Study Material
Topics covered

CHB- 401

Section(A): Inorganic Chemistry-II

Unit -II

Non-aqueous solvents: Physical properties of a solvent for functioning as an effective reaction medium, types of solvents and their general characteristics. Liq. NH_3 as a non-aqueous solvent

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Most of the reactions that Chemists observe in laboratory take place in a solution. Water is the best known solvent but, not of the only importance for the chemists. For example, non-polar solvents are used to dissolve non-polar compounds such as hexane, CS_4, benzene, CCl_4 etc. In addition, solvents such as H_2SO_4, NH_3, glacial CH_3COOH, SO_2 and various non metal halides have been studied extensively. The study of solution chemistry is intimately connected with acid-base theory. Non aqueous solvents are often interpreted in terms of the solvent system concepts which basically tells that formation of solvates involve acid- base interactions.

"A solvent may be considered as a substance which has a power to dissolve other substances."

Why we require a solvent for a reaction?

1. In a solvent, it is possible to achieve its maximum or ultimate.
2. The solvent is required to accelerate the rate of reactions.
3. Sometimes, it is required to slow down or optimize the rate of reaction as some reactions are violent in absence of solvents.
4. It may be possible to separate the desired product from other products by using difference in solubility.
5. Many reagents are more conveniently handled in solution than in pure state such as BF_3.

There are several physical properties of a solvent that are of importance in determining its behaviour. Two of the most important are melting point and boiling point. Because it determines the range of liquid state, and tells the potential range of chemical operations. Another fundamental is its permittivity (dielectric constant). A high permittivity is necessary for the chemical operation involving ionic substances.

Why is water considered as the best solvent?

1. In standard conditions, it is found in liquid state. Its MP/FP (0°C) and BP (100°C) is a very large range.
2. It is found very easily in pure state and it is very cheap.

3. It has high dielectric constant which donates the ability to ionize the ionic substances. I actually reduces the binding electrostatic forces of ions.
4. It is a neutral solvent.

Limitations:

1. Reactions involving acids stronger than H_3O^+ and bases stronger than OH^- cannot be carried out in aqueous conditions.
2. Reactions involving strong reducing agents cannot be carried out in aqueous solution because such reagents would react with water itself causing the evolution of H_2.
3. A salt of weak acids/ bases undergo considerable hydrolysis in water

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$$2Na+ + 2H_2O \rightleftharpoons NaOH + H_3O^+$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Note: A solvent is a liquid, but sometimes can also be a solid, a gas or a supercritical fluid (SCF).

Any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist, may behave as SCF. It can effuse through solids like a gas, and dissolve materials like a liquid. Close to a critical point, small changes in temp. and pressure results in large changes in density, allowing many properties of a supercritical fluid to be fine tuned. CO_2 and H_2O are most commonly used SCFs.

CO_2 - used for decaffeination

H_2O - for power generation

Physical Properties of a Solvent:

1. MP and BP: It indicates the range of temperature across which a substance exists in liquid state.

If this range is large - it is beneficial

Data for some common solvents may be compared:

Solvent	Melting Point (°C)	Boiling Point (°C)
H_2O	0	100
NH_3	-77.7	-33.5
SO_2	-75.5	-10
HF	-89.4	19.5
N_2O_4	-11.2	21

2. **Heat of fusion and Heat of vaporization:**

Heat of fusion is the energy needed for one gram of a solid to melt without any change in temperature and heat of vaporization is the energy needed for one gram of a liquid to vaporize (boil) without a change in pressure.

$$\underbrace{\text{Solid} \longrightarrow \text{Liquid}}_{\text{Molar heat of fusion}}\ \underbrace{\longrightarrow \text{Vapour}}_{\text{Molar heat of vaporization}}$$

Solvents	Molar heat of fusion (KJmol^{-1})	Molar heat of vaporization (KJmol^{-1})
H_2O	6.02	40.65
NH_3	5.65	23.34
SO_2	7.40	24.93
HF	4.58	30.28

Both are indicative of bond strengths and nature of forces by which the molecules of the solvent are held together in the solid or liquid state, respectively.

$$\left.\begin{array}{l}\text{Molar heat of fusion}\\ \text{Molar heat of vaporization}\end{array}\right\} \propto \quad \text{Bond Strength}$$

Mostly, polar molecules are found associated to each other and non-polar molecules are found in monomeric form. In this context, Trouton constant gives a better idea of intermolecular binding forces by dividing molar heat of vaporization by boiling point (K):

$$\text{Trouton constant} = \frac{\text{Molar heat of vaporization}}{\text{Boiling point (K)}}$$

Trouton’s rule states that the entropy of vaporization is almost the same value, about 85–88 $J\ K^{-1}\ mol^{-1}$, for various kinds of liquids at their boiling points. It signifies that:

If = 90; No association (exist as monomer)
> 90; Association increases

For H_2O and NH_3, the value of Trouton constant is 109 and 101, respectively.

Since both are > 90 that indicates, bith are found in associated forms.

Web Link: https://en.wikipedia.org/wiki/Trouton%27s_rule

3. **Dielectric Constant:**

The dielectric constant (symbol ε) is a physical property that has a dimensionless numeric value for every distinct substance. It determines the ability of solvents to dissolve ionic substances. The large dielectric constant of water means that the force between the ions in a salt is very much reduced permitting the ions to separate. These separated ions become surrounded by the oppositely charged ends of water dipoles and become hydrated. This ordering reduces the thermal motion of the molecules. Water molecules are associated with each other through as many as four hydrogen bonds and this ordering greatly resists the thermal random motion. This H-bonding is responsible for its large dielectric constant.

Solvents	**Dielectric constant**
H_2O	80.4 (20 °C)
Liquid NH3	22 (-33.5 °C)
Glycerin	42.5 (20 °C)
Benzene	2.284 (20 °C)
HF	83.6 (25 °C)

4. **Dipole moment:**

The electric dipole moment is a measure of the separation of positive and negative electrical charges, that is, a measure of the system's overall polarity. The dipole moment of polar molecules is high.

Solvents	**Dipole moment (debye)**
H_2O	1.85
NH_3	1.47
SO_2	1.61
HF	1.9

5. **Viscosity:**

For any solvent, low viscosity is favourable because it does not attach with solutes.

Precipitates easily comes in low viscosity solvents i.e. why conc. H_2SO_4 is not commonly used as solvent because of high viscosity.

Dissolution and crystallization is not easy in high viscosity solvents.

Classification of Solvents:

Solvents may be commonly classified as:

1. **Protic and aprotic:** Based on ability to derive H^+ ions.

eg. protic NH_3, HF, H_2O, etc.

aprotic CCl_4, C_6H_6, hexane etc.

These can be explained and well supportive of Bronsted-Lowry concept of acids and bases.

2. **Acidic, Basic and Amphoteric or amphiprotonic solvents:**

Acidic: Extra tendency to release protons. e.g. HF, H_2SO_4 etc.

Basic: Extra tendency to accept protons. e.g. NH_3, NH_2-NH_2 etc.

Amphoteric: Solvents which have either tendency to release as well as accept protons. e.g. H_2O, alcohol etc.

Also, based on Bronsted-Lowry concept.

3. **Ionizing and non-ionizing solvents:**

Solvents which are capable to undergo auto-ionization.e.g. NH_3, H_2SO_4, N_2O_4 etc. and those which are not capable called non-ionizing solvents. e.g. hydrocarbon solvents such as benzene, hexane, cyclohexane etc. They generally have high dielectric constant.

Non-aqueous Solvents

Many non-aquoeous solvent systems have been studied but there are few representative solvents such as liquid ammonia – basic, sulphuric acid – acidic and BF_3 – aprotic solvent. As well as molten salts are also included.

Ammonia

Ammonia is probably the most studied non-aqueous solvent. Its physical properties resembles to water, like, it is a protonic solvent, polar etc. except that the permittivity is considerably very small. The lower dielectric constant results in generally decrease in ability to dissolve the ionic compounds especially those containing highly charged ions such as, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, are practically insoluble. But in some cases, the solubility is higher than, might be expected as per the permittivity factor. In these cases, there is stabilizing interactions between solute and ammonia. One such interaction is between certain metal ions such as Ni^{2+}, Cu^{2+} and Zn^{2+} and the ammonia molecule, where NH3 acts as ligand to form stable complexes (amine complexes, $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_6]^{2+}$, $[Zn(NH_3)_6]^{2+}$. Second type of interaction may be polarizability factor.

Ammonia is a better solvent than water towards non-polar molecules. Though, ionic compounds containing large polarizable ions (I^-, SCN^- etc) are also quite soluble.

Water like properties - A comparison

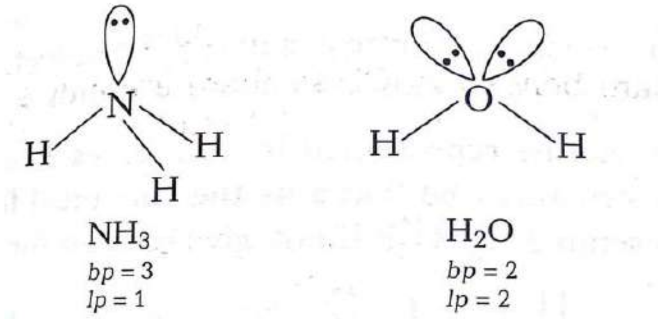
1. **Hydrogen bonding:**

NH_3 have strong H-bonding like water. Some other data of comparison may be given as:

	Water	Ammonia
M.P.	0 °C	-77.7 °C
B.P.	100 °C	-33.5 °C
Density	1.0 g/cc	0.68 g/cc
Dielectric constant	80.4	22
Specific conductance	6×10^{-8} ohm^{-1}cm^{-1}	1×10^{-11} ohm^{-1}cm^{-1}
Viscosity	0.959 centipoise	0.254 centipoise
Dipole moment	1.85 debye	1.47 debye
Trouton constant	109 JK^{-1}mol^{-1}	101 JK^{-1}mol^{-1}

2. **Polarity:**

Both are polar molecules. Geometry of both is tetrahedral



Shape: **Pyramidal** **V-shaped**

3. **Both are ionizing solvents:**

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\ ^\circ\text{C}$$

Similarly:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \quad \text{Amide ion}$$

$$K_w = [NH_4^+][NH_2^-] = 1.9 \times 10^{-33} \text{ at } 25\ ^\circ\text{C}$$

$$3NH_3 \rightleftharpoons 2NH_4^+ + NH^{2-} \quad \text{Imide ion}$$

$$4NH_3 \rightleftharpoons 3NH_4^+ + N^{3-} \quad \text{Nitride ion}$$

4. Liquid ammonia feebly conducts electricity due to its low dielectric constant i.e. low conductor of electricity.

5. Due to low dielectric constant, liq. NH_3 is a poor solvent for polar solvates but due t very low viscosity as compared to water, it promotes the ionic movements therefore, compensate this weakness up to some extent because of low value of dielectric constant.

Chemical reactions of liquid ammonia

1. **Precipitation reaction:**

(a) As in aqueous medium:

$$KCl + AgNO_3 \longrightarrow AgCl\ (ppt) + KNO_3$$

Precipitation of AgCl occurs due to covalent nature of AgCl

However, liq. NH_3 is a good solvent for covalent compounds but poor solvent for ionic compounds. So, the backward reaction is favoured here:

$$AgCl + KNO_3 \xrightarrow{\text{Liq. } NH_3} KCl\ (ppt) + AgNO_3\ (soluble)$$

$$2AgCl + Ba(NO_3)_2 \xrightarrow{\text{Liq. } NH_3} BaCl_2\ (ppt) + 2AgNO_3$$

Ammonia exhibit parallel reaction of auto-ionization like water as shown above.

(b) Various nitrates and ammonium halides reactions:

$$2NH_4Br + Sr(NO_3)_2 \xrightarrow{\text{Liq. } NH_3} SrBr_2\ (ppt) + 2NH_4NO_3\ (soluble)$$

$$2NH_4I + Zn(NO_3)_2 \xrightarrow{\text{Liq. } NH_3} ZnI_2\ (ppt) + 2NH_4NO_3\ (soluble)$$

(c) Ammonium sulphide in liq. NH_3:

$$(NH4)_2S + 2Ag(NO_3)_2 \xrightarrow{\text{Liq. } NH_3} Ag_2S\ (ppt) + 2NH_4NO_3$$

$$(NH4)_2S + Cu(NO_3)_2 \xrightarrow{\text{Liq. } NH_3} CuS\ (ppt) + 2NH_4NO_3$$

$$(NH4)_2S + Cd(NO_3)_2 \xrightarrow{\text{Liq. } NH_3} CdS\ (ppt) + 2NH_4NO_3$$

Many soluble halides are precipitated as complex amines:

$$2NaCl + Cu(NO_3)_2 + 4NH_3 \xrightarrow{\text{Liq. } NH_3} [Cu(NH_3)_4]Cl_2 + 2NaNO_3$$

2. **Acid-base reactions: (Neutralization reaction)**

As in H_2O acid-base neutralization reactions can be shown as:

$$\begin{array}{rcl} HCl + H_2O & \rightleftharpoons & H_3O^+ + Cl^- \\ KOH & \rightleftharpoons & K^+ + OH^- \\ \hline H_3O^+ + OH^- & \rightleftharpoons & 2H_2O\ (unionized) \end{array}$$

Similarly, in liq. ammonia:

$$\begin{array}{lcccl} HCl + NH_3 & \rightleftharpoons & NH_4Cl & \rightleftharpoons & NH_4^+ + Cl^- \\ KOH + NH_3 & \overset{-\ H_2O}{\rightleftharpoons} & KNH_2 & \rightleftharpoons & K^+ + NH_2^- \\ \hline \end{array}$$

$$NH_4^+ + NH_2^- \longrightarrow 2NH_3\ (unionized)$$

Reactions of ammonoacids and ammonobases:

1. Reactions of ammonoacids:

Ammonoacids are substances those furnish NH_4^+ ions in liq. NH_3 solution.

(a) Neutralization:

Similar to neutralization in water e.g.

$$NH_4Cl + KNH_2 \longrightarrow KCl + 2NH_3$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$KNH_2 \longrightarrow K^+ + NH_2^-$$

$$NH_4^+ + NH_2^- \longrightarrow 2NH_3$$

(b) Replacement of proton by active metals:

In water, $H_2SO_4 + Co \longrightarrow CoSO_4 + H_2$ (gas)

In liq. NH_3, $2NH_4NO_3 + Co \longrightarrow Co(NO_3)_2 + 2NH_3 + H_2$(gas)

Such reaction explains why ammonium slats decolorize blue solution of alkali metals in liq. NH_3.

$$NH_4^+ + Na \longrightarrow Na^+ + NH_3 + \tfrac{1}{2} H_2 \text{ (gas)}$$

(c) Protolysis: Protolysis means release of protons in aqueous medium. There are some compounds which do not release proton (acid) in aqueous media but release NH_4^+ (ammonoacid) in liq. NH_3.

i) Urea is neutral in aq. Medium but is an ammonoacid:

$$H_2NCONH_2 + NH_3 \longrightarrow NH_4^+ + H_2NCONH^-$$

ii) Acetamide also is anammonoacid:

$$H_3CCONH_2 + NH_3 \longrightarrow NH_4^+ + H_3CCONH^-$$

iii) Sulphamide

$$H_2NSO_2NH_2 + NH_3 \longrightarrow NH_4^+ + H_2NSO_2NH^-$$

iv) Sulphamic acid is dibasic in liq. NH_3 but monobasic in aqueous medium:

$$H_2NSO_2OH + 2NH_3 \longrightarrow NH_4^+ + HNSO_2O^{2-}$$

$$H_2NSO_2OH + H_2O \longrightarrow H_3O^+ + H_2NSO_2O^-$$

2. **Reactions of ammonobases:**

Ammonobases are substances those release NH_2^-, NH^{2-} and N^{3-} ions in liq. NH_3 solution commonly called as amide, imide and nitride ions, repectively.

Metal amides, imides and nitrides are generally having low solubility in liq. NH_3 except KNH_2. So, they can be easily isolated from reactions:

$$\mathrm{AgNO3 + KNH2 \longrightarrow AgNH_2\ (ppt) + KNO3}$$

$$\mathrm{PbI2 + KNH2 \longrightarrow PbNH\ (ppt) + KI + HI}$$

$$\mathrm{BiI3 + KNH2 \longrightarrow BiN\ (ppt) + KI + 2HI}$$

3. **Amphoteric behavior:** Some salts can be dissolved in acids as well as in base both, called amphoteric. e.g. $Zn(OH)_2$, $Al(OH)_3$ are amphoteric in nature both in H_2O and in liq. NH_3

In water:

$$\mathrm{Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + H_2O}$$

$$\mathrm{Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O}$$

In liq. NH_3:

$$\mathrm{Zn(NH_2)_2 + 2NH_4Cl \longrightarrow ZnCl_2 + 4NH_3}$$

$$\mathrm{Zn(NH_2)_2 + 2NaNH_2 \longrightarrow Na_2Zn(NH_2)_4\ or\ Na_2Zn(NH)_2 + 2NH_3}$$

4. **Ammonolysis:**

It is equivalent to hydrolysis in aq. Medium

(a) Ammonolysis of $SnCl_4$:

$$\mathrm{SnCl_4 \longrightarrow Sn^{4+} + 4Cl^-}$$

$$\mathrm{4NH_3 + 4NH_3 \longrightarrow 4NH_4^+ + 4NH_2^-}$$

$$\mathrm{Sn^{4+} + 4NH_2^- \longrightarrow Sn(NH_2)_4\ (ppt)\ \ tin\ tetramide}$$

(b) Ammonolysis of $TiCl_4$:

In presence of excess of liq. NH_3, each of the Cl^- unit is gradually replaced one by one by amide ion

$$\mathrm{TiCl_4 \xrightarrow[-HCl]{Liq.\ NH_3} TiCl_3(NH_2) \xrightarrow[-HCl]{Liq.\ NH_3} TiCl_2(NH_2)_2 \xrightarrow[-HCl]{Liq.\ NH_3} TiCl(NH_2)_3 \xrightarrow[-HCl]{Liq.\ NH_3} Ti(NH_2)_4}$$

For organic halides, very slow ammonolysis occur in liq. ammonia:

$R\text{-}X + 2NH_3 \longrightarrow R\text{-}NH_2 + NH_4X$

$RNH_2 + R\text{-}X + NH_3 \longrightarrow R\text{-}NH\text{-}R + NH_4X$

$R\text{-}NH\text{-}R + R\text{-}X + NH_3 \longrightarrow R_3N + NH_4X$

This way, a mixture of 1°, 2°, and 3° amines may be obtained with ammonium salt.

Alkali metal hydrides and oxides also undergo ammolysis reaction to give amide:

$NaH + NH_3 \longrightarrow NaNH_2 + H_2O$

$Na_2O + 2NH_3 \longrightarrow 2NaNH_2 + H_2O$

5. **Ammonation:** This is similar to hydration in water.

Here, one or more molecules of ammonia is arre attached with the solute pairs by a chemical bond.

Hydration ⟶ hydrates likewise Ammonation ⟶ ammoniates

$SO_3 + 2NH_3 \longrightarrow SO_3.2NH_3$ (1:2 adduct)

$SiF_4 + 2NH_3 \longrightarrow SiF_4.2NH_3$ (1:2 adduct)

$BF_3 + NH_3 \longrightarrow BF_3.NH_3$ (1:1 adduct)

6. **Complex formation reactions:**

In water,

$Zn(NO_3)_2 + 2NaOH \longrightarrow Zn(OH)_2$ (ppt) $+ 2NaNO_3$

$Zn(OH)_2 + 2NaOH \longrightarrow Na_2[Zn(OH)_4] \xrightarrow{-2H_2O} Na_2ZnO_2$

Sodium zincate (soluble hydroxo complex)

In liq. ammonia:

$Zn(NO_3)_2 + 2NaNH_2 \longrightarrow Zn(NH_2)_2$ (ppt) $+ 2NaNO_3$

$Zn(NH_2)_2 + 2NaNH_2 \longrightarrow Na_2[Zn(NH_2)_4] \xrightarrow{-2NH_3} Na_2Zn(NH)_2$

Sodium ammonozincate (soluble complex)

$AgNH_2 + KNH_2 \longrightarrow K[Ag(NH_2)_2]$

$Al(NH_2)_3 + KNH_2 \longrightarrow K[Al(NH_2)_4]$

7. **Reduction reactions:**

When alkali metals dissolve in liq. ammonia the medium is very suitable for reduction reactions by donating their electrons. This solution is blue in colour.

For reduction reactions, liq. ammonia is better medium than water

$CuI + Na \longrightarrow Cu + NaI$

8. **Oxidation reactions:**

Liq. ammonia is very poor oxidizing medium. Nitric acid and $KMnO_4$ act as strong oxidizing agents in aq. medium but poor oxidizing in liq. NH_3. In case of $KMnO_4$, following reaction is carried out in presence of NH_3:

$$K + NH_3 \longrightarrow KNH_2 + \tfrac{1}{2} H_2 \text{ (gas)}$$

$$6KMnO_4 + 6KNH_2 \longrightarrow 6K_2MnO_4 + 4NH_3 + N_2$$

$$K_2MnO_4 + 4K + 3NH_3 \longrightarrow MnO + 3KNH_2 + 3KOH$$

9. **Solubility of substances:**

Due to poor dielectric constant of ammonia it is very poor solvent for ionic compounds. However, inorganic salts like nitrates, thiocyanates, perchlorates, cyanides are dissolved in liq. ammonia. On the other hand, oxides, hydroxides, carbonates, phosphates, sulphates and sulphides are insoluble in liq. NH_3.

I^- ⟶ soluble

Br^- ⟶ sparingly soluble

F^- and Cl^- ⟶ insoluble (except $BaCl_2$ and NaCl)

Most of the ammonium salts are soluble. Organic compounds – halogens, ketones, alcohol, ether, phenol etc. are soluble. Aromatic hydrocarbons are sparingly soluble. Non-metals (S, P, I) are soluble and react with solvent itself.

In summary, the chemistry of ammonia solutions is markedly parallel to that of aqueous solutions. The principal differences are in the increased basic character and low dielectric constant. The latter not only reduces the solubility of ionic materials but also promotes the formation of ion pairs and ion clusters. Hence, even strong acids, bases and salts are highly associated in liq. ammonia.

Solution of metals in Ammonia

If a small piece of alkali metal is dropped in liquefied ammonia, the solution immediately assumes intense deep blue colour. If more alkali metal is dissolved in ammonia, a point is reached where a bronze coloured phase separates and floats on the blue solution. Further addition of alkali metal in the solution results in gradual conversion of blue solution to bronze solution until the blue colour completely disappears. After this, no more metal get dissolve in liq. NH_3 i.e. its kind of saturated solution. Evaporation of bronze solution allows one to recover the alkali metal. This unusual behavior has fascinated chemists since its discovery in 1864. Complete agreement has not yet achieved on the theoretical background of what is experimentally observed but, there are some popular interpretations based on observed changes and properties which are discussed here.

The characteristics of blue coloured solution:

1. It is independent of metal dissolved.
2. Its density is almost similar to liquid ammonia (pure ammonia).
3. Its conductivity has been found to be in the range of electrolytes.
4. Its paramagnetic resonance g-factor is close to that of value found for free electrons.

It leads to an interpretation that alkali metals dissociates to form alkali metal cations and solvated electrons.

$$M \xrightarrow{\text{dissolve in liq. } NH_3} M^+ + [e(NH_3)_x]^-$$

The interpretation could explain the characteristics of blue solution as:

- The dissociation into cation and anions accounts for electrolytic conductivity.
- Its paramagnetic character, as solution contains a very large number of unpaired electrons.
- The g-value indicates that interaction between solvents and electrons is weak. Commonly it is considered that electrons existing in a cavity in the NH_3 and loosely solvated by the surrounding molecules.
- Blue colour is observed due to broad absorption peak max. at ~1500 nm which probably arise from the absorption of photons by electrons as it is excited to a higher energy level. However, many disagree with this statement.

The very dilute solution of alkali metals in liq. ammonia thus represents a hypothetical ultimate base i.e. free electrons. Such solutions are metastable (equilibrium and has very small disturbances)

When catalyzed they give amide ions:

$$[e(NH_3)_x]^- \xrightarrow{Fe_2O_3} NH_2^- + \tfrac{1}{2} H_2 + (x-1)NH_3$$

The characteristics of bronze coloured solution:

1. Bronze colour exhibits a definite metallic lustre.
2. Very low density.
3. Conductivity has been found to be in the range of metals.
4. Magnetic susceptibility similar to those of pure metals.

So, all these properties are consistent with the description of such solution as a ‘dilute metal’ or an ‘alloy’ in which the electrons behave as they are in a metal, but the metal atoms moved apart by interspersed molecules of ammonia.

Such solutions are very good one electron reducing agents. e.g. pure samples of alkali superoxides may be readily prepared in these solutions:

$$M^+ + e^- + O_2 \longrightarrow M^+ + O_2^-$$

The superoxide is further reducible to peroxides:

$$M^+ + e^- + O_2^- \longrightarrow M^+ + O_2^{2-}$$

In dilute solution, both the alkali metal and electrons are ammoniated:

$$M^+ + xNH_3 \longrightarrow [M(NH_3)_x]^+$$

$$e^- + yNH_3 \longrightarrow [e(NH_3)_y]^-$$

Note: Solution must be dilute for the formation of ammoniated cation and electrons.

As the concentration of metal increases, association starts between the ammoniated cation and ammoniated electrons and blue colour changes to bronze colour and finally blue colour disappears completely. From this solution, metals can be recovered by evaporation.

In dilute solutions, cations and electrons are in dissociated form so electrical conductivity is very high. As the concentration increases cations and electron species becomes associated resulting into decrease in conductivity.

Explanation of colour and paramagnetic nature of this solution:

This property is explained by assuming that the metal in solution is present as the solvated cations and the valence electrons are trapped in the cavities of the NH_3 molecules. The size of these cavities is in between 300 to 340 picometers. The electrons are believed to be present as solvated electrons as $[e(NH_3)_y]^-$. The colour of the solution is due to the presence of the electrons which interacts with protons of the NH_3 molecules and show characteristic spectrum due to 1s → 2p changes.

The presence of free electrons makes the solution a powerful reducing agent. This solution is paramagnetic and this paramagnetism decreases with increase in concentration of metal ions because of the formation of electrons pairs or ion pairs. It may be because they cancel out the paramagnetism of each other.

Advantages of liq.NH_3 as a solution:

1. Dissolution of alkali metal without any chemical reaction is a great advantage of Liq. NH_3 as a solvent. The dissolved alkali metals are recovered from the solution up on evaporation.
2. Alkali metal solutions are strong reducing agents, even stronger than hydrogen.
3. ammonium salts dissolved in liq. NH_3 finds applications in synthetic chemistry. They can be used in precipitation of sulphides, halides and sulphates.
4. The tendency of solvolysis is less in liq. NH_3 than in water.

Disadvantages:

1. Low temperature or high pressure is necessary while working with liq.NH_3 because the liquid range is in netween –33.5 °C to –77.7 °C.
2. Liq. NH_3 is hygroscopic in nature hence all the reactions are to be carried out in sealed tubes.
3. The use of liq. NH_3 as a solvent and as reaction medium requires special techniques because of its offensive odour.

Reference books for further reading:

1. *Inorganic Chemistry*, J.E. Huheey, E.A. Keiter and R.L. Keiter, 4th Edition (2006), Addison Wesley Publishing Co, NY.
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3. *Concise Inorganic Chemistry*, J. D. Lee, 5th Edition (1996), Chapman & Hall, London.