

CHAPTER 4

NON-AQUOUS SOLVENTS

The ability of water to dissolve materials of a wide variety of types, structures and composition has led to the general assumption that water is a universal solvent and has unique properties. No other solvent is so versatile in terms of its availability, wide liquid range, ease of handling and ability to display a wide range of physical and chemical properties. However, many other liquids possess similar properties though to different extent and the difference between these and water is only of degree rather than a difference of behaviour. Many liquids have ability to dissolve inorganic substances and solvents such as alcohol, ether, benzene, esters etc. act as electrolytic solvents for inorganic substances and are useful on a qualitative basis and have almost no scientific value. On the other hand there are many other non aqueous solvents in which ionic reactions take place and such solvents in which ionizations take place and which are described as water like solvents include liquid ammonia, sulphur dioxide, hydrofluoric acid, hydrocyanic acid, sulphuric acid, acetic acid, bromine trifluoride and many others which are of great use for inorganic chemists and have been investigated in detail.

4.10 Classification

The solvents have been classified in following two types depending upon their physical and chemical properties.

4.10(a) Protionic Solvents

The protionic solvents are those which contain hydrogen which provides protons. These undergo auto ionization to give a solvated proton e.g., H_3O^+ in H_2O , NH_4^+ in NH_3 and H_2F^+ in HF , while aprotic solvents do not give protons e.g. SO_2 .

The protionic solvents may be acidic if these have a strong tendency to donate proton e.g., H_2SO_4 , HF basic if possess strong affinity for

proton like NH_3 or amphoteric which can act as both proton-donors and acceptors like water.

The protonic solvents can also be of non polar type *e.g.*, dichloro methane, carbon tetra chloride and polar type like acetonitrile and dimethyl sulphoxide.

4.10(b) Ionizing and Non-ionizing Solvents

This classification is based on the polar and non-polar nature of solvents. The polar solvent is composed of molecules in which there is separation between positive and negative charge, *i.e.*, dipoles and the solvent molecules align themselves in a manner so as to weaken inter ionic attraction within the ionic crystal and thus bring ions into solution. Because of their polar nature, these have strong tendency to form associated species and also undergo self ionization *e.g.*, water, ammonia, sulphur dioxide and hydrochloric acid. Non-ionizing solvents have low dielectric constant such as benzene and carbon tetrachloride and dissolve only non polar compounds and, do not initiate ionic reactions and also do not undergo self-ionization.

4.20 Properties of Ionizing Solvents

Familiar examples of solvents of this type are water, liquid ammonia, hydrogen fluoride etc. and these exist as ions only to a limited extent and are weak conductors of electric current. The following are the important properties of these solvents.

(i) These dissociate into ions in pure state as shown below:



(ii) These solvents are polar molecules which can solvate the ions through ion-dipole inter-action and weaken the inter ionic forces.

An ionic compound is composed of positive ions inter-spaced with negative ions and the forces between these affect the type as well as the properties of crystal lattice. Such compounds go into solution only when the dipole forces produced by solvents weaken the interionic forces within the lattice and the extent to which these forces are reduced depends upon the dielectric constant of the solvent. Thus a solvent with a high dielectric constant is a good solvent for electrovalent compounds and vice versa.

(iii) The polar solvents tend to associate due to dipole-dipole interactions present. This association is more pronounced in protonic solvents due to inter-molecular hydrogen bonding which increases the boiling point of solvent. Association is a condition where various molecules with oppositely charged ends attract each other to produce chains, rings or clusters. Such associated liquids are good solvents for polar compounds, which are capable of penetrating the associated structure, rupturing the associated bonds and entering the intermolecular space of solvent. The non polar compounds cannot behave in this manner and thus do not dissolve in these associated solvents.

(iv) The solvent should be easily available, in liquid state and should possess fairly large liquid range.

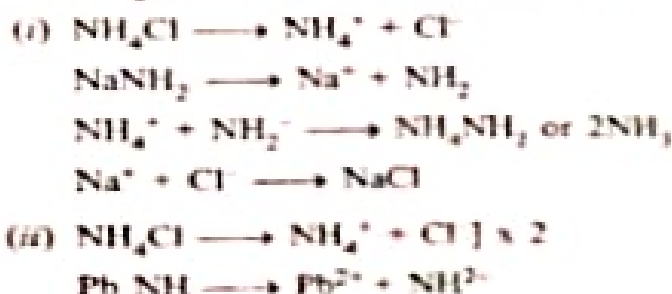
(v) However it is not necessary that all these properties may be associated with a given solvent. Most of the organic solvents as alcohol, carbon tetrachloride, Chloroform, benzene though easy to handle are not suitable as ionizing solvents, HF and HCN are dangerous to health, NH_3 , SO_2 and H_2S have low boiling points while acetic acid and dioxan have low dipole moment.

4.30 Type of Reactions

4.30 (1) Acid-base Reactions

From the definition of acids and bases using solvent system any substance which by ionization in a solvent produces the cation characteristic of that solvent behaves as an acid. Similarly a base is a substance which gives the anion characteristic of solvent. This acid base behaviour depends upon the acid-base nature of solvent, nature of solute, solute-solvent inter-action and high dielectric constant of solvent.

The view that a cation of a protonic solvent is a solvated proton is retained in both Bronsted Lowry concept as well as in solvent system concept. Thus in liquid ammonia NH_4^+ or ammonium ion behaves as an acid and NH_2^- , NH^{2-} or N^{3-} ions as bases as shown in following examples.





In non-protic solvents like benzene or carbon tetrachloride auto ionization does not occur and only Lewis type acid base reactions are possible and thus the solvent system definition of acid base is no more valid. In case of self ionizing non-protic solvents like SO_2 , typical type of acid base reaction is:



The acidity or basicity of a solvent is a property which influences the different behaviour of solutes in different solvents. As an example the case of acetic acid may be taken which behaves as a strong acid in liquid ammonia, a weak acid in water but a base in sulphuric acid as shown below:



The differentiating range of a solvent is governed by auto ionization constant of a solvent which varies from 0-14 for water, 0-3 for sulphuric acid and 0-27 for liquid ammonia. All acids stronger than characteristic cation of the solvent behave as strong acids and are levelled to the solvent cation while all bases stronger than the characteristic anion of solvent similarly behave as strong base and are levelled to solvent anion.



In non-protonic solvents like benzene or carbon tetrachloride auto ionization does not occur and only Lewis type acid base reactions are possible and thus the solvent system definition of acid base is no more valid. In case of self ionizing non-protonic solvents like SO_2 , typical type of acid base reaction is:



The acidity or basicity of a solvent is a property which influences the different behaviour of solutes in different solvents. As an example the case of acetic acid may be taken which behaves as a strong acid in liquid ammonia, a weak acid in water but a base in sulphuric acid as shown below:



The differentiating power of a solvent is measured by its protonic activity.

4.30 (2) Metathetical Reactions

If the solubility products of solute are known in a solvent only then the metathetical reactions can be predicted. These precipitation reactions depend mainly on the nature of solvent used in the reaction and the same solute may give different products in different solvents. Hence, it is not possible to generalise such reactions which are given for different solvents separately later in the chapter.

4.30 (3) Solvolytic Reactions

These are those reactions in which solvent reacts with a solute producing cations or anions and both get attached to solute molecule or ion thereby increasing the normal concentration of these in the solvent. Thus, in solvolysis reaction in water, liquid ammonia and liquid sulphur dioxide, the concentration of H_3O^+ and OH^- , NH_4^+ and NH_2^- and SO_2^+ and SO_3^{2-} is increased respectively. Though these reactions are also described separately for each solvent some typical examples are given below.



In a non-protonic solvent these reactions are represented as:



4.30 (4) Redox Reactions

In both aqueous as well as non aqueous media similar type of redox reactions occur. One important requisite is that the solvent should not undergo any kind of redox reaction itself. The principles applicable in aqueous medium also apply to non-aqueous media. Thus if a hydrogen electrode is to be used as a reference in liquid ammonia the cell should be:



These E^0 values vary considerably in different solvents and depend upon the difference in solvation energy and chemical reactivity of solvent. In many cases the order of reactivity also gets altered so that in non-aqueous media, the same reaction appears unique. Thus sodium metal can be electrolytically produced using pyridine medium and also can be electro deposited from ammonia solution.

The order of oxidation potential E_a in volts for alkali and alkaline earth metals in water is:



Which decreases to following values in liquid ammonia:



4.40 Individual Protogenic Solvent Systems

4.40 (1) Liquid Ammonia

A. General Theory

One of the most comprehensively studied non-aqueous solvents is liquid ammonia which shows a striking resemblance to water in its solvent action. It is less strongly associated than water thus indicating weaker hydrogen bonding because of which its boiling point and freezing point are less than water. Further its dielectric constant (22) is also lower than that of water (78.5) and therefore solubility of salts is less in liquid ammonia than water though many molecules dissolve to appreciable extent among which important are any ammonium salt, polarizable molecules like iodine and metal ions as Ni^{2+} , Co^{2+} , Pd^{2+} and Pt^{2+} . Most of the nitrites, nitrates, cyanides, thiocyanates are soluble but highly charged ions with high charge density like fluoride, hydroxide, oxide, sulphate, carbonate, phosphate and sulphites are insoluble. In case of halides solubility decreases from iodide to chloride therefore most iodides are soluble, bromides less soluble and only sodium, ammonium and beryllium chlorides are soluble.

One main difference between the solvent action of liquid ammonia and water is its ability to dissolve alkali metals without any chemical action so that these be recovered as such by the evaporation of solvent. The alkaline earth metals also dissolve in liquid ammonia but undergo some reaction as the evaporation of solvent leaves behind the metal hexammonate $\text{M}(\text{NH}_3)_6$. These metals dissolve in water to undergo no apparent reaction.

The structure and bond polarity of ammonia are very important as these confer some interesting properties on the solvent. The molecule possesses dipole moment and is capable of forming protogenic bridges, which means that the molecule is associated in liquid state as shown by its relatively high boiling point and heat of vaporisation. Because of the above two factors two significant properties are conferred on the molecule

when acting as a solvent. One is the power of auto ionization and the other is the property to solute charged particles giving the solvent an ability to dissolve polar substances which can dissociate under solvent influence.

Two ammonia molecules coming together tend to become oriented as expected from their dipoles and may form protonic bridges and normally the bridging proton tends to remain nearer to its original nitrogen atom. However, in the course of constant vibrations of atoms about their equilibrium position a situation may arise in which the bridging proton comes nearer to the other nitrogen atom. In effect one ammonia molecule removes a proton from other and this situation is equivalent to extracting an proton from amide ion NH_2^- , as shown in the following figures:



The amide ion is therefore a better electron donor than ammonia and if the NH_4^+ ion comes in contact with NH_2^- , the latter will at once take back its proton forming two ammonia molecules. Within an overwhelming excess of undissociated ammonia molecules, however the ammonium ion is easily lost from amide ion, specially since the extra proton on ammonium ion can transfer very freely from one ammonia molecule to next. Thus within the bulk of liquid ammonia appreciable amount of ammonium and amide ions are produced and this continues till the rate of combination equals rate of dissociation:



The amide ion is a better electron donor than OH ion as illustrated by the complete hydrolysis of amide ion in water.



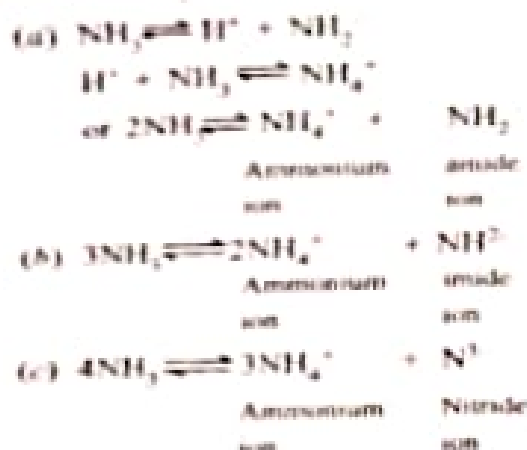
This means that a ammonia molecule does not give up a proton as easily as does water. Hence the autoionization does not proceed to the same extent as in water and this is confirmed from the experimental fact that the ion product constant (10^{-33}) for liquid ammonia is smaller than water (10^{-14}).

Two major problems arise when liquid ammonia is used as a solvent. Ammonia exists as a liquid only at low temperature and this temperature range is small. The studies are therefore to be made at low temperature,

liquid ammonia is also very hygroscopic and a special apparatus is to be used for making studies in it.

B. Auto Ionization in Liquid Ammonia

Liquid ammonia undergoes auto ionization which can be represented in the following modes.



It is seen from the above equations that in whatever manner liquid ammonia ionises, one solvent cation or acid ion and one solvent anion or basic ion is formed. It is further indicated that those substances which produce NH_4^+ ion or the solvent cation will act as acids, while those substances which produce NH_2^- , NH_2^{2-} and N^{3-} ions or the solvent anion will behave as bases in liq. ammonia. The former are called *ammino acids* and later are *ammino bases* and some typical examples of these are given below.

Ammino Acids: Substances such as ammonium salts, organic amides, acetic acid and sulphuric acid, all act as acids in liquid ammonia as clear from their ionization reactions:



urea



acetamide





Behaves as dibasic because it produces two NH_4^+ ions.

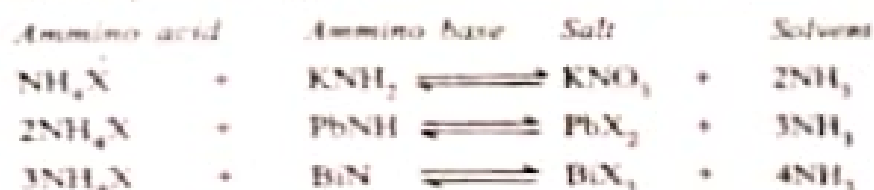
Ammino bases: Substances such as potassium amide, lead imide and bismuth nitride behave as ammino bases as these react to form the solvent anions:



C. Type of Reactions

Since ammonia is water like in its properties the chemical reactions which take place in liquid ammonia are quite similar to those taking place in water and can thus be studied under the same general types, which are described below:

(i) Acid-Base or Salt Formation Reaction: The auto ionization of ammonia gives ammonium ion and amide ion and hence ammonium salts will behave as acids and amide, imide and nitride ions as bases in liquid ammonia as given in section 4.4(iii). Thus, neutralisation reactions which are defined as the reaction between an acid and base to produce salt and solvent take place in liquid ammonia and some examples are:



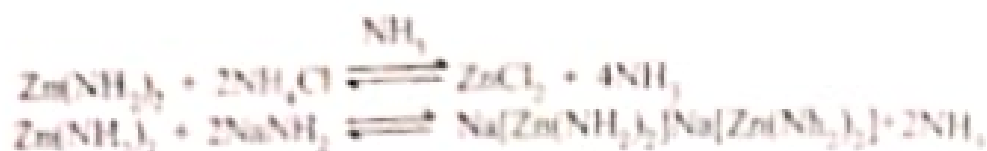
In these reactions ammonium ion is to be regarded as acid, amide as monoacidic base, the imide as diacidic base and nitride as triacidic base.

These reactions may be studied either conductometrically or using an acid base indicator such as phenolphthalain, which is colourless in liquid ammonia but develops a red colour in the presence of alkali amides. Thus the titration of an alkali amide with ammonium salts can be done using this indicator.

The fact that an ammonium salt is acidic in liquid ammonia is confirmed by the observation that ammonium salts dissolve alkali metal oxides and hydroxides and this reaction may be considered as acid-base phenomenon.



Amphoteric behaviour is shown by zinc (II) and Aluminium (III) salts and reactions in case of former are shown as



All the acids in water having pK_a II 12 are levelled to NH_4^+ ions in ammonia and act as strong acids. Molecules showing no acidic behaviour in water may behave as acids in liquid ammonia.



Substances behaving as bases in water are either insoluble or behave as weak bases. Strong bases are levelled off to NH_2^- ion



Ammonium salts in liquid ammonia react with active metals evolving hydrogen, but such reactions cannot be classified as acid base reaction.

(ii) *Metathetical Reactions:* Whenever two ions having low solubility product are brought together these reactions take place and proceed in the same manner as in aqueous medium. Thus when two ions capable of forming a sparingly soluble compound are brought together a precipitate is formed, and such compounds are considerably different from those which are insoluble in water.

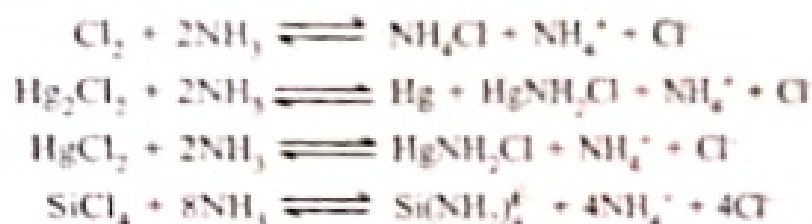
Chlorides in general are insoluble in liquid ammonia (except sodium, ammonium and beryllium chlorides) and if liquid ammonia solutions of



Many insoluble halides are not precipitated as simple halides but as complex amines similar to compounds containing water of crystallisation in water



(iii) **Solvolysis Reaction:** The solvolysis reactions in liquid ammonia are given the special name of ammonolysis or ammonolytic reactions and are similar to hydrolysis reactions in water. These may be considered as double decomposition or metathetical reactions in which ammonia is a reactant. These reactions have been studied very extensively and some important examples are following:



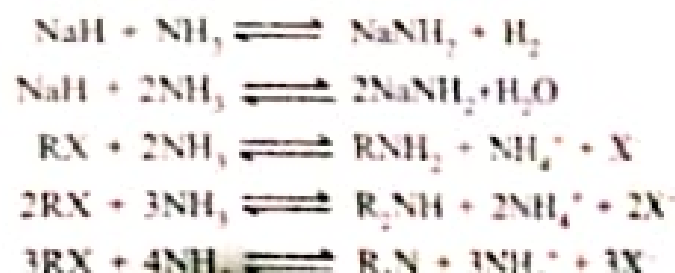
In such reactions the following pH scale can be devised which is similar to water:

$$\text{pH} = 13.5 \text{ or neutral when } [\text{NH}_4^+] = [\text{NH}_2^-]$$

$$\text{pH} = 0 \text{ or } 1\text{M } [\text{NH}_4^+]$$

$$\text{pH} = 27 \text{ or } 1\text{M } [\text{NH}_2^-]$$

Alkali metal hydrides (NaH) and oxides undergo ammonolysis to produce alkali metal amides, while alkyl halides RX (R = alkyl group, X = Cl, Br, I) produce primary, secondary and tertiary amines. These reactions are shown below:



(b) Complex Formation Reactions: The complex formation reactions in liquid ammonia have not been studied in detail but those studied appear to be similar to those in water. Thus in aqueous solution addition of KCN to a silver salt gives a white ppt of AgCN which dissolves in excess cyanide due to the formation of soluble $\text{Ag}(\text{CN})_2^-$ ion. In a similar manner zinc is precipitated as $\text{Zn}(\text{NH}_2)_2$ in liq. ammonia which dissolves in excess amide to form soluble ammonio zincate:



Aluminium salts also undergo the following analogous reaction:



Soluble ammonio aluminate

Similarly, many metal amides, imides and nitriles dissolve in a solution of potassium amide in liquid ammonia to form soluble amide complexes.



Soluble complex

(c) Redox Reactions: Redox reactions take place in liquid ammonia and are similar to that in water. Although most of the investigated reactions are found to be reduction processes and strong oxidising agents do not exist in liquid ammonia. But process of reduction and oxidation have to occur simultaneously and hence the study of these reactions in liquid ammonia is somewhat obscure.

Nitric acid is non oxidising and converted to ammonium nitrate while permanganate and dichromate are only weakly oxidising. But the reducing agents are very reactive and these effects are due to the presence of solvated electron. The reason why oxidising agents are not so active is that these have to compete against the solvent to take up the electron from the reducing agent. For reducing agents the transfer of electron is facilitated by the solvent. The alkali metals act as strong reducing agents in liquid ammonia due to the reaction.



The conversion of NaNH_2 to NaNO_2 is an oxidation reaction.

Nitrous oxide oxidises metallic potassium in liquid ammonia to K^+ and is reduced to N itself



Metallic Sodium in liquid ammonia undergoes following redox reaction with NH_4Br



Sulphur in elemental form reacts with a solution of sodium in liquid ammonia and gets reduced to sulphide ion S^{2-} which is ultimately precipitated as Na_2S



Potassium permanganate is reduced to K_2MnO_4 when treated with a solution of potassium in liquid ammonia. In the second stage K_2MnO_4 is reduced slowly to MnO .



Iodine in liquid ammonia also acts as a weak oxidising agent, oxidising ammoniosulfate to ammoniosulfate



D. Solutions of Metals in Liquid Ammonia

The metals dissolve in liquid ammonia and the resulting solution acts as powerful reducing agent due to the presence of free electrons in solution, which can be easily captured by reacting substances if these are electron acceptors.

If a small piece of alkali or alkaline earth metal is put in liquid ammonia it dissolves freely and a blue solution is formed. If more metal is added the colour is deepened and a brown phase separates which floats on the surface. This process continues till no more metal dissolves. The blue coloured solution has following characteristic properties:

(a) The colour of the solution in almost all cases is blue with a broad absorption maximum at 1450 nm and is independent of the metal dissolved.

(b) The solutions are very good conductors of electric current almost as good as free metal and better than an ordinary electrolytic conductor. The difference in the conductance being due to the difference in the conduction of cations only. The conductivity initially decreases with

(ii) Nitrous oxide to N_2 

(iii) Sulphur to sodium sulphide



(iv) Elemental oxygen to peroxide



(v) Copper iodide to copper

(vi) $KMnO_4$ to MnO 

Besides alkali metals, alkaline earth metals also give blue solutions possessing almost the same properties.

(g) Evaporation of solution leaves behind pure metals.

4.40 (2) Sulphuric Acid

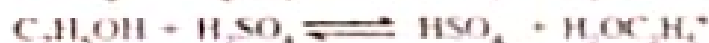
Sulphuric acid has a very viscous appearance and its dielectric constant is very high $\epsilon = 110 \pm 10$ and thus suggests that it should act as a better solvent than water. But due to its viscous nature the dissolution and crystallisation of solutes is a difficult and slow process. The acid solvent auto ionizes as



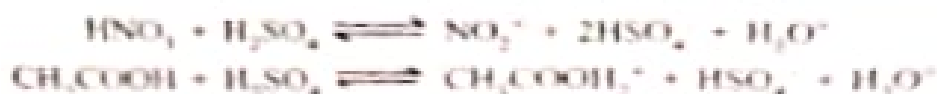
All substances behaving as bases in water also behave as bases in H_2SO_4 .



Those species which are otherwise neutral in water such as alcohol and urea have a tendency to accept proton from the acid solvent to form basic solutions:



Acetic acid and nitric also tend to behave as bases in this solvent due to following reactions:



Because of the strong tendency of the solvent to donate protons very few substances behave as acids amongst which are peroxydisulphuric acid and orthoboric acid.



4.10 (3) Liquid Hydrogen Cyanide

A. General Theory

The important properties such as low molecular weight, high boiling point, high dielectric constant which can make any substance a good solvent are all associated with this liquid. It has a very high boiling point of 297K, a low molecular weight, and a high dielectric constant of 2.93 which is higher than that of any other water like solvent. It is thus expected that it should be, as good if not better, a solvent as water. Most of the substances which dissolve and ionise in water should do the same in liquid HCN. But these expectations are not true and HCN is a far inferior solvent for ionic compounds than water and has a tendency to dissolve covalent compounds only instead. Few alkali metal salts such as NaCl, KCl, NH₄Cl, NaNO₃, K₂SO₄ and KI and many covalent chlorides in POCl₃, SOCl₂, SnBr₄, SnI₄, benzene, aniline, methanol and urea dissolve but do not ionise. The poisonous nature of the compound is a hazard in using it as a solvent.

B. Type of Reactions

(i) **Acid Base reactions:** The auto ionization reactions of hydrogen cyanide may be represented as



Thus those substances that furnish protons should act as acids and those compounds which produce cyanide ions should act as base. Thus soluble acids like H₂SO₄ and HCl may be neutralised using alkali cyanide ions thus furnishing example of acid base reaction. These reactions may be studied conductometrically or by using indicators which change colour in the solvent.



Substances which can dissolve in this solvent may roughly be classified into three groups:

- A Group of substances which dissolve without any appreciable reaction and this includes organic substances and some covalent inorganic compounds like HCl, HBr, AlCl_3 , As_2S_3 and Sb_2S_3 .
- This group includes those substances which dissolve and react either as oxidising solutes, or because of thiohydrolysis. These are aniline and PCl_5 .
- Under this group come those substances which are otherwise insoluble but undergo chemical reaction. E.g., are Na, Cu, Na_2O and AgNO_3 .

B. Type of Reactions

(i) **Acid Base Reaction:** The solvent autoionizes very slowly as



It is thus clear that hydrosulphides which can furnish HS^- ions should act as strong bases. This is found to be true and these bases can be titrated against strong acids as HCl, HBr conductometrically undergoing following neutralisation reactions.



(ii) **Metathetical Reactions:** Some important examples of metathetical reactions possible are:



(iii) **Solvolysis Reactions:** A number of solvolysis reactions have been studied in lg hydrogen sulphide and the product are either a sulphide, hydrosulphide or a thiohydrolysed chloro compound as shown below:

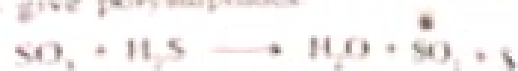


(iv) **Redox Reactions:** Highly electropositive metals like Na, K or Cu can reduce H_2S to produce hydrogen and a metal sulphide as the other product.

Non-Aqueous Solvents



SO_3 or peroxydisulphuric acid oxidise the solvent to SO_2 while free sulphur dissolves to give polysulphides:



4.4 (5) Liquid Hydrogen Fluoride

A. General Theory

Two important physical properties of liquid hydrogen fluoride are high dielectric constant and strong hydrogen bonds make it a solvent quite similar to water and its lower solvating power is not due to dissimilarity in physical behaviour but is due to difference in chemical properties. Its extreme chemical reactivity prohibits the dissolution of substances without chemical reaction.

A solute may dissolve in liquid hydrogen fluoride and may follow any of the following four courses.

(i) The HF may dissociate into ions e.g. H^+ and F^- ions just like other ionising solvents.



(ii) HF is chemically added to a solute such as acetic acid followed by its dissociation to give a complex ion and a fluoride ion.



(iii) The solute may dissolve and exchange its anion with fluoride ion. Eg is the reaction of HF and KCN.



(iv) The dissolution may occur with a distinct chemical reaction, e.g., reaction of H_2SO_4 .



Only fluorides, fluoroborates and perchlorates dissolve unreacted. Most of the halides are either insoluble and unreacted or react with evolution of hydrogen halide in solvent. Oxides and hydroxides react violently to produce fluoride ion and water reacts as shown below giving hydronium and bifluoride ions.



Sodium and potassium sulphates are readily soluble and form free sulphuric acid which reacts slowly giving fluoro sulphates. Other sulphates are insoluble.

B. Type of Reactions

(i) **Acid Base Reaction:** The auto ionization of liquid hydrogen fluoride may be represented by the equation



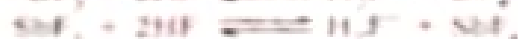
Thus those species which dissociate to produce fluoride ions in the solvent will behave as bases while those substances which protonate it will behave as acids. Thus all fluorides, behave as bases and some oxygen containing organic compounds like alcohols, ethers, ketones and many acid anhydrides also act as bases due to protonation of oxygen as shown



Even strong acids like HNO_3 and H_2SO_4 behave as bases in liquid HF since these produce F^- ions, while perchloric acid shows amphoteric behaviour as shown below:



Only a few substances such as BF_3 , AsF_5 and SbF_5 which are strong Lewis acids in aqueous solution function as acids in liquid HF probably due to the apparent protonation of solvent



These are often called super acids as these protonate even alkanes.



Typical neutralisation reaction in hydrogen fluoride can be illustrated by the following examples:



(ii) **Metathetical Reactions:** Anions such as sulphate and periodate are quite stable in solvent and precipitate metal salts if their sodium or potassium salts are added to a metal fluoride solution:



Perchlorates also tend to behave similarly:



The precipitation reaction resulting in the formation of AgBF_4 is very important and the compound is obtained as a white precipitate when HF solutions of AgNO_3 and BF_3 are mixed



(iii) **Solvolysis Reactions:** Certain covalent halides dissolve in anhydrous hydrogen fluoride to form metal fluorides and this reaction is analogous to solvolysis reaction.



(iv) **Miscellaneous Reactions:** Many organic compounds as alcohols, phenols, ethers, aldehydes and ketones dissolve to give highly conducting solutions which is due to the organic molecule accepting a proton to form a complex positive ion.



4.10 (6) Acetic acid

A. General Theory

Though acetic acid cannot be labelled as a water like solvent in physical properties like melting point (289°K) boiling point (330°K) stability and above all non toxic nature make it a solvent convenient to be used in laboratory. The most common difficulty encountered is to keep it in anhydrous condition as it is highly hygroscopic in nature and simple distillation is not sufficient to remove water and some tedious methods are to be used for purification.

The acid is associated in liquid state but because it exists as a dimer its dipole moment is zero. The low dielectric constant (7.14) predicts that it should be a poor solvent for ionic compounds but a large number of ionic compounds are found to dissolve in it. Main amongst these are Li^+ , NH_4^+ , Ca^{2+} nitrates, Li^+ , K^+ , NH_4^+ , Pb^{2+} , Cd^{2+} acetates, Ca^{2+} , Zn^{2+} , Fe^{2+} chlorides; AlCl_3 , HgCl_2 , HgI_2 are sparingly soluble while Cdl_2 and phosphates are insoluble.

B. Type of Reactions

(i) **Acid Base Reaction:** Typical acid base reactions take place between soluble acetates and strong acids. Its autoionization is expressed as



1.18

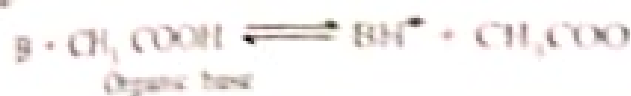
Thus soluble acetates will behave as bases and protonic acids as acids. A typical acid base and neutralisation reaction is shown below:



Zn²⁺ and Al³⁺ salts show amphoteric behaviour



It is also found that such weak organic bases like acetamide and ureamide which cannot be titrated in aqueous medium can be titrated in acetic acid medium using perchloric acid as a titrant. The following reactions occur



(ii) **Metathetical Reactions:** There is a large variation in the solubility of salts in acetic acid and this permits many metathetical reactions to occur. Some such examples are given below:



(iii) **Complex Formation Reactions:** These reactions are similar to those taking place in aqueous medium. Typical examples are the reaction between ferric chloride and ammonium thiocyanate in which a deep red coloured complex is formed $[\text{Fe}(\text{CNS})_6]^{3+}$ and between Co (II) and thiocyanate ion to give a deep blue coloured complex $(\text{NH}_4)_2[\text{Co}(\text{CNS})_4]$:



is a poor conductor of electric current and auto ionizes as:



on this basis thionyl compounds which are freely soluble and give conducting solutions will function as acids as these ionize to give thionyl ions the cation characteristic of solvent and soluble sulphides will behave as bases.

The solvent is not associated as expected because it has no hydrogen atoms responsible for associations in liquids. The thionyl halides and acetates are freely soluble and thus miscible in all proportions while other salts have solubilities of order 0.2-2% because of its weak solvating properties. The solubility of halides decreases from iodide to fluoride. The alkali and alkaline earth metal sulphides are fairly soluble, while sulphates, cyanides and thiocyanates have limited solubility in liquid sulphur dioxide. It is far better solvent for covalent compounds than ionic and this property is used for purification of petroleum products on industrial scale.

B. Type of Reactions

As the solvent is similar to water in its behaviour the reactions taking place in the solvent may be described in terms of the same general types as given below:

(i) **Acid Base Reactions:** In liquid sulphur dioxide thionyl compounds producing SO^{2+} ion will behave as acids while sulphites giving SO_3^{2-} will behave as bases. Thus thionyl chloride can be labelled as acid and calcium sulphite as base. These are freely soluble and dissolve to undergo reaction:



This reaction can be followed conductometrically and a typical neutralisation curve is obtained.

Zn(II) and Al(III) show amphoteric behaviours by analogy to water:



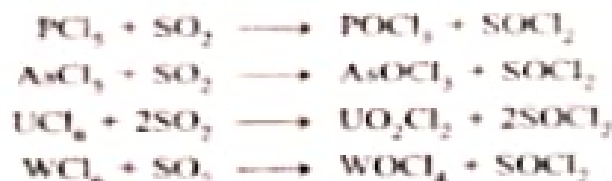
of substances in the solvent which permits precipitation reactions to be carried out in the solvent



The free solubility of thionyl chloride in liquid sulphur dioxide is utilised for the preparation of new thionyl derivatives. These can be prepared by the precipitation of an insoluble compound such as AgCl as given below:



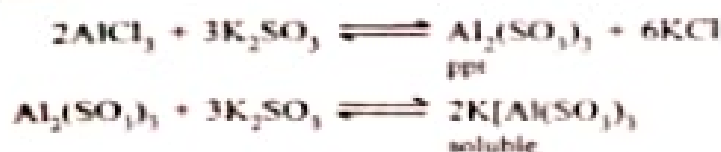
(iii) *Solvolysis Reactions:* These PCl_5 reactions have been observed in case of certain covalent halides like PCl_5 , AsCl_3 , UCl_6 and WCl_6 , which form oxyhalides and the concentration of SO_2^{2-} ions is increased.



(iv) *Complex Formation Reactions:* The type of complex ions formed in liquid sulphur dioxide are analogous to those formed in water. Typical behaviour of this type is the dissolution of the ppt of an amphoteric metal ion in its own anions e.g., the formation of halo complexes by the interaction of covalent halides and alkali metal halides.



Another example is the soluble complex formed between Al(III) and SO_3^{2-} ions



Solubility of iodine in liq sulphur dioxide is increased when an alkali metal iodide (MI) is added due to the formation of complex MI_3



When HgI_2 or CdI_2 are dissolved in liq SO_2 in presence of KI, the solubility increases due to the formation of complex K_2MI_4 .



(i) **Redox Reactions:** If a reaction is carried out in liquid sulphur dioxide may either act as a weak oxidising agent depending upon the type of substance with which it reacts. Sulphur dioxide has no such properties but it can act as a reducing agent. Many reactions can take place, though very few such reactions are known. One example is the oxidising action of metal ions upon sulphur dioxide illustrated by the following reaction



which can be studied conductometrically

The concept of autoionization of sulphur dioxide into SO_2^+ and SO_2^{2-} is not found to be true but using radioactively labelled sulphur SO_2 exchanges radiosulphur S^{35} with labelled $S^{35}O_2$, or $S^{35}O_2$ with $S^{35}O_2$ and suggests a complicated mechanism for the ionization of SO_2



(ii) **Sulphur Dioxide of Crystallisation:** Due to the high solubility of salts in liquid sulphur dioxide compounds containing sulphur dioxide of crystallisation similar to water and ammonia of crystallisation are produced. Some examples are Na_4SO_2 , K_4SO_2 , Li_2SO_2 , Al_2SO_2 and KCN_2SO_2 and these are analogous to hydrates and ammoniates.

4.5 (2) Bromine Trifluoride

A. General Theory

Bromine trifluoride has a wide liquid range from mp 282°K to bp 397°K, a high specific conductance as well as a tendency to remain associated in liquid state and these properties make it a good solvent for ionic solutes. But its highly reactive and corrosive nature prohibits the study of reactions in this medium.

B. Type of Reactions

(i) **Acid base Reactions:** The auto ionization of the solvent may be expressed as: