Chapter
15

Nonaqueous Solvents

15.1 INTRODUCTION

As a solvent, ***water is a universal*** one from the standpoint of its liquid range, ease of handling, innocence towards health, ability to dissolve the versatile types of inorganic and organic compounds and low viscosity.

However, many nonaqueous solvents have been studied to extend our knowledge.

15.2 CLASSIFICATION OF SOLVENTS

The solvents can be classified from the standpoint of different properties. Classification **based on the proton donor and proton acceptor properties** of the solvents is well known. These are as follows :

	Solvent type	*Proton donor/acceptor property*	*Examples*
(1)	**Protic or Protonic:**		
	(i) Protogenic, *i.e.* acidic	Proton donor	HF, CH_3CO_2H, HCN, H_2SO_4, etc.
	(ii) Protophilic, *i.e.* basic	Proton acceptor	NH_3, N_2H_4, amines
(2)	**Aprotic or Nonprotonic** (polar and nonpolar)	No tendency either to accept or donate protons	CCl_4, C_6H_6, SO_2, etc.
(3)	**Amphiprotic**	Both the tendencies to accept and donate protons	H_2O, ROH

Sometimes, the **aprotic solvents** are described as the solvents having no protons to be donated (but they may accept protons). They may be classified into the following groups :

1. ***Nonpolar*** **(*or weakly polar*)**, ***nondissociated and nonsolvating solvents*** **:** These are CCl_4 and other hydrocarbons.
2. ***Strongly solvating but nonionised (or weakly ionised) solvents*** **:** These are CH_3CN, *DMF*, *DMSO*, *THF*, etc. (see donor numbers, Sec. 14.7.8).
3. ***Highly polar and autoionising solvents*** **:** These are BrF_3, IF_5, $OPCl_3$, etc. Their autoionisation modes will be discussed later.

From the standpoint of dissolving the ionic and nonionic compounds, the solvents can be classified as: (i) ***ionising*** and (ii) ***nonionising solvents***. Generally the ionising solvents are efficient in dissolving the ionic compounds while the nonionising solvents predominantly dissolve the nonionic compounds.

- **Some Common Solvents:** The properties of some common solvents are given in Table 15.2.1.

Table 15.2.1. Properties of some common solvents.

	Solvents	*Liquid range* (0°C)	$\varepsilon/\varepsilon_o$ *(dielectric constant)*
(i)	Water (H_2O)	0 to 100	78
(ii)	*N*-methylacetamide (NMA)	28 to 206	165
(iii)	Propylene carbonate (PC)	–55 to 240	70
(iv)	Acetonitrile (CH_3CN)	– 45 to 82	38
(v)	Dimethylformamide (*DMF*) $HC(O)NMe_2$	– 60 to 153	38
(vi)	Dimethylsulfoxide (*DMSO*)	18 to 189	47
(vii)	Nitromethane (CH_3NO_2)	– 29 to 101	35
(viii)	Glycol-dimethylether (glyme, $CH_3OCH_2CH_2OCH_3$)	– 58 to 83	3.5
(ix)	Tetrahydrofuran (*THF*)	– 65 to 65	7.5
(x)	Dichloromethane (CH_2Cl_2)	– 98 to 40	9.0
(xi)	Ammonia (NH_3)	– 78 to –33	22 (–33°C)
(xii)	Hydrogen cyanide (*HCN*)	– 14 to 26	107 (25°C)
(xiii)	Sulfuric acid (H_2SO_4)	– 10 to ~ 300	110 (20°C)
(xiv)	Hydrogen fluoride (*HF*)	– 83 to 19	84 (0°C)

- **Inert organic solvents:** Water being redox active, may itself participate in redox reactions with the solutes (*cf.* **redox stability field of water,** Sec. 16.8.3). Because of the **amphiprotic character** of water, it may also participate in acid-base reactions with the dissolved solutes. These **two serious limitations** of water as a solvent are absent in many inert organic solvents which may be classified in two groups.

i. **Nonpolar or weakly polar traditional organic solvents** like benzene, hexane, $CHCl_3$, CH_2Cl_2, etc. are widely used for dissolving nonpolar or slightly polar covalent compounds.
ii. **Polar organic solvents** with the high dielectric constants (ε) are widely used for dissolving the polar species. Examples of such polar organic solvents are: *N*-methylacetamide (*NMA*) ($\varepsilon = 165$), propylene carbonate (*PC*) ($\varepsilon = 70$), dimethylsulfoxide (*DMSO*) ($\varepsilon = 47$), dimethylacetamide (*DMA*) ($\varepsilon = 38$), acetonitrile ($\varepsilon = 38$), dimethylformamide (*DMF*) ($\varepsilon = 38$), etc.

- **Determination of water (in small quantities) present in solids or liquid samples (soluble in anhydrous methanol) by Karl-Fischer titration:** The sample is dissolved in anhydrous CH_3OH and titrated with the reagent made of SO_2 and I_2 as the pyridine adducts (*i.e.* $py \cdot SO_2$ and $py \cdot I_2$) in anhydrous CH_3OH. Here the solvent CH_3OH reacts with SO_2 to form methyl sulfite ($CH_3OSO_2^-$) which is subsequently oxidised by I_2 to methylsulfonate ($CH_3OSO_3^-$) in presence of water. The reaction can be followed by using the conventional **iodometric indicator** or by coulometrically to generate I_2 from the reduced I^-.

$$CH_3OH + py \cdot SO_2 \rightarrow pyH^+ + CH_3OSO_2^-$$

$$CH_3OSO_2^- + py \cdot I_2 + py + H_2O \rightarrow 2pyH^+ + 2I^- + CH_3OSO_3^-$$

The overall reaction is: $I_2 + SO_2 + 3py + CH_3OH + H_2O \rightarrow 3pyH^+ + 2I^- + CH_3OSO_3^-$

The stoichiometry indicates that **one mole of I_2 consumes one mole of H_2O to oxidise SO_2 to sulfate**. Because of the objectionable odour of pyridine, it is now replaced by **imidazole** as the required base.

15.3 CHARACTERISTICS OF THE IONISING SOLVENTS

- **Dielectric constant and solubilising power :** The electrostatic attractive force between the oppositely charged ions (q^+ and q^-) separated by r-distance in a medium of dielectric constant (K) is given by:

$$F = \frac{1}{K}(q^+ q^- / r^2), \text{(in CGS system)}$$

In SI units, $F = q^+q^-/(4\pi\varepsilon r^2)$ where ε is called the *permitivity* of the medium. In free space, $\varepsilon_o = 8.854 \times 10^{-12}$ Farad per metre. The ratio $\varepsilon/\varepsilon_o$ is called the ***relative permitivity*** of a medium and it is related with the ***dielectric constant*** of the medium.

It is evident that with the increase of the dielectric constant (*i.e.* permitivity), the force of attraction between the cation and anion is decreased and it facilitates the separation of the oppositely charged ions. In the ionic solids, the lattice energy arises from the electrostatic interaction. Hence to reduce this electrostatic interaction, the solvents of higher dielectric constant will be more promising. This is why, the **ionising solvents** are of high dielectric constant.

In fact, water (having the much higher K) can dissolve many **2–2 salts** (particularly, if the cation is already hydrated as in $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, etc.) of higher lattice energy while liquid NH_3 having a relatively lower K-value dissolves mainly the **1–1 salts of less lattice energy**.

The dielectric constant property of a solvent determines the possibility of **ion-pair formation**. In fact, in liquid NH_3, ion-pair formation is an important phenomenon and consequently, dissociation of many strong acids occur to a less extent (see Sec. 15.4). Autoionisation of the solvent is also disfavoured for the low K values.

- **Autoprotolysis constant of solvent and acid-base strength:** The autoprotolysis constant (K_s) of different solvents are given in Table 14.11.1. Besides the inherent acid-base strength of the solvent, its dielectric constant (K) plays a crucial role to determine the K_s-value which decreases with the decrease of K. In general, **acids and bases become weaker in strength in solvents of low autoprotolysis constant**. It is illustrated below:

Solvent	**Water**	**Methanol**	**Ethanol**	Water *vs.* primary alcohol as the solvent (effect of dielectric constant and K_s).
~ K_s:	10^{-14}	10^{-17}	10^{-19}	
~ K:	80	30	25	
pK_a of CH_3CO_2H:	4.8	9.5	10.5	Decreasing trend of strength with the decrease of K_s.
pK_b of $Ph—NH_2$:	9.5	11.0	13.3	

- **Dipole moment and solubilising power:** If the solvent molecules are polar then the solute-solvent interaction through the ion-dipole interaction will favour the dissolution of the ionic compounds. For the ionic compounds, both the cations and anions are to be solvated. The cations are generally smaller in size and for the metal salts, the solvation of the cations is actually metal-ligand interaction in the language of coordination chemistry. The order of coordinating power (see donor number, *i.e.* D.N., Sec. 14.7.8) of some common solvents towards some typical cations is: $DMSO > DMF \approx H_2O >$ acetone $\approx CH_3CN > CH_3NO_2 > C_6H_5NO_2 \gg CH_2Cl_2$. Generally, the polarity and coordinating power of a solvent are interrelated and both these properties simultaneously increase.

- **Polarisability and hard-soft character and solubilising power:** The permanent dipole moment of H_2O is higher than that of NH_3, but the polarisability of NH_3 (2.21 Å^3) is higher than that of H_2O

(1.48 Å^3). **Thus the solubilities of salts in water is *mainly controlled by ion-dipole interaction*. On the other hand, for solubilities in liquid NH_3, the van der Walls interaction including the London dispersion force arising from its polarisability and mutal polarisation are also quite important besides the ion-dipole interaction (*cf.* Sec. 11.4.3).** In other words, because of the higher polarisability, NH_3 is a softer Lewis base (compared to H_2O) and liq. NH_3 appears as a good solvent for the salts with the electron rich and soft cations like Ag^+, Cd^{2+}, etc. ***Because of this fact, liquid NH_3 appears to be a good solvent for the solutes having a large number of electrons and polarisable moieties.***

Besides the ion-dipole interaction, different types of solute-solvent interactions may favour the dissolution process. Sometimes, the π-bonding interactions may play an important role in this regard. $AgClO_4$ gets dissolved in C_6H_6 because of the **π-type interaction** between the filled metal *d*-orbitals and empty π* of C_6H_6. Acetonitrile can readily dissolve *Cu*(*I*) and *Ag*(*I*) salts because of the complexation of the metal centre with the solvents.

● **Ionic mobility of the autoprotolysis products and Grotthus mechanism of ion transport:** The ionic mobility of H_3O^+ and OH^- in aqueous media is very high and it is explained in terms of ***Grotthuss mechanism*** (*i.e.* proton jump/switching mechanism, Fig. 11.1.7.12) through the *H*-bonded network of the solvent (*cf.* Sec. 14.3.8). In fact, for the stronger '$X—H\cdots X$' *H*-bond (*i.e.* more symmetric *H*-bond), the **energy barrier for proton transfer** at the middle of the **potential-energy well** (*cf.* Figs. 11.1.4.3, 11.1.7.12, 11.9.2) is small. For the weaker $X—H\cdots X$ *H*-bond (*i.e.* more asymmetric *H*-bond) having the ***W*-shaped potential energy well**, the energy barrier for proton transfer is higher. It explains why the ionic mobilities of the autoprotolysis products of the protic solvents like H_2O or HF experiencing the stronger *H*-bond are so high. On the other hand, the ionic mobility of NH_4^+ and NH_2^- in liquid NH_3 is normal compared to the other ions. ***It indicates the better and stronger H-bonding network in water.*** This is also reflected in its higher boiling point (*cf.* 100°C for H_2O, –33°C for liquid NH_3). The lower proton transfer rate constant also supports the same fact.

$$NH_4^+ + NH_3 \rightleftharpoons NH_3 + NH_4^+, k = 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(cf. H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+, k \approx 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

(almost diffusion controlled rate)

● **Viscosity :** The viscosity of the solvent molecules drastically influences the mobility of the solute particles. Highly viscous solvents hinder the crystallisation, precipitation, mobility and diffusion of the ions.

Table 15.3.1: Physical properties of some ionising solvents

Solvent	*Dielectric Constant ($\varepsilon/\varepsilon_o$)*	*Viscosity (millipoise)*	*Dipole moment (D)*	*Autoionisation*	*Ionic product*
Water	78.5 (25°C)	10.1	1.84	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	10^{-14}
Ammonia	22 (– 33.5°C)	2.6	1.46	$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$	10^{-27}
Hydrogen fluoride	83.6 (0°C)	2.4	1.90	$3HF \rightleftharpoons H_2F^+ + HF_2^-$	$> 10^{-14}$
Hydrogen cyanide	107 (25°C)	2.0	2.93	$2HCN \rightleftharpoons H_2CN^+ + CN^-$	10^{-19}
Sulfur dioxide	17.3 (– 16.5°C)	2.3	1.61	$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$	–

15.4 LIQUID AMMONIA AS A SOLVENT

(A) **Solvent character :** Boiling point = – 33°C. Freezing point = – 77.7°C. Relative dielectric constant = 22 (at – 33.5°C). Ionic product = 10^{-27}. Dipole moment = 1.46 D. Polarisability = 2.21 Å^3.

(B) **Dissolution power :** It has been already pointed out (see Sec. 15.3) that the solvents with the lower diectric constants are less efficient to separate the highly charged cations and anions from their salts. Similarly, the solvents with the lower dipole moments are less efficient to solvate the cations and anions through the ion-dipole interaction to dissolve their salts. From the standpoint of dielectric constant, ionic product and dipole moment, ***liquid NH_3 appears to be a weaker ionising solvent compared to water***. In fact, the salts of **low lattice energy** (*i.e.* salts constituted by large ions of small charge) are generally soluble in liquid NH_3. In general, water (having the higher dielectric constant and dipole moment) can dissolve many 2-2 salts while liquid NH_3 dissolves mainly 1-1 salts of low lattice energy. However, other properties like **polarisability, hard-soft character, complex forming power** etc. of liquid NH_3 as a solvent are to be considered to assess the solubilisation process in liquid NH_3.

The **higher polarisability** of NH_3 (*cf.* 2.21 Å^3 for NH_3, 1.48 Å^3 for H_2O) can favour the solubilisation process through the van der Walls interaction including the London force (*cf.* Sec. 11.3.1 to understand the dependence on polarisability) which is favoured by the **higher polarisability of solvent**. In fact, the salts constituted by the **polarisable cations** are easily soluble in liquid NH_3. The higher polarisability makes NH_3 a **softer Lewis base** and this property makes it a good solvent for the salts **having the softer cations** like Ag^+, Pd^{2+}, Pt^{2+}, Zn^{2+}, etc.

Consideration of the abovementioned factors can explain why liquid NH_3 can dissolve the following types of salts: (i) ammonium salts irrespective of the character of the associated anions (except those of multivalent anions), (ii) salts having the polarisable ionic moieties, (iii) salts having the metal ions capable of forming the ammine complexes (*e.g.* salts of Ni^{2+}, Cu^{2+}, Co^{2+}, Pd^{2+}, Pt^{2+}, etc.).

It favours the salts having the uni-negative large anions (e.g. $NO_3^-, NO_2^-, CN^-, SCN^-$) but disfavours the satls having the small anions and polyvalent anions (e.g. F^-, OH^-, $O^{2-}, SO_4^{2-}, PO_4^{3-}$ etc.). ***Actually, the satls having the high lattice energies are insoluble in liquid NH_3.*** The small anions and polyvalent anions yield large lattice energies.

For the halides, the solubility order runs as: $I^- > Br^- > Cl^- > F^-$. It can be explained in terms of lattice energy or covalency introduced into the salt from the polarisability of the anionic parts. **Mutual polarisation in the interaction between the solvent and constituent ions** of the salt also supports the sequence (*cf.* Secs. 15.3, 11.4.3 for the importance of **mutual polarisation**).

Note **:** Solubility sequence of halide salts :

$$I^- > Br^- > Cl^- > F^- \text{ (in liquid } NH_3)$$

$$F^- > Cl^- > Br^- > I^- \text{ (in water)}$$

The opposite order supports that water is a much better ionising solvent. The higher dipole moment (1.84 D vs. 1.46 D) and higher dielectric constant (78.5 vs. 22) of water make it a much better ionising solvent.

(C) **Strength of *H*-bond in the *H*-bonded network of solvent and ionic mobilities of the autoprotolysis products (see Sec. 14.3.8):** The said *H*-bond strength order is: $H_2O > NH_3$ and it is supported by the boiling point order: $H_2O > NH_3$. Mobility of the autoprotolysis products of protic solvents occurs through **the *H*-bonded network** of the solvent (**Grotthuss mechanism**, Sec. 14.3.8). The stronger $X—H\cdots X$ *H*-bond makes it more symmetric. In terms of the **potential-energy well** of the $X—H\cdots X$ segment, the **energy barrier of proton transfer** in the middle of the potential well is smaller for the more symmetric *H*-bonding (*cf.* Figs. 11.1.4.3, 11.9.2), *i.e.* stronger *H*-bond. **This is why, the proton transfer rate is much higher in H_2O or *HF* experiencing the better *H*-bonding interaction than in liquid NH_3.** In fact, ionic mobilities of NH_4^+ and NH_2^- (*i.e.* autoprotolysis products of liquid NH_3) are only modestly higher than those of other ions in liquid NH_3 which experiences relatively a much weaker *H*-bond (*i.e.* higher energy barrier in the middle of the ***W*-shaped potential well** for the $N—H\cdots N$ segment). It may be mentioned that the proton transfer rate in liquid NH_3 is about 10^3 times slower than that occurring in H_2O.

(D) **Solution of metals :** *Metals having the low ionisation energies, low sublimation energies and high solvation energies for the corresponding metal ions, the metals* (forming M^{n+}) *are dissolved in liquid* NH_3 *to produce* ***a blue coloured solution***. Such metals are the alkali and alkaline earth metals (*e.g. Ca, Sr, Ba* forming M^{2+}), europium (*Eu* forming Eu^{2+}) and ytterbium (*Yb* forming Yb^{2+}). These metals dissolve in liquid NH_3 through ionisation (*i.e.* $M \rightarrow M^{n+} + ne$) *where the products of ionisation are solvated.* On evaporation of metal-liquid NH_3 solution, the metal is completely recovered (*i.e.* ***no net chemical reaction in solution***). Such solutions have the ***following characteristic properties.***

(i) **Colour:** The **blue colouration** changes into the metallic **bronze colouration** with the increase of metal concentration. This fine blue colouration was first noticed by Sir Humphry Davy in the interaction of potassium with liquid NH_3.

(ii) **Colour metal independent:** The blue colouration and its spectral behaviour are independent of the nature of the metal dissolved.

(iii) **Conductivity:** The conductivity of the blue solution is somewhat better than that of a strong electrolyte solution. The conductivity of the blue solution varies from metal to metal because of the variation of the ionic conductivity of the metal ions. The conductivity decreases with the increase of concentration of the particular metal, then after passing through a minimum (*ca.* 0.05 M for *Na*, *cf.* Fig. 15.4.3), it again increases sharply and the saturated solution conducts electricity like the liquid metals described as the **expanded metal** (*cf.* specific conductivity: $\sim 10^4$ ohm^{-1} cm^{-1} for *Hg* and *Na* in liquid NH_3).

(iv) **Magnetic susceptibility:** The dilute blue coloured solutions are **paramagnetic** indicating the presence of **unpaired electrons**. The electron paramagnetic resonance (*epr*) ***g*-factor** observed for the paramagnetic solution is very close to that of the **free electrons**. It suggests that the interaction between the solvent and unpaired electrons responsible for paramagnetism is rather weak and this is why, these unpaired electrons of blue solutions are described as the **quasi-free electrons**. For the dilue blue coloured solutions, the magnetic susceptibility supports the presence of **one quassi-free electron per alkali metal atom**. This paramagnetic susceptibility decreases with the increase of concentration of the metal and the solution becomes **diamagnetic in the region of the conductivity minimum**. But the solution becomes again **weakly paramagnetic** at still higher concentrations leading to the saturated solution showing the metallic bronze colour.

(v) **Density:** The density of blue coloured dilute solution is appreciably lower than that of liquid NH_3 itself. The bronze coloured solution obtained at very high concentration is lighter than the dilute blue coloured solution (*cf.* **liquid-liquid phase separation, floating of the bronze coloured solution on the blue coloured solution**).

(vi) **Thermodynamic stability:** ***The blue solution of alkali metals in liquid NH_3 is not thermodynamically stable with respect to the following reaction* :**

$$M + NH_3 \rightarrow MNH_2 + \frac{1}{2}H_2 \text{ or, } e^-(\text{solvated}) + NH_3 \rightarrow NH_2^- + \frac{1}{2}H_2$$

Thus the blue solution on standing becomes colourless due to removal of solvated electrons responsible for the blue colour. ***Here it should be mentioned that the said thermodynamically unstable solution enjoys the kinetic stability due to overvoltage for the evolution of H_2*** (*cf.* Sec. 16.1.9, electrochemistry in liquid NH_3). However, the process is efficiently catalysed by Fe_2O_3 and transition metal ions. In absence of the catalytic impurities, **completely anhydrous solution** decomposes very slowly.

(vii) **Reducing activity:** The solutions are highly reducing.

(viii) **As an expanded metal at high concentration:** The concentrated bronze coloured solution shows a metallic lustre. Its conductivity, magnetic susceptibility, etc. are comparable to those of the metals.

Understanding the properties of metal-ammonia solution (R. Hoffman *et al*, *Angew. Chem. Int. Ed.* **48**, 8198-8232, 2009): It is believed that metals get ionised giving rise to the ammoniated metal ions and electrons. It is illustrated for the **monovalent alkali metals (*M*)**.

$$M + (x + y)\ NH_3 \xrightleftharpoons{K} M(NH_3)_x^+ + e(NH_3)_y^+,\ i.e.\ e^-\ @\,(NH_3)_y\ ;\ K \approx 10^{-2}$$

• **Cavity concept to house the solvated electron:** It is suggested that the solvated electron, *i.e.* $e(NH_3)_y^-$ is ultimately housed in the **cavities generated through the rearrangement / reorientation of the solvent NH_3 molecules**. In the cavity (radius in the range, 320–340 pm), the electron is kept held by the **electrostatic potential barriers** produced by the cavity forming NH_3 molecules. The H-atoms of these cavity forming NH_3 molecules are projected towards the inside ("***H-in***") to establish the **$H^{\delta+}\cdots e^-\cdots H^{\delta+}$ electrostatic stabilising interaction**. Thus the trapped or encapsulated electron does not reside at the centre of the cavity but **near the *H*-atoms**. This **encapsulation** of electron is denoted by the standard convention, **$e^-@(NH_3)_y$** where @ stands for encapsulation (*cf.* Sec. 10.11.5, Vol. 2).

The detailed theoretical calculations (Ref. *Angew. Chem Int. Ed.*, **48**, 8198-8232, 2009) have shown that among the cavity forming NH_3 molecules, there is no H-bonding interaction and the electron occupies a diffuse *MO* (*i.e.* **singly occupied *MO* or *SOMO***) built up largely from the lowest unoccupied *MOs* of the cavity forming NH_3 molecules. **The *SOMO* brings about the bonding interaction among the *H*-atoms of the nearest cavity forming NH_3 molecules**. This bonding interaction (different from the well-known H-bond) has been represented by **$H\leftrightsquigarrow H$**.

• **Cavity formation model (Catterall-Mott model) for $e^-@(NH_3)_y$ to explain the reduced density:** It is argued that the strongly polarising electron reorients the NH_3 molecules around it with the H-atoms pointed inwards ("***H-in***") through the destruction of H-bonded liquid NH_3 structure to bring about the $H^{\delta+}\cdots e^-\cdots H^{\delta+}$ interaction (*i.e.* **$H\leftrightsquigarrow H$** in terms of *MOT*). Thus to form the cavity to encapsulate the electron, the **normal *H*-bonded liquid NH_3 structure is destroyed** (Fig. 15.4.1) due to their **reorientation** (H-atoms of the cavity forming NH_3 molecules pointing towards the centre, *i.e.* "***H-in***") to establish the **$H\leftrightsquigarrow H$ stabilising interaction**.

Thermal agitation, **hydrogen-hydrogen repulsion and dipole-dipole repulsion** lead to the **expansion of cavity**. This cavity formation model was first proposed by Catterall and Mott. **Formation of such expanded cavity** along with the **rupture of *H*-bonded liquid NH_3 structure** can explain the volume expansion, *i.e.* **reduced density** (compared to that of pure liquid NH_3).

• **Cavity model (Jortner model) to explain the blue colour of dilute metal-ammonia solution:** The trapped or encapsulated electron within the cavity (*i.e.* $e^-@(NH_3)_y$) mimicks the model, **particle in a box** (see Sec. 3.5.2, Vol. 1). The **wavefunctions of the energy states** of the trapped electron can be written to describe the distribution of the electron density. The wave functions roughly resemble those of the H-atoms. The ground state and the immediate excited state correspond to the **1*s* and 2*p***

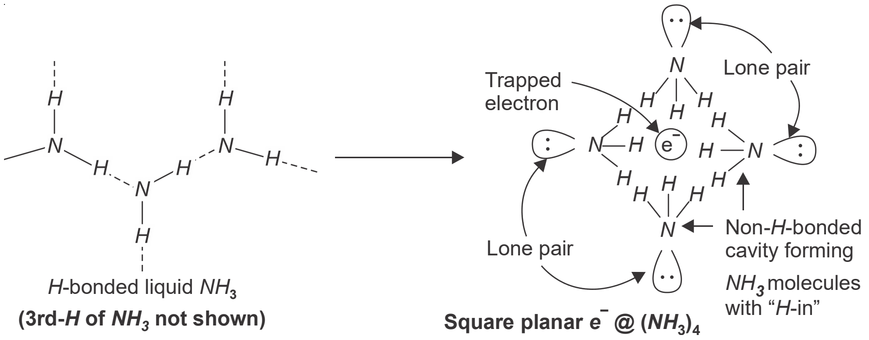


Fig. 15.4.1. Schematic representation of cavity formation from the *H*-bonded liquid NH_3 structure to accommodate/encapsulate the electron.

(**Note:** Probability of finding the electron is maximum not at the centre of cavity but near the *H*-atoms of the reoriented NH_3 molecule with "***H-in***").

like wavefunctions of *H*-atom (**Jortner model**). The electron transition, $1s \longrightarrow 2p$, produces a **broad absorption band** (Fig. 15.4.2) having the peak at ~ 1500 nm (≡ 0.82 eV) (*i.e.* infrared region) with the molar extinction coefficient about 4.5×10^4 $\text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$ at –70°C. The absorption band

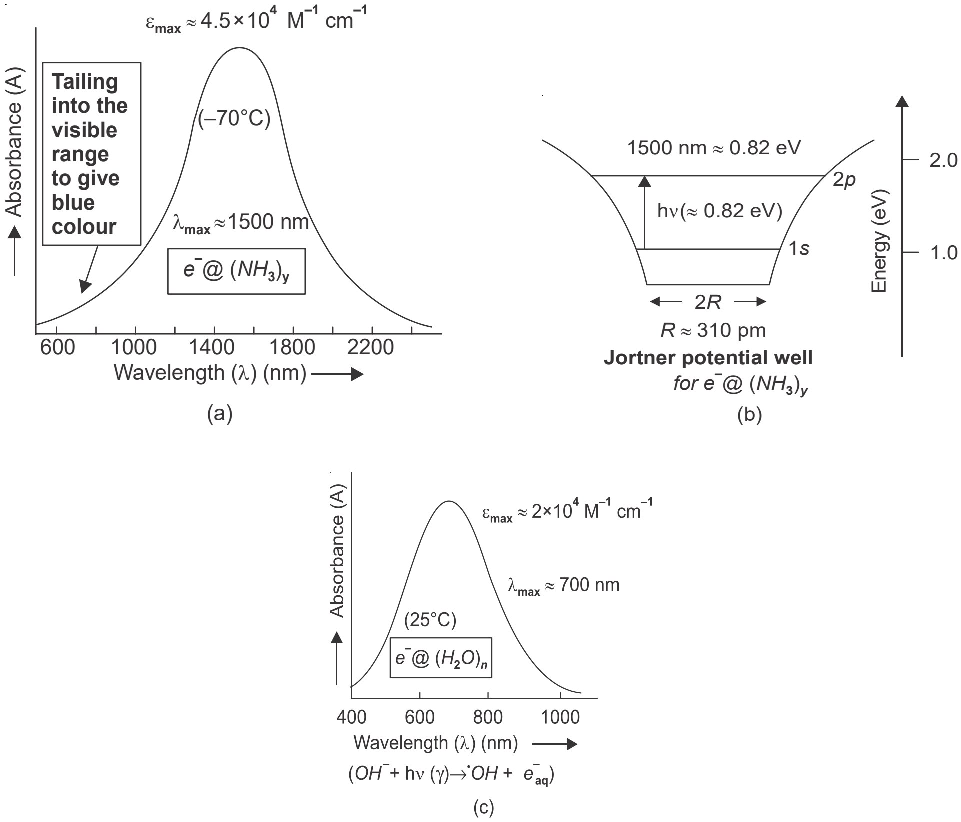


Fig. 15.4.2. (a) Electronic absorption spectrum of the cavity trapped electron in liquid NH_3 (*i.e.* $e^-@(NH_3)_y$ or simply e^-_{am}) in terms of Jortner's potential well model. (b) Jortner's potential well of $e^-@(NH_3)_y$; (c) Absorption spectrum of $e^-@(H_2O)_n$

further extends into the infrared region and **tails into the visible range to produce the characteristic blue colour**. This is the source of Sir Humphry Davy's fine blue colour. This absorption band is the characteristic feature of the trapped electron and it explains why the colour of the dilute solution is **independent of the nature of metal**.

- **Cavity trapped electron described as the quasi-free electron:** This quasi-free state of the trapped electron is supported by the facts like **high reducing activity**, **high mobility** in **an electrical field**, and **electron spin resonance (*esr*) *g*-value**.

- **Rationalisation of magnetic susceptibility and electrical conductivity of metal-ammonia solution in terms of different species prevailing in different concentration regions:** It is illustrated by taking the alkali metal as the representative one. In very dilute solutions, the ionised products, *i.e.* solvated M^+ (*i.e.* $M(NH_3)_x^+$ denoted by M_{am}^+) and solvated electron *i.e.* $e^-@(NH_3)_y$ (denoted by e_{am}^-) remain **well separated.** Thus the very dilute solution represents the **behaviour of a strong electrolyte**. The **paramagnetism** arises due to the **unpaired quasi-free electron** (e_{am}^-) and the electrical conductivity arises due to M_{am}^+ and e_{am}^- whose mobility is about **10 times higher** than that of the solvated alkali metal ion, *i.e.* M_{am}^+. It explains the electrical conductivity of dilute solutions **somewhat higher than that of a representative strong electrolyte like KNO_3 in liquid** NH_3 (Fig. 15.4.3).

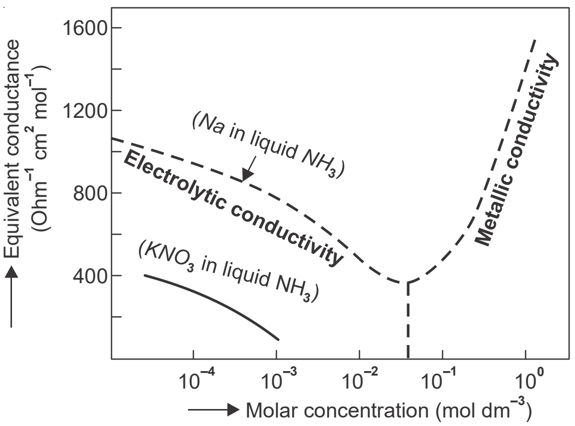


Fig. 15.4.3. Variation of equivalent conductance (ohm^{-1} cm^2 mol^{-1}) of *Na* and KNO_3 (a strong electrolyte) in liquid NH_3 with the molar concentration (mol dm^{-3})

At higher concentration, concentration of M_{am}^+ and e_{am}^- increases. With the increase of concentration of M_{am}^+ and e_{am}^-, they will come closer to allow the formation different species and some of them are nonconducting, less conducting and diamagnetic (spin paired, $S = 0$). This can explain the decrease of electrical conductivity, and magnetic susceptibility with the increase of concentration. Formation of these new species with the increase of concentration are discussed below.

(a) Formation of **overall electrically neutral ion-pair** (*i.e.* $M_{am}^+ \cdot e_{am}^-$) and **solvated metal atom** (*i.e.* M_{am}^0):

$$M_{am}^+(S=0) + e_{am}^-\left(S=\frac{1}{2}\right) \xrightleftharpoons{K_1} M_{am}^+ \cdot e_{am}^-\left(S=\frac{1}{2}\right) \xrightleftharpoons{K_2} M_{am}^0\left(S=\frac{1}{2}\right);\ K_1K_2 \approx 10^2$$

The limiting situation of a strong ion-pair represents M_{am}^0. Both are **paramagnetic** $\left(S=\frac{1}{2}\right)$ but **nonconducting**.

(b) **Formation of cluster of ion triples (*i.e.* $e_{am}^- \cdot M_{am}^+ \cdot e_{am}^-$)** having the stoichiometry M_{am}^- which is **less conductivity** (compared to e_{am}^-) and **diamagnetic** ($S = 0$).

$$M_{am}^+ \cdot e_{am}^- \left(S = \frac{1}{2}\right) + e_{am}^- \left(S = \frac{1}{2}\right) \rightleftharpoons e_{am}^- \cdot M_{am}^+ \cdot e_{am}^- \equiv M_{am}^- \ (S = 0)$$

i.e. $M_{am}^0 + e_{am}^- \rightleftharpoons M_{am}^-, K \approx 10^3$

(c) **Formation of cluster of ion-quadruples** (*i.e.* $e_{am}^- \cdot M_{am}^+ \cdot e_{am}^- \cdot M_{am}^+$) having the stoichiometry $(M_2)_{am}$ which is **nonconducting** and **diamagnetic** ($S = 0$).

$$e_{am}^- \cdot M_{am}^+ \cdot e_{am}^- \ (S = 0) + M_{am}^+ \ (S = 0) \rightleftharpoons e_{am}^- \cdot M_{am}^+ \cdot e_{am}^- \cdot M_{am}^+ \equiv (M_2)_{am} \ (S = 0)$$

$$\text{or } 2M_{am}^0 \rightleftharpoons (M_2)_{am}, K \approx 10^{-4}$$

Formation of such clusters like **ion-pairs**, **ion-triples**, **ion-quadruples** and even higher clusters in concentrated solutions is quite reasonable in liquid NH_3 because of its **low dielectric constant** which enhances the attraction between the opposite charges. It has been established that the **spin-paired clusters** ($S = 0$, *i.e.* diamagnetic are more stable than the paramagnetic clusters). These **diamagnetic clusters** have been described as the **bipolarons**.

(d) **Combination of two singly charged cavities in close proximity into a single large cavity trapping two paired electrons** (*i.e.* **2 electrons paired in a cavity**):

$$e^- @(NH_3)_y + e^- @(NH_3)_y \rightleftharpoons e^- @(NH_3)_y \cdot e^- @(NH_3)_y \rightleftharpoons 2e^- @(NH_3)_n \equiv (e_2)_{am}^{2-}$$

This paired electron pair, *i.e.* $(e_2)_{am}^{2-}$ is **less conducting** and **diamagnetic** ($S = 0$).

It is evident that all the above mentioned processes (a–d) are important at the relatively higher concentration (*i.e.* the intermediate concentration range) and they **remove the highly conducting and paramagnetic species**, *i.e.* e_{am}^- leading to the formation of nonconducting/less conducting and diamagnetic cluster species and **it explains the decrease of conductivity and paramagnetic susceptibility with the inverse of concentration**.

• **Metallic reflectivity, metallic conductivity and metallic weak paramagnetism in extremely concentrated solution (*i.e.* saturated solution):** For a **very dilute** alkali metal-liquid NH_3 solution, it behaves like a **strong electrolyte solution** consisting of the isolated M_{am}^+ and e_{am}^- species. In the **intermediate concentration range**, pairing of the electrons in a hole; ion-pair, spin paired ion-triple, spin paired ion-quadruple formation occur and it approaches towards the '**transition to metallic state**' (***TMS***) through the formation of small metallic clusters. At this relativily higher concentration range, the conductivity and paramagnetic susceptibility tend to attain the minimum value. At this concentration range, if the solution is cooled, it leads to **liquid-liquid phase separation** (*i.e.* two **immiscible liquid phase**) where the more concentrated bronze coloured metallic phase (less dense) floats on top of the bluish dilute layer. If the metal concentration is further increased to give the **saturated solution**, then it shows the **metallic properties**, *i.e.* **metallic reflectivity** or **metallic lustre (metallic bronze colour), metallic conductivity and metallic paramagnetism**.

It is suggested that in the saturated bronze coloured solutions, larger clusters (*i.e.* $[M(NH_3)_x]_r$) through the association of M_{am}^+ and e_{am}^- are formed. In such large crystals (resembling the metallic crystals), ammoniated metal ions (*i.e.* M_{am}^+) occupy the cationic sites of the **liqud metal crystal** (*i.e.* **expanded metallic lattice**) and e_{am}^- occupy the nearby sites. This saturated solution is rightly described as a "**dilute metal**" or "**expanded metal**" because at this condition, the metal centres are placed apart (compared with the pure metallic crystal) by the interspersed molecules of NH_3. At this stage of concentration, the ammoniated electrons are so near that their wave functions can overlap to form a **half-filled metallic band** (*cf.* band structure of solids).

Because of the above reasons, the saturated metal-liquid NH_3 solution is described as a "**liquid expanded metal**" whose conductivity (about 10^7 S m^{-1}) is comparable to that of mercury or a representative solid metal. Thus at this stage, the **genuine free electron behaviour** is noted.

● **Hydrated electron (e_{aq}^-) *vs.* ammoniated electron:** For the hydrated electron, λ_{max} ($\approx$ 700 nm, $\varepsilon_{max} \approx 2 \times 10^4$ M^{-1} cm^{-1}) is **shorter** and it indicates that the cavity diameter to trap the electron in water is much smaller compared to that in liquid NH_3. It is believed that this **smaller cavity size** for e_{aq}^- imparts its **instability** (life time ~ 10^{-3} s) with respect to the following reaction.

$$2e_{aq}^- \xrightarrow{H_2O} H_2 + 2OH^-, k \approx 6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

It may be noted that for e_{am}^-, the corresponding reaction is kinetically much slower to impart its **kinetic stability**.

$$2e_{am}^- \xrightarrow{NH_3} H_2 + 2NH_2^-, \text{ (slow reaction).}$$

Alkalides and Electrides (see Sec. 11.5.9 and Vol. 4)

Alkali metals (except Li) may ionise in ether and ammine solvents as :

$$M(s) \rightleftharpoons M_{solv}^+ + e_{solv}^-$$

$$2M(s) \rightleftharpoons M_{solv}^+ + M_{solv}^-, \textbf{(disproportionation)}$$

The above disproportionation equilibrium can be driven towards the right through the **stabilisation of the cation by using the suitable macrocyclic ligands like cryptands or crown ethers.** It will allow the isolation of solid crystalline solids having the anion (M^-). Such solids are called **alkalides.** Sometimes, complexed cations may crystallise with the solvated electrons giving rise to **electrides.**

Some representative examples of alkalides and electrides are:

Alkalides: $[Na(\text{crown-6})]^+Na^-$, $[K(\text{crown-6})]^+Na^-$, $[Rb(\text{crown-5})_2]^+Na^-$, $[M(\text{crypt-[2,2,2]})]^+M^-$ ($M = Rb$, Na, K) (**origin of colour:** charge transfer (CT) from M^- to solvent).

Electrides: $[Cs(\text{crown-6})_2]^+e^-$, $[K(\text{crown-6})]^+e^-$, $[Cs(\text{crown-5})_2]^+e^-$; $[K(\text{crypt-[2,2,2]}]e^-$ (**Origin of colour:** From the trapped electrons acting like the ***F*-centres**)

● ***Formation and stabilisation of alkalides and electrides*** **:** Here it is worth mentioning that the studies of alkali metal-liquid ammonia system could lead to the *discovery of alkalide* (M^-) *ions*, but the **high solvation energies of M^+ and e^- in liquid NH_3 favour the following reactions** in dilute solution.

$$M(\text{solvated})^- \rightleftharpoons M(\text{solvated}) + e(\text{solvated})$$

$$M(\text{solvated})^- \rightleftharpoons M(\text{solvated})^+ + 2e(\text{solvated})$$

However, concentrated solutions of Na in liquid ethylenediamine (en) and methylamine may produce the solvated Na^- and Na^+ ions characterised by the electrical conductivity of normal 1:1 electrolyte.

In fact, by using the same principle of preparation of alkali metal-ammonia blue solution, it has been possible to prepare the ***alkalide ions*** (*e.g.* Na^-, K^-, Cs^-, etc.) and ***electrides*** (*i.e.* solvated electrons). Alkali metals can dissolve in the solvents like alkylamines to give the alkalide ions and in such cases, the **spectral characteristics depend on the nature of the metal because it arises due to the charge transfer (CT) from M^- to solvent.** Let us consider the alkalide formation by using Na-metal in ethylenediamine (en) as a solvent.

$$2Na(s) \rightarrow Na(en)_x^+ + Na(en)_y^-; \text{ (both diamagnetic, } S = 0)$$

It is interesting to note that when Na-K alloy (1:1) is dissolved in *en*, the **metal dependent spectral band** is the same as for Na itself dissolved in *en*. It supports the following equilibrium.

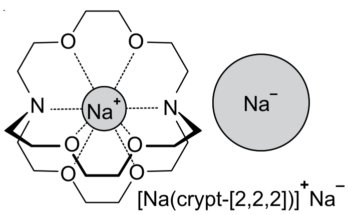
$$NaK \xrightarrow{en} K(en)_x^+ + Na(en)_y^-; \; (cf.\ \text{Ionisation energy: } Na > K)$$

Thus both Na and NaK alloy produce the same alkalide (Na^-) called **sodide** (more correctly **natride**) whose ionic radius is somewhat greater than that of I^-. Other alkalides like **potasside**, **rubidide**, and **caeside** (except **lithide**, Li^-) have been prepared. **Caeside (Cs^-)** is probably **the largest anion with the highest polarisability**.

The use of suitable macrocyclic ligands like cryptand and crown ether (see Chapter 11 for their structural details) can allow the ***isolation of solid sodide***, *e.g.* $[Na(crypt)]^+[Na]^-$ where *crypt* stands for a **cryptand** ligand. This has been prepared by dissolving sodium in cold ethylamine in presence of the cryptand-[2,2,2].

$$2Na \text{ (dissolved in } EtNH_2) + \text{crypt-[2,2,2]} \longrightarrow [Na(\text{crypt-[2,2,2]})]^+Na^-$$

(**Diamagnetic golden crystal**)



$[Na(\text{crypt-[2,2,2]})]^+Na^-$

The Na^+ ion is encapsulated within the cavity of the macrocyclic ligand like cryptand or crown ether. The Na^+ ion is encapsulated within the cavity of the macrocyclic ligand and consequently, it cannot interact with the anion Na^- (having apparent radius larger than that of I^-). ***In fact, the macrocyclic ligand produces a barrier between Na$^+$ and Na$^-$* and the corresponding crystal is quite stable.**

In the alkalides like $[Rb(\text{crown-5})_2]^+Na^-$ or $[K(\text{crown-6})(\text{crown-4})]^+Na^-$, the cation is **sandwiched** between two crown ethers and it gives a favourable situation to stablise Na^-.

Inverse sodium hydride consisting of Na^- and H^+ ion (encapsulated in 3^6-adamanzane) has been prepared (see Sec. 4.6.5; Vol. 4).

Here it is worth mentioning that the alkalides are **highly reducing** (*i.e.* strong 2*e*-reductants) and consequently, the selected macrocycles must be **resistant to reduction by alkalide** to provide the stability of the system.

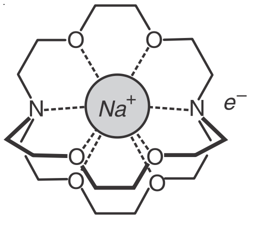
It is also possible to isolate the solvated electrons (called ***electrides***) as the anions in ionic solids where the cation is shielded in a macrocyclic cavity. However, compared to alkalides, **isolation of crystalline electrides is relatively more difficult** (*cf.* J.L. Dye, *Science*, **247**, 663, 1990). In general, in electrides, the positive ions are the complexed cations and the negative ions are the trapped **electrons or electrons pairs** depending on the condition. It should be remembered that the electrons **are not the massive particles** and due to the **quantum effect** (*cf.* **tunneling effect** for such light particles), they can move beyond the boundaries of the cavity to interact with each other and with the cations depending on the conditions. By using the **bulky sandwich alkali metal cations**, ML_2^+ (where M = alkali metal, L = appropriate **crown ether** ligand), several electrides have been prepared.

The representative examples of **sandwich electrides** are: $[Cs(\text{crown-6})_2]^+e^-$ and $[Cs(\text{crown-5})_2]^+e^-$ (Fig. 15.4.4). Besides these, by using the less bulky encrypted cation, the electride, $[K(\text{crypt-}[2,2,2]^+e^-$ has been prepared.

$$K + \text{crypt-}[2,2,2] \xrightarrow{Me_2O,\ -50°\text{C}} [K(\text{crypt-}[2,2,2]^+e^-$$

The electride, $[Na(2,2,2\text{-crypt})]^+e^-$, can be prepared as follows:

$$Na \xrightarrow{\text{liquid } NH_3} Na(NH_3)_x^+\ (i.e.\ Na_{am}^+) + e(NH_3)_y^-\ (i.e.\ e_{am}^-)$$



$[Na(2,2,2\text{-crypt})]^+e^-$

$$\Big\downarrow \begin{array}{l}\text{(i) Addition of 2,2,2-cryptand}\\ \text{(ii) Evaporation of } NH_3\end{array}$$

$$[Na(2,2,2-\text{crypt})]^+e^-$$

(Blue - black paramagnetic salt)

Here it is worth mentioning that in the electrides, the extent of **electron-electron interaction** largely depends on the size of the complex cation. In the crystal structure of $[Cs(\text{crown-6})_2]^+e^-$, the **free electron** is **localised** as the **anion** at **each anionic site** (*cf.* ***F*-centre** in alkali halides). This **paramagnetic compound** shows the **low electrical conductivity** consistent with the idea of localisation of the electron in the geometric anion sites. On the other hand, in the electride, $[K(\text{crypt-}[2,2,2]]^+e^-$ having the **less bulky complexed cation**, the electrons can interact fairly strongly with each other leading to the paired electrons in the elongated cavities to produce the **diamagnetic singlet state** ($S = 0$) but with a **thermally accessible paramagnetic state**. The electride, $[Cr(\text{crown-5})_2]^+e^-$ produces the condtion of an **intermediate state of electron-electron interaction** in terms of bulkiness of the complex cation. In fact, the crystal shows the **antiferromagnetic behaviour** below 4.6 K (*i.e.* antiparallel spins of the electrons). Thus it is evident that the size of the complexed cation is crucially important to determine the state of electron in the electride.

$[Cs(\text{crown-6})_2]^+e^-$	**$[Cs(\text{crown-5})_2]^+e^-$**	**$[K(\text{crypt-}[2,2,2])]^+e^-$**
Paramagnetic, free electron localised at the anionic site.	**Antiferromagnetic** (distorted body-centred type cubic lattice housing the electron at the centre of cube, see Fig. 15.4.4)	Electron pairs trapped; diamagnetic ground state

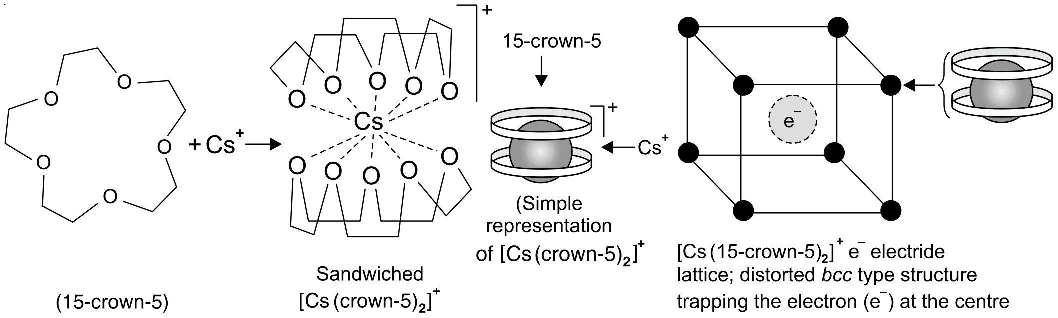


Fig. 15.4.4. Structure of the cation and electride $[Cs(15\text{-crown-5})_2]^+e^-$

In fact, it has been possible to isolate the *golden crystals of* $[Na(crypt)]^+Na^-$ **from the concentrated bronze coloured solution. From the blue solution**, *dark blue crystals of* $[Na(crypt)]^+e(NH_3)_m^-$ have been isolated. The anions Na^- and $e(NH_3)_m^-$ are believed to be responsible for the said colours.

- ***Formation and isolation of Zintl anions*** **:** It is well known that by dissolving the post-transition metals in liquid NH_3, in the presence of alkali metal ions, the highly ***coloured cluster anions*** (known as ***Zintl anions***) like Sn_9^{4-}, Pb_9^{4-}, Pb_7^{4-}, Pb_5^{2-}, Sb_7^{3-}, Bi_3^{3-} etc. can be prepared. Their structure and bonding have been explained in Sec. 13.8.4 (Vol. 3A). These large ***homopoly-atomic*** anions can be isolated by using the large cations, *e.g.* $[Na(crypt)]_2Pb_5$, $[Na(crypt)]_4Sn_9$, etc.

(E) **Reactions of metal-ammonia solutions :** The free electrons, *i.e.* ammoniated electrons, $e^-_{(amm)}$ are highly mobile and these can act as the strong reducing agents. In aqueous solutions, highly reducing agents cannot survive because of the possible reduction of H^+ to H_2 (*i.e.* generation of H_2 from H_2O), but in the case of metal-ammonia solution which is very much reducing, such a problem does not arise. *This is why, the metal-ammonia solution can bring about a number of powerful reduction in liquid* NH_3.

The blue solution is decolourised by the ammonium salts or by any other acid, *i.e.*

$$NH_4^+ + e^-_{(amm)} \rightarrow NH_3 + \frac{1}{2}H_2$$

The colour disappears due to the removal of the trapped quasi-free electron. Similarly, in reduction, the electrons are used up and the solutions become colourless.

(F) **Acid-base neutralisation reactions :** From the knowledge of the autoionisation pattern, all the ammonium salts are acidic in liquid NH_3 while the amides, imides and nitrides are basic according to the **concept of solvent system defining acids and bases**. Some examples of acid-base neutralisation are given below :

$$NH_4Cl + KNH_2 \rightleftharpoons KCl + 2NH_3;\ 3NH_4I + BiN \rightleftharpoons BiI_3 + 4NH_3;$$

$$2NH_4I + PbNH \rightleftharpoons PbI_2 + 3NH_3$$

In fact, the amides and imides in liquid ammonia are equivalent to hydroxides in water; and nitride (N^{3-}) in liquid ammonia is equivalent to oxide (O^{2-}) in water.

Amphoteric behaviour of Zn(II) and Al(III) salts in liquid NH_3 can be explained by considering the following acid-base reactions.

$$ZnCl_2 + 2KNH_2 \rightleftharpoons Zn(NH_2)_2 + 2KCl$$

$$Zn(NH_2)_2 \text{ (as an acid)} + 2KNH_2 \rightleftharpoons K_2[Zn(NH_2)_4]$$

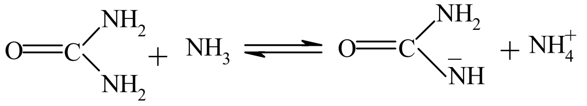
$$Zn(NH_2)_2 \text{ (as a base)} + 2NH_4Cl \rightleftharpoons ZnCl_2 + 4NH_3$$

(*cf. Amphoteric behaviour of Zn(II)-salts in water*)

$$Zn(OH)_2 + 2OH^- \rightleftharpoons [Zn(OH)_4]^{2-};\ Zn(OH)_2 + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$$

$Al(NH_2)_3$ can also function like $Zn(NH_2)_2$ in liquid ammonia.

Liquid NH_3 being basic in nature can act as a **levelling solvent** for different weak acids. The compounds having no acidic property in aqueous media may also display an acidic property in liquid ammonia. Urea is an example of this group.



$$O{=}C(NH_2)_2 + NH_3 \rightleftharpoons O{=}C(NH_2)(\overset{-}{N}H) + NH_4^+$$

It may be noted that in spite of the favourable proton transfer process producing the **ion-pair** $NX_4^+\cdot X^-$ from HX, the observed acid strength is not high (*cf.* $pK_a \approx 4$ for both HCl and CH_3CO_2H) because the **tight ion-pair dissociates weakly** to release the free NH_4^+ ion in liq. NH_3 due to the **low dielectric constant** (≈ 22). **Thus liq. NH_3 can level the acid strength but the observed acid strength is not high** (effect of ion-pair formation, discussed below).

On the other hand, many aqueous strong bases like alkoxide (RO^-) act as the weak bases in liquid NH_3 (*cf.* **differentiating effect**).

$$RO^- + NH_3 \rightleftharpoons ROH + NH_2^-$$

In fact, only the very strong bases like hydride (H^-) can act as the strong bases in liquid NH_3.

$$H^- + NH_3 \longrightarrow H_2\uparrow + NH_2$$

(G) **Ion-pairing in liquid NH_3 and its effect on electrical conductivity and acid dissociation constant:** Ion-pair formation is energetically more probable in solvents having the **low dielectric constant**. Thus ion-pair formation is more favoured in liquid NH_3 than in water. It is understandable from the expression of **ion-pairing potential energy** (E_{IP}).

$$E_{IP} = -\frac{q_1 q_2}{K r_{12}}$$ (CGS system), K = dielectric consant ≈ 78 for water, ≈ 22 for liquid NH_3.

For the **singly charged ions**, $E_{IP} \approx 3$ kJ mol^{-1} (in water), ≈ 10 kJ mol^{-1} (in liquid NH_3). Thus, E_{IP} (in water) is almost comparable to room-temperature thermal energy ($k_BT \approx 2.5$ kJ mol^{-1}) and consequently, ion-pair formation is not so important at least for the singly charged ions in aqueous media. In liquid NH_3, the studies are made **at much lower temperatures** (*cf.* liquid range of liquid NH_3) where the thermal energy is much less than that of E_{IP}. Consequently, in liquid NH_3, **ion-pair formation** leading to the overall electrically neutral species is an important phenomenon and this aspect has been pointed out in explaining the **electrical conductivity** of metal-liquid NH_3 solution.

***HCl* and *CH_3CO_2H*: Both are almost equally weak acids in liquid *NH_3* but *HCl* is a strong acid and *CH_3CO_2H* is a weak acid in water.**

Let us illustrate the **effect of ion-pair formation on the acid strengths** of HCl and CH_3CO_2H in liquid NH_3. For the acid HX ($X^- = Cl^-$ or $CH_3CO_2^-$), the **total proton transfer process** to the solvent can be argued to occur in two steps:

$$\textbf{Step-I: } HX + NH_3 \xrightleftharpoons{K_{\text{prot}}} (NH_4^+)(X^-) \textbf{ (ion-pair)};$$

$$\textbf{Step-II: } (NH_4^+)(X^-) \xrightleftharpoons{K_{\text{sep}}} NH_4^+ + X^-$$

Step-I represents the proton transfer from HX to basic NH_3 to produce the **tightly bound ion pair** (an effect of **low dielectric constant** and **low thermal energy**). This proton transfer step is reasonably almost complete (*i.e.* K_{prot} **very high**). Step-II leads to **separation of the ion pair** and this step is unfavoured (*i.e.* K_{sep} very low). The overall acid dissociation constant (K_a) is the product of K_{prot} and K_{sep} (*i.e.* $K_a = K_{\text{prot}} K_{\text{sep}}$) and **$K_a$ appears to be small due to the very low value of K_{sep}** in spite of the large value of K_{prot}. For any acid, step-I is almost complete (*i.e.* levelling effect) and the K_a value is mainly determined by K_{sep}. In fact, for both HCl and CH_3CO_2H, K_a is about 10^{-4} (*i.e.* $pK_a \approx 4$; levelling effect). Thus CH_3CO_2H appears somewhat stronger in liquid NH_3 (compared with that in aqueous media where its pK_a value is about 4.7) but HCl appears to be a weak acid. **Thus the acid strengths of HCl and CH_3CO_2H are levelled off but HCl acts as a weak acid in liquid** NH_3.

(H) **pH-scale in liquid ammonia:** By considering the ionic product of this solvent ($K_{\text{ion}} = 10^{-27}$, see Table 14.11.1), a **conventional pH scale** can be defined as follows in the range 0–27:

$$pH = 0\ (1\ \text{mol dm}^{-3}\ NH_4^+),$$

$$pH\ (\text{neutral}) = 13.5\ \ ([NH_4^+] = [NH_2^-]);\ pH = 27\ (1\ \text{mol dm}^{-3}\ \ NH_2^-)$$

(I) **Precipitation reactions :** In the *metathetical reactions* (*i.e.* double decomposition reactions; the Greek word *metathesis* means *interchange*), if a salt of low solubility in liquid NH_3 is formed, then the salt is precipitated. Some examples are :

$$NaCl + KI \rightleftharpoons KCl\downarrow + NaI;\ 2NH_4I + Zn(NO_3)_2 \rightleftharpoons ZnI_2\downarrow + 2NH_4NO_3;$$

$$2NH_4Br + Sr(NO_3)_2 \rightleftharpoons SrBr_2\downarrow + 2NH_4NO_3.$$

Here it is interesting to note that in the reaction between $AgNO_3$ and $NaCl$, $AgCl$ does not get precipitated. Thus the possibility of complexation may play an important role in determining the chance of precipitation.

(J) **Complex formation reactions :** In aqueous solutions, if the precipitated hydroxides have the amphoteric properties then they go into solution in the presence of the excess base (*i.e.* OH^-) due to the formation of soluble hydroxo complexes, *e.g.*

$$Zn(OH)_2\downarrow + 2NaOH \xrightarrow{\text{aq. soln.}} Na_2[Zn(OH)_4]$$

Similar reactions may occur in liquid NH_3, *e.g.*

$$Zn(NO_3)_2 + 2KNH_2 \rightleftharpoons Zn(NH_2)_2\downarrow + 2KNO_3;$$

$$Zn(NH_2)_2\downarrow + 2KNH_2 \rightleftharpoons K_2[Zn(NH_2)_4],$$

$$Al(NH_2)_3\downarrow + NH_2^- \rightleftharpoons [Al(NH_2)_4]^-.$$

Thus addition of KNH_2 to $Zn(NO_3)_2$ dissolved in liquid NH_3 gives first the precipitate of $Zn(NH_2)_2$ which redissolves in presence of excess KNH_2 due to the formation of soluble amido complex. Similarly, $Al(NH_2)_3$ redissolves as $[Al(NH_2)_4]^-$. $IrBr_3$ in liquid NH_3 precipitates as $Ir(NH_2)_3$ which redissolves as $[Ir(NH_2)_6]^{3-}$ in presence of excess KNH_2.

(K) **Solvolysis reactions :** As in the hydrolysis reaction (in H_2O), in *ammonolysis or ammonolytic reactions*, the concentration of either NH_4^+ or NH_2^- ion is increased.

$[Co(OH_2)_6]^{3+} + H_2O \rightleftharpoons [Co(OH_2)_5(OH)]^{2+} + H_3O^+$ (Hydrolysis through proton transfer)

$[Co(NH_3)_6]^{3+} + NH_3 \rightleftharpoons [Co(NH_3)_5(NH_2)]^{2+} + NH_4^+$ (Ammonolysis through proton transfer)

Some examples of ammonolysis reaction are:

$$SiCl_4 + 8NH_3 \rightleftharpoons Si(NH_2)_4 + 4NH_4^+ + 4Cl^-;$$

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

$$SO_2Cl_2 + 4NH_3 \rightleftharpoons SO_2(NH_2)_2 + 2NH_4^+ + 2Cl^-;$$

$$HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_2)Cl + NH_4^+ + Cl^-,\ \text{(incomplete solvolysis)};$$

$$SnX_4 + 6NH_3 \rightleftharpoons SnX(NH_2)_3 + 3NH_4^+ + 3X^-,\ \text{(incomplete solvolysis)}$$

$$RX + 2NH_3 \rightleftharpoons R\text{–}NH_2 + NH_4^+ + X^-,\ (RX = \text{alkyl halide}).$$

(L) **Electrochemistry in liquid NH_3 :** The aspect has been discussed in Sec. 16.18.

(M) **Redox stability field (Fig. 15.4.5) of liquid NH_3 as a solvent:** Pourbaix diagram ($E°$ *vs.* pH) can give the redox stability field of a particular solvent (see Fig. 16.7.1, discussed in details for H_2O). For liquid NH_3, the $E°$ (reduction potentials) of the following two couples determine its redox stability field (Fig. 15.4.4).

$$NH_4^+ + e^- \rightleftharpoons NH_3 + \frac{1}{2}H_2, E° = 0 \text{ V (defined for } NH_3)$$

$$\frac{1}{2}N_2 + 3NH_4^+ + 3e^- \rightleftharpoons 4NH_3, E° = +\,0.04 \text{ V}$$

Thus the **thermodynamic redox stability range** is only 0.04 (*cf.* 1.23 V for water) which is so narrow that practically no oxidising or reducing agent is thermodynamically stable in liquid NH_3. But **very high overvoltage** (about 1 V) for both reactions expands the **kinetic redox stability** range to about 2 V (*cf.* about 2.2 V for H_2O; Fig. 16.7.1). This is why, **many strong reducing agents** are **kinetically stable in liquid NH_3** and many unusual reductions are carried out in liquid NH_3.

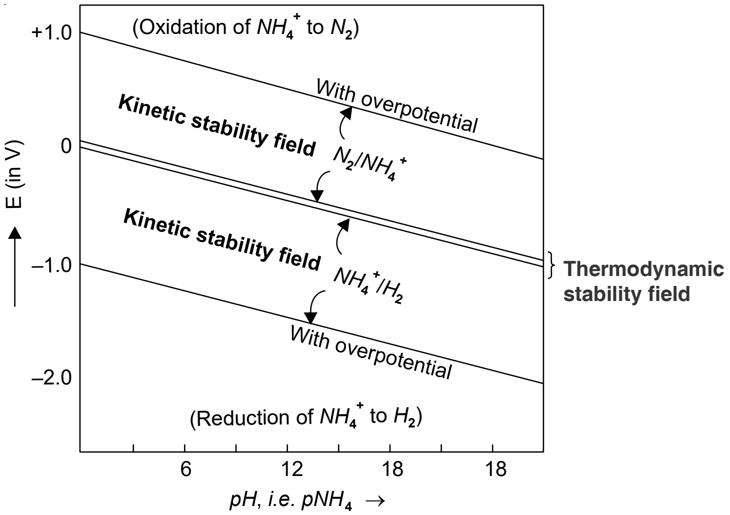


Fig. 15.4.5. Redox stability field of liquid NH_3 in pH range, 0–27. **Note:** Thermodynamic stability range is very narrow but the kinetic stability (due to overpotential) range is quite large.

(N) **Redox reactions :** In liquid NH_3, generally, oxidising power of the common powerful oxidising agents (in aqueous media) is significantly decreased. Nitric acid is nonoxidising; permangnate and dichromate are poorly oxidising in liquid NH_3. In general, the oxidising agents are to compete with the solvent which is present in large excess to accept the electron from the reducing agents. The electrons are solvated and stabilised in the solvent. ***This is why, the oxidising power of the external oxidising agents gets decreased.*** Besides this, the oxidising agents (*e.g.* $Cr_2O_7^{2-}$, MnO_4^-, etc.) which require protons to display their oxidising activity are the weaker oxidising agents in liquid NH_3, ***because of the low availability of protons in liquid NH_3.*** On the other hand, for the reducing agents, the transfer of electron to the solvent is facilitated. This is why, the alkali metals are the **powerful reducing agents** in liquid NH_3. Some examples of the redox reactions are given below:

$$2Na + 2NH_4Br \rightleftharpoons 2NaBr + 2NH_3 + H_2;\ K + KMnO_4 \rightleftharpoons K_2MnO_4;$$

$$K_2MnO_4 + 4K + 3NH_3 \rightleftharpoons MnO + 3KNH_2 + 3KOH;$$

$$K_4[Sn^{II}(NH_2)_6] + I_2 \rightleftharpoons K_2[Sn^{IV}(NH_2)_6] + 2KI;\ CuI + Na \rightleftharpoons Cu + NaI;$$

$$[Ni^{II}(CN)_4]^{2-} \xrightarrow{+e^-} [Ni^{I}(CN)_3]^{2-} + CN^- \xrightarrow{+e^-} [Ni^0(CN)_4]^{4-},$$

$$[Pt^{II}(NH_3)_4]^{2+} \xrightarrow{+2e^-} [Pt^0(NH_3)_4],\ NH_4^+ \xrightarrow{+e^-} NH_3 + \frac{1}{2}H_2$$

$$[Mn_2(CO)_{10}] \xrightarrow{+2e^-} [Mn(CO)_5]^-, [Fe(CO)_5] \xrightarrow{+2e^-} [Fe(CO)_4]^{2-} + CO$$

$$O_2 \xrightarrow{+e^-} O_2^- \text{ (superoxide)} \xrightarrow{+e^-} O_2^{2-} \text{ (peroxide)},\ S_8 \xrightarrow{+2e^-} S_8^{2-}$$

By using the above reaction, **alkali metal superoxides and peroxides** may be readily prepared. Alkali-metal-ammonia solution can be used to prepare **graphitic interacalates** (see Sec. 10.11.2) and **fullerides**.

$$8C_{graphite} + K_{am}^+ + e_{am}^- \longrightarrow [K_{am}]^+ [C_8^-]$$

$$C_{60} + 3Rb_{am}^+ + 3e_{am}^- \longrightarrow [Rb_{am}]_3 [C_{60}] \xrightarrow{\Delta} Rb_3C_{60}$$

Alkali metals in liquid NH_3 can reduce the elements like Ge, Sn, Pb, As, Sb, S, Se, Te, etc. and produce the ***homopolyatomic cluster anions*** (*Zintl ions*)**.** Reduction of Se and Sn by Na/NH_3 is shown below :

$$Na \xrightarrow{Se} Na_2Se \xrightarrow{Se} \underset{\text{(bright red)}}{Na_2Se_2} \xrightarrow{Se} \underset{\text{(wind red)}}{Na_2Se_3} \xrightarrow{Se} \underset{\text{(green)}}{Na_2Se_4}$$

$$Na_2Se_4 \xrightarrow{Se} Na_2Se_5 \xrightarrow{Se} Na_2Se_6 \text{ (reddish green)}$$

$$4Na + 9Sn \longrightarrow Na_4Sn_9\ (i.e.\ 9Sn + 4e^- \longrightarrow Sn_9^{4-})$$

Similarly, Pb can be reduced to Pb_9^{4-} and it can be isolated as $[Na(crypt)]_4[Pb_9]$.

In fact, in this way, different types of ***Zintl anions*** (*i.e.* ***homopolyatomic anions***) can be prepared.

- **Liquid NH_3 - a good host medium to stabilise the very strong Lewis bases like carbanions** (*cf.* superacid - a good host medium to stabilise the very strong Lewis acids like carbocations).
- **Liquid NH_3 - a good medium to carry out the powerful reduction reactions producing the highly electron rich species** (*e.g.* Zintl anions) acting as the very good Lewis bases (*cf.* strongly acidic solvents — chosen to carry out powerful oxidation reactions producing the unusually strong Lewis acids; see H_2SO_4 as a solvent).

Very strong 'Lewis bases are **easily destroyed through the Lewis acid-base adduct formation**. Hence to stabilise such species in free state, the host medium must be a strong Lewis base like liquid NH_3. Similarly to stabilise a strong Lewis acid, the host medium must be a very weak Lewis base.

(O) **Advantages in using liquid ammonia as a solvent :** (i) In aqueous solutions, reducing agents stronger than hydrogen cannot exist, because they will liberate H_2 from H_2O. But in liquid NH_3, alkali metals are dissolved without suffering any chemical reaction (*as on evaporation of* *the alkali metal-ammonia solution, the alkali metals can be recovered*). Such alkali metal-ammonia solutions are highly reducing. It can carry out many powerful reductions which cannot go on in aqueous solutions. (ii) Many salts show a lesser tendency to undergo solvolysis in liquid NH_3 compared to that in water.

(P) **Disadvantages in using liquid ammonia as a solvent :** (i) The liquid range of the solvent is very narrow. Its boiling point is –33.5 ºC. This is why, to investigate the reactions, **a lower temperature is to be maintained**. It requires a special type of experimental set-up. (ii) Due to the hygroscopic nature of liquid NH_3, the reactions are to be carried out in a moisture free atmosphere. (iii) Due to the favoured formation of ion-pair (a consequence of low dielectric constant), ionisation of salts and acids remains incomplete.

(Q) **Water *vs.* liquid ammonia solvent** (Summary)

- **Dielectric constant**—solubilisation of salts; autoprotolysis constant; ion-pair formation (its effect on electrical conductivity and acid dissociation constant (see text).
- **Dipole moment**—solubilisation of salts (see text).
- **Polarisability**—induced dipole interaction in the solubilisation process (see text).
- **Hard-soft character**—hard-hard interaction in water while soft-soft interaction in liquid NH_3.
- **Autoprotolysis constant**—*pH* scale; acid-base strength (see text).
- **Ionic mobility of the autoprolysis products**—very high mobility in water and almost normal mobility in liquid NH_3.
- **Solvated electron**—colour and stability (see text).
- **Redox stability**—survival of powerful reducing agents in liquid NH_3 (see text).
- **Host medium (liquid NH_3) for the highly charged anionic species** (see text).
- **Basicity**—levelling effect, differentiating effect, strength of acids and bases (see text).
- **Advantages and disadvantages as solvents** (see text).

(R) **NH_3 *vs.* RNH_2 as solvents:** The alkyl amines (RNH_2) possess **a more convenient liquid temperature range** than ammonia but **solvating power** of the alkyl amines to solubilise the ionic compounds is weaker than that of ammonia. In spite of the higher Lewis basicity of the alkyl amines, the **steric factor reduces their solvating ability**.

(*cf.* **H_2O *vs.* ROH as solvents:** The primary alcohols like *MeOH* and *EtOH* are quite polar and have the dielectric constant comparable to that of liquid NH_3. Because of their less *H*-bonding power and steric factor, their **solvating power is weaker** than that of water. Because of their reduced solvating ability, they appear as the **more inert solvents** than water for studying the Lewis acid-base reactions. Their **autoprotolysis constants** (10^{-17} for *MeOH*, 10^{-19} for *EtOH*) are smaller than that of water (10^{-14}) and the **weak acids** (*e.g.* $MeCO_2H$) and **weak bases** (*e.g.* $PhNH_2$) **appear weaker in primary alcohols than in water**. This aspect has been discussed in Sec. 15.3).

15.5 LIQUID HYDROGEN FLUORIDE AS A SOLVENT

(A) **Solvent character :** Boiling point = 19.5ºC; Freezing point = –83ºC; relative dielectric constant = 84 (at 0 ºC); Dipole moment = 1.90 D. This hydrogen bonded solvent covering a wide liquid range is **a good solvent for the ionic compounds** because of its high dielectric constant. But its corrosive behaviour limits its application.

(B) **Solute-solvent interaction :** It may protonate many organic and inorganic compounds having protonation sites (*e.g.* *O*-sites). The fluorides may carry out complexation giving rise to the fluoro-complexes. Actually these are basically the acid-base reactions. But different fluoroborates and perchlorates dissolve in hydrogen fluoride without any reaction.

(C) ***H*-bond strength and ionic mobilities:** In terms of electronegativity ($F > O$), hydrogen bonding in liquid HF is stronger than in water; and liquid HF is a **stronger Kamlet-Taft acid** (*i.e.* better proton donor in H-bond). Because of the strong H-bonded network in liquid HF, mobilities of its autoprotolysis ions (*i.e.* H_2F^+ and HF_2^-) are much higher (*cf.* higher mobilities of H_3O^+ and OH^- in water) than for other ions because of the **Grotthuss type of ion transport** (*i.e.* **ionic motion without actual diffusion** of the autoionisation products through the H-bonded network of the solvent, see Sec. 14.3.8, Fig. 11.1.7.12).

(D) **Acid-base behaviour:** In terms of electronegativity ($F > O$), HF is a weaker electron donor (*i.e.* weaker Lewis base) than H_2O but HF is a stronger acidic solvent (both Lewis and Brönsted sense) than water. HF is a **stronger Kamlet-Taft acid** (*i.e.* better H-donor in H-bond).

(E) **Acid-base reactions :** The autoionisation of HF can be represented as follows :

$$3HF \rightleftharpoons H_2F^+ \ (i.e.\ H^+.HF) + HF_2^- \ (i.e.\ F^- .HF)$$

Symmetrical FHF^- (*i.e.* HF_2^-) ion is linear and its MO energy level diagram has been already discussed (Chapter 11) and bent HFH^+ is isoelectronic with H_2O and its bonding can be explained as for H_2O.

In fact, F^- may be solvated as follows : $xF^- + nHF \rightleftharpoons HF_2^- + H_2F_3^- + H_3F_4^- +$

Hence the species which can increase the concentration of H_2F^+ (*i.e.* H^+) are regarded as acids while the species which can enhance the concentration of HF_2^- (*i.e.* F^-) are regarded as bases. In the relatively stronger acidic liquid HF solvent, **weak bases in water appear as the stronger bases**. In addition to this, many acids in water appear here as the bases. On the other hand, **only very strong acids in water** can act **here as the weak acids**. These aspects are illustrated in the following examples.

Oxides and hydroxides can act as the strong bases in liquid HF.

$$M_2O + 2HF \rightleftharpoons 2MF + H_2O,\ H_2O + HF \rightleftharpoons H_3O^+ + F^-$$

$$HF + F^- \rightleftharpoons HF_2^-$$

Organic compounds (*e.g.* ketones, aldehydes, ethers, etc.) having the protonation sites act as the bases,

$$i.e.\ R\text{—}OY + 2HF \rightleftharpoons RO^+HY + HF_2^-.$$

Strong inorganic acids like HNO_3 and H_2SO_4, and weak fatty acids act as the bases in HF as follows.

$$HNO_3 + HF \rightleftharpoons H_2NO_3^+ + F^-;\ H_2SO_4 + HF \rightleftharpoons H_3SO_4^+ + F^-;$$

$$CH_3CO_2H + HF \rightleftharpoons CH_3CO_2H_2^+ + F^-;\ KNO_3 + 2HF \rightleftharpoons K^+ + H_2NO_3^+ + 2F^-$$

$HClO_4$ ($pK_a \approx -10$), the strongest acid in aqueous media shows an amphoteric character in liquid HF, *i.e.*

$$HClO_4 + HF \rightleftharpoons H_2ClO_4^+ + F^-;\ HClO_4 + HF \rightleftharpoons ClO_4^- + H_2F^+$$

However, FSO_3H ($pK_a \approx -15$), a **superacid** can act as the proton donor, *i.e.*

$$FSO_3H + HF \rightleftharpoons FSO_3^- + H_2F^+$$

Thus we can conclude: liquid HF can act as a **differentiating solvent** for the strong acids in water while it can act as a **levelling solvent** for the weak bases in water.

Lewis acids, especially the fluoride acceptors act as the strong acids, *e.g.* $SbF_5 + 2HF \rightleftharpoons SbF_6^- + H_2F^+$. This resultant mixture is referred to as ***a superacid*** (see Sec. 14.6) which can protonate even the hydrocarbons.

Other fluoride acceptors like, BF_3, AlF_3, GeF_4, SnF_4, PF_5, SeF_4, etc. also act as acids but are weaker in strength than SbF_5.

AlF_3 goes into solution because of the fluoro-complex formation (i.e. acidic property) but in the presence of a better fluoride acceptor (i.e. stronger acid), it again precipitates.

$$AlF_3\downarrow + HF \rightleftharpoons H^+AlF_4^-\ (dissolved) \xrightarrow{BF_3} H^+BF_4^- + AlF_3\downarrow$$

The $Al(III)$ fluoro-complex may be $[AlF_6]^{3-}$.

AlF_3, CrF_3 etc. can also show the *amphoteric properties* in liquid HF.

$$AlF_3\ \text{(an acid)} + 3KHF_2 \rightleftharpoons 3HF + K_3[AlF_6]$$

$$K_3[AlF_6]\ \text{(as a base)} + 3HBF_4 \rightleftharpoons AlF_3\downarrow + 3HF + 3KBF_4$$

(*cf.* Amphoteric behaviour of Al^{3+} in aqueous media)

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3\downarrow;\ Al(OH)_3 + OH^- \rightleftharpoons [Al(OH)_4]^-\ (\equiv AlO_2^- + 2H_2O)$$

$$[Al(OH)_4]^- + H^+ \rightleftharpoons Al(OH)_3\downarrow + H_2O\ \text{ or, } AlO_2^- + H^+ + H_2O \rightleftharpoons Al(OH)_3\downarrow$$

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$

(F) **Precipitation reactions :** Sulphate, nitrate and perchlorate salts of alkali metals are sufficiently soluble but the corresponding heavy metal salts are insoluble.

$$Na_2SO_4 + 2AgF \rightleftharpoons Ag_2SO_4\downarrow + 2NaF;\ NaClO_4 + TlF \rightleftharpoons TlClO_4\downarrow + NaF$$

$$AgNO_3 + BF_3 + 2HF \rightleftharpoons AgBF_4\downarrow + H_2NO_3^+F^-;\ NaClO_4 + AgF \rightleftharpoons AgClO_4\downarrow + NaF$$

(G) **Solvolysis reactions :** Formation of covalent fluorides occurs through the solvolysis reaction, *e.g.*

$$TiCl_4 + 4HF \rightleftharpoons TiF_4 + 4HCl.$$

(H) **Formation of addition compounds :** A number of so-called addition compounds, *e.g.* $KF\cdot HF$, $KF\cdot 2HF$, $NH_4F\cdot HF$, etc. are reported.

15.6 LIQUID HYDROGEN CYANIDE AS A SOLVENT

(A) **Solvent character :** Boiling point = 26 °C; Freezing point = –14 °C; Relative dielectric constant, 107 (at 25 °C). In spite of extensive hydrogen bonding and high dielectric constant, **it is inferior to water as an ionising agent**. Besides these, its deadly toxicity limits its application.

(B) **Dissolution power :** Many covalent compounds such as $SnCl_4$, $SnBr_4$, benzene, aniline, urea, glycerine, alcohols, etc. are soluble in HCN. Some covalent chlorides like $POCl_3$, $SOCl_2$, $BiCl_3$, $SbCl_5$, etc. are soluble in HCN. A few alkali metal salts like $NaCl$, KCl, NH_4Cl, $NaNO_3$, K_2SO_4 and KI are also soluble in HCN.

(C) **Acid-base reactions :** It autoionizes as, $2HCN \rightleftharpoons H_2CN^+ + CN^-$.

Thus protonic acids (*e.g.* HCl, H_2SO_4, HNO_3, etc.) are acids and cyanide producing substances are bases. A representative neutralisation reaction is :

$$HCl\ \text{(acid)} + NaCN\ \text{(base)} \rightleftharpoons NaCl\ \text{(salt)} + HCN\ \text{(solvent)}.$$

Such neutralisation reactions can be followed conductometrically.

(D) **Complex formation reactions :** Formation of the cyano-complexes can also be regarded as the acid-base reactions.

$$FeCl_3 + 3[(C_2H_5)_3NH][CN] \rightleftharpoons Fe(CN)_3\downarrow + 3[(C_2H_5)_3NH]Cl;$$

$$Fe(CN)_3\downarrow + 3[(C_2H_5)_3NH][CN] \rightleftharpoons [(C_2H_5)_3NH]_3[Fe(CN)_6],\ \text{(soluble)}$$

Here, triethylammonium cyanide acts as a cyanide donor (*i.e.* base).

(E) **Solvolysis reactions :** Formation of metal cyanides can be regarded as the representative solvolysis reaction.

$$Ag_2SO_4 + 2HCN \rightleftharpoons 2AgCN + H_2SO_4$$

15.7 ACETIC ACID (CH_3CO_2H) AS A SOLVENT

(A) **Solvent character :** Liquid range = 17°C to 118°C; Dipole moment = 0 (in the dimeric form); Relative dielectric constant = 7.0 (at 25°C). The zero dipole moment arises from the dimeric structure in its liquid state. Though its dielectric constant is low, it can dissolve a number of ionic salts.

(B) **Acid-base reactions :** It autoionises as, $2CH_3CO_2H \rightleftharpoons CH_3CO_2H_2^+ + CH_3CO_2^-$.

Thus the proton donors can act as the acids while the acetate donors can act as the bases. A typical acid-base reaction is :

$$CH_3CO_2Na \text{ (base)} + HCl \text{ (acid)} \rightleftharpoons NaCl \text{ (salt)} + CH_3CO_2H \text{ (solvent)}.$$

It can act as a differentiating solvent for the strong acids while it acts as a levelling solvent for the weak organic bases. The weak organic bases like aniline, acetamide and acetanilide cannot be titrated in aqueous media but behave as the strong bases and they can be titrated by using $HClO_4$ in acetic acid media. Actually the following reaction occurs as :

$$B \text{ (weak base)} + CH_3CO_2H \rightleftharpoons BH^+ + CH_3CO_2^-,$$

$$CH_3CO_2^- + HClO_4 \rightleftharpoons CH_3CO_2H + ClO_4^-$$

(C) **Amphoteric reactions :** Zn(II), Al(III) can show the amphoteric behaviour.

$$ZnCl_2 + 2CH_3CO_2Na \rightleftharpoons Zn(OCOCH_3)_2\downarrow + 2NaCl$$

$$Zn(OCOCH_3)_2\downarrow + 2CH_3CO_2Na \rightleftharpoons Na_2[Zn(OCOCH_3)_4], \text{ (soluble)}$$

(D) **Complex formation reactions :** $Fe(III)$ forms a red-coloured complex with SCN^- in liquid acetic acid. Similarly, $Co(II)$ gives the blue coloured thiocyanato complex.

$$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+};\ Co^{2+} + 4SCN^- \rightleftharpoons [Co(NCS)_4]^{2-}$$

(E) **Solvolysis reaction :** This is being illustrated in the following example.

$$SO_2Cl_2 + 4CH_3CO_2H \rightleftharpoons SO_2(CH_3CO_2)_2 + 2CH_3CO_2H_2^+ + 2Cl^-$$

15.8 SULFURIC ACID AS A SOLVENT

(A) **Solvent character :** Boiling point = 300°C (with decomposition); Freezing point = 10.4°C; Density = 1.83 g cm^{-3} (25°C); Relative dielectric constant = 110 (at 20°C); Viscosity = 245.4 millipoise.

In spite of the high dielectric constant, it is not being treated as a promising ionising solvent because of its high viscosity (~ 25 times higher than that of water) which prevents the rapid diffusion, dissolution and crystallization of the solutes. Besides these, the adhered solvents cannot be easily removed.

(B) ***H*-bonding and ionic mobilities of the autoionisation products:** The high autoionisation constant ($\sim 10^{-4}$) makes the high abundance of the autoionisation products, *i.e.* $H_3SO_4^+$ and HSO_4^- which show the relatively **higher ionic mobilities** through the strongly *H*-bonded network of solvent as in water (*cf.* **Grotthuss mechanism of ion transport**, see Sec. 14.3.8, Fig. 11.1.7.12).

(C) **Acid-base reactions :** The autoionization process ($K = 10^{-4}$) takes place as :

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

Thus $KHSO_4$ acts as a base. In fact, all the bases in water also act as bases in the present solvent. Even the compounds which have got no basic property in water may act as the strong bases in sulfuric acid.

$$OH^- + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^-;\ NH_3 + H_2SO_4 \rightleftharpoons NH_4^+ + HSO_4^-;$$

$$R{-}OH + H_2SO_4 \rightleftharpoons ROH_2^+ + HSO_4^-;$$

$$O{=}C(NH_2)_2 + H_2SO_4 \rightleftharpoons O{=}C(NH_2)(NH_3^+) + HSO_4^-$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

The last example producing H_3O^+ does not make the solution acidic (*cf.* acidity is measured by the abundance of $H_3SO_4^+$) and here **H_3O^+ acts just like another cation**.

Because of the strong acidic property of H_2SO_4 solvent, most of the solutes and salts act as the bases to increase the concentration of HSO_4^-.

$$NH_4ClO_4 + H_2SO_4 \rightleftharpoons NH_4^+ + HClO_4 + HSO_4^- \quad (\textit{i.e.}\ \textbf{solvolysis}\ \text{of}\ NH_4ClO_4).$$

Acetic acid and HNO_3 can also act as the bases in H_2SO_4, *i.e.*

$$CH_3CO_2H + H_2SO_4 \rightleftharpoons CH_3CO_2H_2^+ + HSO_4^-;$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+.$$

Here actually the protonated intermediate species $H_2NO_3^+$ produces $H_2O + NO_2^+$. A mixture of conc. nitric acid and conc. sulfuric acid is used as the ***nitrating mixture*** in which the effective nitrating agent, nitronium ion (NO_2^+) exists.

The mode of ionisation through the acid-base interaction can be evidenced through the *cryogenic studies, i.e. depression of freezing point*, *i.e.* $\Delta T = kmn$, m = stoichiometric molality, n = number of particles formed on dissolution of one molecule of the solute = 4 for HNO_3, k = molal cryoscopic constant.

- **Conc. H_2SO_4 is a good medium to stabilise the cation like NO_2^+ –Why?** The cations like NO_2^+ where the central atoms present in **high oxidation states** are highly electronegative and consequently, they are **strong Lewis acids** which will be destroyed easily through the Lewis acid-base adduct formation. To stabilise such strong Lewis acid cations in free state, the host medium must be a very weak Lewis base. In fact, H_2SO_4 is a very weak Lewis base and it is very often chosen as a solvent **for carrying out the oxidation reactions producing the highly electron deficient Lewis acids**. It may be noted that **superacids** are chosen as the host medium to stabilise the **carbocations** which are the powerful Lewis acids.

  It may be noted that conversely, the Lewis basic solvents like liquid NH_3 is generally chosen to stabilise the **strong Lewis bases like the carbanions** and carrying out the reduction reactions producing the electron rich and strong Lewis bases (see Sec. 15.4).

H_2SO_4 is a very strong acid. Only a very few compounds can show the acidic functions in H_2SO_4. ***$HClO_4$, the strongest acid in aqueous media acts only as a weak acid in conc. H_2SO_4,***

$$HClO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + ClO_4^-.$$

Pyrosulfuric acid (*i.e.* disulfuric acid), $H_2S_2O_7$ acts also as a weak acid. It is formed in the reaction between SO_3 and H_2SO_4.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7,\ H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

Here, ***SO_3* (*a Lewis acid*) *acts as an acid*** as it enhances the concentration of the **lyonium** (*i.e.* $H_3SO_4^+$) and reducing the concentration of **lyate** (*i.e.* HSO_4^-). The above reaction can be written as :

$$2H_2SO_4 + SO_3 \rightarrow H_3SO_4^+ + HS_2O_7^-$$

Fluorosulfuric acid (*FSO_3H*) and chlorosulfuric acid (*$ClSO_3H$*) can also act as the weak acids.

$$FSO_3H + H_2SO_4 \rightleftharpoons H_3SO_4^+ + FSO_3^-$$

Boron *tris*(*hydrogen sulfate*), a Lewis acid can also act as an acid in the same way.

$$B(HSO_4)_3 + 2H_2SO_4 \rightarrow H_3SO_4^+ + [B(HSO_4)_4]^-$$

The above reaction can be understood as follows :

$$B(HSO_4)_3 + H_2SO_4 \rightarrow H[B(HSO_4)_4]^-$$

$$H[B(HSO_4)_4] + H_2SO_4 \rightarrow H_3SO_4^+ + [B(HSO_4)_4]^-$$

Hydrogen **tetrakis(hydrogensulfato)borate, *$H[B(HSO_4)_4]$*** prepared *in situ* shows a strong acidic function in H_2SO_4.

$$H_3BO_3 + 6H_2SO_4 \rightarrow [B(HSO_4)_4]^- + 3H_3O^+ + 2HSO_4^-$$

To the above mixture, addition of SO_3 removes H_3O^+ and HSO_4^- :

$$[B(HSO_4)_4]^- + 3H_3O^+ + 2HSO_4^- + 3SO_3 \rightarrow H_3SO_4^+ + [B(HSO_4)_4]^- + 4H_2SO_4$$

In terms of the coordinating mode of HSO_4^-, $[B(HSO_4)_4]^-$ actually represents $[B(OSO_3H)_4]^-$. Thus the net reaction is:

$$B(OH)_3 + 3SO_3 + 2H_2SO_4 \longrightarrow [B(OSO_3H)_4]^- + H_3SO_4^+$$

Here it is interesting to note that the above reaction leading to the formation of $H[B(HSO_4)_4]$ is nothing but the dehydration of $B(OH)_3$ by SO_3 in sulfuric acid solution. In fact, the present reaction can be regarded as the **solvolysis of *$B(OH)_3$***.

(D) **Solvolysis reaction:** We have already mentioned that because of the high autoprotolysis constant ($K_s \approx 10^{-4}$) there is an abundance of HSO_4^- to favour the solvolysis reaction (*cf.* solvolysis of $B(OH)_3$ producing $[B(HSO_4)_4]^-$. $SnCl_4$ solvolyse and the solvolysis product (*i.e.* $Sn(HSO_4)_4$) remain as a **solvated species** which acts as an acid.

$$SnCl_4 + 6H_2SO_4 \longrightarrow [Sn(OSO_3H)_4(H_2SO_4)_2] + 4HCl$$

$$[Sn(OSO_3H)_4(H_2SO_4)_2] + H_2SO_4 \longrightarrow [Sn(OSO_3H)_5(H_2SO_4)]^- + H_3SO_4^+$$

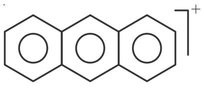
(E) **Redox reaction:** It has been already pointed out that H_2SO_4 is a good solvent to carry out the oxidation reaction producing the unusual cations acting as the very strong Lewis acids. One such example is the oxidation of I_2 to I_2^+ (**blue coloured**) in oleum ($H_2S_2O_7$, *i.e.* $H_2SO_4 + SO_3$ where SO_3 is the effective oxidising species).

$$2I_2 + 2SO_3 + H_2SO_4 \longrightarrow 2I_2^+ \text{ (blue)} + SO_2 + 2HSO_4^-$$

By using other oxidising agents like IO_3^- or $S_2O_8^{2-}$ instead of SO_3, I_2 can be oxidised to IO^+, I_3^+ and I_5^+.

Aromatic hydrocarbon (*AHC*) radical cations (*ESR* active) can be generated from the corresponding *AHC* in H_2SO_4 (as a solvent) which protonates the *AHC* followed by oxidation of the protonated *AHC* by the H_2SO_4 solvent itself. The overall oxidation of anthracene (*A*, a representative *AHC*) is shown here.

$$2A + 3H_2SO_4 \longrightarrow 2A^+ + SO_2 + 2H_2O + 2HSO_4^-; A^+ \equiv$$



Thus this **strongly protonic solvent** (H_2SO_4) can also act as an **oxidising solvent**.

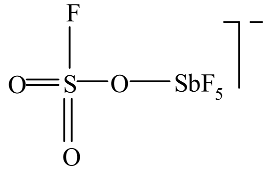
15.9 FLUOROSULFONIC ACID (HSO_3F) AS A SOLVENT AND SUPERACIDS

(A) **Solvent character :** Boiling point = 163°C; Melting point = – 89°C. Viscosity = 15.6 millipoise (at 25 °C); Density = 1.73 g cm^{-3}. ***As an acidic solvent, it has got some distinct advantages over HF and H_2SO_4.*** If free from *HF*, it can be easily handled in glass vessels. Its liquid range is more suited. *Its low viscosity also favours the solvent character.*

(b) **Acid-base reactions :** The autoionisation occurs as : $2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-$. In connection with the **superacids** (see Sec. 14.6), this acidic solvent is of much importance. Some examples are given below.

(i) ***SbF_5 and HSO_3F mixture*** : The mixture produces the product which is stronger than HSO_3F and the mixture is a ***superacid.*** The superacid is sometimes described colourfully as the ***magic acid*** because of its superacidity.

$$SbF_5 + HSO_3F \rightarrow H[SbF_5(OSO_2F)] \xrightleftharpoons{HSO_3F} H_2SO_3F^+ + [SbF_5(OSO_2F)]^-$$



(ii) **($SbF_5 + SO_3$) and *HSO_3F mixture*** : Addition of SO_3 in the molar ratio up to 3:1 of SO_3 to SbF_5 in HSO_3F enhances the acidity function and the mixture can be treated as a ***superacid.***

$$SO_3 + SbF_5 \rightleftharpoons SbF_4(OSO_2F),\ 2SO_3 + SbF_5 \rightleftharpoons SbF_3(OSO_2F)_2;$$

$$3SO_3 + SbF_5 \rightleftharpoons SbF_2(OSO_2F)_3;$$

$$SbF_3(OSO_2F)_2 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + [SbF_3(OSO_2F)_3]^-$$

$$SbF_2(OSO_2F)_3 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + [SbF_2(OSO_2F)_4]^-$$

The superacids are so strong acids that even the highly electron deficient species like $C_6H_3(NO_2)_3$ behaves as a strong base in superacids. Such superacids can protonate hydrocarbons leading to the **synthesis of carbonium ions** (*cf.* Sec. 14.6).

15.10 LIQUID SULFUR DIOXIDE AS A SOLVENT

(A) **Solvent character :** Boiling point = –10.2°C; freezing point = –75.5°C; relative dielectric constant = 17.3 (at –16.5°C). Because of the low dielectric constant, it is not a good solvent for the ionic compounds, but it is good for many types of organic compounds. In general, iodides and thiocyanates are soluble. Among the alkali metal halides, the solubility runs as : $MI > MBr > MCl > MF$. The **thionyl halides and acetates** are practically miscible in liquid SO_2. Many **sulphuryl compounds**, *e.g.* SO_2X_2, are also highly soluble.

(b) **Acid-base reactions :** It is proposed that the autoionization occurs as :

$$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}.$$

Thus thionyl halides capable of providing the SO^{2+} cations are the acids while the compounds which can provide SO_3^{2-} ions are regarded as the bases. Thus the following type of acid-base neutralisation reactions can be studied conductometrically.

$$SOX_2\ \text{(acid)} + K_2SO_3\ \text{(base)} \rightleftharpoons 2KX\ \text{(salt)} + 2SO_2\ \text{(solvent)}$$

Zn(*II*) and *Al*(*III*) salts show the amphoteric behaviour.

$$2AlCl_3 + 3K_2SO_3 \rightleftharpoons Al_2(SO_3)_3\downarrow + 6KCl;$$

$$Al_2(SO_3)_3\downarrow + 3K_2SO_3 \rightleftharpoons 2K_3[Al(SO_3)_3],\ \text{(soluble)}$$

$$2K_3[Al(SO_3)_3] + 3SOCl_2 \rightleftharpoons 6KCl + 6SO_2 + Al_2(SO_3)_3\downarrow$$

(*cf. Amphoteric behaviour of Al*(III)-*salts in aqueous media.*

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow;\ Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-,\ i.e.\ AlO_2^- + 2H_2O$$

$$[Al(OH)_4]^- + NH_4^+ \rightarrow Al(OH)_3 \downarrow + H_2O.)$$

Similarly, $ZnSO_3$ may undergo complexation to produce $K_2[Zn(SO_3)_2]$.

Here it is important to mention that the **solvent system concept of acid and base** is applied in liquid SO_2 based on its proposed autoionisation mode but unfortunately, the **experimental evidences** (see Sec. 14.11) **do not support the existence of SO^{2+} cation in liquid SO_2.**

(C) **Metathetical and precipitation reactions :** Two soluble salts may led to precipitations.

$$BaI_2 + Zn(SCN)_2 \rightleftharpoons Ba(NCS)_2\downarrow + ZnI_2;\ AlCl_3 + 3NaI \rightleftharpoons NaCl\downarrow + AlI_3$$

Thionyl derivatives are highly soluble in liquid SO_2. By taking the advantage of the metathetical reactions, a large number of thionyl derivatives have been prepared.

$$2CH_3CO_2Ag + SOCl_2 \rightleftharpoons 2AgCl\downarrow + SO(OCOCH_3)_2;$$

$$2NH_4SCN + SOCl_2 \rightleftharpoons 2NH_4Cl\downarrow + SO(SCN)_2;\ 2KI + SOCl_2 \rightleftharpoons 2KCl\downarrow + SOI_2$$

(D) **Redox reactions :** In aqueous media, SO_2 shows both its oxidising and reducing activities but the liquid SO_2 does not display any pronounced oxidising or reducing activity but simply, it provides a medium for the reaction.

$$6KI + 3SbCl_5 \rightleftharpoons 2K_3[SbCl_6] + SbCl_3 + 3I_2.$$

(E) **Solvolysis reactions :** Many covalent halides undergo solvolysis in liquid SO_2.

$$2LiBr + 2SO_2 \rightleftharpoons Li_2SO_3 + SOBr_2$$

$$PCl_5 + SO_2(l) \rightleftharpoons POCl_3 + SOCl_2;\ NbCl_5 + SO_2(l) \rightleftharpoons NbOCl_3 + SOCl_2$$

(F) **Complex formation reactions :** The amphoteric behaviour shown by *Zn*(*II*) and *Al*(*III*) salts actually involves the complexation with sulphite. Besides these, a large number of halo-complexes of *Sb*(*III*) and *Sb*(*V*) are reported to be formed in liquid SO_2 in the following reactions.

$$SbCl_3 + 3KCl \rightleftharpoons K_3[SbCl_6];\ SbCl_5 + KCl \rightleftharpoons K[SbCl_6];$$

$$SbCl_5 + CH_3COCl \rightleftharpoons [CH_3CO][SbCl_6];\ SbCl_5 + NOCl \rightleftharpoons [NO][SbCl_6]$$

(G) **Organic reactions :** Because of the high solubility of many organic compounds in liquid SO_2, many synthetic reactions are carried out in liquid SO_2. Some representative examples are given below.

Sulphonation : $C_6H_6 + ClSO_3H \rightarrow C_6H_5SO_3H + HCl.$

Friedel crafts reactions : $C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl.$

15.11 BROMINE TRIFLUORIDE AS A SOLVENT

(A) **Solvent character:** Boiling point = 126°C; Melting point = 9 °C; Specific conductance = 0.008 Ω^{-1} m^{-1} at 25 °C. The fairly high specific conductance indicates its autoionisation process. Thus it is expected to be a good solvent for the ionic compounds. But because of its high reactivity and corrosiveness, very few reactions have been investigated in this solvent.

(B) **Acid-base reactions:** The mode of autoionisation is : $BrF_3 + BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-$. Thus the *fluoride acceptors* (*e.g.* SbF_5, TiF_4, etc.) *will enhance the concentration of* BrF_2^+ *and they will act as the acids, e.g.* $MF_5 + BrF_3 \rightleftharpoons [BrF_2]^+ + [MF_6]^-$; $M = Sb, Nb, Ta, P,$ etc.

$$MF_4 + 2BrF_3 \rightleftharpoons 2[BrF_2]^+ + [MF_6]^{2-},\ M = Si,\ Ti,\ \text{etc.}$$

On the other hand, the *fluoride donors will act as the bases* because they enhance the concentration of BrF_4^- as follows.

$$MF + BrF_3 \rightleftharpoons M^+ + [BrF_4]^-, \; M = K, Na, Ag, \text{ etc.}$$

IF_5 (as a solvent): $2IF_5 \rightleftharpoons [IF_4]^+ + [IF_6]^-$ (autoionisation)

SbF_5 – an acid to increase $[IF_4^+]$: $SbF_5 + IF_5 \longrightarrow [SbF_6]^- + [IF_4]^+$

KF – a base to increase $[IF_6^-]$: $KF + IF_5 \rightleftharpoons K^+ + [IF_6]^-$

Thus the acid-base neutralisation reactions can be studied conductometrically. The acid-base reactions between SbF_5 and KF will produce the salt $K^+[SbF_6]^-$ as follows :

$$KF + BrF_3 \rightleftharpoons K^+ + [BrF_4]^-; \; SbF_5 + BrF_3 \rightleftharpoons [BrF_2]^+ + [SbF_6]^-$$

i.e. $$KF + SbF_5 + 2BrF_3 \rightleftharpoons K^+[SbF_6]^- + 2BrF_3$$

or, $K^+[BrF_4^-]$ (*base*) + $[BrF_2]^+[SbF_6]^-$ (*acid*) $\rightleftharpoons$ $K^+[SbF_6^-]$ (*salt*) + $2BrF_3$ (*solvent*)

Similarly, $$Ag^+[BrF_4]^- + [BrF_2]^+[AuF_4]^- \rightleftharpoons Ag^+[AuF_4]^- + 2BrF_3$$

i.e. $$AgF + AuF_3 \rightleftharpoons Ag^+[AuF_4]^-$$

$$2Ag^+[BrF_4]^- + ([BrF_2]^+)_2[SnF_6]^{2-} \rightleftharpoons Ag_2[SnF_6] + 4BrF_3$$

i.e. $$2AgF + SnF_4 \rightleftharpoons Ag_2[SnF_6]$$

$$Ag^+[BrF_4]^- + [BrF_2]^+[SbF_6]^- \rightleftharpoons Ag[SbF_6] + 2BrF_3$$

i.e. $$AgF + SbF_5 \rightleftharpoons Ag[SbF_6]$$

(C) **Fluorination reactions :** It can favourably fluorinate metals and metal oxides, *e.g.*

$$3SiO_2 + 4BrF_3 \rightleftharpoons 3SiF_4 + 2Br_2 + 3O_2;$$

$$6Sb_2O_3 + 20BrF_3 \rightleftharpoons 12SbF_5 + 10Br_2 + 9O_2;$$

$$2WO_3 + 4BrF_3 \rightleftharpoons 2WF_6 + 2Br_2 + 3O_2.$$

(D) **Redox reactions :** Metals (*e.g.* Nb, Ta, Au, etc.) which can form stable fluoro-complexes can get dissolved in BrF_3 with the liberation of bromine.

$$6Nb + 16BrF_3 \rightleftharpoons 6[BrF_2][NbF_6] + 5Br_2.$$

15.12 OXYHALIDES AS THE SOLVENTS

A number of oxychlorides can function as solvents. The modes of autoionisation of some representative oxyhalides are given below (ignoring the solvation of the ions produced).

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-; \; SeOCl_2 \rightleftharpoons SeOCl^+ + Cl^-;$$
$$COCl_2 \rightleftharpoons COCl^+ + Cl^-; \; CH_3COCl \rightleftharpoons CH_3CO^+ + Cl^-$$

Here we shall pay attention only to $SeOCl_2$ and $POCl_3$ in connection with the involved acid-base reactions.

Thus the compounds which can enhance the concentration of Cl^- ions are regarded as bases while the compounds which can accept the chlorides are referred to as acids in $SeOCl_2$. Thus $NaCl$ acts as a base:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Similarly, pyridine (*py*), quinoline and alkaline earth metal chlorides show the basic properties in $SeOCl_2$:

$$py + SeOCl_2 \rightleftharpoons [SeOCl.py]^+ + Cl^-.$$

$FeCl_3$ being a chloride acceptor acts as an acid :

$$FeCl_3 + SeOCl_2 \rightleftharpoons SeOCl^+ + [FeCl_4]^-.$$

Similarly, the chloride acceptors such as $SnCl_4$, $SiCl_4$, $AsCl_3$, SO_3 show the acidic functions:

$$SnCl_4 + 2SeOCl_2 \rightleftharpoons 2SeOCl^+ + [SnCl_6]^{2-}.$$

Different acid-base titrations such as, pyridine–$SnCl_4$, KCl–$SnCl_4$, pyridine – SO_3, $CaCl_2 - SnCl_4$, can also be studied in $SeOCl_2$ conductometrically.

Phosphorous oxychloride $POCl_3$, an aprotic solvent suffers autoionization as,

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-.$$

Considering the possibility of solvation of the ions, the autoionization process can be represented in a general way as,

$$(x + y)POCl_3 \rightleftharpoons [POCl_2.(POCl_3)_y]^+ + [Cl(POCl_3)_{x-1}]^-$$

Thus the chloride donors, e.g. $Et_4N^+Cl^-$, *are the bases while the chloride acceptors, e.g.* $FeCl_3$, $SbCl_5$, $AlCl_3$, $TiCl_4$, etc., *act as the acids.* A typical acid-base reaction is represented as follows.

$$SbCl_5 + POCl_3 \rightleftharpoons [POCl_2]^+[SbCl_6]^-$$

$$[POCl_2]^+\ [SbCl_6]^- \text{ (acid)} + [Et_4N]^+Cl^- \text{ (base)} \rightleftharpoons [Et_4N][SbCl_6] \text{ (salt)} + POCl_3 \text{ (solvent).}$$

Titrations can be monitored conductometrically. Et_3N and KCl can also show basic functions in $POCl_3$.

$$Et_3N + POCl_3 \rightleftharpoons Et_3N.POCl_2^+ + Cl^-, KCl \rightleftharpoons K^+ + Cl^-.$$

15.13 MOLTEN SALTS (*i.e.* IONIC LIQUIDS) AS THE SOLVENTS

Several molten salts can also act as the non-aqueous solvents. The molten inorganic salts are resistant to drastic reaction conditions (*i.e.* electrolytic production of F_2). They can provide the higher concentration of the coordinating anions. Many high temperature reactions (*e.g.* blast furnace reactions) are known to occur in molten conditions. Some molten salts as the solvents are discussed below.

Covalent halides **:** The covalent halides like HgX_2 can experience autoionisation on melting.

$$2HgX_2 \rightleftharpoons HgX^+ + HgX_3^-$$

In terms of the concept of *solvent system*, the species which can generate HgX^+ ions are the acids and the species which can produce HgX_3^- ions are the bases. Solution of Hg in molten $HgCl_2$ leads to:

$$Hg + HgCl_2 \rightarrow Hg_2Cl_2$$

Similarly, addition of Cd in molten $CdCl_2$ produces Cd_2^{2+} (**cadmus ion**) which can be isolated with the addition of Al_2Cl_6 which offers the large anion $AlCl_4^-$ to stabilise Cd_2^{2+} in the solid lattice.

$$Cd + CdCl_2 \rightarrow Cd_2Cl_2 \xrightarrow{Al_2Cl_6} Cd_2[AlCl_4]_2$$

Alkali halides **:** On melting, though the *long range order* (present in crystals) is destroyed, the local order is maintained; and the coordination number 6:6 is reduced to 4:4. The molten (*i.e.* fused) salt is a good conductor of electricity. When Al_2Cl_6 is added to the fused alkali metal chloride, $[AlCl_4]^-$ anion is produced.

$$2M^+Cl^- + Al_2Cl_6 \rightarrow 2M^+ + 2[AlCl_4]^-$$

In $M[AlCl_4], [AlCl_4]^-$ can autoionise as follows :

$$2[AlCl_4]^- \rightleftharpoons [Al_2Cl_7]^+ + Cl^-, \ pK_{eq} = 7.0\ (175\ ^{o}\mathrm{C})$$

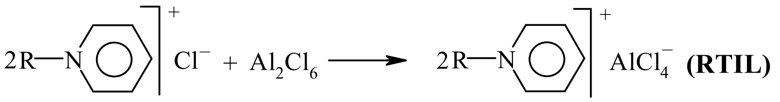
A ***pCl* scale** (similar to pOH scale in aqueous media) can be formulated as :

$pCl = 3.5$ (neutral point), $pCl < 3.5$ (basic condition), $pCl > 3.5$ (acidic condition).

[*cf.* In aqueous media, $pOH = 7$ (neutral point), $pOH > 7$ (acidic condition), $pOH < 7$ (basic condition)].

The alkali metal halides can dissolve the alkali metals ($M \rightarrow M^+ + e$, the released electron remains trapped into the solvent cavities). Formation of the chloro-complexes in such melts is favoured because of the very high concentration of Cl^- (*e.g.* concentrated HCl solution can give $[Cl^-] = 12$ mol dm^{-3} while molten $LiCl$ can produce $[Cl^-] = 35$ mol dm^{-3}). It allows the formation of the chloro-species like $[FeCl_4]^{2-}, [CrCl_6]^{3-}$, $[TiCl_6]^{3-}$ which are not stable in aqueous media with respect to the hydrolysis reaction.

***Room-temperature molten salts* or *Room-temperature ionic liquid (RTIL)* :** Generally, the concept of molten salts projects the idea of **high temperature fused systems**. But, some typical salts can remain in molten conditions even at room temperature. When alkyl **pyridinium chlorides** are added to aluminium chloride, the resultant salt remains in liquid condition.



Such molten salt systems can be studied at ~ 25°C while it needs ~ 175°C for $MAlCl_4$ (produced by the addition of Al_2Cl_6 to MCl).

When the solid salts like **triethylammonium chloride** and cuprous chloride ($CuCl$) are mixed together, it produces a light green liquid of the molten salt produced.

$$Et_3NH^+Cl^- \text{ (solid)} + CuCl \text{ (solid)} \rightarrow [Et_3NH][CuCl_2] \text{ (molten state)} \ \ \textbf{(RTIL)}$$

It may be mentioned that such solvents (molten salts) are very much sensitive towards the moisture which can initiate the hydrolytic cleavages of the chlorocomplexes.

Note* :** The ***melting point of ionic liquids which are basically ionic salts depends on the extent of electrostatic attraction between the cations and anions. ***The large interionic separation reduces the electrostatic attraction and consequently reduces the melting point.*** In organic ionic liquids, the positive charge in the organic cation very often delocalises. It disfavours the formation of stable ionc organic crystal. ***This reduced lattice energy lowers the melting point also.***

***Room temperature organic ionic liquids* :** We have already mentioned two such liquids (*RTIL*). In fact, a large number of such liquids constituted by **an organic cation and an inorganic anion** have been prepared and these are widely used in organic synthesis. The organic cations commonly used for this purpose are shown in Fig. 15.13.1.

The anions are like : $Cl^-, Br^-, NO_3^-, BF_4^-, ClO_4^-, PF_6^-, AlCl_4^-, Al_2Cl_7^-, CF_3SO_3^-, CH_3SO_3^-$, etc. By using a suitable combination of the cation and anion, a large number of organic ionic liquids may be prepared (***tailor-made solvents***).

The halocomplexes as the anions are generally sensitive to hydrolysis but using the suitable anions, ***organic ionic liquids resistant to air and moisture can be prepared.***

Properties, uses and advantages of the organic ionic liquids

(i) They are the nonaqueous polar solvents to dissolve a wide range of both organic and inorganic substances.

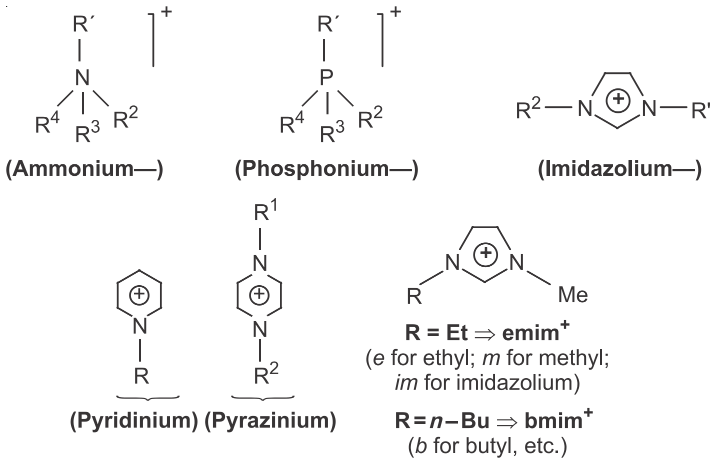


Fig. 15.13.1. Organic cations used in preparing the organic ionic liquids.

(ii) By making the suitable combinations, a large number of solvents can be prepared (*tailor-made solvents*) according to the requirements.

(iii) By using a suitable anion, the ionic liquids can be made resistant to air and moisture (*i.e.* water).

(iv) The ionic liquids can be made by using the poorly coordinating anions (*i.e.* ***polar but noncoordinating solvents***).

(v) The ionic liquids are immiscible with a number of *organic nonpolar solvents*. Thus, such ionic liquids may be used to prepare **two-phase systems with a nonaqueous polar phase.**

(vi) Hydrophobic ionic liquids may be used to prepare **two immiscible polar phases including water.**

(vii) Ionic liquids are **nonvolatile** and they can be used safely in high vacuum systems. In fact, based on this ground, ***they can replace the volatile organic solvents to avoid the environmental hazards.*** This is why, such ionic liquids may be treated as the ***green solvents*** (see the authors' book, **Environmental Chemistry with Green Chemistry**, Books & Allied, Kolkata). **To make the ecofriendly organic ionic liquids, halogen free *anions like tosylate, octyl sulfate, ethyl sulfate, methyl sulfate etc. may be used.***

(viii) The organic ionic liquids are ***nonflammable***. This is an added advantage compared to the conventional organic solvents.

(ix) These ionic liquids are quite stable and safer in *microwave mediated synthesis*.

(x) The organic cation very often delocalises the charge and the organic component of the salt prevents the formation of stable organic crystal.

(xi) These organic ionic liquids are widely used in carrying out organic reactions.

EXERCISE XV

A. General Questions

(1) What are the different types of solvents? Discuss the properties of the ionising solvents.

(2) Discuss the advantages and disadvantages of liquid NH_3 as a solvent.

(3) Discuss the acid-base reactions in different protic and aprotic solvents.

(4) What do you mean by superacids? Discuss their characteristics.

(5) What do you mean by ionic liquids as the solvents? Discuss the different types of ionic liquids. What are the advantages of these solvents?

B. Justify the Following Statements

(1) The oxidising power of different so-called potential oxidising agents is significantly reduced in liquid NH_3.
(2) There are many highly reducing agents which cannot survive in aqueous solutions but they can exist in liquid NH_3, and the reducing agents are facilitated in liquid NH_3.
(3) The colour of metal-ammonia solution does not depend on the nature of the metal dissolved.
(4) On increasing the concentration of metal, the blue coloured alkali metal-ammonia solution becomes bronze coloured having some metallic properties.
(5) The conductivity and paramagnetism of the alkali-metal ammonia solution initially decrease with the increase of concentration of the metal, but after passing through a minimum, the properties increase again.
(6) Alkali metals do not survive in aqueous solution but in liquid NH_3.
(7) Hydrogen fluoride is a poorer solvent than water.
(8) Experimental evidences do not support the proposed mode of autoionisation of liquid SO_2.
(9) In spite of the wider liquid range and higher dielectric constant of H_2SO_4, it is a poorer solvent than H_2O for the ionic solutes.
(10) Very few compounds can only display the acidic functions in H_2SO_4 solvent.
(11) SO_3 and H_3BO_3 can enhance the acidity in H_2SO_4 solvent.
(12) SbF_5 increases the acidity as well as the conductivity of liquid HF.
(13) Neither BrF_5 nor AsF_5 is a good conductor of electricity but their mixture is a good conductor.
(14) AlF_3 gets dissolved in HF in the presence of NaF but it again gets precipitated on passing BF_3 gas through the solution.
(15) The higher dielectric constant, dipole moment and fluidity favour the ionising solvents.
(16) Many ionic salts having the uni-univalent ions get dissolved in liquid NH_3 but the salts having the polyvalent ions do not get favourably dissolved.
(17) The mixture of SbF_5 and HF is a superacid.
(18) The weak bases like acetamide and acetanilide cannot be titrated by any acid in aqueous media but these can be done by $HClO_4$ in acetic acid media.
(19) $Zn(II)$ salts and $Al(III)$ salts may display the amphoteric behaviour in many nonaqueous solvents.
(20) Pure HNO_3 cannot act as a nitrating reagent but it can perform the task in the presence of the concentrated H_2SO_4.
(21) H_3BO_3 is a weak acid in aqueous media but it acts as a strong acid in H_2SO_4.
(22) The mixture of SbF_5 and HSO_3F is a superacid and the superacidity can be increased with the addition of SO_3.
(23) Many organic synthesis reactions can be easily carried out in liquid SO_2.
(24) The conductivity of BrF_3 can be enhanced with the addition of SbF_5 or TiF_4.
(25) In BrF_3, KF can be conductometrically titrated by SbF_5.
(26) In $SeOCl_2$, pyridine can be titrated conductometrically by $SnCl_4$.
(27) SO_3 and $B(HSO_3)_3$ are Lewis acids and they can act as acids in H_2SO_4.
(28) It is relatively easier to characterise sodide and electride in liquid ethylenediamine solvent than in liquid ammonia.

(29) The macrocyclic ligands like cryptands and crown ethers can be used to characterise the unusual anions like Na^-, Bi_3^{3-}, Pb_5^{2-}, Sn_9^{4-} etc. in liquid NH_3.

(30) The proton transfer rate is slower in liquid NH_3 than in water.

(31) Some salts can be used as ionic liquid solvents.

(32) *Na*-liquid NH_3 can be used to prepare homopolyatomic cluster anions.

(33) Alkyl pyridinium chloride on being treated with aluminium chloride can produce an ionic liquid at room temperature.

(34) Two solids – triethylammonium chloride and cuprous chloride on mixing produces a light green liquid at room temperature.

(35) Organic ionic liquids can be used as the *green solvents*.

(36) There are many advantages of organic ionic liquids over the conventional organic solvents.

(37) Dielectric constant and autoprotolysis constant are the two important parameters of a solvent to determine the acid-base strength.

(38) In Karl-Fischer titration to determine water (present in small quantities in a solid or liquid sample involves the oxidation of SO_2 by iodine to sulfate in presence of water and a base.

(39) Water can dissolve many 2-2 salts while liquid NH_3 dissolves mainly 1-1 salts consisting of the polarisable ions.

- Liquid NH_3 is a good solvent for the salts bearing the soft cations.

(40) Ionic mobilities of the autoprotolysis products in a particular protic solvent depends on the *H*-bond strength in the solvent network.

- Grotthuss transport does not lead to the actual diffusion of the ions.

(41) Alkali metal dissolved in liquid NH_3 is described as the '**expanded metal**'.

- Density of the metal-ammonial blue solution is less than that of pure solvent.
- Paramagnetic susceptibility of the metal-ammonia solution depends on the concentration of metal.
- Colour and conductivity of the metal ammonia solution depend on the concentration of metal.
- Colour of a dilute metal-ammonia solution is independent on the nature of metal and it can be explained by Jortner cavity model.
- Formation of cluster of ions (*e.g.* ion-pairs, ion-triples, ion-quadruples) is quite reasonable in liquid NH_3 but not in water.
- Extremely concentrated metal-ammonia solution shows the metallic conductivity and metallic weak paramagnetism.
- Electronic absorption spectra and stabilities of hydrated electron and ammoniated electron are different. These can be explained by cavity model.
- In a moderately concentrated metal-ammonia solution, there is a liquid-liquid phase separation leading to the floating of a bronze coloured liquid on a blue liquid.

(42) Liquid NH_3 is a good host medium to stabilise the unstable anionic species like carbanion while H_2SO_4 as a solvent is good host medium to stabilise the unstable catioonic species like NO_2^+.

- Superacids can stabilise the carbocations.

(43) Dissolution of *Na–K* alloy (1:1) in ethylenediamine (*en*) produces sodide not potasside.

(44) In the alkalides, generally the cations are stabilised by the macrocyclic ligands like crown ether, cryptand, etc.

- In many alkalides, the cation remains **sandwiched** between the macrocyclic ligands.
- Compared to alkalides, isolation of crystalline electrides is relatively more difficult.
- Depending on the bulkiness of the complexed cations, the electride may be paramagnetic, diamagnetic and antiferromagnetic.

(45) Many so called strong bases like RO^- (alkoxide) act as the weak bases in liquid NH_3.

- In liquid NH_3, the very strong bases like H^- (hydride) can act as the strong bases.

(46) Thermodynamic redox stability range of liquid NH_3 is only 0.04 V while it is 1.23 V for water.

- Kinetic redox stability range is about 2 V for both water and liquid NH_3.
- Because of the kinetic factor, many strong reducing agents are stable in liquid NH_3.

(47) Solvating power of $R–NH_2$ (as a solvent) is less than that of liquid NH_3, though $R—NH_2$ is more basic than NH_3.

- Solvating power of $R–OH$ is less than that of H_2O.
- Acids and bases appear weaker in $R–OH$ than in water.

(48) Only very strong acids like FSO_3H can act as the acid in HF or H_2SO_4 solvent.

(49) The reaction, $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$, producing H_3O^+ in H_2SO_4 solvent does not make the solution acidic.

- Conc. H_2SO_4 is a good medium to stabilise NO_2^+.
- Oleum ($H_2S_2O_7$) becomes blue coloured when I_2 is passed through it.
- Aromatic hydrocarbon (AHC) radicals are produced when the corresponding AHC is passed through conc. H_2SO_4 as a solvent.

(50) The spectral characteristics of dilute metal-ammonia solutions are metal independent but the spectral characteristics of alkalides are metal dependent.

- Spectral characteristics of electrides are metal (alkali metal) independent but metal dependent for alkalides.