# Liq. $NH_3$ :

- * M.P & B.P of $NH_3$ are abnormal with respect to $PH_3$, $AsH_3$ & $SbH_3$
- * f.p & b.p are lower than those of $H_2O$
- * dielectric constant = 22 water (78.5)
- * Hydrocarbons are soluble in $NH_3$.
- * Nitrates, ~~ex~~ thiocyanates, perchlorates, & most cyanides are soluble in $NH_3$.
- * oxides, hydroxides, sulphates, carbonates, phosphates, sulphites and most sulphides are insoluble.
- * general order of solubilities of halides in $NH_3$ $I^- > Br^- > F^- >$ [illegible]
- * most iodides are soluble
- * bromides are less soluble
- * most of the ammon. salts such as $NH_4NO_3$, $NH_4SCN$, $NH_4(CH_3COO)$ are soluble
- * All metal amides, except those of alkali metals, are insoluble. $LiNH_2$ is also insoluble

- alcohols, halogen compounds, ketones, esters, simple ethers & phenols and its derivatives are soluble

- non-metals (P, S, I) dissolve in $NH_2$.

$$\frac{3}{4} S_8 + 16 NH_3 \longrightarrow N_4S_4 + 6(NH_4)_2S$$

## Advantages:

- without reacting dissolves alkali-metals. The dissolved alkalin metals can be recovered from $NH_3$ by evaporation.

- $NH_3$ has lesser tendency than $H_2O$ to undergo solvolysis ~~rxns~~ with solutes.

## Disadvantages:

- b.p of $NH_3$ is −33.5°c
- lower temprature is maintained
- high pressure are to be avoided.
- It is used as solvent required elaborate equipment & special techniques are to be used.

- Due to the hydroscopic nature of $NH_3$ rxns are done in sealed tubes so as not allow contact with maisture.

## Auto ionisation:

$$NH_3 + NH_3 \rightleftharpoons \underset{\text{ammono acid}}{NH_4^+} + \underset{\text{Ammano base}}{NH_2^-}$$

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

undergo auto ionisation silimilar to $H_2O$ but lesser extent than $H_2O$

## Chemical rxns:

1) metathetical or pricipitation rxns

$$KI + NH_4Cl \xrightleftharpoons{liq.\ NH_3} \underset{\text{white ppt}}{KCl} + NH_4I$$

(ii) $Sr(NO_3)_2 + 2NH_4Br \xrightleftharpoons{Liq.\ NH_3} SrBr_2\downarrow + 2NH_4NO_3$

$$Zn(NO_3)_2 + 2NH_4I \xrightleftharpoons{''} ZnI_2\downarrow + 2NH_4NO_3$$

(iii) Sodium carbamide is precipitated in liq. $NH_3$

$$NH_4[NH_2CO.O] + NaNO_2 \xrightarrow{''} \underset{\text{Sod. carbomate}}{Na[NH_2CO.O]} + NH_4NO_3$$

2) Ammonia as Proton acceptor:

Strong tendency to pick up $H^+$ from neutral or weakly basic substances.

$$H_2O \rightleftharpoons OH^- + \cancel{H^+}$$

$$NH_3 + \cancel{H^+} \rightleftharpoons [NH_3 \leftarrow H]^+$$

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$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

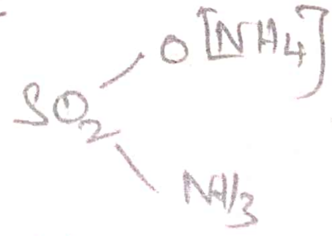
a) $CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$

b) $CH_3CONH_2 + NH_3 \longrightarrow CH_3CONH^- + NH_4^+$

$NH_2CONH_2 + NH_3 \longrightarrow NH_2CONH^- + NH_4^+$

3) Ammonation rxns:

$SO_3 + 2NH_3 \longrightarrow$



$SO_2\begin{smallmatrix} O[NH_4] \\ NH_3 \end{smallmatrix}$

$SiF_4 + 2NH_3 \longrightarrow SiF_4 \cdot 2NH_3$

$BF_3 + NH_3 \longrightarrow BF_3 \cdot NH_3$

### ④ Reactions of ammono acids:

$Na + NH_4^+ \xrightarrow{liq.NH_3} Na^+ + \frac{1}{2}H_2 + NH_3$

$Na_2O + 2NH_4Cl \xrightarrow{liq.NH_3} 2NaCl + 2NH_3 + H_2O$

$NaOH + 2NH_4Ng \xrightarrow{''} NaCl + NH_3 + H_2O$

### (5) Reactions of ammono base:

$AgNO_3 + KNH_2 \xrightarrow{NH_3} \underset{amide}{AgNH_2} \downarrow + KNO_3$

$PbI_2 + 2KNH_2 \xrightarrow{''} \underset{imide}{PbNH_3} + 2KI + NH_3$

$BiI_3 + 3KNH_2 \xrightarrow{''} \underset{Nitride}{BiN} \downarrow + 3KI + 2NH_3$

### 6) Acid - base rxns:

Ammo. acid + Ammono. base $\xrightarrow{''}$ Ammono salt + solvent

$NH_4NO_3 + KNH_2 \xrightarrow{''} KNO_3 + 2NH_3$

$CH_3CONH_2 + KNH_2 \xrightarrow{''} K^+[CH_3CONH]^- + NH_3$

$2NH_4I + PbNH_2 \longrightarrow PbI_2 + 3NH_3$

$3NH_4I + BiN \longrightarrow BiI_3$

⑦ Ammonolysis rxns:

$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

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

$H^- + NH_3 \rightleftharpoons NH_2^- + H_2$

~~ammonolysis~~

$SO_2Cl_2 \longrightarrow SO_2(NH_2)_2 + NH_4Cl$

⑧ Complex formation:

$Zn(OH)_2 + 2NaOH \longrightarrow Na_2[Zn(OH)_4]$

$Zn(NH_2)_2 + 2KNH_2 \longrightarrow K_2[Zn(NH_2)_4]$

$Al^{3+} + 3NH_2^- \rightleftharpoons Al(NH_2)_3 \downarrow \overset{liq.\ NH_3}{\rightleftharpoons}$

$[Al(NH_2)_4]^-$

## Lewis concept for acids & bases :

* It explain $e^-$ structure of the acid & base along with the formation of a coordinate covalent bond.

* according to acids is any Species that can accept an $e^-$ pair to form a Co-ordinate covalent bond.

* base is any Species that can donate an $e^-$ pair to the formation of a ~~covalent~~ coordinate covalent bond.

* In the Lewis system acid is an $e^-$ pair acceptor and base is an $e^-$ pair donor.

* Simply formation of coordinate bond between an acid & a base.

$$H^+ + :NH_3 \longrightarrow (H \leftarrow NH_3)^+$$

acid Base Adduct

* $H^+$ accept one pair $e^-$s from $:NH_3$ there fore an acid.

* $NH_3$ donates an pair of $e^-$s is a base

* Adduct is $NH_4^+$ ion.

* Lewis & Bronsted - Lowry bases are the same substances, since the molecule (or) ion accepts protons.

* In the above ~~eass~~ example $NH_3$ molecule is a proton acceptor (ie Bronsted base) & an $e^-$ pair donar (ie Lewis base)

* Bronsted & Lewis Theories are identiatial. definition of ~~for~~ the bases is differend in ~~the~~ both the theories.

* $NH_3$, $H_2O$, $O^{2-}$, $I^-$, $Cl^-$, $CN^-$ etc. are the bases on the Bronsted as well as on the Lewis system.

* amides, ethers, nitriles, $C_2H_4$, $C_2H_2$, $C_6H_6$ etc which have little or no tendency to accept protons but react readily with lewis acids -

Classification of Lewis acids.

Any Lewis acid must contain atleaset one empty orbital in the valance shell. of one of its atoms accept an $e^-$ pair from Lewis base

Lewis acid + Lewis bas $\longrightarrow$ Adducts

$F_3B + (O C_2H_5)_2 \longrightarrow F_3B \leftarrow O$

Lewis acid Lewis base Adducts

$F_3B + O(C_2H_5)_2 \longrightarrow F_3B \leftarrow (O C_2H_5)_2$

$Cl_3Al + NC_5H_5 \longrightarrow Cl_3Al \leftarrow NC_5H_5$

$Me_3B + N_2H_4 \longrightarrow Me_3B \leftarrow N_2H_4$

$H^+ + :NH_3 \longrightarrow (H \leftarrow NH_3)^+$

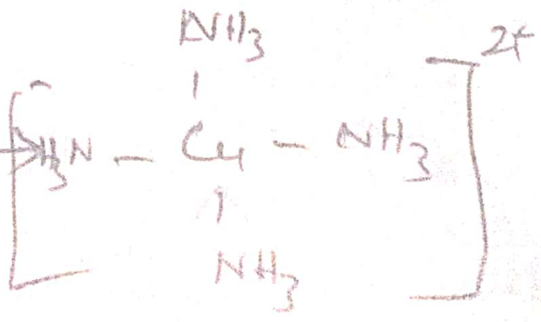
- * The central metal atom of the halides such as $SiX_4$, $GeX_4$, $TiCl_4$, $SnX_4$, $PX_3$, $PF_5$, $SF_4$, $SeF_4$, $TeCl_4$ etc have vacant d-orbitals
- * These substances accept $e^-$s pair from Lewis base to accommodate their orbital and can form adducts.

Lewis acid + base $\longrightarrow$ Adduct (or) Addition complex

Ammonation : $Ag^+ + 2(:NH_3) \longrightarrow [NH_3 \rightarrow Ag \leftarrow NH_3]^+$

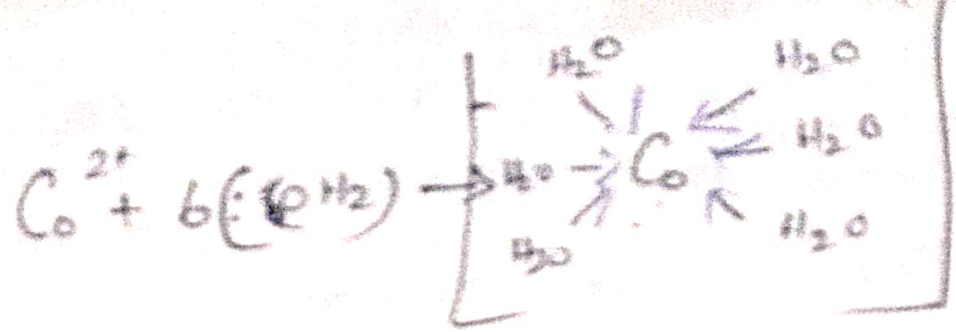
Lewis

$Cu^{2+} + 4(:NH_3) \longrightarrow$



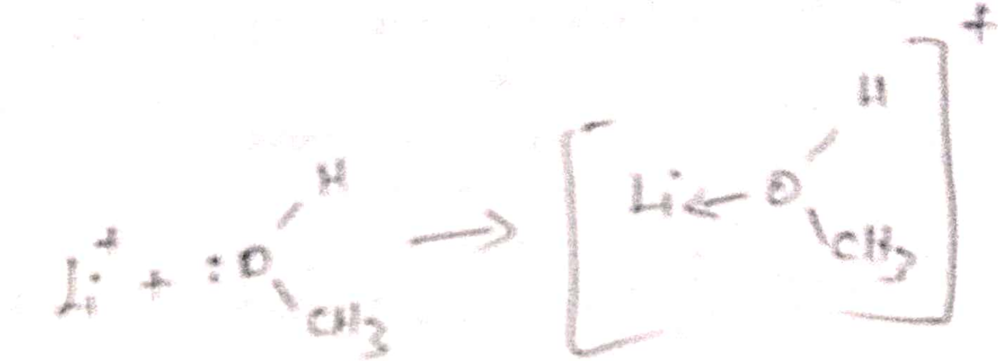
$$\left[\begin{array}{c} NH_3 \\ | \\ H_3N - Cu - NH_3 \\ | \\ NH_3 \end{array}\right]^{2+}$$

Hydration :



~~Alcholation~~

Alcoholation:



* Lewis acid Strength depending on

(a) an increases in the +ve charged carried by the cation

(b) increases nuclear charge for atoms in any period of the periodic table

(c) decrease in ionic radii

(d) decrease in the no of Shielding $e^-$ shells

* Acid Strength of simple cations increases $\longrightarrow$ Strength of Lewis acid increases

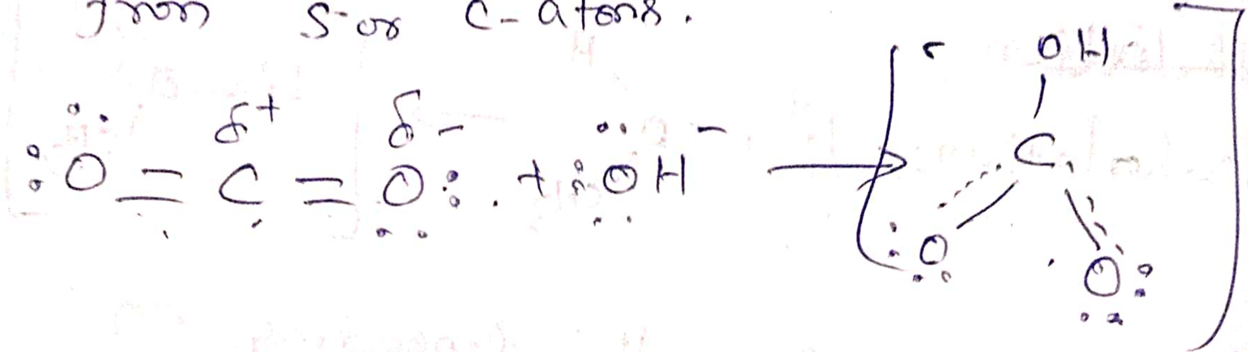
$Fe^{2+} < Fe^{3+}$ ( +ve charge increases $+2 \rightarrow +3$)

$K^+ < Na^+$ ( on moving a bottom to top in a gp)

$Li^+ < Be^{2+}$ ( on moving for L – R in a period)

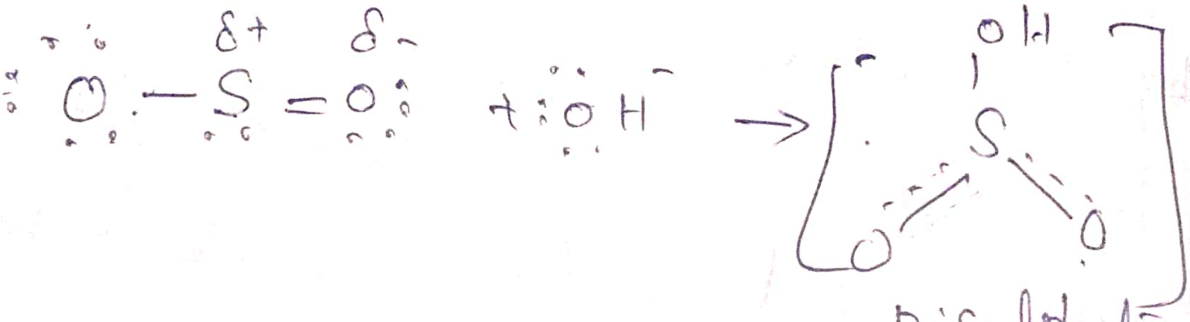
* Lewis acids are $CO_2$, $SO_2$ + $SO_3$. in these compd ~~acids~~ the O-atoms are more $e^-$ -ve than S or C-atom.

* $e^-$ density of π $e^-$s is displaced by from S or C-atoms.



Bicarbonate ion

$SO_2$ also reacts in the same manner



Bisulphate ion

* O & S atoms contain 6$e^-$s in their valance shell and therefore regarded as Lewis acid.

$$\overset{\text{base}}{SO_3^{2-}} + \overset{\text{acid}}{:\ddot{O}} \longrightarrow \overset{\text{Adduct}}{[O \leftarrow SO_3]^{2-}}$$

$$SO_3^{2-} + :\ddot{S} \longrightarrow [S \leftarrow SO_3]^{2-}$$

## HSAB principle: Hard & Soft acids and bases

### Hard & Soft bases:

- * Soft Lewis bases are easily polarised & have low electronegativity.
- * Hard bases are low polarisabilities & have high electronegativity.
- * Softness of Lewis bases increases with the increase in the size of the donor atom.

$F^- < Cl^- < Br^- < I^-$

F − hardest, $I^-$ softest Lewis base

| Hard bases | Borderline | Soft bases |
|---|---|---|
| $H_2O$, $OH^-$, F, $CH_3COO^-$ | $C_6H_5NH_2$, $C_5H_5N$ | $R_2S$, RSH, $RS^-$, $I^-$ |
| $PO_4^{2-}$, $SO_4^{2-}$, $Cl^-$, $CO_2^{2-}$ | $NO_2^-$, $SO_3^{2-}$, $N_2$ | $SCN^-$, $S_2O_3^{2-}$, $R_3P$, |
| $ClO_4^-$, $NO_3^-$, ROH, $RO^-$ | | $R_3AS$, $(RO)_3P$, |
| $R_2O$, $NH_3$, $RNH_2$, $N_2H_4$ | | $CN^-$, RNC, CO, |
| | | $C_2H_4$, $C_6H_6$, $H^-$ |

### Hard & Soft acids:

- * A hard acid difficult to polarise
- * $Al^{3+}$, generally has

(i) small size (ii) high +ve charge

(iii) nobal gas configuration

## Soft acids

- * Soft acids are readily polarised
- * Large size
- * low +ve (or) zero charge
- * do not have a nobal gas electronic configurati

### Hard acids

$H^+$, $Li^+$, $Na^+$, $K^+$,
$Be^{2+}$, $Ca^{2+}$
$Sr^{2+}$, $Mn^{2+}$, $Al^{3+}$, $Ga^{3+}$
$In^{2+}$, $La^{3+}$, $Lu^{2+}$, $Cr^{3+}$
$Co^{2+}$, $Fe^{3+}$, $As^{3+}$, $Si^{4+}$,
$Ti^{4+}$, $Zr^{2+}$
$Th^{4+}$, $U^{4+}$, $Ce^{3+}$, $Sn^{4+}$
$VO^{2+}$, $UO_2^{2+}$, $MoO^{3+}$, $BF_3$
$SO_3$, $Cr^{6+}$, $I^{6+}$, $CO_2$
$I^{7+}$, $(HF)_n$

### Borderline

$Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$,
$Zn^{2+}$, $Pb^{2+}$, $Sn^{2+}$, $Sb^{3+}$
$Br^{3+}$, $Rh^{3+}$, $SO_2$, $NO^+$,
$GaH_3$

### Soft acids

$Cu^+$, $Ag^+$, $Au^+$, $Tl^+$,
$Hg^+$,
$Pd^{2+}$, $Cd^{2+}$, $Pt^{2+}$, $Hg^{2+}$
$Tl^{3+}$, $BH_3$, $GaCl_3$, $InCl_2$
$I^+$, $Br^+$, $I_2$, $Br_2$
Zero valent metal ~~ion~~ .atoms

## Relative Strength of oxyacids:

- Strong acid has a Strong tendency to donate a proton.
- Strong base has a Strong tendency to accept proton.
- Comparison of proton-donating tendencies of different acids
- Compare the acidic Strength of $CH_3COOH$ & HCN
- Experimentally it has been observed that the ionisation or acidic constant Ka for AcOH & HCN at 25° is $1.8 \times 10^{-5}$ & $4.0 \times 10^{-10}$ respectively.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \quad K_a = 1.8 \times 10^{-5}$$

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^- \quad K_a = 4.0 \times 10^{-10}$$

- $CH_3COOH$ is Stronger acid than HCN. $CN^-$ ion is a Stronger base than $CH_3COO^-$
- <u>Competitive</u> protolysis method.
- One acid is added to conjugated base of another and equilibrium Con. of are determined

$H_2O + C_2H_5O^- \longrightarrow C_2H_5OH + OH^-$

stronger acid | stronger base | weaker acid | weaker base

* $C_2H_5O^-$ is stronger base than $OH^-$

* $H_2O$ is stronger acid than

**Levelling effect (or) levelling solvent:**

* apparent strength of a protonic acid dependent on the solvent.

* $HClO_4$, $H_2SO_4$, $HCl$ & $HNO_3$ are added to $H_2O$.

* ~~$H_2O$~~ They donate a $H^+$ to $H_2O$, form ~~equal~~ form $H_3O^+$ ~~strength of $H_3O^+$~~

* acids are levelled to the strength of a $H_3O^+$ ion

* strength of all acids becomes equal to that of $H_3O^+$ is called levelling effect of the solvent.

* $H_2O$ is a levelling solvent.

* very strongs bases like $Na^+H^-$, $Na^+$

$NaOC_2H_5$ are levelled to the strength of $OH^-$ ion. for they react completely with $H_2O$ to produce $OH^-$ ion.

* Solvent completely ~~produced~~ proton-transfer occurs are called levelling solvent.

* Solute ~100% ionised are called levelling solvent.

* HF & HCl both are ~100% ionised in liq-$NH_3$ to give ~100% $NH_4^+$ ions

* In $H_2O$, HF is only partially ionised whereas HCl & HBr are ~100% ionised. Thus $H_2O$ is diffiiciating solvent

& HCl + HBr levelling Solvent

* Several mineral acid are partially ionised in $CH_3COOH$.

* But for bases $CH_3COOH$ act as a levelling solvent.