

1/10/19

Inorganic chemistry

~~Let~~ Some fundamental Physical Properties of atoms/molecules :-

- Consequences of Electronic configuration

[1] Ionisation P/E
 [2] Electron Affinity
 [3] Electronegativity

} Vital importance of chemical/Physical properties.

ionic radii
 covalent radii
 van der Waal's radii

} known

~~b~~ Interactions based on electronegativity :-

<u>A</u>	<u>B</u>	<u>Interaction</u>
Low	High	Ionic \checkmark
comparable	"	covalent \checkmark
Low	low	metallic \checkmark

~~Let~~ Inert - pair / shielding effect :-
Screening "

The Inner orbital e^- in an atom reduces the effective nuclear charge.....

Pb^{2+} Pb^{4+} ...

Screening : $s > p > d > f$

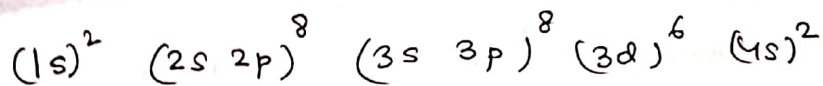
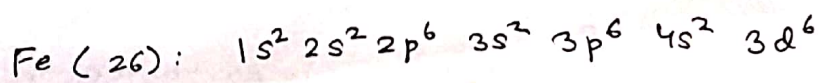
Power
(σ/A)

~~Let~~ Slater's rule

- grouping of orbitals.
- effect only from lower or same energy orbital.

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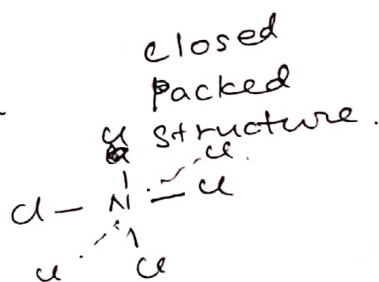
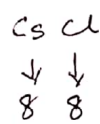
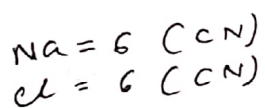
Q. Cal. effective nuclear charge (Z^*) for one $2s e^-$



$$\begin{aligned} S &= 7 \times 0.35 + 2 \times 0.85 \\ S &= 2.45 + 1.7 \\ S &= 4.15 \end{aligned}$$

$$\begin{aligned} Z^* &= Z - S \\ &= 26 - 4.15 \\ &= 21.85 \end{aligned}$$

Ionic Bonding



Lattice energy

The min^m amt of energy (potential) released when a definite number oppositely charged ions or molecules combines to form one mole of solid crystal is known as

May be defined as energy required to break the crystals into its constituents.

L.E can't be determined usually calculated from

directly: It is Born Lande eqⁿ:

$$U = \frac{N_0 A Z^+ Z^- e^2}{4 \pi \epsilon_0 r} \left(1 - \frac{1}{n} \right)$$

stabilisation gained or energy is released.

$$NaCl_u = -791 \text{ KJ/mole}$$

u : lattice energy (LE)

Z^+ : cation charge

Z^- : Anion "

$N_0 A$: At. no.

r : interatomic dist.

ϵ_0 : Permittivity of vacuum

A : Madelung const. (value of which depends upon geometry of crystal)

n : Born exponent (associated with repulsion arising from identical charge of ions).

ratio \rightarrow outside the bracket \downarrow denotes attractive force
 \rightarrow inside the bracket \downarrow repulsive force.

$$u \propto \frac{1}{r}$$

$$u \propto Z^+ \cdot Z^-$$

A cannot be changed without changing r and vice versa.

increasing A , increases LE. Hence, the effect of increase in A and r may largely cancel each other.

n - Born exponent (n)

outer e^- conf
 $1s^2$ (He)
 $2s^2 2p^6$ (Ne)

$\frac{n}{5}$ (exp. attained).

7

$3s^2 3p^6$ (Ar) or $3s^2 3p^6 3d^{10}$ (Cu^+)

9

$4s^2 4p^6$ (Kr) or $4s^2 4p^6 4d^{10}$ (Ag^+)

10

$5s^2 5p^6$ (Xe) or $5s^2 5p^6 5d^{10}$ (Au^+)

12

eg n_{NaCl}

$Na^+ \rightarrow 2s^2 2p^6 - 7$
 $Cl^- \rightarrow 3s^2 3p^6 - 8$

$$\frac{9+7}{2} = 8$$

	A-X dist (in Å)	L.E. (in kJ/mole)
LiF	2.01	-1021
LiCl	2.57	-845
LiBr	2.75	-803
LiI	3.00	-753

↓
decreasing

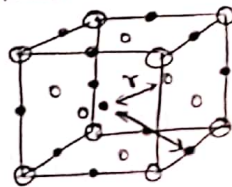
MgO > NaCl (u)

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A Madelung constant

The value of which depends upon geometry of crystals.

NaCl



• → Na⁺
• → Cl⁻
body centre + cell edge length
each corner + face centre

body centred Na⁺ ion is the centre atom of unit cell.

interatomic distance = r

6 Cl⁻ ions are at a dist. of r.

12 Na⁺ " " " " " " $\sqrt{2}r$

8 Cl⁻ " " " " " " $\sqrt{3}r$

6 Na⁺ " " " " " " $\sqrt{4}r = 2r$

NaCl M-X Type

The potential Energy of the central atom (Na⁺/M^{Z+}) is to brought from infinity to it's position in the lattice (lt).

left side repulsive.
right side attractive.

$$U = \frac{-e^2}{4\pi\epsilon_0} \left[\frac{6Z^+Z^-}{r} - \frac{12 \times (Z^+)^2}{\sqrt{2}r} + \frac{8Z^+Z^-}{\sqrt{3}r} - \frac{6 \times (Z^+)^2}{\sqrt{4}r} + \dots \right]$$

$$= - \frac{e^2 z^+ z^-}{4\pi\epsilon_0 r} \left[6 - \frac{12}{\sqrt{2}} \frac{z^+}{z^-} + \frac{8}{\sqrt{3}} - \frac{6 z^+}{\sqrt{9} z^-} + \dots \right]$$

The ratio $\frac{z^+}{z^-} = \text{constant}$ for a particular crystal.

So, the algebraic sum within the bracket is constant. This constant is called Madelung constant.

Imp
Z

M. Constant	
NaCl	→ 1.747
CaF ₂	→ 2.519

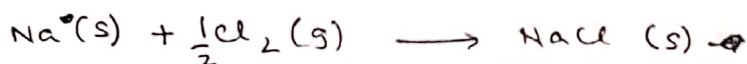
Imp
Z

Born - Haber cycle

use to obtain ΔH_f experimentally which is different from the

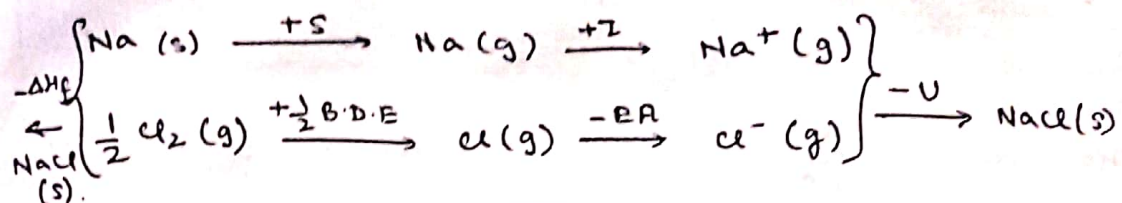
let's consider formation of 1 mol of NaCl.

Process	Energy terms	Full Name
Na(s) → Na(g)	+S	Sublimation
Na(g) → Na ⁺ (g)	+I	
$\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$	$+\frac{1}{2} \text{B.D.E}$	
Cl(g) → Cl ⁻ (g)	-EA	
Na ⁺ (g) + Cl ⁻ (g) → NaCl(s)	-U	



$$-\Delta H_f = S + I + \frac{1}{2} \text{B.D.E} - \text{EA} - U$$

↑
Heat of formation



$$\boxed{1919 - \text{B.D.E.}}$$

by Born & Haber.

$$U_{\text{NaCl}} = \Delta H_f + S + I + \frac{1}{2} \text{B.D.E.} - EA$$

$$= 414 + 109 + 494 + 121 - 347$$

$$= 791 \text{ kJ/mol} \quad (\text{consider this inherently -ve}).$$

as U is always -ve.

LTE can be calculated provided all other E terms are given.

H_f is always -ve. (for a crystal).

Theoretical

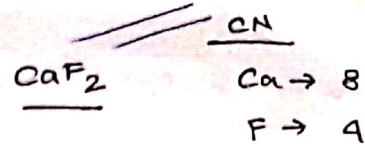
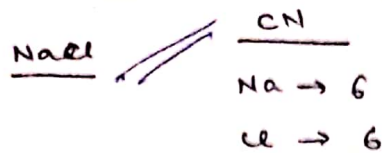
$$U_{\text{NaCl}} \text{ (using same value of Madelung const)} = \underline{2154 \text{ kJ/mol.}}$$

$$\begin{aligned} \Delta H_f &= S + I_1 + I_2 + \text{B.D.E.} - 2 \cdot E \cdot A - U \\ &= 2560 \text{ kJ/mole} \\ &\quad (\text{+ve}). \end{aligned}$$

not practical.

Co-ordination Number

The number of oppositely charged ions which remain surrounding central ion in an ionic crystal is known as C.N of the central ion.



$$\text{Radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion.}}$$

Radius ratio Rule

Limiting radius ratio value.
predicting the C.N and geometry
of the ionic crystal i.e.

<u>R_r</u>	<u>C.N</u>	<u>Geometry</u>
0 - 0.155	2	Linear
0.155 - 0.255	3	Trigonal Planar
0.255 - 0.414	4	Tetrahedral
0.414 - 0.732	4	Square Planar
0.414 - 0.732	6	Octahedral
0.732 - 1.00	8	BCC (CsCl)
≥ 1	12	hcp

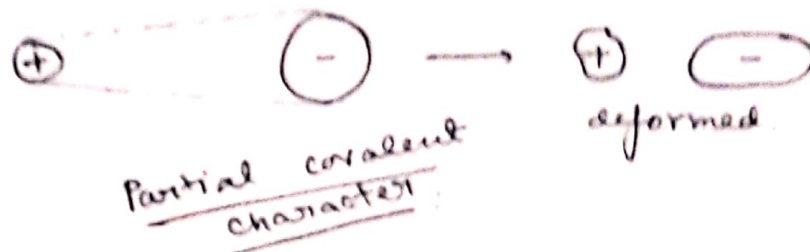
exception

CaO }
BaO } do not
SrO } follow
R_r rule

$$R_r = 0.732 - 1.00 \quad (\text{C.N} \sim 8)$$

as all these compounds are made of high +ve & -ve charge, there will be high repulsion i.e. cation-cation & anion-anion. There should be an optimum repulsive & attractive forces.

Fajan's rule (1924)



Covalent character is favoured

- 1) small cation, large anion
- 2) high charges on the ions.
- 3) M.P of ionic crystals will be always high if (rather than covalent compounds), b'coz ionic compounds are closed packed structures.

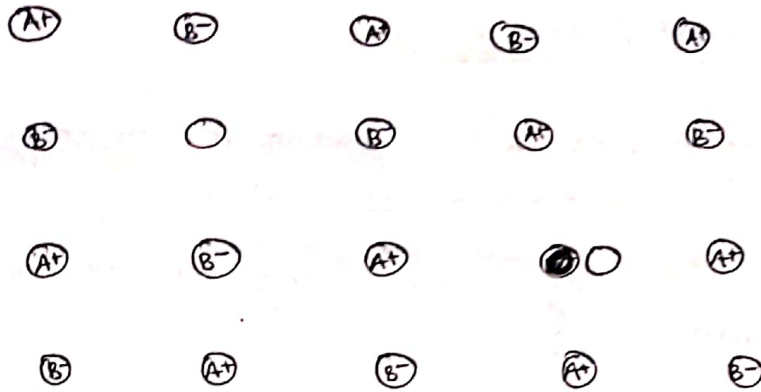
		M.P
↑ in covalent character ↓	(1+) NaBr	755
	(2+) MgBr ₂	700
	(3+) AlBr ₃	907.5

↓ in ionic character and hence decrease in M.P.

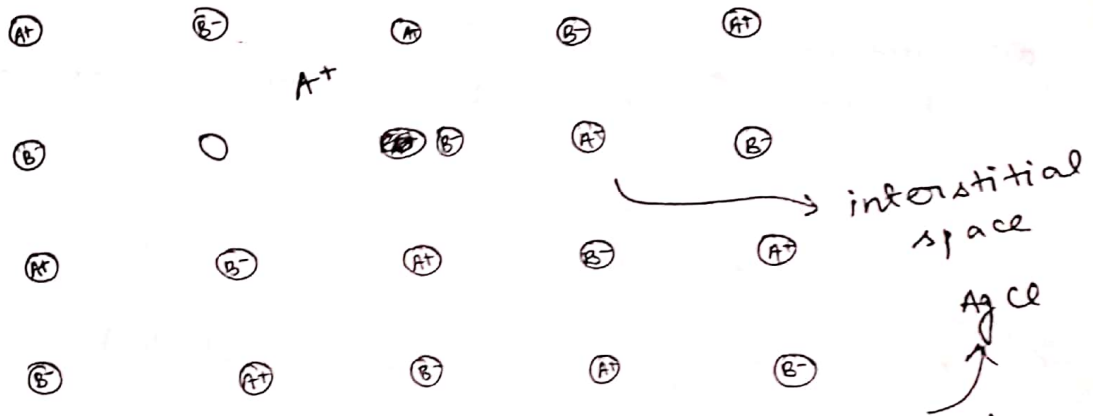
Crystal defects

In a perfect crystal, all atoms would be on their correct lattice points in the structure & this situation happens only at absolute temperature i.e. 0 K. Above this we will have crystal defects.

Schottky Defects (w. Schottky)



Frenkel Defects (J. Frenkel)



{ tetrahedral hole or octahedral hole }

Only A^+ can move, Only B^- can move,
Both A^+ & B^- can move.

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Acids & Bases

1) Arrhenius concept / water ion concept :-

Acids \rightarrow H^+ containing subs. giving H^+ ion in aq. solⁿ : $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

Bases \rightarrow OH^- containing subs. giving OH^- ion in aq. solⁿ : $NaOH + H_2O \rightleftharpoons Na^+ + OH^- + H_2O$

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

Limitations

- restricted to aq. solⁿ.
It could not be observed in other solvents or in absence of solvents.
- $AlCl_3$ which is acidic can't be explained with this theory.

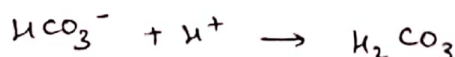
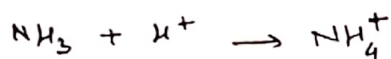
2) Bronsted - Lowry Concept :- (1923)

Acids \rightarrow H^+ donors.

Bases \rightarrow H^+ acceptors.

Protonic acids : $HCl \rightarrow H^+ + Cl^-$

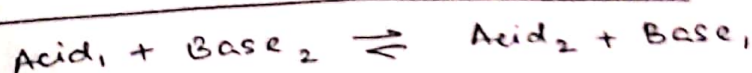
Protonic Bases : $[Al(OH)_6]^{3-} \rightarrow [Al(OH)_5OH]^{2-} + H^+$



Acids can act as acid only when it is in contact with base.

Acid₁ \rightleftharpoons H^+ + Base₁ \leftarrow conj. base of acid₁

Base₂ \rightleftharpoons H^+ + Acid₂ \leftarrow conj. acid of base₂

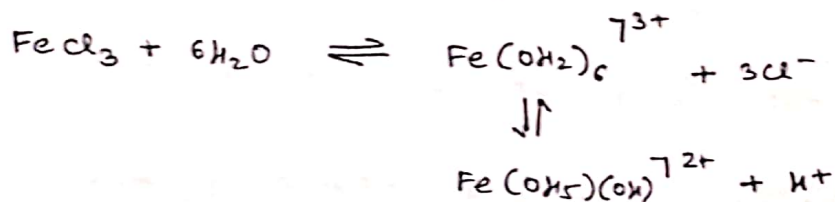


$\text{Acid}_1 - \text{Base}_1$ } conj. acid - base pair
 $\text{Acid}_2 - \text{Base}_2$ }

~~conj~~ base of a stronger acid must be weak and vice versa.

Advantages

- a) Not restricted to / dependent on any solvent.
- b) FeCl_3 is acidic in aq. medium.



Limitation

- a) Too many emphasis on protons ($\text{AlCl}_3, \text{SO}_2, \text{CO}_2$, etc. acidic but can't be explained by this theory).

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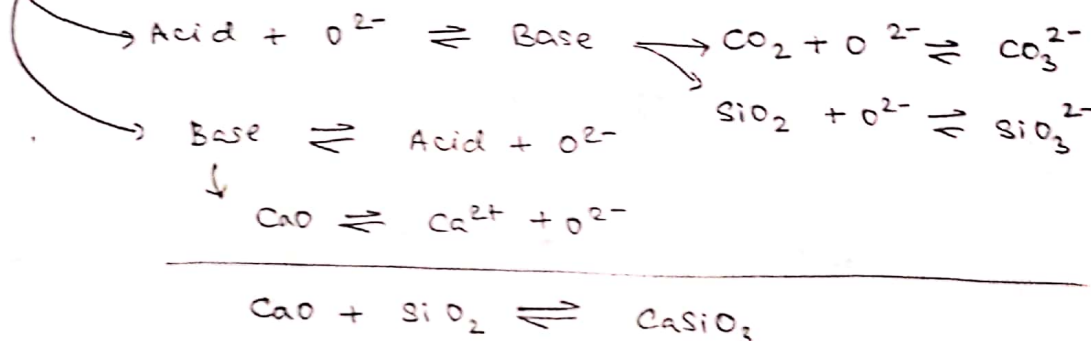
Lux - Flood Concept :-

Defines acids, base characters of mainly oxides.

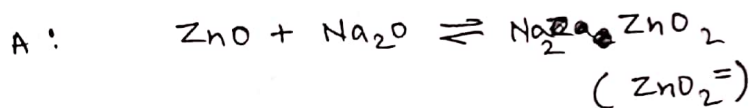
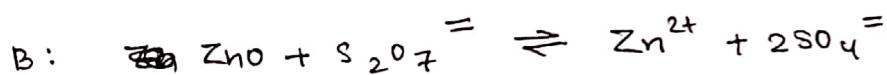
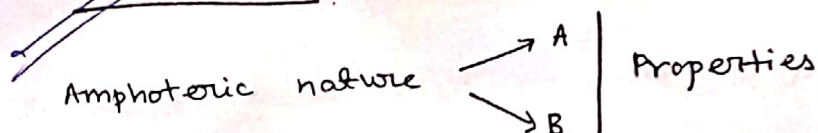
Acids \rightarrow oxide ions acceptor.

Bases \rightarrow oxide ions donor.

useful for high temp chemistry



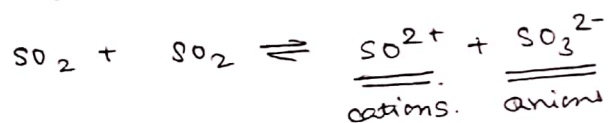
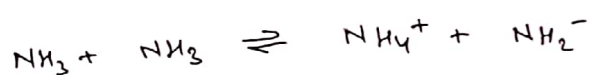
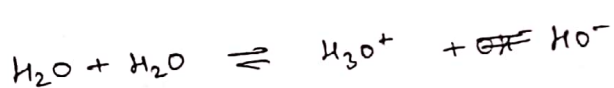
Amphoterism



Limitation

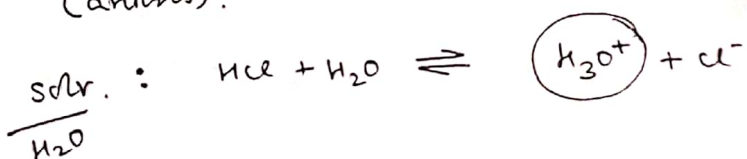
a) only restricted to oxides.

General Theory of solvent systems :- (E.C. Franklin 1905)



Auto-
ionisation
of
solvents.

Acid(A) is any substance which either by direct dissociation or by reaction with solvent gives cationic characteristics of the solvents. and similarly for bases (B) (anions).



gmp

Advantages

- a) could explain A & B characteristics other than aqueous solvent.
i.e. Protic / Aprotic.

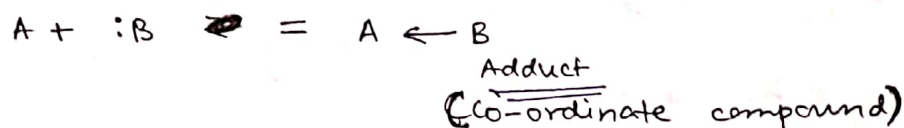
Limitation

- a) can't explain A-B behaviour without the presence of solvents.

5) Lewis Acid-Base Electronic concept :- (1923)

A Electron pair acceptor

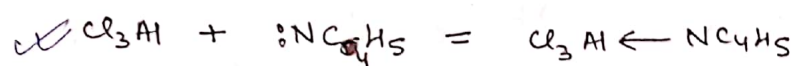
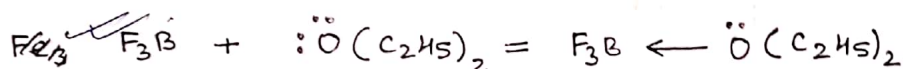
B Electron pair donor



To behave as Lewis acid (LA) central atom of species must contain at least one empty orbital & depending upon the empty orbital L.A are classified into 5 heads \rightarrow

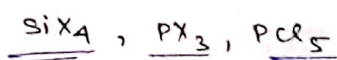
- i) Molecules having central atom with incomplete octet.

Electron deficient molecules (Be, B, Al)

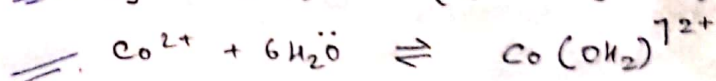


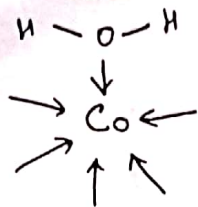
- ii) Molecules having central atom with vacant 'd' orbitals.

3rd / 4th period elements.

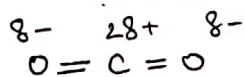


- iii) simple metal ions.



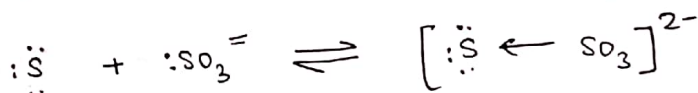
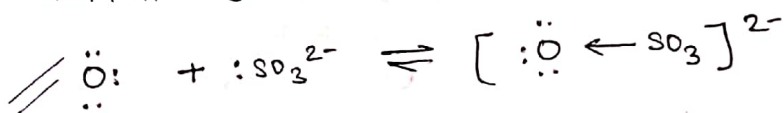


iv) Molecules having multiple bonds with dissimilar electronegativity.



oxygen being ^{more} electronegative than carbon pulls the electron pair towards itself and attains the partial negative charge and here carbon attains partial positive charge.

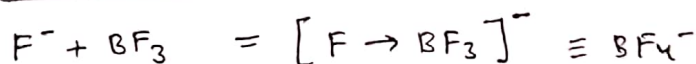
v) Element 'e' sextet.



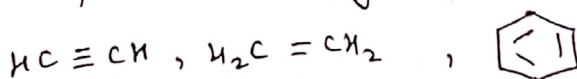
L.B.

i) Molecules having one/two LPs. ($\ddot{\text{NH}}_3$, $\text{H}_2\ddot{\text{O}}$, $\ddot{\text{OEt}}_2$, $-\ddot{\text{NH}}_2$)

ii) Almost anions : $\text{F}^- / \text{Cl}^- / \text{HO}^- / \text{CN}^-$



iii) Compounds having multiple bonds.



π electron clouds.

Advantages

a) does not depend upon any particular solvent.

Limitations

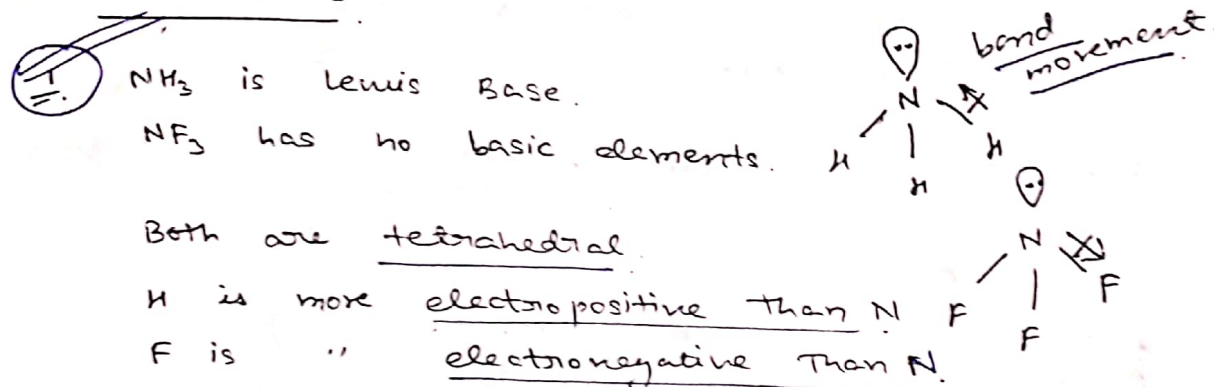
a) Relative strength couldn't be measured.

67. Usanovich Concept

'A' is any species capable of ^{giving} giving cations, combining with anions or 'e's' or neutralising a base to give a salt.

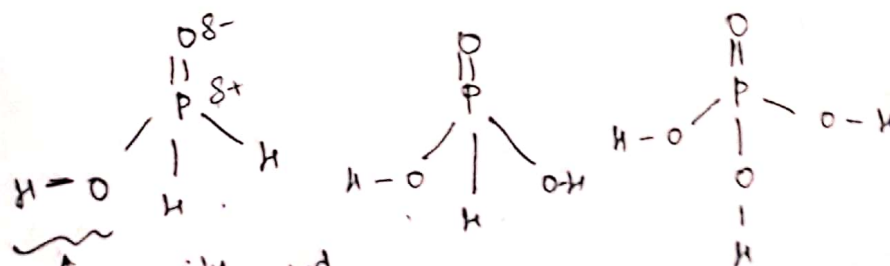
A 'B' is any species capable of giving up anions or 'e's', combining with cations or neutralising an acid to form a ~~solvent~~ salt.

Some Facts



∴ Band movement in NH_3 towards N
 → electron density on N is more ^{high}
 → easily donates electrons.

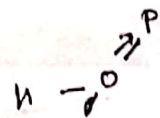
∴ Electron band movement towards F in NF_3 .
 → L.P. on N will be more tight situation i.e. tightly held
 → It will not be easily donated.



↑
 more easily
 bond is dissociated
 to give the
 proton.

Between P & O, oxy O is
 more electronegative, O attains
 partial δ^- charge & δ^+ P

P pulls electrons towards itself.



'e' is pulled towards O between O & H.

∴ ~~B~~ HfO, H is easily released.

For H_3PO_3 , two O-H bonds.

Pulling power of P is distributed & hence releasing nature of either protons is less as compared to that of H_3PO_2 . less acidic.

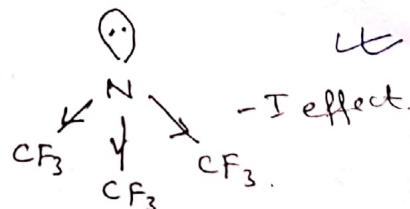
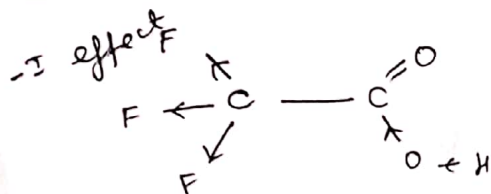
For, H_3PO_4 , Pulling power
3. lt.

∴ least acidic

formed +ve charge of P attracts 'e' pair of 'O-H' bonds
This force of attraction $\xrightarrow{1/2} \text{H}_3\text{PO}_3$
 $\xrightarrow{1/3} \text{H}_3\text{PO}_4$.

3. L.A of BF_3 , BCl_3 , BBr_3 , BI_3 , Arrange.
H/W.

4. (Strong L.A) CF_3COOH No L.B property.
 $(\text{CF}_3)_3\text{N}$



Pauli Rules Regarding Relative strength of oxy acids :-

* $O_{2n} \times (OH)_m$ $pK_a \approx 8 - 5n$

* polyprotic acid ($m > 1$),

successive pK_a values increases by 5 unit.

* $n \rightarrow$ non-hydrogenated oxygen atom

<u>n</u>	<u>pKa</u>	<u>oxy acid (obs)</u>	<u>structure</u>
0	8	$HOCl$ (7.2)	$H-O-Cl$
1	3	H_2CO_3 (3.6)	$H-O-C(=O)-O-H$
	$pK_1 = 5 (8 - 5 \times 1)$ $pK_2 = 8 (pK_1 + 5)$ $pK_3 = 13 (pK_2 + 5)$	H_3PO_4 $\begin{bmatrix} 2.1 \\ 7.4 \\ 12.7 \end{bmatrix}$	 $\therefore 3 \text{ pKa values.}$
2	$-2 (8 - 5 \times 2)$	HNO_3 (-1.4)	
3	$-7 (8 - 5 \times 3)$	$HClO_4$ (-10)	

{Carter wilkinson, inorganic chemistry} (125-127).