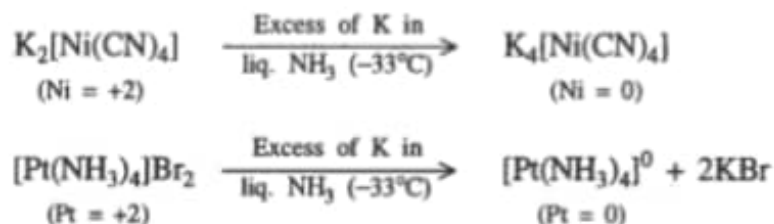
(f) K in liq. NH_3 reduces KMnO_4 to MnO and is itself oxidised to KNH_2 .



(g) Na in liq. NH_3 reduces ZnI_2 to NaZn_4 and is itself oxidised NaI .



(h) Excess of K in liq. NH_3 reduces $\text{K}_2[\text{Ni}(\text{CN})_4]$ and $[\text{Pt}(\text{NH}_3)_4]\text{Br}_2$ to $\text{K}_4[\text{Ni}(\text{CN})_4]$ and $[\text{Pt}(\text{NH}_3)_4]^0$ respectively.



Advantages of using liquid ammonia as a solvent

(i) We have seen above that alkali metals, without reacting with liq. NH_3 , are soluble in this solvent. The dissolved alkali metals can be recovered by evaporating the alkali metal-liq. NH_3 solution.

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

(iii) We have seen under the study of precipitation reactions taking place in liq. NH_3 that these reactions can be used to precipitate metallic halides, sulphides, alcoholates, amides, imides and nitrides.

Disadvantages of using liq. NH_3 as a solvent

(i) 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°C .

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

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

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 temperature and pressure, sulphur dioxide is a gas but can be readily liquefied. It has a wide liquid range from -10.0°C to -75.5°C (b.pt. = -10.0° and m.pt. = -75.5°C) and hence can be used as a solvent. Its dielectric constant is low (= 17.4 at -20°C) and hence it is a poor solvent for ionic compounds but acts as a good solvent for covalent compounds.

Solubility of various substances in liq. SO_2

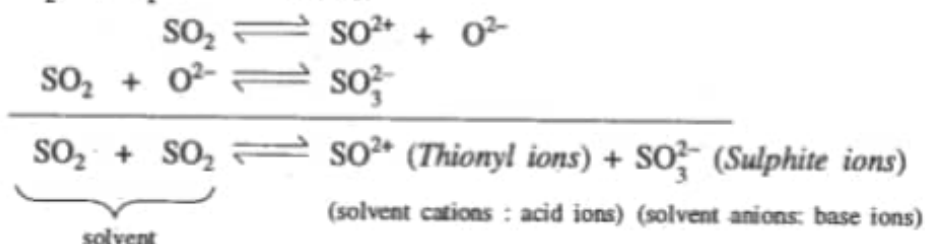
(a) **Solubility of ionic compounds (inorganic salts).** Iodides and thiocyanates are the most soluble. Sulphates, sulphides, oxides and hydroxides are practically insoluble. Many of the ammonium, thallium and mercuric salts are soluble.

(b) **Solubility of non-ionic compounds (inorganic and organic covalent compounds).** Covalent halides like IBr , BCl_3 , AlCl_3 , AsCl_3 , PBr_3 , CCl_4 , SiCl_4 and SnCl_4 are soluble in liq. SO_2 . Organic compounds like amines, ethers, alcohols, benzene, alkenes, pyridine, quinoline, halogen derivatives and acid chlorides are soluble. Alkanes are insoluble.

(c) **Solubility of metals.** Metals are insoluble in liq. SO_2 .

Auto-ionisation of liq. SO₂

Self-ionisation of liq. SO₂ takes place as follows:



When we compare the self-ionisation of liq. SO₂ with that of water and liq. NH₃, we find that SO²⁺ ion is analogous to H₃O⁺ and NH₄⁺ ions while SO₃²⁻ ion is analogous to OH⁻ and NH₂⁻ ion produced by the self-ionisation of H₂O and liq. NH₃ respectively. Thus all those compounds which contain or make available SO²⁺ ions (solvent cations-acid ions) will act as acids in liq. SO₂. Similarly all those compounds which contain or make available SO₃²⁻ ions, will behave as bases in liq. SO₂.

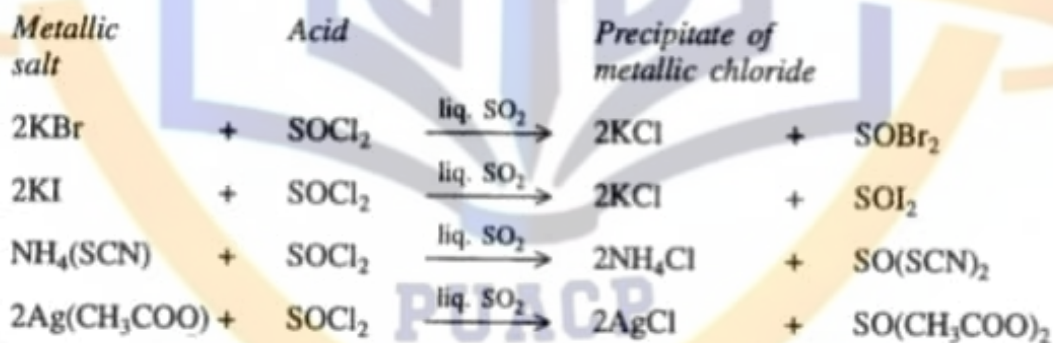
The above discussion shows that since SOCl₂, SOBr₂, SO(SCN)₂ etc., give SO²⁺ ions in liq. SO₂, they behave as acids in this solvent. On the other hand, the substances viz., Cs₂SO₃, [N(CH₃)₄]₂SO₃, K₂SO₃ which give SO₃²⁻ ions in this solvent act as bases.

Chemical Reaction Taking Place in Liq. SO₂

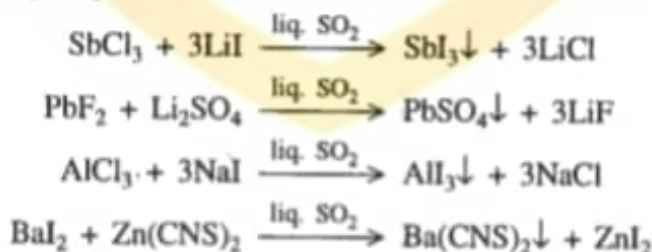
The chemical reactions that take place in liq. SO₂ can be of the following types:

1. Precipitation reactions

(i) When a substance which acts as an acid in liq. SO₂ (e.g., SOCl₂) reacts with the metallic salts like KBr, KI, NH₄(SCN), Ag(CH₃COO) etc. in liq. SO₂, chloride of the metal is precipitated.

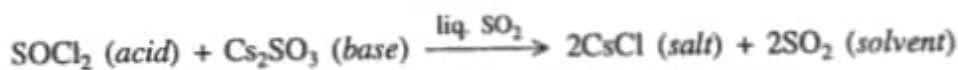


(ii) Examples other precipitation reactions that can be carried in liq. SO₂ are:

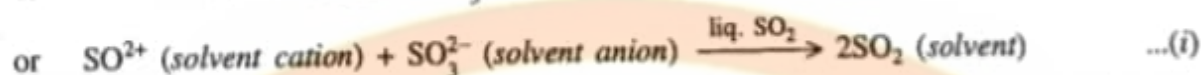
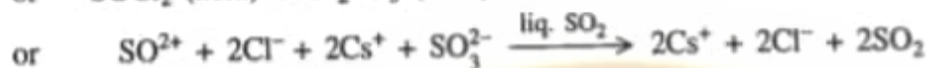
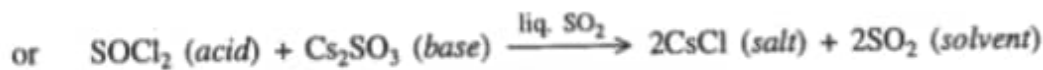
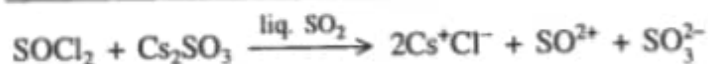
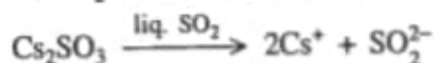
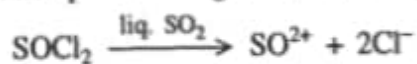


2. Acid-base neutralisation (salt formation) reactions

In liq. SO₂, acid-base reaction is that in which a compound containing or making available SO²⁺ ion (*acid*) combines with a compound containing or making available SO₃²⁻ ion (*base*) to form the salt and the solvent (i.e., SO₂), e.g.,

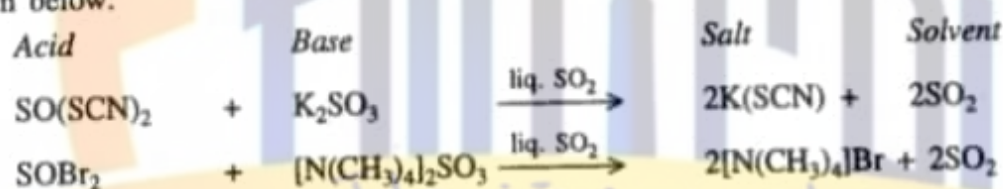


Actually the above reaction takes place through the following steps:



It may be seen from equation (i) that neutralisation reaction in liq. SO_2 can also be defined as the combination of the solvent cation (SO^{2+}) and solvent anion (SO_3^{2-}) to produce the solvent (SO_2).

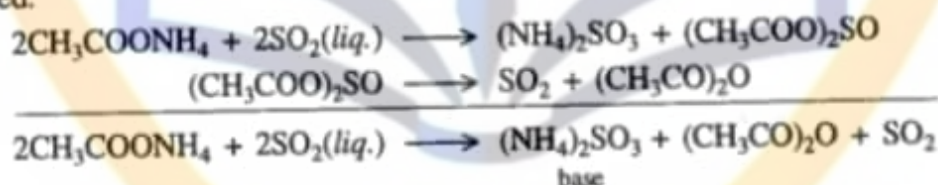
Examples of some other acid-base neutralisation reactions taking place in liq. SO_2 are given below:



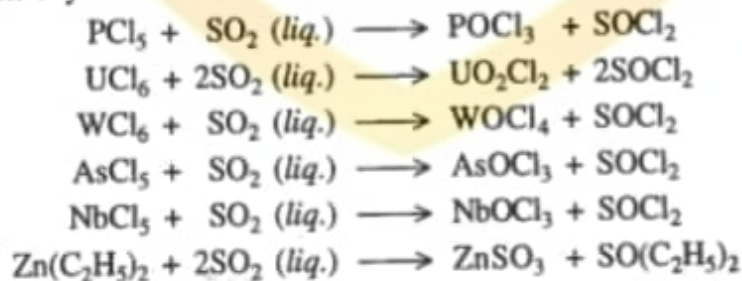
3. Solvolysis (solvolytic) reactions in liq. SO_2

Examples of solvolysis reactions occurring in liq. SO_2 are given below:

(a) $\text{CH}_3\text{COONH}_4$ undergoes solvolysis reaction in liq. SO_2 . Here the concentration of SO_3^{2-} ions is increased.



(b) Some covalent halides like PCl_5 , UCl_6 , WCl_6 , AsCl_3 etc. undergo solvolysis reactions in liq. SO_2 and form oxyhalides. In all these reactions the concentration of SO^{2+} ion is increased.

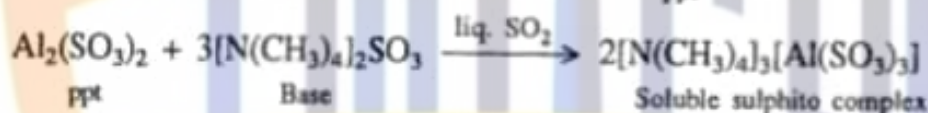
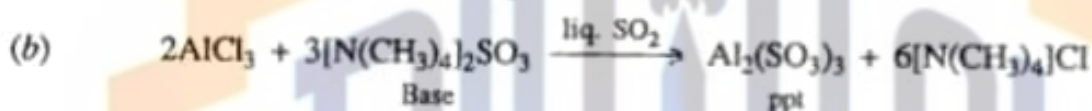
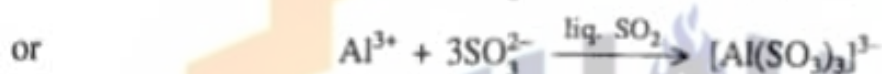
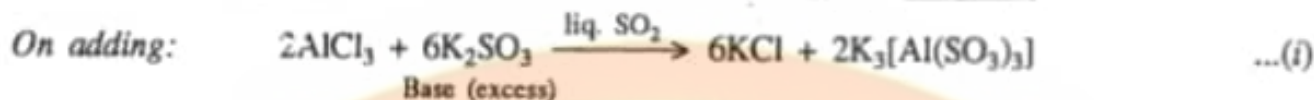
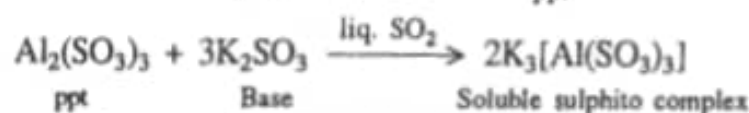


4. Formation of solvates

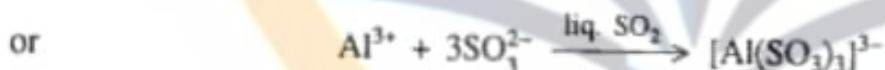
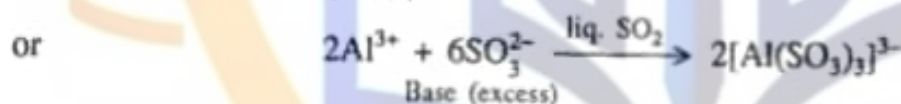
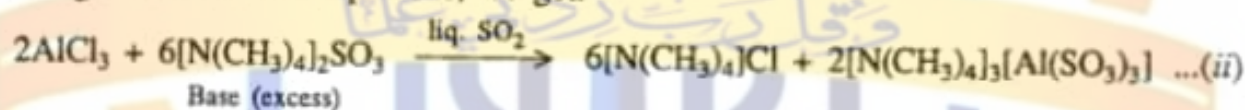
Like water and liq. NH_3 , liq. SO_2 also forms addition compounds with solutes. These addition compounds are called solvates and contain one or more molecules of sulphur dioxide as sulphur dioxide of crystallisation. Examples of some solvates formed in liq. SO_2 are $\text{LiI} \cdot 2\text{SO}_2$, $\text{KBr} \cdot 4\text{SO}_2$, $\text{Ml} \cdot 4\text{SO}_2$ ($\text{M} = \text{Na}, \text{K}$ or Rb), $\text{Ml}_2 \cdot 4\text{SO}_2$ ($\text{M} = \text{Ca}, \text{Sr}$ or Ba), $\text{AlCl}_3 \cdot 2\text{SO}_2$, $\text{KCNS} \cdot n\text{SO}_2$ ($n = 0.5, 1$ or 2), $[(\text{CH}_3)_4\text{N}]\text{Cl} \cdot \text{SO}_2$, $[(\text{CH}_3)_4\text{N}]_2\text{SO}_4 \cdot 3\text{SO}_2$.

5. Complexes formation reactions

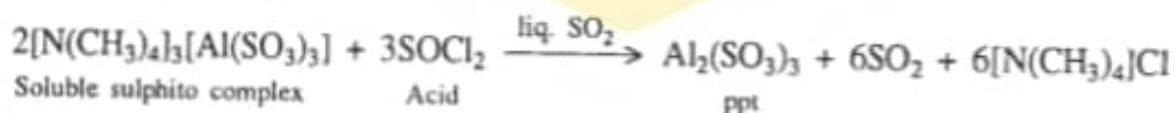
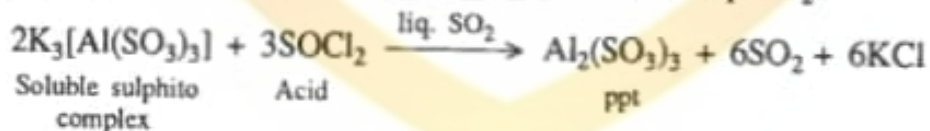
(i) When Al(III) or Ga(III) salt (e.g., AlCl_3 , GaCl_3) is treated with a compound containing SO_3^{2-} ions (which act as base in liq. SO_2) in liq. SO_2 , ppt. of $\text{Al}_2(\text{SO}_3)_3$ is obtained. This ppt. dissolves in the excess of the base due to the formation of a soluble sulphito complex of Al(III). Thus,



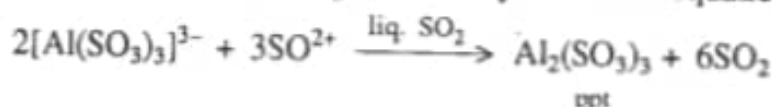
On adding the above two equations, we get:



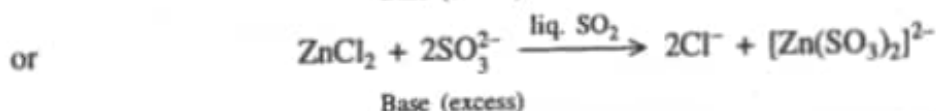
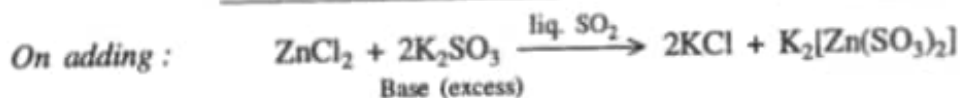
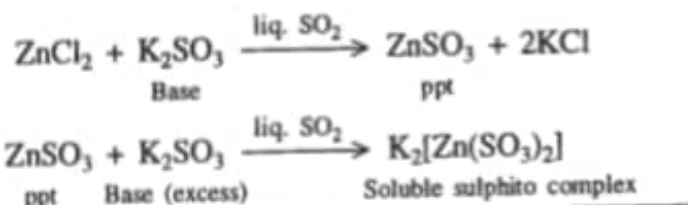
When SOCl_2 (which acts as an acid in liq. SO_2) is added to the solution containing Al(III) sulphito complex, $\text{Al}_2(\text{SO}_3)_3$ is again precipitated. The precipitation of $\text{Al}_2(\text{SO}_3)_2$ indicates that AlCl_3 (and also GaCl_3) behaves as an amphoteric substance in liq. SO_2 .



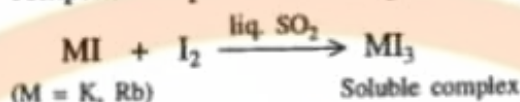
Both the above equations can be represented by the ionic equation:



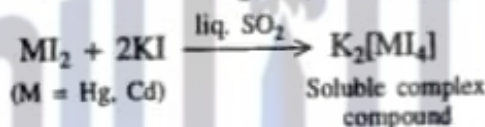
(ii) When Zn(II) salts [e.g., ZnCl_2] react with a compound containing SO_3^{2-} ions (which behaves as base in liq. SO_2) in liq. SO_2 , ppt. of ZnSO_3 is obtained. This ppt. dissolves in the excess of the base due to the formation of a soluble sulphito complex of Zn(II)



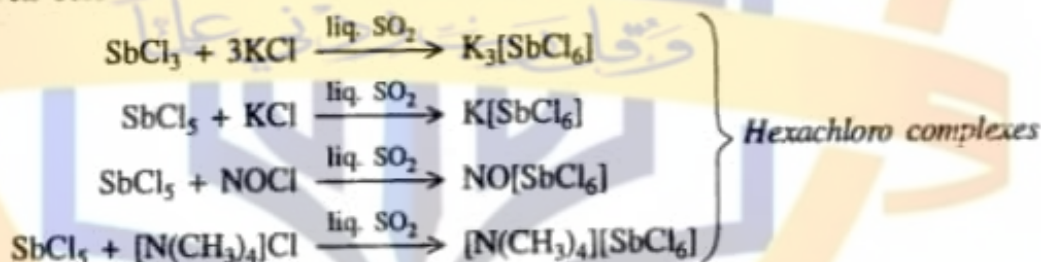
(iii) Solubility of I_2 in liq. SO_2 is greatly increased when KI or RbI is added to it. This is due to the formation of complex compounds viz. KI_3 or RbI_3 .



(iv) When HgI_2 or CdI_2 is dissolved in liq. SO_2 in presence of KI, the solubility of these iodides is increased due to the formation of $\text{K}_2[\text{MI}_4]$ which is a complex compound.



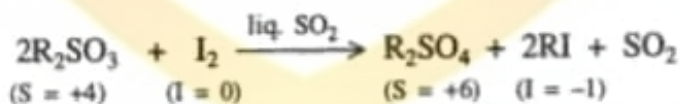
(v) Other reactions showing the formation of hexahalo complexes in liq. SO_2 by the action of covalent halides (e.g., SbCl_3 , SbCl_5 etc.) on alkali metal halides (e.g., KCl) or NOCl or $[\text{N}(\text{CH}_3)_4]\text{Cl}$ are given below:



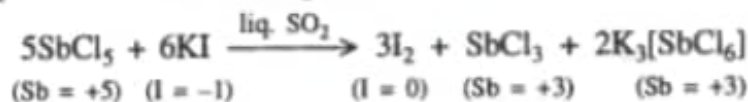
6. Redox reactions

Liq. SO_2 itself does not act as any strong oxidising/reducing agent. It serves only as a medium for any redox reactions. For example:

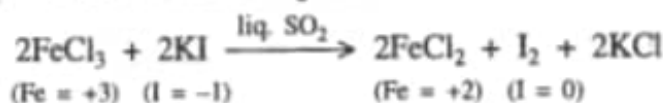
(a) A sulphite (R_2SO_3) in liq. SO_2 reduces iodine to iodide and itself oxidised to sulphate (R_2SO_4).



(b) SbCl_5 in liq. SO_2 oxidises KI to free I_2 and is itself reduced to SbCl_3 .



(c) FeCl_3 in liq. SO_2 oxidises KI to free I_2 and is itself reduced to FeCl_2 .



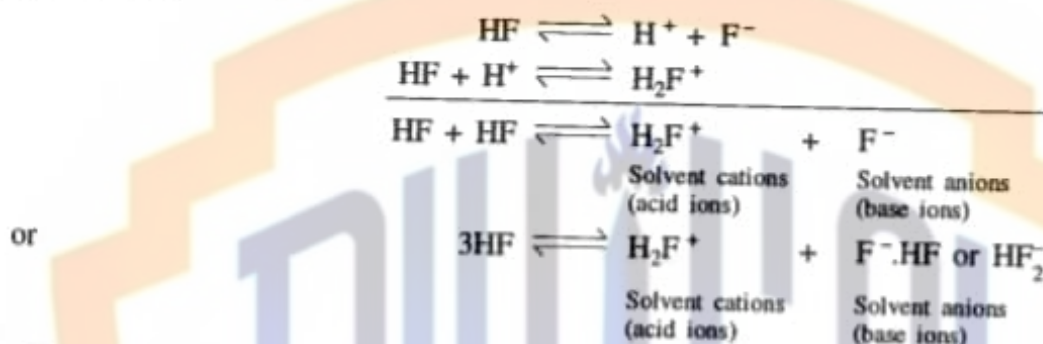
Liquid Hydrogen Fluoride, (Liq. HF)

Liq. HF has a wide but convenient liquid range (-83°C to 19.4°C). The disadvantages of using HF as a solvent and reaction medium are that it can dissolve only relatively few substances without chemical reaction and that it has poisonous character.

Although HF has a rather low specific conductance, its high dielectric constant makes it an excellent ionising solvent. It is regarded as one of the most water-like of all non-aqueous solvents. It dissolves many inorganic and organic compounds to give highly conducting solutions. Inorganic substances are generally more soluble than organic compounds.

Auto-ionisation of liq. HF

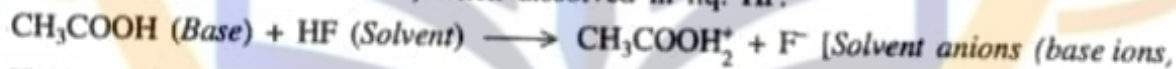
The high specific conductance of liq. HF suggests a relatively high degree of auto-ionisation of liq. HF shown below:



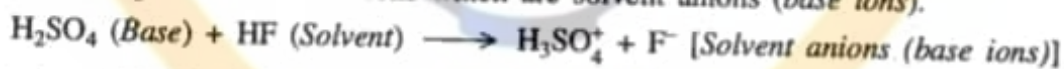
Behaviour of different substances in liq. HF

The auto-ionisation of liq. HF as shown above indicates that any substance that gives H_2F^+ ions in liq. HF behaves as an acid in this solvent and the substance that furnishes F^- or HF_2^- ions acts as a base in this solvent. This point would be more clear from the following examples:

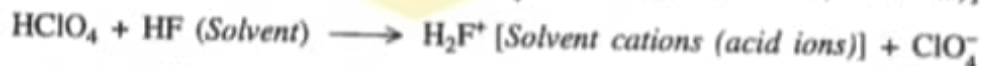
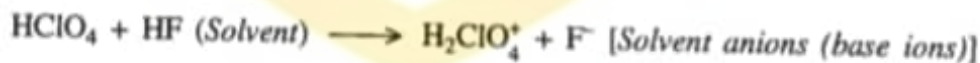
(i) CH_3COOH (which acts as a *weak acid* in water) acts as a base in liq. HF, because it gives F^- ions (solvent anions-base ions) when dissolved in liq. HF.



(ii) H_2SO_4 and HNO_3 both act as strong acids in aqueous medium, but show basic character in liq. HF, due to the production of F^- ions which are solvent anions (base ions).



(iii) HClO_4 behaves as the *strongest acid* in water, but in liq. HF it acts as an *amphoteric substance*, since it produces both H_2F^+ (solvent cations-acid ions) and F^- (solvent anions-base ions) in this solvent.



(iv) Electron-acceptor fluorides (e.g., BF_3 , AsF_3 , PF_5 and SbF_5) act as acids in liq. HF.



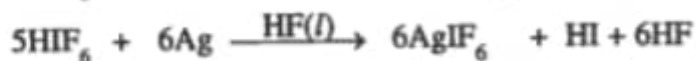
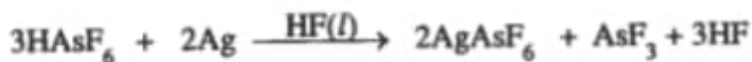
These acceptor molecules dissolve in HF to give solutions which dissolve electropositive metals like Mg. This is an evidence in favour of the acidic nature of these solutes.

Chemical Reactions Taking Place in Liq. HF

Chemical reactions that take place in liq. HF are of the following types:

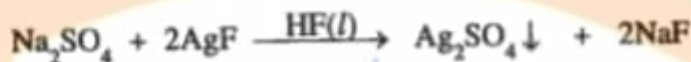
1. Oxidation-reduction reactions

Oxidation-reduction reactions between hydrofluoro acids and metals in HF are not generally different from those taking place between HNO_3 and metals in the aqueous system, e.g.,



2. Precipitation reactions

Some of the precipitation reactions occurring in liq. HF are exemplified by the following reactions.



The precipitation reaction resulting in the formation of silver tetrafluoroborate, AgBF_4 is the most important. AgBF_4 is obtained as a precipitate when AgNO_3 and BF_3 solutions in HF are mixed.



3. Formation of addition compounds

HF also forms a number of addition compounds with metallic fluorides, e.g., $\text{KF} \cdot \text{HF}$, $\text{KF} \cdot 2\text{HF}$, $\text{KF} \cdot 3\text{HF}$, $\text{NH}_4\text{F} \cdot \text{HF}$, etc.

SOME TYPICAL PROBLEMS WITH SOLUTIONS

Problem 1. (a) Classify the following solvents as ionising and non-ionising solvents: HF, liq SO_2 , liq. N_2O_4 , H_2SO_4 , POCl_3 , pyridine and acetic acid.

(b) Classify the following solvents as protonic (protic) or non-protonic (aprotic) solvents: HF, liq. SO_2 , C_6H_6 , H_2SO_4 and liq. NH_3 .

Solution. (a) Ionising solvents : HF, H_2SO_4 , acetic acid

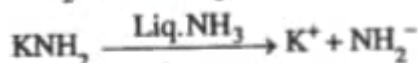
Non-ionising solvents : liq. SO_2 , liq. N_2O_4 , POCl_3 , pyridine.

(b) Protic solvents : HF, H_2SO_4 , liq. NH_3

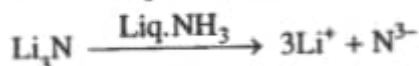
Aprotic solvents : liq SO_2 , C_6H_6

Problem 2. What will be the effect of adding (a) KNH_2 (b) Li_3N (c) CH_3COOK to liq. NH_3 on the acidity/basicity of the solvent.

Solution. (a) Since KNH_2 gives NH_2^- ions (amide ions) in liq. NH_3 , it behaves as a base in this solvent. Thus the addition of KNH_2 to liq. NH_3 increases the basic character of the solvent



(b) Since Li_3N produces nitride ions (N^{3-} ions) in liq. NH_3 , it behaves as a base in this solvent. Thus the addition of Li_3N to liq. NH_3 increases the basic nature of the solvent.

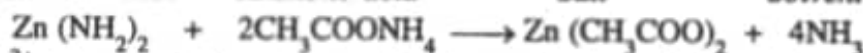


(c) Since CH_3COOK does not have any of the ions viz NH_4^+ , NH_2^- , NH^{2-} , N^{3-} , the addition of this compound to liq. NH_3 has no effect on the acidity/basicity of liq. NH_3 .

Problem 3. Guess the reaction between $\text{Zn}(\text{NH}_2)_2$ and $\text{CH}_3\text{COONH}_4$

Solution. Auto-ionisation of liq. NH_3 gives NH_4^+ (ammonio acid ion) and NH_2^- (ammonio base ion) ions. Thus $\text{Zn}(\text{NH}_2)_2$ will act as a base and $\text{CH}_3\text{COONH}_4$ will act as an acid in liq. NH_3 and the reaction between these substances is a neutralisation reaction.

Ammonio base Ammonio acid Salt Solvent

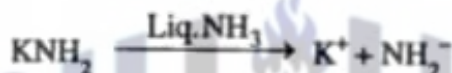


Zn^{2+} ions obtained by the dissociation of $\text{Zn}(\text{CH}_3\text{COO})_2$ will react with 4NH_3 to give tetramminezinc (II) ion, $[\text{Zn}(\text{NH}_3)_4]^{2+}$

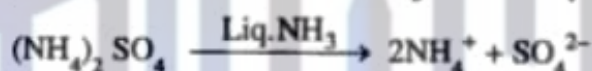


Problem 4. How do the following solutes behave in the solvents given in parentheses? (a) $\text{KNH}_2(\text{NH}_3)$ (b) $(\text{NH}_4)_2\text{SO}_4(\text{NH}_3)$ (c) $\text{SiCl}_4(\text{NH}_3)$ (d) $\text{SO}_2\text{Cl}_2(\text{NH}_3)$ (e) $\text{PCl}_5(\text{SO}_2)$ (f) $\text{AgCl}(\text{NH}_3)$ (g) $\text{Zn}(\text{C}_2\text{H}_5)_2(\text{SO}_2)$ (h) $\text{Cs}_2\text{SO}_3(\text{SO}_2)$ (i) $\text{NbCl}_5(\text{SO}_2)$

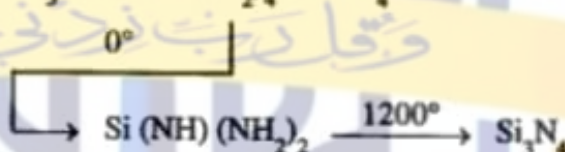
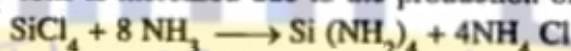
Solution (a) KNH_2 behaves as a base in liq. NH_3 , since it gives NH_2^- (base anion) in this solvent.



(b) $(\text{NH}_4)_2\text{SO}_4$ behaves as an acid in liq. NH_3 , since NH_4^+ ions are produced.



(c) SiCl_4 is covalent and hence undergoes ammonolysis reaction in liq. NH_3 . In this reaction the concentration of NH_2^- ions is increased due to the production of $\text{Si}(\text{NH}_2)_4$



(d) SO_2Cl_2 undergoes ammonolysis reaction in liq. NH_3 , since $\text{SO}_2(\text{NH}_2)_2$ is produced. This compound increases the concentration of NH_2^- ions.



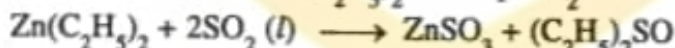
(e) In liq. SO_2 , PCl_5 undergoes solvolysis reaction and POCl_3 is formed.



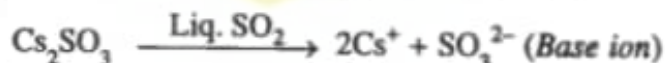
(f) AgCl dissolves in liq. NH_3 due to the formation of a complex compound, $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$.



(g) The reaction between $\text{Zn}(\text{C}_2\text{H}_5)_2$ and liq. SO_2 is an example of solvolysis reaction



(h) Since Cs_2SO_3 gives SO_3^{2-} ions in liq. SO_2 , this compound acts as a base in this solvent



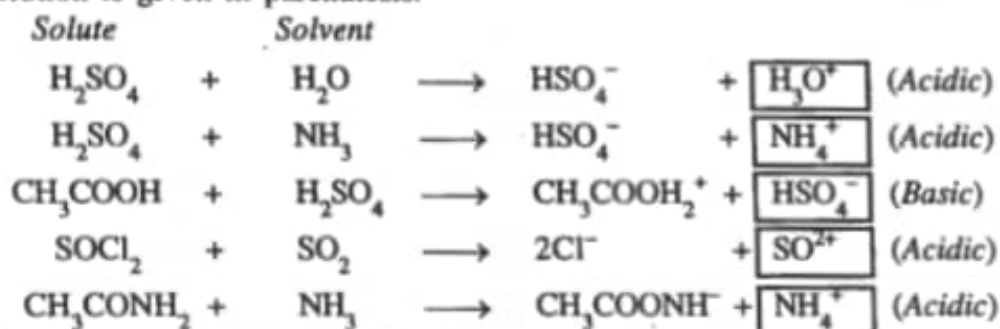
(i) NbCl_5 shows solvolysis reaction in liq. SO_2 .



Problem 5. How will the following solutes react with the solvents given in the parenthesis. State whether the solution formed in each case will be more acidic or more basic than the solvent:

$\text{H}_2\text{SO}_4(\text{H}_2\text{O})$, $\text{H}_2\text{SO}_4(\text{NH}_3)$, $\text{CH}_3\text{COOH}(\text{H}_2\text{SO}_4)$, $\text{SOCl}_2(\text{SO}_2)$ and $\text{CH}_3\text{CONH}_2(\text{NH}_3)$.

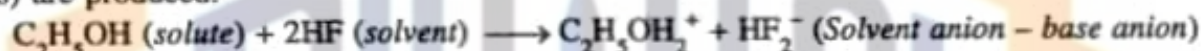
Solution. The reactions between the solutes and the solvents are given below. The nature of the solution is given in parenthesis.



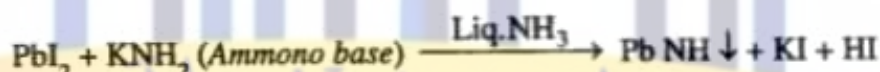
Problem 6. Complete the following equations:



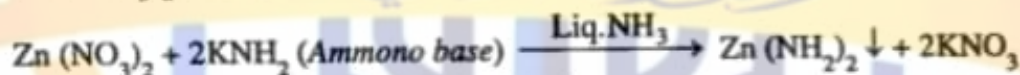
Solution. (i) In HF (solvent), $\text{C}_2\text{H}_5\text{OH}$ (solute) behaves as a base, since HF_2^- ions (solvent anions) are produced.



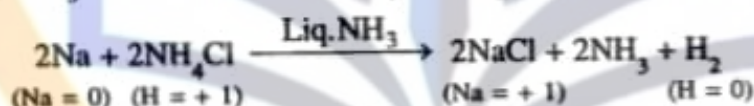
(ii) PbI_2 is a metal salt. It reacts with the base viz KNH_2 and gives the ppt. of lead imide (PbNH).



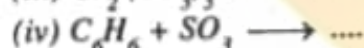
(iii) $\text{Zn}(\text{NO}_3)_2$ is a metal salt. It reacts with the base, KNH_2 and gives the ppt. of ZnNH_2 .



(iv) In liq. NH_3 , Na metal reduces NH_4Cl to H_2 .

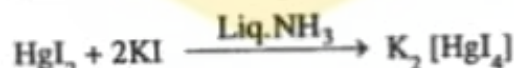


Problem 7. Complete the following reactions in liq. SO_2

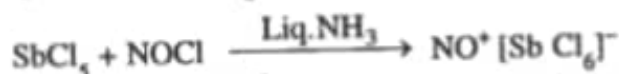


(P.U. April 1996, Kurukshetra 1994)

Solution. (i) When HgI_2 is dissolved in liq SO_2 in presence of KI, the solubility of HgI_2 in liq SO_2 is increased due to the formation of $\text{K}_2[\text{HgI}_4]$ (a complex compound)

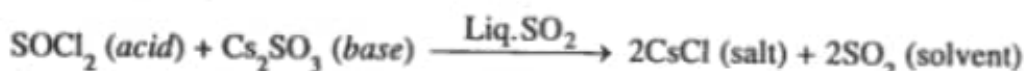


(ii) The reaction between SbCl_5 (covalent halide) and NOCl in liq. SO_2 leads to the formation of hexachloro complex, $\text{NO}^+[\text{SbCl}_6]^-$

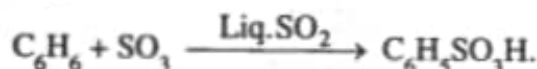


(iii) Since $\text{Cr}_2(\text{SO}_3)_3$ contains SO_3^{2-} ions, this compound acts as a base in liq. SO_2 . Similarly, since SOCl_2 gives SO^{2+} ions in liq. SO_2 , this salt behaves as an acid in liq SO_2 . Thus the

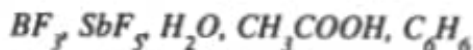
reaction between $\text{Cr}_2(\text{SO}_3)_3$ and SOCl_2 in liq. SO_2 is an acid-base (neutralisation) reaction and gives salt and solvent (i.e., SO_2)



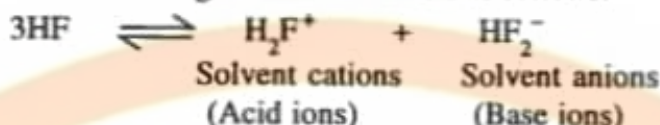
(iv) In presence of liq. SO_2 , C_6H_6 undergoes sulphonation.



Problem 8. Show whether each of the following compounds acts as an acid or a base in liq. HF.



Solution. We know that HF undergoes self-ionisation as follows:



This equation shows that the compounds producing H_2F^+ ions in liq HF act as acids in this solvent while the compounds giving HF_2^- ions behave as bases in this solvent. Thus:



(Acid)



(Acid)



(Base)



(Base)



(Base)

Problem 9. Account for the following, giving appropriate reasons.

(i) K_2SO_3 is soluble in liq. SO_2

[M.D. Rohtak 1997]

(ii) SO_2 acts both as a Lewis acid and as a Lewis base.

[M.D. Rohtak 1998]

(iii) The electrical conductivity of liq. NH_3 is increased when NH_4Cl is dissolved in it.

[M.D. Rohtak 1997, Agra 1993]

(iv) A liq. NH_3 solution of phenolphthalein is colourless but becomes red coloured on addition of KNH_2

[M.D. Rohtak 1994]

(v) Liq. NH_3 exhibits association whereas liq. SO_2 does not.

[M.D. Rohtak 1992, Punjab 1996]

(vi) Acetamide behaves as a base in aqueous solution but shows acidic properties in liq. NH_3

(vii) HNO_3 acts as an acid in aqueous solution but in HF it behaves as a base.

[H.P.W. 1997]

(viii) CH_3COOH behaves as a base in HF but SbF_5 behaves as an acid in this solvent.

[Guru Nanak pev 1997]

(ix) Liq. NH_3 behaves as a differentiating solvent for NaH , NaNH_2 acid NaOC_2H_5

(x) Solution of sodium metal in liq. NH_3 is blue and has strong reducing property and high electrical conductance.

[Punjab 1996]

Solution. (i) K_2SO_3 is soluble in liq. SO_2 , since this compound forms a solvate, $\text{K}_2\text{SO}_3 \cdot \text{SO}_2$ (an addition compound) with liq. SO_2 . This solvate contains one molecule of SO_2 as sulphur dioxide of crystallisation. In this solvate, K_2SO_3 acts as a solute.

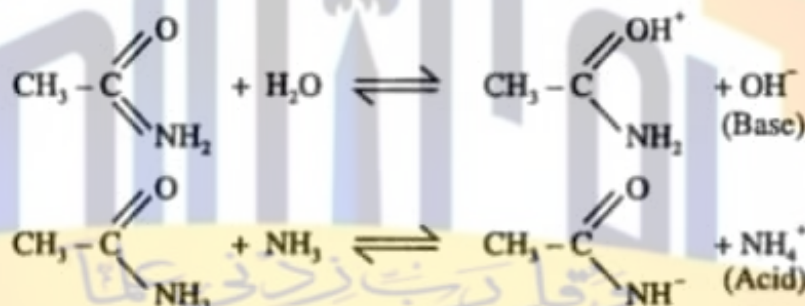
(ii) In the formation of solvates like $\text{CaI}_2 \cdot 4\text{SO}_2$, $\text{LiI}_2 \cdot 2\text{SO}_2$ etc, SO_2 donates electrons to the solutes and hence acts as Lewis base. In the formation of solvates like $\text{C}_5\text{H}_5\text{N} \cdot \text{SO}_2$, $\text{C}_6\text{H}_7\text{N} \cdot \text{SO}_2$, SO_2 accepts electrons from the solutes and hence acts as Lewis acid. Thus SO_2 acts both as a Lewis acid and as a Lewis base.

(iii) Since NH_4Cl gives NH_4^+ ions in liq. NH_3 , this compound acts as an acid in this solvent. Due to the production of NH_4^+ ions, the concentration of these ions in liq. NH_3 increases. The increase of NH_4^+ ions increases the electrical conductivity of liq. NH_3 .

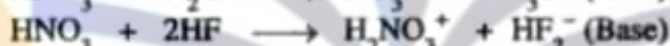
(iv) Addition of KNH_2 to liq. NH_3 increases the concentration of NH_2^- ions and hence this solution behaves as an ammonio base. As soon as the concentration of NH_2^- ions increases in solution, the solution behaves as a base and hence imparts red colour to phenolphthalein just as an aqueous basic solution imparts red (pink) colour.

(v) Due to small size and high electronegativity of N-atom, many molecules of liq. NH_3 get associated together through H-bonding. This type of association is not possible in case of liq. SO_2 , since sulphur atom has bigger size. ($\text{N} = 0.75 \text{ \AA}$, $\text{S} = 1.02 \text{ \AA}$) and lower electronegativity ($\text{N} = 3.0$, $\text{S} = 2.5$) than N-atom.

(vi) Since acetamide, CH_3CONH_2 gives OH^- ions in aqueous solution, this compound behaves as a base in water. On the other hand, since CH_3CONH_2 gives NH_4^+ ions in liq. NH_3 , it behaves as an acid in this solvent.



(vii) Since, in aqueous solution, HNO_3 gives H^+ or H_3O^+ ions, this compound behaves as an acid in this solution. On the other hand HNO_3 acts as a base in HF , since, in this solvent, this compound gives HF_2^- ions.



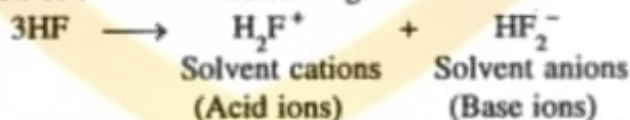
(viii) CH_3COOH gives HF_2^- ions in HF by accepting H^+ ion.



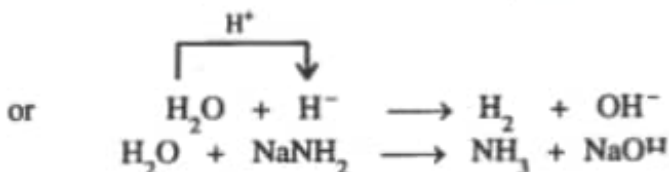
SbF_5 ionises as an acid in HF by accepting F^- ion. Thus SbF_5 gives H_2F^+ ions

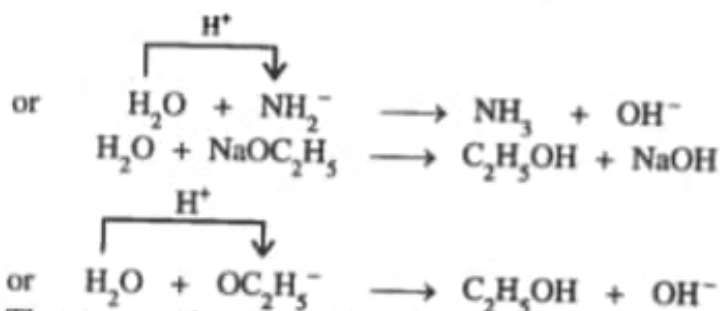


Here the self ionisation of HF can be noted as given below:



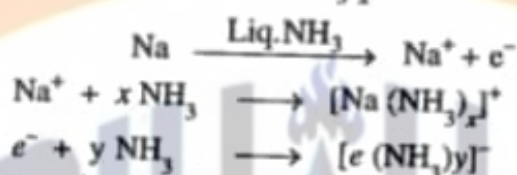
(ix) When strong bases like NaH , NaNH_2 and NaOC_2H_5 react with H_2O (solvent), a proton is donated by H_2O molecule to these bases and NaOH is produced.





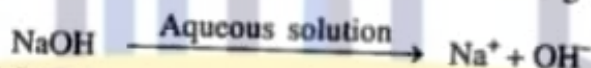
Thus we see that these bases are levelled to the base strength of OH^- ions, and hence these bases cannot be differentiated as bases in aqueous solution. On the other hand, since liq. NH_3 is a poor proton donor, these bases can be differentiated as bases in liq. NH_3 . Thus liq. NH_3 behaves as a differentiating solvent for NaH , NaNH_2 and NaOC_2H_5 .

(x) Blue colour is due to an absorption band having its maximum at 5000\AA . Strong reducing property and high electrical conductance shown by the solution of sodium in liq. NH_3 is due to the production of ammoniated cations, $[\text{Na}(\text{NH}_3)_x]^+$ and ammoniated electron, $[e(\text{NH}_3)_y]^-$



Problem 10. What are the principal species formed in the solutions of NaOH , $(\text{NH}_4)_2\text{SO}_4$ and H_2O in water, anhydrous H_2SO_4 and liq. NH_3 ?

Solution. NaOH (a) In water: In water, NaOH dissociates to give Na^+ and OH^- ions.

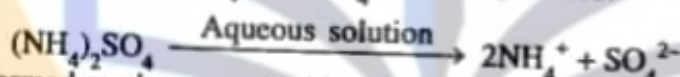


(b) In anhydrous H_2SO_4 : OH^- ions formed as above further react with H_2SO_4 to produce HSO_4^- and H_3O^+ ions.

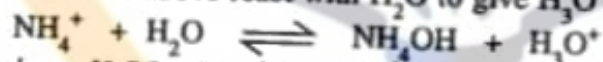


(c) In liq. NH_3 : In liq. NH_3 , no species are formed.

$(\text{NH}_4)_2\text{SO}_4$ (a) In water: NH_4^+ and SO_4^{2-} ions are formed.



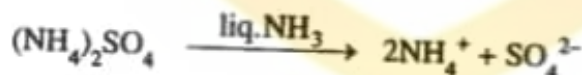
NH_4^+ ions formed as above react with H_2O to give H_3O^+ ions.



(b) In anhydrous H_2SO_4 : NH_4^+ and SO_4^{2-} ions are obtained.

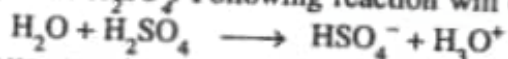


(c) In liq. NH_3 : NH_4^+ and SO_4^{2-} ions are formed. Due to the production of NH_4^+ ions, the solution becomes acidic.

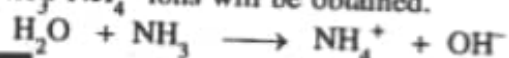


H_2O . (a) In water. there will be no reaction

(b) In anhydrous H_2SO_4 Following reaction will occur.



(c) In liq. NH_3 , NH_4^+ ions will be obtained.

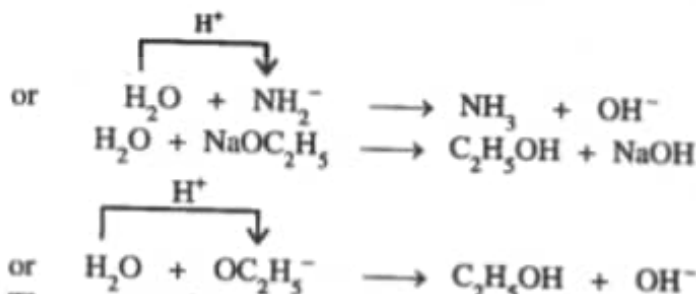


Problem 11. Predict the behaviour of urea in water, liq. NH_3 and anhydrous H_2SO_4

Solution. Urea is NH_2CONH_2 .

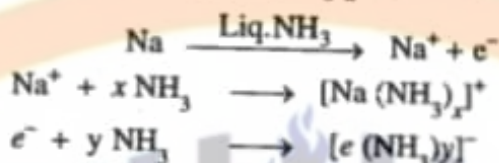
In water: NH_2CONH_2 is expected to behave as a non-electrolyte.

In liq. NH_3 : NH_2CONH_2 behaves as a weak acid in liq. NH_3 , since this compound produces NH_4^+ ion in this solvent.



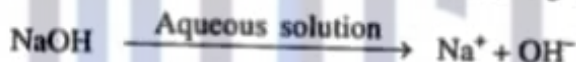
Thus we see that these bases are levelled to the base strength of OH^- ions, and hence these bases cannot be differentiated as bases in aqueous solution. On the other hand, since liq. NH_3 is a poor proton donor, these bases can be differentiated as bases in liq. NH_3 . Thus liq. NH_3 behaves as a differentiating solvent for NaH , NaNH_2 and NaOC_2H_5 .

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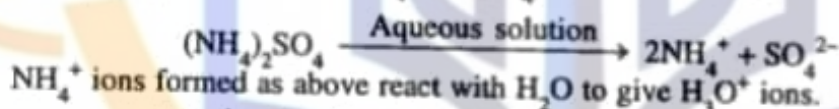


(b) In anhydrous H_2SO_4 : OH^- ions formed as above further react with H_2SO_4 to produce HSO_4^- and H_3O^+ ions.

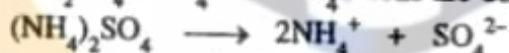


(c) In liq. NH_3 : In liq. NH_3 , no species are formed.

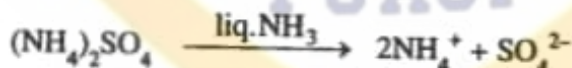
$(\text{NH}_4)_2\text{SO}_4$ (a) In water: NH_4^+ and SO_4^{2-} ions are formed.



(b) In anhydrous H_2SO_4 : NH_4^+ and SO_4^{2-} ions are obtained.



(c) In liq. NH_3 : NH_4^+ and SO_4^{2-} ions are formed. Due to the production of NH_4^+ ions, the solution becomes acidic.

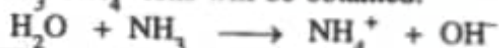


H_2O . (a) In water, there will be no reaction

(b) In anhydrous H_2SO_4 , Following reaction will occur.



(c) In liq. NH_3 , NH_4^+ ions will be obtained.



Problem 11. Predict the behaviour of urea in water, liq. NH_3 and anhydrous H_2SO_4

Solution. Urea is NH_2CONH_2 .

In water: NH_2CONH_2 is expected to behave as a non-electrolyte.

In liq. NH_3 : NH_2CONH_2 behaves as a weak acid in liq. NH_3 , since this compound produces NH_4^+ ion in this solvent.

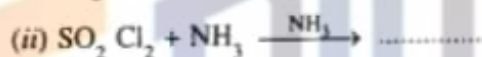


In anhydrous H_2SO_4 : When NH_2CONH_2 reacts with H_2SO_4 , HSO_4^- ion is produced. Thus NH_2CONH_2 behaves as a base in H_2SO_4

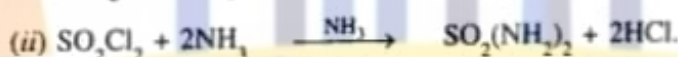


University Questions

- (a) Discuss in detail the classification of solvents.
(b) Discuss the following in liquid NH_3 and liquid SO_2 :-
(i) Oxidation-reduction reaction
(ii) Precipitation reaction. (Nagpur 2002)
- Compare the self-ionisation of water, liq. NH_3 and anhydrous acetic acid. (Delhi 2002)
- (a) Predict the behaviour of the following solutes in liquid SO_2 :
(i) SOCl_2 (ii) CS_2SO_3 (iii) $(\text{CH}_3)_4\text{N}^+\text{Br}^-$.
(b) Predict the solubility of the following solutes in liquid SO_2 :-
(i) NH_4SCN (ii) Na_2S .
(c) Complete the following equations :

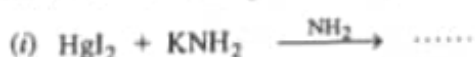


(Delhi 2002)



- (a) Explain chemical reactions in non-aqueous solvents with reference to those occurring in liq. NH_3 .
(b) Discuss the role of non-protonic solvents in chemical reactions with special reference to the reactions occurring in liquid SO_2 . (VBS, Purvanchal 2003)
- (a) What is meant by protic and aprotic solvents? Give examples.
(b) Give only one example for each of the following in liquid sulphur dioxide :
(i) Acid-base reaction (ii) Redox reaction
(iii) Precipitation reaction (iv) Complex formation reaction
(v) Reactions with organic compounds (Rohildkhand 2003)
- Explain the following reactions which take place in liq. SO_2 as medium : (Delhi 2003)
(i) Acid base reactions (ii) Precipitation reactions.
- (a) Classify the solvents on the basis of their proton-donor and proton-acceptor property. Give the following reactions in liquid NH_3 (Delhi 2003)
(i) Redox reaction (ii) Precipitation reaction.
(b) Give the following reactions in liquid SO_2
(i) Solvolysis
(ii) Complex formation. (Nagpur 2003)

- (a) Write notes on (in non-aqueous solvent)
(i) Ammonolysis (ii) Acid-base reactions (iii) Redox reactions
(b) What are non-aqueous solvents? Explain the following reactions in liquid HF.
(i) Auto ionisation reaction (ii) Precipitation reactions (iii) Solvation reactions
(iv) Reaction with $\text{C}_2\text{H}_5\text{OH}$ (Bhopal 2004)
- What do you understand by ionising and non-ionising solvents? Give examples. (GND Amritsar 2004)
- Discuss acid-base reactions in liq. SO_2 and metathetical reactions in liq. HF. (GND Amritsar 2004)
- How do the following reactions proceed?



(GND Amritsar, 2004)