In a similar way, in case of liq. NH_3, the neutralization reaction involves combination of NH_4^+ and NH_2^- ions to form un-ionised NH_3. For ex, the neutralization of NH_4Cl with KNH_2 may be written as

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
$$KNH_2 \longrightarrow NH_2^- + K^+$$
$$NH_4^+ + NH_2^- \longrightarrow 2NH_3 \text{ (neutralization)}$$

Obviously, the role of NH_4Cl in liq. NH_3 soln is the same as that of HCl in aq. soln and of KNH_2 in liq. NH_3 to KOH in aq. soln.

Thus, NH_4Cl may be ~~sefo~~ regarded as a strong acid and KNH_2 as a strong base in liq. NH_3 and are termed as ammono acids and ammono bases, respectively.

ⓐ **Reactions of ammono acids** — Ammono acid is a substance which in liq. NH_3 furnishes NH_4^+ ion. The following reactions show their behaviour to be similar to that of aqua acids.

1. **Neutralisation** — discussed above
2. **Replacement of protons by reactive metals** — Acids give out hydrogen with metals in aq. solns. Likewise, the soln's of Amm. salts in liq. NH_3 react with alkali and other metals to give hydrogen.

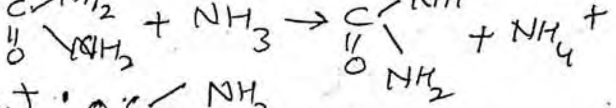
$$Na + NH_4^+ \xrightarrow{liq.\,NH_3} Na^+ + \tfrac{1}{2}H_2 + NH_3$$
$$Co + 2NH_4NO_3 \xrightarrow{liq.\,NH_3} H_2 + 2NH_3 + Co(NO_3)_2$$

This is analogous to the reaction

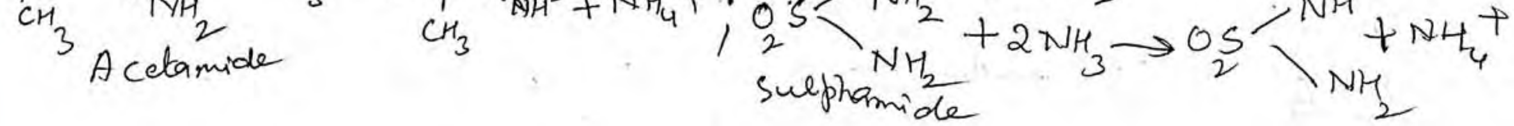
$$Co + H_2SO_4 \longrightarrow CoSO_4 + H_2$$

Ammonium salts decolourise blue solutions of alkali metals in liq. NH_3

③ **Protolysis** — Certain compd. like urea, acetamide, sulphamide etc, which are incapable of donating protons to water, can readily undergo protolysis in liq. NH_3, i.e. they can donate protons to NH_3 in liq. NH_3. Hence org. amides act as acids in liq. NH_3. for ex.



$$O{=}C(NH_2)_2 + NH_3 \rightarrow O{=}C(NH^-)(NH_2) + NH_4^+$$

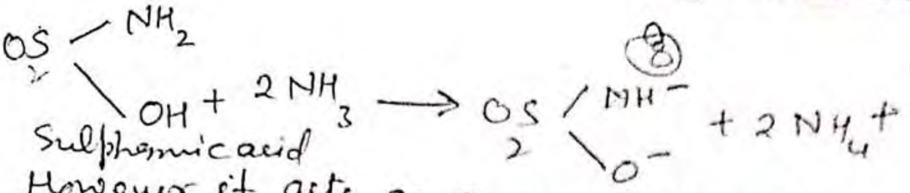


$$CH_3C({=}O)NH_2 + NH_3 \longrightarrow CH_3C({=}O)NH^- + NH_4^+$$

Acetamide

$$O_2S(NH_2)_2 + 2NH_3 \longrightarrow O_2S(NH^-)(NH_2) + NH_4^+$$

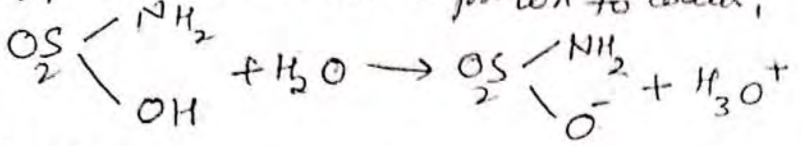
Sulphamide



$$O_2S\langle^{NH_2}_{OH} + 2NH_3 \longrightarrow O_2S\langle^{NH^-}_{O^-} + 2NH_4^+$$

Sulphamic acid

However it acts as a monobasic acid in aq. sol^n. This is because NH_2 grp. cannot donate a proton to water,



$$O_2S\langle^{NH_2}_{OH} + H_2O \longrightarrow O_2S\langle^{NH_2}_{O^-} + H_3O^+$$

(b) Reactions of Ammono Bases

— Ammono base is a substance which in liq. NH_3 furnishes NH_2^- ion. Consequently, amides ($-NH_2$), imides ($=NH$) and nitrides ($\equiv N$) behave as bases in liq. NH_3 as shown below:

$$-NH_2 + NH_3 \longrightarrow -NH_3^+ + NH_2^-$$
$$=NH + NH_3 \longrightarrow =NH_2^+ + NH_2^-$$
$$\equiv N + NH_3 \longrightarrow \equiv NH^+ + NH_2^-$$

Since in all the above rea^ns, the NH_2^- ion is released, the amide, imide and nitrides all behave as ammono bases.

Since alkaline earth amides and lithium and sodium amides have very low solubility, KNH_2 which is much more soluble is usually employed as an ammono base. Thus, salts of metals in liq. NH_3 are ppted as amides, imides and nitrides by the add^n of a sol^n of KNH_2.

$$AgNO_3 + KNH_2 \xrightarrow{liq.\,NH_3} KNO_3 + AgNH_2 \downarrow$$
$$PbI_2 + KNH_2 \xrightarrow{liq.\,NH_3} KI + HI + PbNH$$
$$BiI_3 + KNH_2 \xrightarrow{liq.\,NH_3} KI + 2HI + BiN \downarrow$$

(3) Amphoterism

— A compd. that dissolves both in acids and bases is said to be amphoteric in character. e.g. in aq. medium Zn and Al hydroxides are amphoteric, In liq. NH_3 Zn amide shows amphoteric behaviour.

$$Zn(OH)_2 + 2HCl \xrightarrow{H_2O} ZnCl_2 + 2H_2O \,;$$
$$Zn(NH_2)_2 + 2NH_4Cl \xrightarrow{liq.\,NH_3} ZnCl_2 + 4NH_3$$
$$Zn(OH)_2 + 2NaOH \xrightarrow{H_2O} Na_2ZnO_2 + 2H_2O$$
$$Zn(NH_2)_2 + 2NaNH_2 \xrightarrow{liq.\,NH_3} Na_2Zn(NH_2)_2 + 2NH_3$$

(4) AMMONOLYSIS

— Ammonolysis in liq. NH_3 is similar to hydrolysis in aq. medium. Just as in hydrolysis, the conc. of H^+ or OH^- ions increases due to interaction of cations or anions of a salt with H^+ or OH^- ions furnished by auto-ionization of H_2O. In ammonolysis the conc. of either, NH_4^+ or NH_2^{4-} ions increases due to interaction of cations or anions of a salt with NH_4^+ or NH_2^- ions furnished by autoionization of NH_3. Consider the following reaction;

Hydrolysis of $CuSO_4$ – $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

$$2H_2O + 2H_2O \rightleftharpoons 2H_3O^+ + 2OH^-$$
$$Cu^{2+} + 2(OH)^- \longrightarrow Cu(OH)_2$$

$$CuSO_4 + 4H_2O \rightleftharpoons \underset{\text{weak base}}{Cu(OH)_2} + SO_4^{2-} + 2H_3O^+$$

Ammonolysis of $SnCl_4$: $SnCl_4 \longrightarrow Sn^{4+} + 4Cl^-$

$$4NH_3 + 4NH_3 \rightleftharpoons 4NH_4^+ + 4NH_2^-$$
$$Sn^{4+} + 4NH_2^- \longrightarrow Sn(NH_2)_4$$

$$SnCl_4 + 8NH_2 \rightleftharpoons Sn(NH_2)_4 + 4NH_4^+ + 4Cl^-$$

⑤ Ammonation and formation of Ammoniates

Ammonation is a type of solvation reaⁿ in which liq. NH_3 is used as a solvent and in which one or more NH_3 molecules are attached to a solute species (a cation, an anion or a neutral molecule) by a chemical bond. The product of solvation are called solvates and in the case of ammonation they are known as ammoniates. Solvation in water is called hydration and the products are known as hydrates. Formation of typical ammoniates is shown below:

$SO_3 + 2NH_3 \longrightarrow SO_3 \cdot 2NH_3$ 1:2 adduct

$SiF_4 + 2NH_3 \longrightarrow SiF_4 \cdot 2NH_3$ 1:2 "

$BF_3 + NH_3 \longrightarrow BF_3 \cdot NH_3$ 1:1 adduct

⑥ Complex formation Reaⁿs

– Several complex formation reactions are known in liq. NH_3. These are similar to reactions occurring in aq. systems. for ex.

$$Zn(NO_3)_2 + 2NaOH \xrightarrow{H_2O} Zn(OH)_2 + 2NaNO_3$$

$$Zn(OH)_2 + \underset{\text{excess}}{2NaOH} \xrightarrow{H_2O} \text{Insoluble}$$

$Na_2[Zn(OH)_4]$

Soluble hydroxo complex

Liq. NH_3 system: $Zn(NO_3)_2 + 2KNH_2 \xrightarrow[NH_3]{liq.} \underset{Insoluble}{Zn(NH_2)_2} + 2KNO_3$

$Zn(NH_2)_2 + \underset{excess}{2KNH_2} \xrightarrow[NH_3]{liq.} \underset{Soluble\ amide\ complex}{K_2[Zn(NH_2)_4]}$

Similaly many metal amides, imides and nitrides dissolve in a solution of KNH_2 in liq. NH_3 forming soluble amide complexes. $AgNH_2 + KNH_2 \xrightarrow{liq. NH_3} \underset{Soluble\ amide\ complex}{K[Ag(NH_2)_2]}$

⑦ Reduction Reactions: solution of alkali metals in liq. NH_3

$CuI + Na \xrightarrow[NH_3]{liq.} Cu + NaI$

⑧ Oxidation Reactions – oxidising action of various oxidising agents is weaker in liq. NH_3 than in aq. solutions. For instance, HNO_3 in liq. NH_3 does not act as an oxidising agent. Similarly $KMnO_4$ in liq. NH_3 acts as a very weak oxidising agent.

⑨ Solubility of substances in Liq. NH_3 – As expected from its very low dielectric const., liq. NH_3 is a poor solvent for ionic substances. Amongst the inorg. compds, nitrates, thiocyanates, perchlorates and most of the cyanides are soluble in liq. NH_3. oxides, hydroxides, carbonates, phosphates, sulphates and most of the sulphides are insoluble.

[redacted]

SOLUTIONS of Metals in NH_3 —

If a small piece of alkali metal is dropped in liq. NH_3, the solⁿ immediately assumes an intense deep blue colour. If more alkali metal is dissolved in NH_3, eventually a point is reached where a bronze-colored phase seperates and floats on the blue solution. Further addⁿ of alkali metals results in gradual conversion of blue solution to bronze solution until the former disappears. Evaporation of NH_3 from the bronze solⁿ allows one to recover the alkali metal unchanged. This unusual behavior has fascinated chemists since its discovery in 1864. Complete aggrement on the theoritical interpretation of exptal observations made on these solutions has not been achieved, but the following somewhat simplified discussion will indicate the most popular interpretations.

The blue solution is characterized by ① its colour, which is independent of the metal ~~s~~ involved; ② its density, which is very similar to that of pure ammonia; ③ its conductivity which is in the range of electrolytes dissolved in NH_3; and ④ its paramagnetism, indicating unpaired electrons. This has been ~~indicated~~ interpreted as indicating that in dilute solution, alkali metals dissociate to form alkali metal cations and solvated electrons; $M \xrightarrow[NH_3]{\text{dissolve in}} M^+ + [e(NH_3)_x]^-$ The dissociation ~~el~~ into cation and anion accounts for the electrolytic conductivity. The solution contains a very large no. of unpaired electrons, hence the paramagnetism. It is common to talk of the electron existing in a cavity ~~of~~ in the ammonia, loosely solvated by the surrounding molecules. The blue colour is a result of a broad absorption peak that has a maximum at ~1500 nm, but there is no aggrement ~~as~~ between the scientest as to the nature of the excited state.

The bronze solutions have the following characteristics: ① a bronze colour with a definite metallic lustre; ② very low densities; ③ conductivities in the range of metals; and ④ mag. sus. similar to those of pure metals. All of these properties are consistent with a model describing the solution as a 'dilute metal' or an 'alloy' in which the electrons ~~to~~ behave essentially as in a metal but the metal atoms have been moved apart (Compared with the pure metal) by interspersed molecules of ammonia.

Solutions of alkali metals in ammonia have been the best studied, but other metals and other solvents give similar results. The alkaline earth metals except Be form similar solutions readily, but upon evaporation a solid "ammoniate," $M(NH_3)_x$, is formed. Other solvents such as various amines, ether etc. show some propensity to form this type of solution.

These solutions of electrons are not only strong bases, ~~and~~ they are also good one-electron reducing agents. For ex., pure samples of alkali metal superoxides may be readily prepared in these solutions

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

The superoxide ion is further reducible to peroxide;

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

The chemistry of metal electrides has been extensively studied and the ~~format~~ formulation M^+e^- is best accepted.

Molten salts - Some of the molten salts are being used as non-aq. solvents since 1960s. On the basis of str of the liquid, molten salts can be conveniently