original.

ACID AND BASE

22/02/24

○ Various defination of acids and bases has been Proposed by different chemists. this definations have tried to cover a large number of acid-base reactions, redox reaction and Complex formation Reaction.

Each definition is correct within its own framework and we should apply the one which is the suited under the given circumstances. How-ever the following concept of acids and bases are so important.

▣ **Prob:** Discuss the "Arrhenius Concept" of acid and base and also discuss its limitation.

◎ ARRHENIUS THEORY ◎

In 1884 Svante Arrhenius theory Proposed a theory which is known as Arrhenius theory.

According to Arrhenius theory, an acid is any hydrogen containing compound which gives $H^\oplus$ ion in aqueous solution and a base which gives $OH^\ominus$ ions in aqueous solution.

Ex: Thus, according to this concept, the substance like HCl, HNO_3, H_2SO_4, CH_3COOH etc are acids, since they give $H^\oplus$ ions, when dissolved in water.

$$HCl + H_2O \rightleftharpoons H_3O^\oplus + Cl^-$$

The substances like NaOH, KOH, $Ca(OH)_2$ etc, are bases since they give $OH^\ominus$ ions in water.

$$NaOH \rightleftharpoons Na^\oplus + OH^\ominus$$

- **Acid-Base Nutralisation Reaction:**

According to this concept acids bases neutrali reaction are nothing but the combination of H⊕ and OH⊖ which is produced water. by the dissociation of the acids and bases respectively in aqueous medium.

$$HCl \rightleftharpoons H^{\oplus} + Cl^{\ominus} \quad [\text{in } H_2O].$$

$$NaOH \rightleftharpoons Na^{\oplus} + OH^{\ominus} \quad [\text{in } H_2O].$$

$$H^{\oplus} + OH^{\ominus} \rightleftharpoons H_2O \quad (\text{Neutralisation})$$

Application of Arrhenius Theory [ADVANTAGE

With the help of this concept we can explain the following ——

① Aqueous solution of non-metalic oxides (CO_2, SO_2, SO_3, N_2O_3, N_2O_5, P_4O_6, P_4O_{10} etc) is acidic, since give H⊕ ion in water.

$$SO_3 + H_2O = H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

(II) Aqueous solution of metallic oxides (eg CaO, Na and the compounds like NH_3, N_2H_4, NH_4OH etc are basic, since this substance gives OH⊖ ions in water.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^{\ominus}$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5 + OH^{\ominus}.$$

(III) This concept can explain the acid base neutrali reactions taking place in water.

(IV) The strength of an acid (HA) a base (BOH) can be expressed quantatively in terms of the ionisat constant of the acid and base in aqueous medium.

$$\underset{\text{acid}}{HA} \rightleftharpoons H^+ + A^\ominus, \quad K_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}}$$

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^\ominus \quad K_b = \frac{C_{B^+} \times C_{OH^-}}{C_{BOH}}$$

(v) The catalytic properties of acids in many reactions can be explained by saying that $H^\oplus$ ions are available from the acids.

Limitation of Arrhenius Concept:

(i) According to this concept, the acid and basic property of a substance is not supposed to be inherent in the substance itself, but it dependent on its aqueous solution.

Eg: According to this concept HCl is an acid, only when it is dissolved in water, but it is not considered an an acid when it is in gaseous state.

(ii) According to this concept, acid-base neutralisation reactions take place only in water and hence can not explain such reactions occuring in other solvents or in the gas phase.

Eg: The formation of NH_4Cl (s) by the combination of NH_3 (g) and HCl (g) can not be explained by this concept.

$$NH_3(g) + HCl\ (g) \rightleftharpoons NH_4Cl\ (s)$$

(iii) According to this concept, acids and bases undergo dissociation only in water (aqueous solvent). Thus, it can not explain the dissociation of acids and bases in non aqueous solvent like liq NH_3, liq SO_2 etc.

"BRONSTED-LOWRY CONCEPT"

In 1923 J.N Bronsted and J.M Lowry independen Proposed a concept of acids and bases. Accordin to it, an acid is a species (amolecule or ion) tha can loss a proton (H+) and base is the species (molecule or ion) that can accept a proton.

In other words, an acid is proton donor and a base is proton acceptor.

- An acid qualifying a ~~base~~ Bronsted Lowry Concep is termed as a Bronsted Lowry acid or simply as a Bronsted acid.

A base qualifying Bronsted Lowry theory is term as a Bronsted Base.

Example:

HCl can loss a proton (H+) to give Cl⁻ ic According to this concept HCl is Bronsted aci

$$\underset{\text{Bronsted acid}}{HCl} \rightleftharpoons H^{\oplus} + Cl^{-}$$

Similarly, since Cl⁻ ion can accept a proton (H+ to form HCl. Cl⁻ ion act as a base.

$$\underset{\text{Bronsted base}}{Cl^{-}} + H^{\oplus} \rightleftharpoons HCl$$

More example:

Bronsted acid (These can loss one or more proton)

Bronsted Base (These can accept one or more proton)

$$HX \underset{+H^{\oplus}}{\overset{-H^{\oplus}}{\rightleftharpoons}} X^{\ominus}$$

$NH_4^\oplus \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} NH_3$

$H_2S \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} SH^\ominus$

$CH_3COOH \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} CH_3COO^\ominus$

$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} \begin{matrix} COO^\ominus \\ | \\ COO^\ominus \end{matrix}$

$H_2SO_4 \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} HSO_4^-$

$HNO_3 \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} NO_3^\ominus$

$H_3PO_4 \underset{+3H^\oplus}{\overset{-3H^\oplus}{\rightleftharpoons}} PO_4^{3-}$

$H_2CO_3 \underset{+2H^\oplus}{\overset{-2H^\oplus}{\rightleftharpoons}} CO_3^=$

$H_2SO_4 \underset{+2H^\oplus}{\overset{-2H^\oplus}{\rightleftharpoons}} SO_4^=$

$H_3O^\oplus \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} H_2O$

$NH_2CONH_3^+ \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} NH_2CONH_2$

$H_2O \underset{+H^\oplus}{\overset{-H^\oplus}{\rightleftharpoons}} OH^\ominus$.

Prob: vu-

All arrhenius acids are also bronsted acids, but all arrhenius base are not bronsted base.

Soln:

Let us consider the behaviour of HCl in the following two reactions

① $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ ⓪ $HCl + NH_3 \longrightarrow NH_4Cl$ $[NH_4^+ + Cl^-]$

Reaction ①

Since HCl gives H_3O^+ ion when dissolved in water, this acids act as an Arrhenius acid in this reaction.

$$HCl \longrightarrow H^\oplus + Cl^\ominus$$
$$H_2O + H^\oplus \longrightarrow H_3O^\oplus$$
$$\overline{HCl\,(\text{Arrhenius acid}) + H_2O \longrightarrow H_3O^\oplus + Cl^-}$$

Reaction: In this reaction HCl loss a proton (H^+) which combine with NH_3 to form $NH_4^\oplus$ ion. HCl acts as a Bronsted acid.

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$NH_3 + H^+ \rightleftharpoons NH_4^\oplus.$$
$$\overline{HCl\,(\text{Bronsted acid}) + NH_3 \longrightarrow NH_4^+ Cl^-}$$

The above reaction shows that HCl both act as ~~an acid~~ ~~as~~ both Bronsted acid and Arrhenius acid.

According to Arrhenius theory, a substance that give OH⊖ ion(s) in aqueous solution, is called Arrhenius base. Such a substance (Arrhenius base) can not accept a proton and hence according to Bronsted-Lowry concept, can not act as a bronsted base.

Thus, an arrhenius base can not act as a bronsted base.

Prob:

● Explain Conjugate acids and bases concept?

Solⁿ: Conjugate Acid-Base pairs:

* Considers a reaction

one proton (H+) going to H2O   one proton (H+) going to Cl−

$$HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^-$$

In this reaction HCl donates a proton to H2O and is, therefore act as an acid. On the other hand, H3O⊕ ion donate a proton to Cl− ion, hence H3O+ ion is an acid. Cl− ion because it accept a proton from H3O⊕ ion, is a base.

So, A Conjugate base of an acid is that part left after proton lost.

Similarly the Conjugate acid of a base is that species formed on the addition of a proton to the base.

$$\overset{\text{acid}}{HCl} + \overset{\text{base}}{H_2O} \rightleftharpoons \overset{\text{conjugate acid}}{H_3O^{\oplus}} + \overset{\text{conjugate base}}{Cl^{\ominus}}$$

● According to this concept, an acid-base nutralisation reaction is that in which a Bronsted acid reacts with Bronsted base and their conjugate base and conjugate acid respectively are produced.

acid base Conj. acid Conj. base

$HCl + NH_3 \rightleftharpoons NH_4^{\oplus} + Cl^- \; [NH_4Cl]$

Some example of Conjugate acid - base pairs :

acid$_1$	Base$_2$	acid$_2$ (Conjugate acid of base$_2$)	Base$_1$ (Conjugate base of acid$_1$)
HCO_3^- +	H_2O ⇌	$H_3O^{\oplus}$ +	$CO_3^{=}$
HCN +	H_2O ⇌	$H_3O^{\oplus}$ +	CN^-
H_2S +	H_2O ⇌	$H_3O^{\oplus}$ +	HS^-
H_2O +	$CO_3^{=}$ ⇌	HCO_3^- +	$OH^{\ominus}$
H_2O +	H_2O ⇌	$H_3O^{\oplus}$ +	$OH^{\ominus}$
NH_4^+ +	H_2O ⇌	$H_3O^{\oplus}$ +	NH_3
HF +	CH_3COOH ⇌	$CH_3COOH_2^{\oplus}$ +	Cl^-
$HClO_4$ +	H_2SO_4 ⇌	$H_3SO_4^{\oplus}$ +	ClO_4^-
$HCOOH$ +	NH_2CONH_2 ⇌	$NH_2CONH_3^{\oplus}$ +	$HCOO^{\ominus}$
HF +	HNO_3 ⇌	$H_2NO_3^{\oplus}$ +	$F^{\ominus}$

Relative strength of Bronsted acids and Bronsted Base :

In a given Conjugate acid-base pairs, if the acid is strong, its conjugate base will be weak. Similarly if the acid is weak, its conjugate base will be strong.

i,e strong base produced weak conjugate acid and weak base produced strong conjugate acid.

HCl (strong acid) ⇌ $Cl^{\ominus}$ (weak Conjugate base)

CH_3COOH (weak acid) ⇌ strong Conj base (CH_3COO^-).

Prob: Comparison between the basic strength of the three bases namely H_2O, Cl^-, $CH_3COO^\ominus$.

Sol^n: $CH_3COO^\ominus$ is the conjugate base of CH_3COOH (weak acid)

$Cl^\ominus$ is . . . . HCl (strong acid)

H_2O . . . . . . $H_3O^\oplus$ (stronger than CH_3COOH)

According to Bronsted Lowry concept conjugate base of weak acid is stronger and conjugate base of strong acid is weaker.

So, CH_3COO^- stronger than Cl^-, H_2O, and Cl^- is weaker than H_2O.

So, Increasing order of basic strength will be

$$H_2O < Cl^- < CH_3COO^-$$
$$\xrightarrow[\text{increasing order.}]{}$$

⊛ Merits of the Bronsted–Lowry concept:

(I) It defines the acid and bases strength in terms of the substance themselves not in terms of the ions generated in the ionisation of the solvent under consideration.

(II) This concept is utilized in ~~explaing~~ explaining the hydrolytic behaviour of salts.

for example:

The aqueous solution of $FeCl_3$ in acidic due to the fact that proton donor ability of hydrated Fe^{3+} ion i.e $[Fe(H_2O)_6]^{3+}$ exceeds the proton acceptor ability of $Cl^\ominus$ ion so that a considerable excess of $H_3O^\oplus$ ion exist in aqueous solution making

$FeCl_3$ solution acidic.

$$FeCl_3 + 6H_2O \longrightarrow [Fe(H_2O)_6]^{3+} + 3Cl^{\ominus}$$

$$[Fe(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_5OH]^{2+} + H^{\oplus}$$

$$H^{\oplus} + H_2O \longrightarrow H_3O^{\oplus}.$$

Similarly aqueous solution of Na_2CO_3 is alkaline because the proton acceptor ability of CO_3^{2-} is more than the proton donor ability of hydrated $Na^{\oplus}$ ion.

$$Na_2CO_3 + 2x\,H_2O \longrightarrow 2\,[Na(H_2O)_x]^{\oplus}\,CO_3^{=}$$

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^{-} + OH^{\ominus}$$

(iii) The concept can explain the amphoteric reaction.

(iv) The concept can explain the acid-base behaviour of organometallic hydrides.

Limitation of the Concep:

Although this concept has several utility yet there are certain drawbacks. This has an over emphasis on the proton transfer / acceptor property. More over there are several compounds eg: SO_2, $AlCl_3$, $SOCl_2$ etc undergo acid / base behaviour although there is no proton transfer occurs.

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{=}$$

$$CaO + SiO_2 \rightleftharpoons CaSiO_3.$$

Levelling and differentiating solvents:

Levelling Solvents:

The strength of protonic acids is dependent on the solvent in which the acids are dissolved. If the solvent is a good proton acceptor (base) then the different acids will donate the protons completely (100%) to the referene base, so that all acids will be qually strong. For example $HClO_4$, H_2SO_4, HCl, HNO_3 are levelled to the strength of $H_3O^{\oplus}$ in solvent H_2O.

$$HClO_4 + H_2O \longrightarrow H_3O^{\oplus} + ClO_4^{\ominus}$$

$$H_2SO_4 + H_2O \longrightarrow H_3O^{\oplus} + HSO_4^{-}$$

$$HCl + H_2O \longrightarrow H_3O^{\oplus} + Cl^{\ominus}$$

$$HNO_3 + H_2O \longrightarrow H_3O^{\oplus} + NO_3^{-}$$

In all cases the acid dissociation constant (K_a) has the value infinity and water acting as a levelling solvent. A solvent in which 100% proton transfer may occur is called a levelling solvent for acids.

~~Differentiating solvent:~~

Similarly liquid NH_3 is acting as a levelling solvent for the acids HF, HBr, CH_3COOH etc when proton transfer is about cent percent so that —

$$HX + NH_3 \longrightarrow NH_4^{\oplus} + X^{\ominus} \quad [X = F, Br, CH_3COO]$$

Differentiating solvent:

If we take CH_3COOH as a solvent then the acid strength of the above strong acids eg. $HClO_4$ H_2SO_4, HCl and HNO_3 can be differentiated.

$$HX + CH_3COOH \rightleftharpoons CH_3COOH_2^{\oplus} + X^{\ominus} \longrightarrow ①$$

[$X = ClO_4, HSO_4, Cl$ and NO_3

Here CH_3COOH is acting as a base, therefore in order to differentiate the acid strength of strong acids we have to take a much weaker acid as a differentiating solvent.

Though it is apparent from equation ① that the strengths of all the strong acids are levelled to the strength of $CH_3COOH_2^{\oplus}$, this is not correct because the proton donation capability of ~~different~~ ~~for different~~ strong acids towards CH_3COOH are different, so that concentration of $CH_3COOH_2^{\oplus}$ will be different for different acid strength as $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$ in anhydrous CH_3COOH medium. Here CH_3COOH act as a differentiating solvent.

What is

LEWIS CONCEPT ? (1923)

The limitation of Bronsted Concept is somewhat rectified by Lewis theory because this concept based on the electronic structure of the acids and bases. According to Lewis

an acid is defined as a species (molecule or radical or ion) which accepts electron pair and a base is a molecular system which donates electron pair.

Thus an acid is an electron deficient species (electrophile) while bases are electron rich molecular system (nucleophile).

According to Lewis Concept

The process of neutralisation then considered as the formation of a donor–acceptor bond (Co-ordinate bond) from a donor base (:B) to acceptor acid (A) as to form an adduct (AB) as.

$$A + :B \longrightarrow A \leftarrow :B$$

Classification of Lewis acids :

ⓐ A species containing a central atom having incomplete octet.

In the molecule viz BF_3, BCl_3, $AlCl_3$, $B(CH_3)_3$ etc the central atom is of sextet and can accept an electron pair to complete the octet.

$$\underset{\text{acid}}{F_3B} + \underset{\text{base}}{\ddot{N}H_3} \longrightarrow \underset{\text{adduct}}{F_3B \leftarrow NH_3}$$

ⓑ All metal cations are acting as Lewis acids to form Co-ordination Compounds eg—

$$Co^{2+} + 6H_2O \longrightarrow [Co(H_2O)_6]^{2+}$$

$$Co^{3+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{3+}$$

$$\underset{\text{acid}}{Ag^{+}} + \underset{\text{base}}{2NH_3} \longrightarrow \underset{\text{adduct}}{[Ag(NH_3)_2]^{\oplus}}$$

Transition metal ion have strong powers of complex formation.

ⓒ Molecules having central atom with vacant d- orbitals :

In the case of halides eg $SiCl_4$, $GeCl_4$, $TiCl_4$, $SnCl_4$, $TeCl_4$ etc, the central atom has vacant d- orbitals which recive the electron pairs from the lewis base.

$$TiCl_4 + 2Cl^{\ominus} \longrightarrow [TiCl_6]^{2-}$$

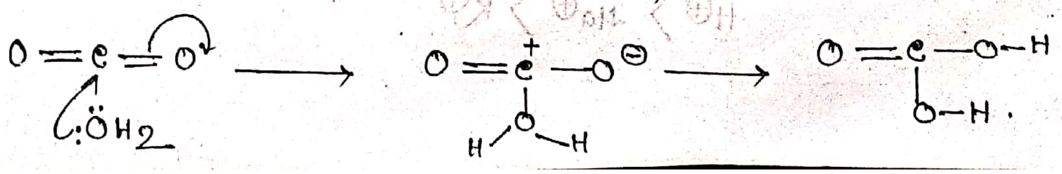
$$\underset{\text{acid}}{SiF_4} + \underset{\text{base}}{2F^{\ominus}} \longrightarrow \underset{\text{adduct.}}{[SiF_6]^{2-}}$$

ⓓ Molecules containing multiple bonds between atoms of different electronegativity:

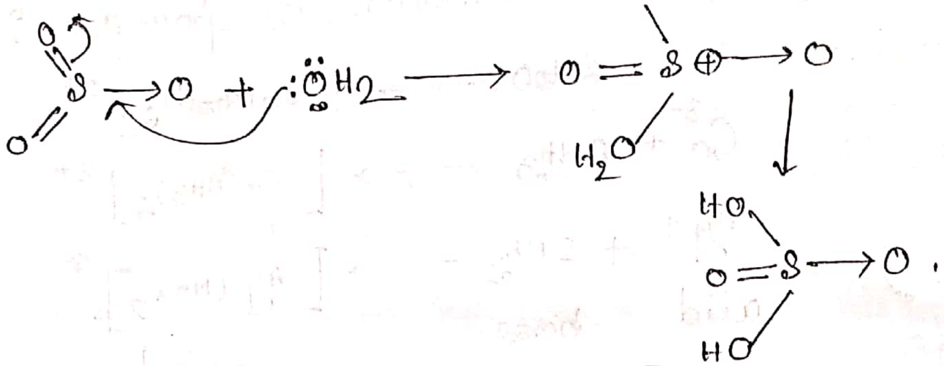
for example CO_2 acting as a Lewis acid when it forms HCO_3^- or H_2CO_3 by accepting electron pairs from the oxygen atom of $OH^{\ominus}$ or H_2O

$$CO_2 + OH^{\ominus} \longrightarrow HCO_3^{\ominus}$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$



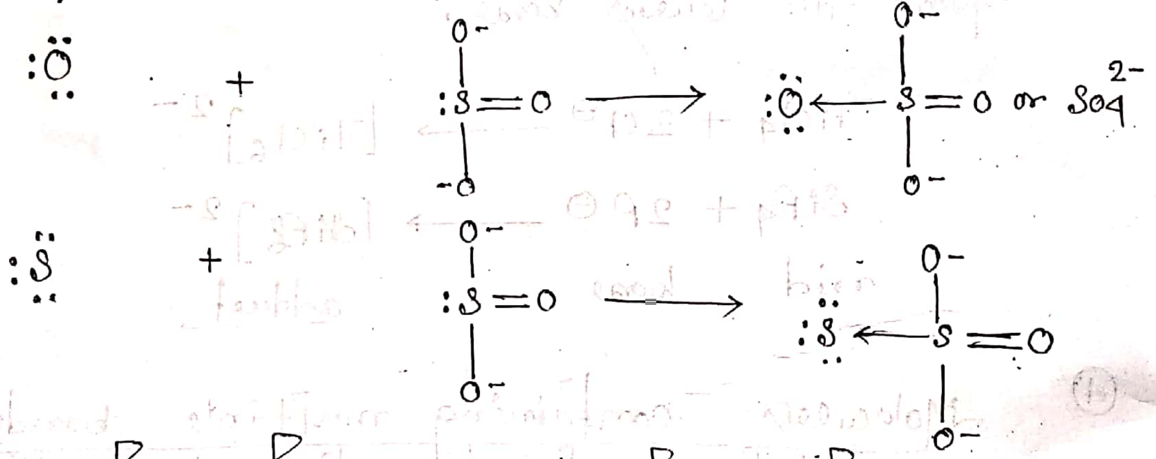
Similarly SO_3 can act as a secondary Lewis acid as



ⓔ Elements which have a sextent of electron in their valence-shell.

Example of such elements are oxygen and sulphur (ns^2np^4 configuration). These elements accept electron pairs from Lewis base like SO_3^{2-} to complete their octet and hence act as Lewis acids. For example

Lewis acid   Lewis base.   Complex ion (adduct).



Variation of Lewis acid strength of simple Cation :

① Size of the Cation :

Smaller is the size of a cation, greater is its tendency to accept the electron pair(s) hence stronger is its Lewis acid strength.

$H^{\oplus} > Na^{\oplus} > K^{\oplus}$

2. Oxidation state of the Cation :

The Lewis acid strength of the cations derived from the same metal atom increases with the increase in its oxidation numbers, since the size of the cation decreases with the increases in oxidation numbers.

For example the Lewis acid strength of Fe^{2+} and Fe^{3+} ions is in the orders: $\underrightarrow{Fe^{2+} < Fe^{3+}}$.

~~The species having suitable electron cloud~~

Classification of the Lewis Bases :

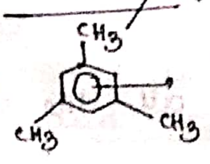
The species having suitable electron clouds for donation are

(i) All anions $Cl^{\ominus}$, $F^{\ominus}$, $Br^{\ominus}$, $O^{=}$, $S^{=}$, $NH_2^{\ominus}$, PH_2, $OH^{\ominus}$, $HS^{\ominus}$, $SO_3^{\ominus}$ etc.

(ii) Molecules having unshared electron pairs :

NH_3, PH_3, H_2S, $:CO$, $H_2O:$, $\ddot{O}::\ddot{O}:$ etc.

(iii) Organic Compounds having suitable pi-electron clouds :



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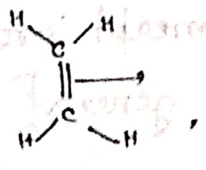

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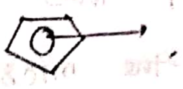
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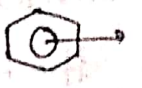
etc.

* Limitation of Lewis Concept :

i) Since the strength of Lewis acid and Lewis bases and is found to depend on the type of reaction not on the absolute power of accepting or donating a pair of electrons. It is not possible to arrange the Lewis acids and Lewis bases in any order of their acid or base strength.

For example, Fluoride complex of Be^{2+} ion is more stable than Cu^{2+} ion. Be^{2+} ion is more stronger Lewis acid than Cu^{2+} ion.

On the other hand the fluoride ammine complex of Cu^{2+} ion is more stable than Be^{2+} ion. So Cu^{2+} ion is more stronger Lewis acid than Be^{2+}.

(ii) The conventional protonic acids, viz H_2SO_4, HCl are not covered under Lewis concept as they do not establish a covalent bond by accepting a pair of electrons.

[c] USANOVICH CONCEPT (1939).

M. Usanovich (1939), Russian chemist, proposed a very wide defination of acids and bases. The merits of this concept are.

i) It is the most general of all the different definitions

(ii) It includes all acids and bases, define by Lewis.

(iii) It states that the donation or acceptance of electrons need not take place as shared pair

According to this Concept

An acid is a substance capable of accepting anions or electrons or giving up cation and react with a base. A base is a substance that can react with acid and accept cations and furnishes anions or electron.

Some example of acid-base reactions in terms of Ushanovich Concept :

(i) SO_3 (acid) + Na_2O (Base) $\longrightarrow$ Na_2SO_4 (salt).

Na_2O (Base) $\longrightarrow 2Na^{\oplus} + O^{=}$, Na_2O gives $O^{=}$ anion and hence acts as base.

SO_3 (acid) $+ O^{=} \longrightarrow SO_4^{=}$, SO_3 accepts $O^{=}$ anion and hence behaves as acid.

(ii) $Fe(CN)_2$ (Acid) + 4 KCN (base) $\longrightarrow$ $K_4[Fe(CN)_6]$ (Salt)

4KCN (Base) $\longrightarrow 4K^{\oplus} + 4CN^{\ominus}$, KCN acts as a base, Since it gives $CN^{\ominus}$ anion.

$Fe(CN)_2$ (acid) $+ 4CN^{\ominus} \longrightarrow [Fe(CN)_6]^{4-}$, $Fe(CN)_2$ acts as a acid.

va' 007

Prob: Write a brief account on Usanovich's Concept of acid and bases.

LUX-FLOOD CONCEPT

- The Concept proposed by Lux (1939) and extended by Flood (1947) defines the acids and bases in term of $O^=$ (oxide) ion transfers. In terms of oxide ion transfers, conjugate acids and bases may defined as follows:

$$\text{Base} \rightleftharpoons O^{2-} + \text{acid (conjugate)}.$$

The acids (eg SiO_2, SO_3 etc) are oxide ion acceptors while the bases (eg CaO, PbO etc) are oxide ion donors.

Example:

$$\underset{\text{base}}{CaO} + \underset{\text{acid}}{SiO_2} \rightleftharpoons \underset{\text{salt}}{Ca^{2+}SiO_3^{=}}$$

$$\underset{\text{base}}{PbO} + \underset{\text{acid}}{SO_3} \rightleftharpoons \underset{\text{salt}}{Pb^{2+}SO_4^{=}}$$

$$\underset{\text{base}}{6\ CaO} + \underset{\text{acid}}{2P_2O_5} \rightleftharpoons \underset{\text{salt}}{2\ Ca_3(PO_4)_2}.$$

According to this concept, the amphoteric substances are having both the tendency to accept and donate the oxide ion.

The example of amphoteric substance are

$$ZnO \rightleftharpoons Zn^{2+} + O^{=}, \quad ZnO + O^{=} \rightleftharpoons ZnO_2^{2-}$$

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{=}, \quad Al_2O_3 + O^{=} \rightleftharpoons 2AlO_2^{-}$$

* ZnO (base) + $S_2O_7^{=}$ (acid) $\rightleftharpoons Zn^{2+} + 2SO_4^{=}$

Na_2O (base) + ZnO (acid) $\longrightarrow 2Na^{+} + ZnO_2^{=}$

TiO_2 (base) + $Na_2S_2O_7$ (acid) $\longrightarrow Na_2SO_4 + TiO(SO_4)$.

Nb_2O_5 (base) + $K_2S_2O_7$ (acid) $\longrightarrow (NbO_2)_2SO_4 + K_2SO_4$.

Xenon fluorides as Lux-Flood acids:

Xenon fluorides are the good oxides acceptors and they can fluoridate the oxide donors. The relative acidity of xenon fluoride —

$XeF_6 > XeO_2F_4 > XeO_3F_2 > XeO_4 > XeOF_4 > XeF_4 > XeO_2F_2 > XeO_3 > XeF_2$.

Example:

$$XeF_6 + OPF_3 \longrightarrow XeOF_4 + PF_5$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + HF \quad \text{(controlled hydrolysis)}$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF.$$

NU

Prob: Considering the following reaction, identify the stronger acid between SiO_2 and CO_2:

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2.$$

NU-08.

Prob: Dissolution of Al_2O_3 is molten $K_2S_2O_7$ is an acid-base reaction. explain this theory of your choice.

Hint:

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{=}$$

$$K_2S_2O_7 + O^{=} \longrightarrow 2K^{+} + 2SO_4^{=}$$

$$3K_2S_2O_7 + 3O^{=} \longrightarrow 6K^{+} + 6SO_4^{=}$$

So, ultimate reaction,

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{=}$$

$$3K_2S_2O_7 + 3O^{=} \rightleftharpoons 6K^{+} + 6SO_4^{=}$$

$$Al_2O_3\,(\text{base}) + 3K_2S_2O_7\,(\text{acid}) \rightleftharpoons Al_2(SO_4)_3 + 3K_2SO_4.$$

Solvent System theory :

extended by Cady - Esley (1928)

This Concept developed by Franklin based on the experimental studies of autoionisation of solvent including water. Franklin (1905)

Definitions in terms of autoionisation of solvent:

In this model, the autoionisation of the solvent is Considered and any substance capable of increasing the Concentration of the cation (i.e lyonium) produced in the autoionisation of the solvent is regarded as an acid in that solvent.

On the other hand, the species which can enhance the Concentration of the anion (i.e lyate) produced in the autoionisation of the solvent is Consider as a base in that solvent.

Hence to characterise the substance as acid or bases in a particular solvent, it is required to know the mode of autoionisation of the solvent under consideration. Some common solvents with their autoionisation mode are given below ——

Protonic solvent

$$H_2O + H_2O \rightleftharpoons \overset{\text{Acid}}{H_3O^{\oplus}} + \overset{\text{Base}}{OH^{\ominus}}$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^{\oplus} + NH_2^{\ominus}$$

$$CH_3COOH + CH_3COOH \rightleftharpoons CH_3CO_2H_2^{\oplus} + CH_3COO^{\ominus}$$

Non-protonic solvent

$$SO_2 + SO_2 \rightleftharpoons \overset{\text{acid}}{SO^{2+}} + \overset{\text{Base}}{SO_3^{=}}$$

$$POCl_3 + POCl_3 \rightleftharpoons OPCl_2^{\oplus} + OPCl_4^{-}$$

$$BrF_3 + BrF_3 \rightleftharpoons BrF_2^{\oplus} + BrF_4^{\ominus}$$

$$N_2O_4 + N_2O_4 \rightleftharpoons 2NO^{\oplus} + 2NO_3^{\ominus}$$

Prob: Write the characteristic of the solvent when ① $NOCl$ ⓘⓘ $NaNO_3$ dissolved in N_2O_4 solvent.

Solⁿ :

N_2O_4 act as non protonic solvent, It is autoionised to produced $NO^{\oplus}$ (solvated Cation) and

$$2N_2O_4 \rightleftharpoons 2NO^{\oplus} + 2NO_3^{\ominus}$$

$NO_3^{\ominus}$ (solvated anion).

When $NOCl$ dissolved in N_2O_4, it is ~~aut~~oionised to Prodused $NO^{\oplus}$ and $Cl^{\ominus}$. Hence $NOCl$ increase

$$NOCl \rightleftharpoons NO^{\oplus} + Cl^{\ominus}$$

the Concentration of solvated Cation. so act as an acid.

Similarly $NaNO_3$ dissociated in N_2O_4 to Prodused $Na^{\oplus}$ and $NO_3^{\ominus}$ (solvated ~~Cation~~) anion)

$$NaNO_3 \rightleftharpoons Na^{\oplus} + NO_3^{\ominus} \text{ (solvated anion)}$$

so, $NaNO_3$ increasing the Concentration of solvated anion so, act as base in N_2O_4 solvent.

Prob: Write the acid - base Neutralisation reaction in liquid ammonia.

Solⁿ :

$$NH_4Cl \rightleftharpoons \underset{\substack{\downarrow \\ \text{(Solvated} \\ \text{Cation)}}}{NH_4^{\oplus}} + Cl^{\ominus}, \qquad NaNH_2 \rightleftharpoons Na^{\oplus} + \underset{\text{Solvated anion}}{NH_2^{\ominus}}$$

In liquid NH_3, NH_4Cl increase the Concentration of Solvated Cation so act as acid. $NaNH_2$ increase the Concentration of solvated anion so act as a base. The acid- base neutralisation in liquid amonia are given below —

$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} \rightleftharpoons \underset{\text{(Solvent)}}{2NH_3} + \underset{\text{(salt)}}{NaCl}$$

(*) In SO_2 as a solvent, $SOCl_2$ is expected to act as an acid while the sulphite salts act as bases:

$$SOCl_2 \rightleftharpoons SO^{2\oplus} + 2Cl^{\ominus}$$

(Solvated cation)

$$Na_2SO_3 \rightleftharpoons 2Na^{\oplus} + SO_3^{2-}$$

(Solvated anion)

Thus the reaction between $SOCl_2$ and Na_2SO_3 can be regarded as an acid - base neutralisation reaction in SO_2:

$$Na_2SO_3 \text{ (base)} + SOCl_2 \text{ (acid)} \rightleftharpoons \underset{\text{(Salt)}}{2NaCl} + 2SO_2 \text{ (solvent)}$$

(*) Autonisation of liquid phosgene ($COCl_2$) can be shown as follows:

$$COCl_2 \rightleftharpoons COCl^{\oplus} + Cl^{\ominus}$$

In this solvent, $AlCl_3$ can act as an acid and $CaCl_2$ can act as a base.

Acidic character of $AlCl_3$:

$$AlCl_3 + COCl_2 \rightleftharpoons COCl^{\oplus} + AlCl_4^{\ominus}.$$

Basic character of $CaCl_2$:

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^{\ominus}.$$

The neutralisation reaction can expected as follows —

$$CaCl_2 + 2\left[COCl^{+}AlCl_4^{-}\right] \rightleftharpoons Ca\left[AlCl_4\right]_2 + 2COCl_2$$

Merits of the Concept :

It can extend the concept of acid and base interaction in both protic and aprotic solvents.

Demerits of the Concept :

① It Pays an excessive attention to the idea of auto ionisation of the solvent ignoring the others physical and chemical properties of the solvents. It even ignores the properties arising from the dielectric constant which in fact, determines the possibility of autoionisation.

(ii) It can not explain many acid-base reaction occuring in the absence of any solvent.

(iii) Many acid-base reactions involving the neutral molecules can not be explained in this model.

Prob: How would you expect CH_3COOH (acetic acid) to behaves in ⓘ waters ⓘⓘ liq NH_3 ⓘⓘⓘ Anhydrous H_2SO_4 and ⓘⓥ liquid HF.

ⓘ In waters CH_3COOH ionise to a small extent to produced $H_3O^{\oplus}$ ions (solvated cation). due to the feeble ionisation of CH_3COOH in water the conce. of $H_3O^{\oplus}$ ions obtained is very low and hence according to solvent system theory, CH_3COOH act as a weak acid in waters.

$$\underset{\text{weak acid}}{CH_3COOH} + \underset{\text{solvent}}{H_2O} \rightleftharpoons \underset{\text{solvated cation.}}{H_3O^{\oplus}} + CH_3COO^{\ominus}$$

ⓘⓘ CH_3COOH dissolved in liquid NH_3, CH_3COOH completely converted into $NH_4^{\oplus}$ ions which are solvent cation. CH_3COOH, therefore, behaves as strong acid in liquid NH_3.

$$CH_3COOH\,(\text{strong acid}) + NH_3\,(\text{solvent}) \rightleftharpoons \underset{\text{(Solvated Cation)}}{NH_4^{\oplus}} + CH_3COO^{\ominus}.$$

ⓘⓥⓘ When CH_3COOH disolved in liquid H_2SO_4, CH_3COOH is protonated, and the concentration of $HSO_4^{\ominus}$ (solvated anion) is increases and hence CH_3COOH behaves as a base in H_2SO_4.

$$CH_3COOH + \underset{\text{solvent}}{H_2SO_4} \rightleftharpoons CH_3COOH_2^{\oplus} + \underset{\text{(Solvated anion)}}{HSO_4^{\ominus}}$$

(iv) When CH_3COOH dissolved in liq HF, it ionise to produced $F^{\ominus}$ ions (solvated anion) and hence behaves as base in liquid HF.

$$CH_3COOH\,(liq) + HF\,(solvent) \rightleftharpoons CH_3COOH_2^{\oplus} + \underset{\text{(solvent anion)}}{F^{\ominus}}$$

Prob:

How would you expect HNO_3 to behaves in i) Water ii) liq HF (iii) H_2SO_4.

Soln: i) HNO_3 completely ionised in water to produced $H_3O^{\oplus}$ ions (solvent cation) is large extent and hence according to solvent system theory HNO_3 behaves as strong acid in H_2O.

$$\underset{\text{(acid)}}{HNO_3} + H_2O\,(solvent) \rightleftharpoons \underset{\text{(Solvent cation)}}{H_3O^{\oplus}} + NO_3^{\ominus}$$

(ii) When HNO_3 put in liq HF, it gets ionised to produced $F^{\ominus}$ (solvent anion) and hence HNO_3 behaves as an base in liq HF.

$$HNO_3 + HF\,(solvent) \rightleftharpoons H_2NO_3^{\oplus} + F^{\ominus}$$

(increase the concentration of solvent cation).

(iii) When HNO_3 is dissolved in H_2SO_4, HNO_3 is protonated and produced $HSO_4^{\ominus}$ ion (solven anion) so, HNO_3 increase the concentration of solvent anion, act as a base.

$$HNO_3 + H_2SO_4\,(solvent) \rightleftharpoons H_2NO_3^{\oplus} + \underset{\text{(solvent anion)}}{HSO_4^{\ominus}}$$

Prob: How would you expect urea to behaves in ⓘ water ⓘⓘ liq NH_3 ⓘⓘⓘ Anhydrous H_2SO_4.

Solⁿ: ⓘ Urea (NH_2CONH_2) does not react with water to produce $H_3O^{\oplus}$ and $OH^{\ominus}$ ions and hence behaves as a neutral substance in this solvent.

(ii) When Urea is dissolved in liq NH_3, $NH_4^{\oplus}$ ion (solvated cation) are obtained in low conc. in the solⁿ and hence Urea behaves as weak acid in this solvent.

$$NH_2CONH_2 \text{ (weak acid)} + NH_3 \text{ (solvent)} \rightleftharpoons H_2NCONH^{\ominus} + NH_4^{\oplus} \text{ (Solvent Cation)}$$

(iii) When Urea dissolved in Conc. H_2SO_4, Urea is Protonated and Produced $HSO_4^{\ominus}$ ion (solvated anion) is large extent. Thus in H_2SO_4 solvent ~~H_2SO_4~~ $CO(NH_2)_2$ behaves as a strong base.

$$H_2NCONH_2 \text{ (strong base)} + \underset{\text{solvent}}{H_2SO_4} \rightleftharpoons H_2NCONH_3^{\oplus} + HSO_4^{\ominus} \text{ (Solvated anion)}$$

⑫

Cosolvating Agents and Acids - Base strength:

The Proton transfers of an acid (HA) in equilibrium measuring the acid strength of HA. HA can derived the proton transfers in equilibrium to the right hand direction to enhance the acid strength.

The agent responsible to derived the Proton transfers equilibrium is described as the Cosolvating agent.

Similarly, a Cosolvating agent can also enhance the basicity of B. In fact, the co-solvating agent interact more strongly with the conjugate acid-base components (i.e HA and $A^\ominus$; $BH^\oplus$ and B) than the solvent itself to influence the proton transfer Process.

Vu-03

Prob: HF is weak acid in H_2O but in presence of BF_3 and SbF_5 it behaves as an strong acid.

Soln: HF slightly dissociated in H_2O, to produced $H_3O^\oplus$ and $F^\ominus$, so, HF act as an weak acid in H_2O. But in presence of BF_3 and SbF_5 the dissociation of HF is largly enhanced. Because BF_3 and SbF_5 act as a $F^\ominus$ acceptor so dissociation will occure in forward direction. Here BF_3 and SbF_5 act as a Co-solvating agent.

$$HF + H_2O \rightleftharpoons H_3O^\oplus + F^\ominus, \quad F^\ominus + BF_3 \rightleftharpoons BF_4^\ominus$$

$$\text{or } F^\ominus + SbF_5 \rightleftharpoons SbF_6^\ominus$$

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Prob: Would the following increase, decrease or have no. effect on the acidity of the solution.

① Addition of Li_3N to liq NH_3?

② " " SiO_2 to FeO?

③ " " $KHSO_4$ " H_2SO_4?

④ " " HgO to an aqueous solⁿ of KI.

⑤ NH_4Cl in liquid NH_3?

⑥ Addition of $CuSO_4$ to an aqueous solⁿ of $(NH_4)_2SO_4$.

⑦ Addition of $Al(OH)_3$ to an aqueous solⁿ of $NaOH$.

⑧ Anhydrous $AlCl_3$ is added to liquid phosgene?

Solⁿ:

① Liquid NH_3 autoionise as

$$\underset{\text{Solvent}}{2NH_3} \rightleftharpoons \underset{\text{Solvent Cation}}{NH_4^{\oplus}} + \underset{\text{solvent anion}}{NH_2^{\ominus}}.$$

According to solvent system theory the substance which increase the concentration of solvated cation are called acid, if increase the concentrati of solvated anion are called base.

Li_3N ionise as

$$Li_3N \rightleftharpoons 3Li^{\oplus} + N^{3-}$$

The nitride ion N^{3-} react with liq NH_3 to produced amide ion (NH_2^-) i.e solvent anion.

$$2NH_3 + N^{3-} \rightleftharpoons 3NH_2^{\ominus}$$

$LiNH_2$ increase the concentration of solvated anion in liquid NH_3, i.e. $LiNH_2$ act as a base.

Hence the acidity of the solution decreases due to the addition of $LiNH_2$ in liq NH_3.

② According to "lux-flood concept" An acid is an oxide ion acceptor while a base is an oxide ion donor.

When SiO_2 added in FeO, SiO_2 act as an oxide ion acceptor and it accept ($O^{=}$) from FeO to form $SiO_3^{=}$ and FeO act as oxide ion donor so, the reaction is acid base neutralisation reaction. i.e. the medium will be neutral in state.

$$\underset{\text{acid}}{SiO_2} + \underset{\text{base.}}{FeO} \rightleftharpoons \underset{\text{salt}}{FeSiO_3}$$

Hence, the basicity decreases and the acidity of the soln increases.

③

H_2SO_4 autoionise as

$$H_2SO_4 \rightleftharpoons H^{\oplus} + \underset{\text{(Solvent anion)}}{HSO_4^{\ominus}}$$

$KHSO_4$ is ionic salt of H_2SO_4 which as

$$KHSO_4 \rightleftharpoons K^{\oplus} + HSO_4^{\ominus}$$

When $KHSO_4$ added in the H_2SO_4, the concentration of $HSO_4^{\ominus}$ increases (solvated anion), Consequently acidity of the soln decreases.

④ Reaction of HgO with KI in aqueous sol^n results in the formation of the stable Complex, K- mercuric iodide, $K_2[HgI_4]$ along with strong base KOH. The equation is given below

$$4KI + HgO + H_2O \rightleftharpoons K_2[HgI_4] + 2KOH.$$

Since in the solution, the concentration of $OH^{\ominus}$ increases, consequently acidity of the solution decreases.

⑤ The liquid NH_3 autoionise as

$$2NH_3 \rightleftharpoons \underset{acid}{NH_4^{\oplus}} + \underset{base}{NH_2^{\ominus}}$$

According to solvent system theory "the substance which increase the concentration of the solvent cation are called acid.

If increase the concentration of solvent ~~Cation~~ anion are called base.

When NH_4Cl is added liq NH_3. It ionise as follows

$$NH_4Cl \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$$

Since NH_4Cl increase the concentration of characteristic solvent cation, so the amount of $NH_4^{\oplus}$ ion increases, consequently acidity of the solution increases and basicity decreases.

⑥ When $CuSO_4$ is added to an aq. sol^n of $(NH_4)_2SO_4$ the Cupric ion Combines with (NH_4^+) Coming from $(NH_4)_2SO_4$ ion to form a stable Complex- cupro- ammonium Sulphate.

Thus addition of $CuSO_4$ ise Cu^{2+} ion in ammonium salt solution, resulting in the formation of complex along with the liberation of $4H^{\oplus}$ ion.

$$CuSO_4 + 4NH_4^{\oplus} \text{ (coming from } (NH_4)_2SO_4\text{)} = \underset{aq}{[Cu(NH_3)_4]}So$$

$$+ 4H^{\oplus}.$$

Due to the formation of $4H^{\oplus}$ ion, the resulting solⁿ becomes acidic, hence the basicity of the solution decreases.

⑦ When $Al(OH)_3$ is added to an aq. solⁿ of NaOH then $Al(OH)_3$ react with NaOH to form a salt ~~NaAl2~~ $NaAlO_2$ (sodium aluminate) and two moles of waters.

$$Al(OH)_3 + NaOH \rightleftharpoons NaAlO_2 + 2H_2O$$

Since the concentration of $OH^{\ominus}$ decreases to a large extent, hence the basicity of the solⁿ decreases and consequently acidity of the solⁿ increases.

⑧ When anhydrous $AlCl_3$ is added to liquid phosgene, $AlCl_3$ react with $COCl_2$ to formed $COCl^{\oplus} + AlCl_4^{\ominus}$, $COCl^{\oplus}$ is solvated cation. So, $AlCl_3$ increase the concentration of solvated cation in the solution so acidity of the solution increases, since $AlCl_3$ act as acid in liquid phosgene ($COCl_2$)

$$2COCl_2 \rightleftharpoons 2COCl^{\oplus} + 2Cl^{\ominus}$$

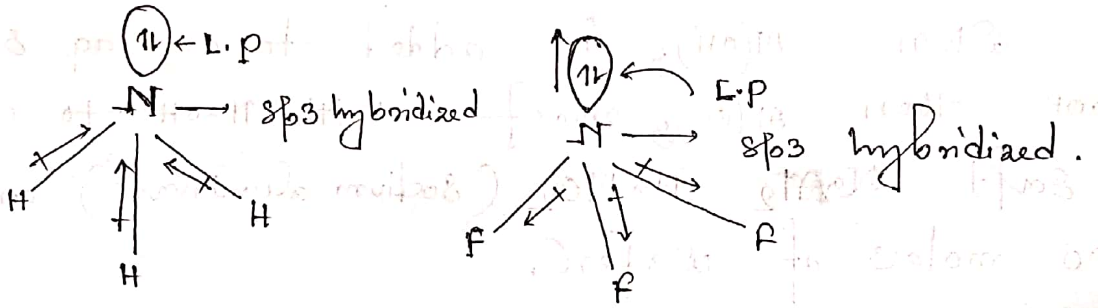
$$AlCl_3 + COCl_2 \rightleftharpoons \underset{\text{(solvant cation)}}{COCl^{\oplus}} + AlCl_4^{\ominus}$$

Prob: Explain with reasons:

ⓐ NH$_3$ is a lewis base but NF$_3$ has practically no basic character.

sol^n:

Both NH$_3$ and NF$_3$, contains one lone pairs in one sp3 hybrid orbitals. so they expected to act as Lewis base by donating the lone pair.



Hydrogen is more electropositive and 'F' is more electronegative than nitrogen atom, so bonding electron pair to each N—H bond shifts towards N- atom to increase the electron density over N- atom. Consequently NH$_3$ donate the lone pair easily and behaves as lewis base.

But in case of 'NF$_3$' the bonding electron pair of each N—F bond shifts towards the more electronegative 'F' atom to decrease the electron density over N- atom. ~~As~~ a result F shows little tendency for donation So it has no basic character.

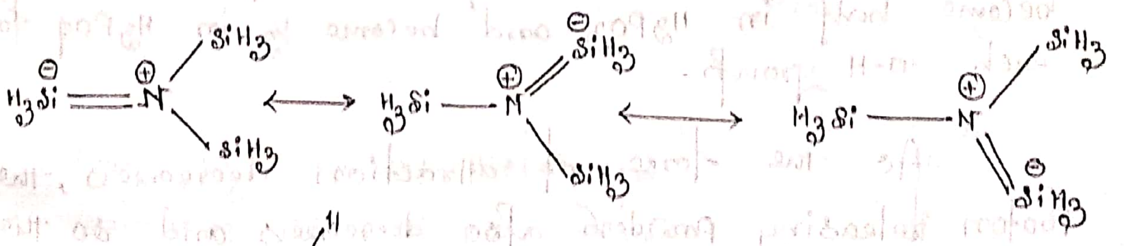
ⓑ $(SiH_3)_3N$ and $(CH_3)_3N$ react with HCl to give different product.

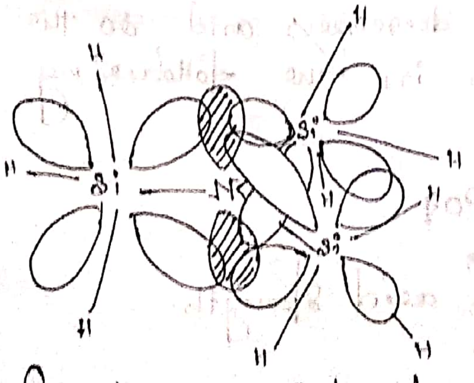
ans Trimethyl amine is pyramidal and has a donor property but trisylil amines is planar does not shows any donor properties. $(CH_3)_3N: + HCl = [(CH_3)_3N-H]^+Cl^-$

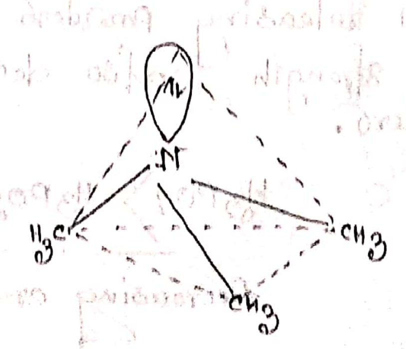
$(SiH_3)_3N: + 4HCl = NH_4Cl + 3SiH_3Cl$.

Soln:

In trimethyl amine, $(CH_3)_3N$, the N is sp^3 hybridised to provide the bond angle, $H_3C-\hat{N}-CH_3 \approx 108°$ while in trisilylamine, the nitrogen is sp^2 hybridised to make the system planar with the bond angle, $H_3Si-\hat{N}-SiH_3 \approx 120°$. In trisylyl amine, N is forced to adopt the sp^2 hybridisation to house the lone pair in a pure p-orbitals which in turn gets involved in N(2p) — Si(3d) π-bonding. As matter of the fact that, the d-orbitals on three Si atoms can participate in the pπ–dπ bonding to delocalise the lone pair over the whole molecule. Because of this involvement of the lone pair on nitrogen, it is not readily available for showing the Lewis basicity.







On the other hand, in trimethyl amine, no such π-bonding operates and the molecule assumes the pyramidal shape as result. Thus it retains the lone pair for Lewis basicity.

Prob: Strength of the oxyacid of P- vary with in the order $H_3PO_2 > H_3PO_3 > H_3PO_4$ —— explain.

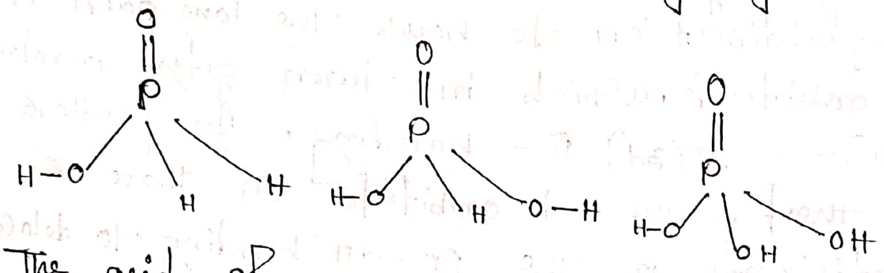
Soln

$\overset{+I}{H_3PO_2}$, $\overset{+III}{H_3PO_3}$, and $\overset{+V}{H_3PO_4}$ with increasing in +ve oxidation state, the acid strength is expected to be the following order.

$$\overset{+5}{H_3PO_4} > \overset{+3}{H_3PO_3} > \overset{+1}{H_3PO_2}$$

$$\xrightarrow[\text{decreasing order}]{}$$

But in Practice the reverse order is observed. This anomaly can be explain considering the str. and Presence of oxygenated hydrogen atoms.



The acid strength not only depends on the oxidation state. The acid strength depends upon the release of proton by braeking -OH bonds. Due to the (+ve) formal charge of 'P' it attracts the electron pair of —O—H bond. This force of attraction become half in H_3PO_3 and become ⅓ in H_3PO_4 for each -O-H group.

As the force of attraction decreases, the Proton releasing power also decreases and so the acid strength also decreases in the following order.

$$H_3PO_2 > H_3PO_3 > H_3PO_4$$

$$\xrightarrow[\text{Decreasing order of acid strength.}]{}$$

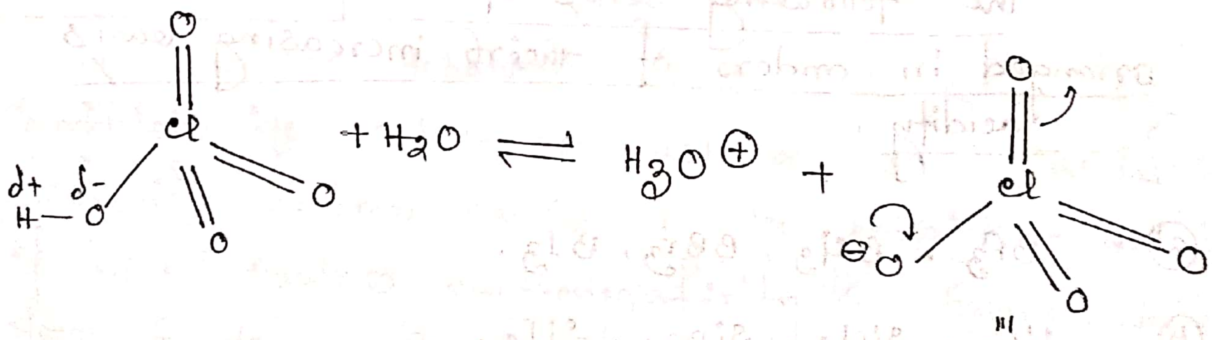
Prob: $HClO_4$ is a strongest of all the acid known— Explain?

Solⁿ:

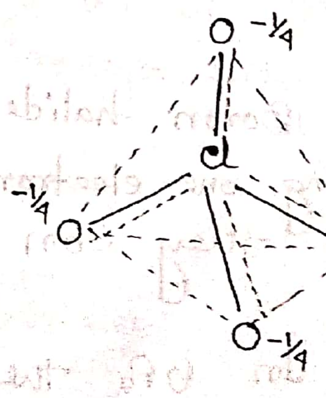
$HClO_4$ is a monobasic acid with 'Cl' atom in +7 oxidation state. For high (+ve) oxidation state of central atom 'Cl' in $HClO_4$, the polarity of $-OH$ bond is very high. So the acid readily ionises to release proton.

$$H-OClO_3 \longrightarrow H^{\oplus} + ClO_4^{\ominus}$$

The strength of the $HClO_4$ also depend on the stability of $ClO_4^{\ominus}$. The $ClO_4^{\ominus}$ is tetrahedral and the −ve formal charge get delocalised over the all oxygen atom. For symmetrical Td structure and symmetrical distribution of −ve formal charge, $ClO_4^{\ominus}$ ion is very stable.



For this reason $HClO_4$ is the strongest of all the known acid.



Prob: Although aq H_2S is stronger acid than H_2O. But liquid H_2S is much less ionise than water.

Solⁿ: For higher dielectric constant and higher dipole moment of H_2O, it brakes S–H bond in H_2S readily. So co-velent H_2S molecule ionises readily in H_2O.

$$H_2S + H_2O \rightleftharpoons H_3O^{\oplus} + HS^{\ominus}$$

$$HS^{\ominus} + H_2O \rightleftharpoons H_3O^{\oplus} + S^{=}$$

for greater degree of proton release the aqueous solution of H_2S acts strongly acidic, S–H bond is pourely co-velent as the electronegativity difference between H and S is negligible, so in absence of H_2O, H_2S ionised very little.

Prob:

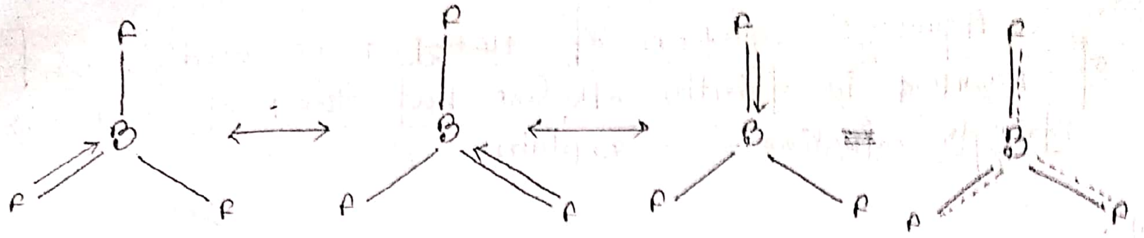
The following series of compounds can be arranged in order of their increasing lewis acidity.

ⓐ BF_3, BCl_3, BBr_3, BI_3.

ⓑ SiF_4, $SiCl_4$, $SiBr_4$, SiI_4.

Solⁿ: Boron halide are electron deficient molecule having one electron pair short to full field octate. So they can act as a lewis acid.

In BF_3 the electron deficiency is removed to some extent by intramolecular back bonding by lateral overlap of field p-orbital of F-atom with empty 2p-orbital of B-atom.



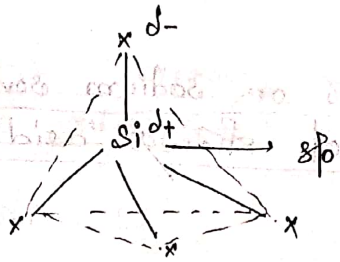
The size of the halogen gradully increase from F to I. With increase the size of halogen atom, π- bonding ability gradully decreases, which making the '2P' - orbital of 'B' atom more and more available for acceptance of electron pairs. So lewis acidity of ~~BnF due to~~ the Boron halide increases with increasing the size of the halogen atom. So increasing lewis acidity order of Boron halide will be —

$$BF_3 < BCl_3 < BBr_3 < BI_3 .$$

$$\xrightarrow{\hspace{4cm}}$$

increasing order of lewis acidity.

ⓑ In silicon tetrahalide SiX_4, Si-atom has completely ~~its~~ octate. It act as lewis acid by accepting electron pairs in the empty 'd' orbitals of 'Si'. Agains electronegativity of halogen decreases from F to I. So formal charge on 'Si' gradully decreases with decrease in electronegativity of halogens.



With the decrease in formal charge on Si the electron accepting powers of the molecule gradully decreases. Hence the following orders of lewis acid strength of silicon halide —

$$SiI_4 < SiBr_4 < SiCl_4 < SiF_4$$

Prob:

Aqueous solution of NaH_2PO_4 is acidic, that of Na_2HPO_4 is faintly alkaline but that of Na_3PO_4 is strongly alkaline — explain.

Solⁿ:

An aq. solution of NaH_2PO_4 ionises into $Na^{\oplus}$ and $H_2PO_4^{\ominus}$ which again ionises to give proton.

$$NaH_2PO_4 \rightleftharpoons Na^{\oplus} + H_2PO_4^{\ominus}$$

$$H_2PO_4^{\ominus} \rightleftharpoons H^{\oplus} + HPO_4^{=}$$

As the proton is released in the second stage so the aq. solution of NaH_2PO_4 is acidic.

In aqueous solution of Na_2HPO_4 hydrolyse partially and reversibly to produced a mixture of weak acid NaH_2PO_4 and strong $NaOH$, $NaOH$ ionise to give $OH^{\ominus}$ ion, so aq solⁿ acts alkaline.

$$Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH$$

$$NaOH \rightleftharpoons Na^{\oplus} + OH^{\ominus}.$$

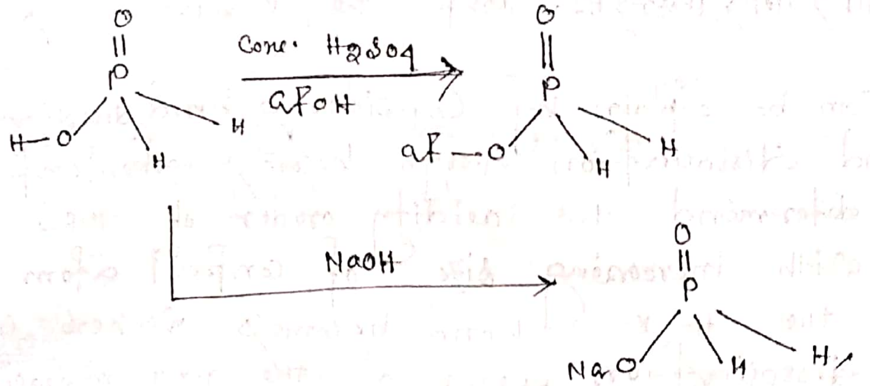
In aq. solⁿ of Na_3PO_4 hydrolyse partially and reversibly producing a mixture of weak base Na_2HPO_4 and a strong base $NaOH$. So the aqueous solⁿ of the salt acts as strongly alkaline.

$$\underset{}{Na_3PO_4} + H_2O \rightleftharpoons \underset{(W.B)}{Na_2HPO_4} + \underset{(S.B)}{NaOH}.$$

Prob:

Mono ethyl ester or sodium salt of hypophosphrous acid does not shows acid characters — Explain.

Solⁿ: Hypophosphrous acid is a monobasic acid containing only one oxygenated hydrogen atom. The hydrogen atom in $-O-H$ group is acidic and is replaced by ethyl group or methyl to form mono-ethyl or methyl esters or salt.



The others two hydrogen atoms which are directly linked with P-atom are not at all acidic. As there is no acidic hydrogen. So mono-ethyl esters of hypohosphohrous acid has no. acidic property.

Prob:

FACTOR EFFECTING THE ACID STRENGTH OF SOME ACIDS:

Ⓐ Bond dissociation energy.
Ⓑ Electronegativity of central atom.
Ⓒ Oxidation state of the central atom.
ⓓ Solvation energy of the central atom.

BOND DISSOCIATION ENERGY:

Ⓐ With decreasing the bond dissociation energy of a hydracid, the acidity of a hydracid increases.

Prob:

Arrange the increasing order of acidity and give reason in this case:

① HF, HCl, HBr, HI
⑪ NH_3, HF, H_2O, CH_4.

① Electronegativity of the halogen obey the following order F > Cl > Br > I and the acidity order of the hydracid should be HF > HCl > HBr > HI. But the observation is reversed.

This can be explain by considering bond dissociation energy. Bond dissociation energy becomes important factor to determind the acidity order of the hydracid. With increasing size of central atom (F, Cl, Br, I) the H–X bond becomes weaker hence bond dissociation energy of the given hydracid are $\underrightarrow{HF > HCl > HBr} > HI$, decreasing the bond dissociation energy, facilitates the release of $H^{\oplus}$ and acidity increases. The increasing order of acidity of hydracid will be $HF < \underrightarrow{HCl < HBr < HI}$.

⑪ It has been observed that, in a periodic electronegativity effect decided the acidity of the hydracid. The central atom of each hydracids belong to 1st Period with electronegativity order F < N < O < F, With increasing the electronegativity of the central atom, H–X bond polarity increases, as a result dissociation of $\overset{\delta+}{H}-\overset{\delta-}{X}$ bond to release $H^{\oplus}$ ions becomes easier. The acidity order of the hydracid will be

$$CH_4 < \underrightarrow{NH_3 < H_2O} < HF$$

increasing order of acidity.

Prob:

Arrange the acidity order of the following hydracid.

H_2Te, H_2Se, H_2S, H_2O.

Similar answer Q. No. ①.

Ⓑ Electronegativity of the central atom:

With increasing the electronegativity of the central atom of an oxiacid, the polarity of a $-O-H$ bond increases (If central atom having same oxidation state) As a result acidity of an oxiacid increases.

Prob: Arrange the acidity order of the following oxiacid.

i) $HClO_4$ and HIO_4 (ii) H_2SO_3 and H_2SeO_3.

Soln (i) The electronegativity of the central atom of an oxiacid plays an important role (If the oxidation state of the central atom is same) to determine the acidity of the oxiacid. With increasing the electronegativity of the central atom for same oxidation state the $-O-H$ bond becomes more polar and acidity of the oxiacid increases.

The electronegativity order of the above two central atom of two compound becomes $Cl > I$ and $S > Se$. So the acidity order of the oxiacid will be $HClO_4 > HIO_4$ and $H_2SO_3 > H_2SeO_3$.

Prob: Arrange the acidity order of the following oxiacid.

(i) $HOCl$, $HOBr$, HOI (ii) $HClO_3$, $HBrO_3$, HIO_3.

Soln: The oxidation state of the central atom of the above oxiacid series are same. So the acidity order of the oxiacid can be explain on the basis of their electronegativity of the central atom (X). As the electronegativity of the central atom decreases as we move from Cl to I, the tendency of the central atom to attract the electron pair of X—O bond towards itself decreases and hence rupture of O—H bond also decreases. The acid having the central atom with maximum electronegativity value will give $H^{\oplus}$ ions quite easily. So the order of the acid strength of the oxiacid will be —

$$\underrightarrow{HOI < HOBr < HOCl}$$

increasing order

Similar answer:

decreasing order of acidity.

① $\underrightarrow{H\overset{+5}{Cl}O_3 > H\overset{+5}{Br}O_3 > H\overset{+5}{I}O_3}$

(ii) $\underrightarrow{H_2SO_4 > H_2SeO_4 > H_2TeO_4}$

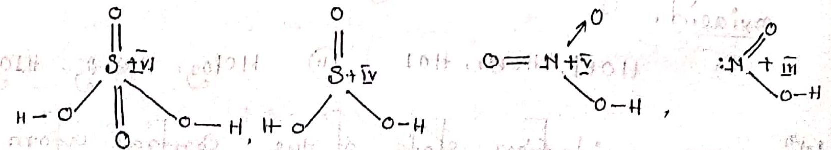
(iii) $\underrightarrow{H_3PO_4 > H_3AsO_4 > H_3SbO_4}$

(iv) $\underrightarrow{HNO_3 > HPO_3 > HAsO_3}$.

ⓔ Compare the acid strength of the following oxiacid.

(i) H_2SO_4 and H_2SO_3 (ii) HNO_3 and HNO_2.

Sol^n Acidity of the oxiacid increases with increasing in the oxidation state of the central atom.



Besides for their non hydrogenated 'O' atom by virtue of their strong −I effect, creates more (+ve) charge density on the central atom.

Which make the -O-H bond in the oxiacids more polar and increase acidity. There are two factors acts in the same line and the acidity order will be the following order.

$$\underrightarrow{H_2SO_4 > H_2SO_3}$$ decreasing order of acidity. , $$\underrightarrow{HNO_3 > HNO_2}$$ decreasing order of acidity.

Similar answer:

$$\underrightarrow{\overset{+1}{HOCl} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}}$$ increasing order of acidity.

$$\underrightarrow{\overset{+1}{HOI} < \overset{+3}{HIO_2} < \overset{+5}{HIO_3} < \overset{+7}{HIO_4}}$$ increasing order.

$$\underrightarrow{\overset{+6}{H_2MnO_4} < \overset{+7}{HMnO_4}}$$

Prob: Identify the conjugate acid and bases of the following species.

$HCO_3^{\ominus}$, $HSO_4^{\ominus}$, $HSO_3^{\ominus}$, $HS^{\ominus}$, $HPO_4^{2\ominus}$, $H_2PO_4^{\ominus}$

Soln:

An acid - release (gives up) proton to produced its conjugate base while a base accepts proton to produced its conjugate acid.

Species

$$H_2CO_3 \xleftarrow{+H^{\oplus}} HClO_3 \xrightarrow{-H^{\oplus}} CO_3^{=}.$$

$$H_2SO_4 \xleftarrow{+H^{\oplus}} HSO_4^{-} \xrightarrow{-H^{\oplus}} SO_4^{=}$$

$$H_2SO_3 \xleftarrow{+H^{\oplus}} HSO_3^{-} \xrightarrow{-H^{\oplus}} SO_3^{2-}$$

$$H_2S \xleftarrow{+H^{\oplus}} HS^{-} \xrightarrow{-H^{\oplus}} S^{=}$$

$$H_2PO_4^{\ominus} \xleftarrow{+H^{\oplus}} HPO_4^{=} \xrightarrow{-H^{\oplus}} PO_4^{3\ominus}$$

$$H_3PO_4 \xleftarrow{+H^{\oplus}} H_2PO_4^{-} \xrightarrow{-H^{\oplus}} HPO_4^{=}$$

Prob: Arrange the following species in order of their increasing proton affinity.

CH_3^-, $I^{\ominus}$, $Cl^{\ominus}$, $OH^{\ominus}$.

Sol^n^: Conjugate acids of the following species are —

Base		Conjugate acid.
$CH_3^{\ominus}$	$\xrightarrow{+H^{\oplus}}$	CH_4
$I^{\ominus}$	$\xrightarrow{+H^{\oplus}}$	HI
$Cl^{\ominus}$	$\xrightarrow{+H^{\oplus}}$	HCl
$OH^{\ominus}$	$\xrightarrow{+H^{\oplus}}$	H_2O

Conjugate base of the weak acid are stronger and their proton affinity will also be stronger and vice versa.

The increasing order of acidity of the conjugate acids are $\underrightarrow{CH_4 < H_2O < HCl < HI}$ so, their corresponding base strength will be $\underrightarrow{I^{\ominus} < Cl^{\ominus} < OH^{\ominus} < CH_3^{\ominus}}$. So proton affinity of the above charged ions are in the following order.

$$\underrightarrow{I^{\ominus} < Cl^{\ominus} < OH^{\ominus} < CH_3^{\ominus}}$$

Increasing order of proton affinity.

Similar

Prob: Arrange the following species in order of their increasing proton affinity $HS^{\ominus}, F^{\ominus}, I^{\ominus}, NH_2^{\ominus}$

Soln: Conjugate acid of the following species are

$$\text{base}\left\{\begin{array}{l} HS^{\ominus} + H^{\oplus} \longrightarrow H_2S \\ F^{\ominus} + H^{\oplus} \longrightarrow HF \\ I^{\ominus} + H^{\oplus} \longrightarrow HI \\ NH_2^{\ominus} + H^{\oplus} \longrightarrow NH_3 \end{array}\right\} \text{— Conjugate acid.}$$

HI is a strongest acid among the all acids of the above series. due to its small dissociation energy. HF is stronger acid than H_2S due to higher electronegativity of F atom and NH_3 is the weakest acid due to its basic character.

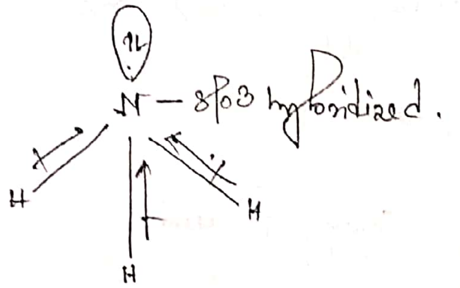
So, the acidity order of the conjugate acid is $\underrightarrow{NH_3 < H_2S < HF < HI}$. The basicity of the above bases are increases with decreasing the acidity of the conjugate acids. So the increasing order of their proton affinity will be $\underrightarrow{I^{\ominus} < F^{\ominus} < SH^{\ominus} < NH_2^{\ominus}}$.

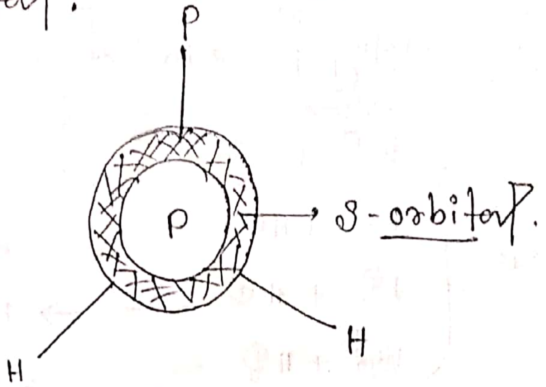
Prob: Discuss the base strength of NH_3 and PH_3.

Soln: From the structural characteristic of NH_3: $H-\hat{N}-H \simeq 107°$ and PH_3: $H-\hat{P}-H \simeq 90°$ it is evident that in NH_3, N- is almost sp^3 hybrid orbital and one hybrid orbital contain one lone pair. As a result NH_3 donate its lone pair easily to the other species act as base.

But due to larger energy difference and size difference between 1s orbital of hydrogen and 3s and 3p orbital of P atom, P- using almost

Pure p-orbital for the formation of PH_3 molecule. In PH_3, lone pair is getting housed in an almost pure s-orbital.





The s-electron are more tightly bound in PH_3 and hence it has no. directive property. the lone pair on PH_3 can not be easily donated compared to the case of NH_3.

Prob:

Pick out and Justify:

(i) Thermally most stable: NH_4Cl, PH_4Br, PH_4I

(ii) Most acidic oxide: Ag_2O, V_2O_5, CO, N_2O_5

(iii) Stronger base towards a proton: $NH_2^{\ominus}$, $PH_2^{\ominus}$.

Solⁿ:

Thermal stability refers to the general reaction type

$$PH_4X \longrightarrow PH_3 + HX$$

In a series of HX acids ($X = Cl, Br, I$) case of decomposition will increase with the stability of HX, that is with decreasing acid strength. HI strongest acid ($I^{\ominus}$ has the lowest proton affinity) and hence PH_4I is expected to be thermally most stable.

However, lattie energy would decrease with increases in anion size, ie from PH_4Cl to PH_4I. This does not significantly alters the primary acid strength.

(ii) The oxide of with the highest positive charge on the element other than O should be most acidic. Oxidation state of V in V_2O_5 and N in N_2O_5 are both +5. But the electronegativity of N is higher making N_2O_5 the most acidic oxide.

(iii) The conjugate acid of the following ~~acids~~ species are $\overset{\ominus}{PH_2} \xrightarrow{H^{\oplus}} PH_3$ and $\overset{\ominus}{NH_2} \xrightarrow{H^{\oplus}} NH_3$ ie PH_3 and NH_3 respectively.

'N' and 'P' belong to the same group in the periodic table, 'P' has the larger size than 'N' hence P–H bond in PH_3 is weaker than N–H bond in NH_3 ie bond dissociation energy of PH_3 is ~~higher~~ smaller than NH_3.

Hence 'PH_3' is a strongest acid than NH_3 Consequently $\overset{\ominus}{NH_2}$ is the strongest conjugate base of weaker acid NH_3.

Prob: Which of the following halides is the most acidic? — Explain.

ⓐ PCl_3 ⓑ $SbCl_3$ ⓒ $BiCl_3$ ⓓ CCl_4

Sol^n:

Since C atom in CCl_4 molecules has no vacant orbitals in its valence shell, this atom can not accept electron pair donated by a donor molecule or ion and hence does not show any acidic properties.

On the other hand, due to the presence of vacant d- orbitals in the valence shell in P, Sb, Bi, PCl_3, $SbCl_3$ and $BiCl_3$ molecule can accept electron pair donated by donor molecule and shows acidic properties.

Since Bi atom is the largest in size, $BiCl_3$ molecule will shows maximum tendency to accept the electrons donated by a Lewis base. Thus $BiCl_3$ is the most acidic.

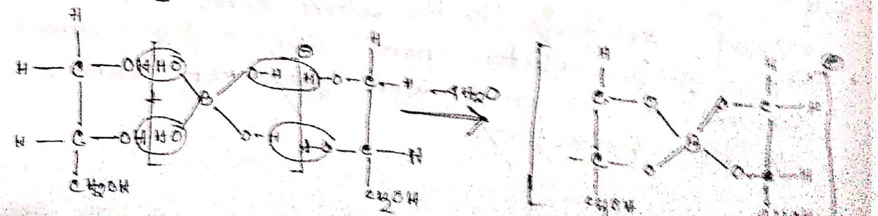
Prob:

"Boric acid behaves as a strong acid in presence of glycerol or any other cis – diol" — Comment.

Solⁿ: H_3BO_3, itself does not ionise in aqueous to produced $H^{\oplus}$. It shows acidic character by the accepting of $OH^{\ominus}$ from H_2O so it is behaves as weak monobasic Lewis acid.

$$H_3BO_3 + H{-}O{-}H \rightleftharpoons [B(OH)_4]^{\ominus} + H^{\oplus}.$$

The acidity of H_3BO_3 in aqueous media depend on the stability of the conjugate base $[B(OH)_4]^{\ominus}$. In presence of cis. diol or glycerol, $[B(OH)_4]^{\ominus}$ got stabilised during the formation of chelate complex. So the concentration of $(H^{\oplus})$ ion increases in aqueous medium as the stability of $B(OH)_4^{-}$ increases. So. in presence of cis - diol or glycerol H_3BO_3 act as strong monobasic acid.



Prob: Arrange the acidic strength of the given oxide with reasons —

① SO_2, P_4O_{10}, Cl_2O_7.
(ii) SO_2, CO, N_2O_5, CO_2
(iii) Na_2O, MgO, Al_2O_3.

Solⁿ:

(i) All the given oxides in ① are the oxide of P, S and Cl which are present in the same period. (3rd Period). Since the metallic characters of P, S, Cl decreases from left to right ($P \rightarrow S \rightarrow Cl$), the basic characters of their oxide also decreases as $P_2O_5 > SO_2 > Cl_2O_7$. or acidic character increases as $P_2O_5 < SO_2 < Cl_2O_7$.

(ii) CO is neutral oxide, since it reacts neither with an acid nor with a base, N_2O_5, SO_2, CO_2 on reacting with H_2O, gives HNO_3, H_2SO_3 and H_2CO_3 respectively. Out of this acids HNO_3 is strongest acid and H_2CO_3 is the weakest acid. Thus the acidic character of N_2O_5, SO_2 and CO_2 is in the order $N_2O_5 > SO_2 > CO_2$. Consequently acidic character of all the given four oxides is in the order

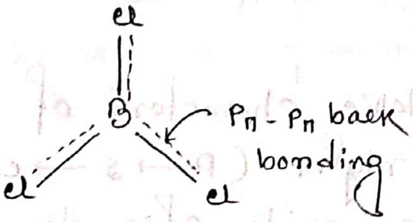
$$\underrightarrow{N_2O_5 > SO_2 > CO_2 > CO}$$

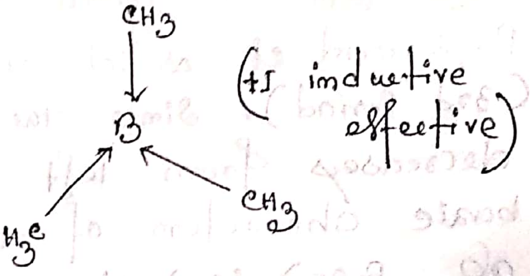
(iii) Since Na_2O and MgO are the oxide of highly electropositive metals (Na - alkali metal and Mg - alkaline earth metal), these are highly basic oxide. Since Mg has lesser metallic (basic) character than Na. MgO is less basic than Na_2O and MgO is more acidic than Na_2O. Al_2O_3 is amphoteric oxide. Thus the acidic character of Na_2O, MgO and Al_2O_3 is in the order

$$\underrightarrow{MgO > Na_2O > Al_2O_3}.$$

Prob: Which would you expect to be a better lewis acid BCl_3 and $B(CH_3)_3$. —— Explain.

Soln: In Both Compound Contains 'B' atom which has vacant 'p' orbitals in its valence shell. So it can accept electron pairs and behaves as a lewis acid.





Due to +I effect of $-CH_3$ group electron density on the 'B' atom in $B(CH_3)_3$ increases i.e electron deficiency of B atom decreases.

But in case of BCl_3, due to the formation of internal Pπ – Pπ bonding between vacant 'p' orbital of 'B' atom and filled 'p' orbital of 'Cl' atom, the electron deficiency of 'B' in BCl_3 decreases.

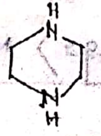
But internal π- bonding predominants over the inductive effect (+I effect) of $-CH_3$ group and the extent of decrease of electron deficiency in BCl_3 ~~because~~ becomes greater than that of $B(CH_3)_3$. Thus $B(CH_3)_3$ is better lewis acid than BCl_3.

Prob: Arrange ~~the~~ basic strength of the following species

(i)

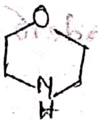
Piperidine.

~~>~~ ,



Piperazine

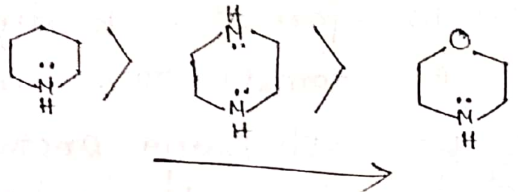
,



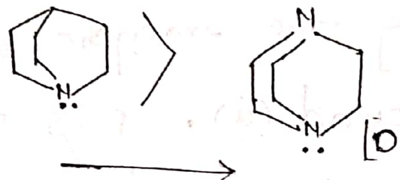
Morpholine

Solⁿ: ① Piperazine is less basic than piperidine, morpholine is less basic than Piperadine.

This is occure due to the introduction of an extra hetero atom (eg N, O) that shows the electron withdrawing inductive effect. Thus the order will be



Similarly



[DABCO]

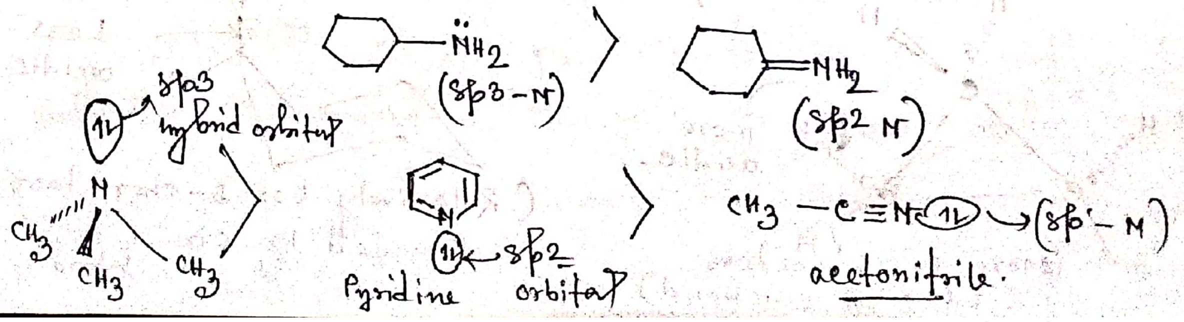
1,4 – Diazabicyclo –[2,2,2] –octane.

Prob: Discuss the role for the state of hybridisation of the central atom governing the acid and basic strength.

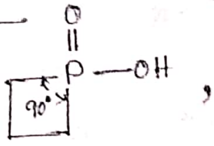
Solⁿ: If the central atom utillises its hybrid orbitals having more s- character to bind an acidic H or -OH group from which the Proton is released, the acid strength become higher, the higher s-character indicates the higher electron withdrawing force. Thus the acid strength run as —

$$HC \equiv C—H\ (sp-c) > H_2C = CH—H\ (sp^2-c) > H_3C—CH_2—H\ (sp^3-c).$$

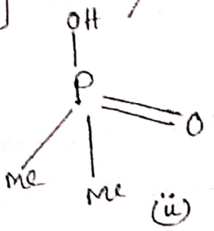
Relative basicity order:



Prob: Among the following species which is more acidic —



(i)



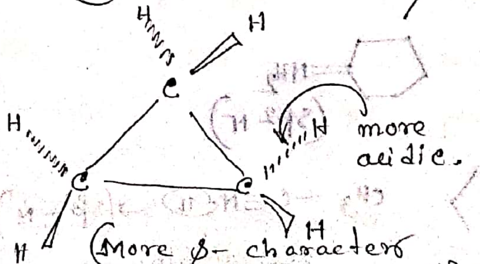
(ii)

Sol^n Between the oxiacids of P, in the cyclic compound (i) the bond angle $-CH_2-P-CH_2-$ is ~90°. For this purpose, 'P' uses its two almost pure p-orbitals for the bonding purpose towards the adjacent C-atoms. Thus in the residual bonds, the s-orbital and another p-orbital of P are distributed. It leads to ~50% s-character to each of the bonding orbitals of P for making the exocyclic bonds.

In compound (ii), P is roughly Td hybridised having s-character about ~25% in each bond. This is why, the cyclic one is stronger acid than the tetrahedral one.

Prob: Compare the acid strength cyclopropane and cyclohexane.

Sol^n: The C—Ĉ—C bond angle in cyclopropane is much smaller compared to that in cyclohexane. This is why, it making the C—C bonds, more p-character is concentrated in cyclopropane compared to that in cyclohexane. Consequently, more s-character is concentrated it making the outer C—H bonds in cyclopropane. It make the C—H bonds of cyclopropane more acidic.



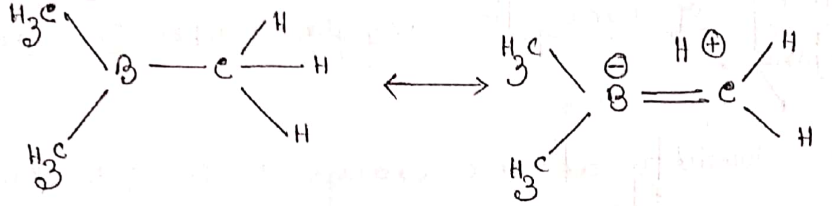
(More s- character provided by C in C—H bond)

(Relatively less s-character provided by C in C-H bond)

Prob: Compare the Lewis acidity, BMe_3 Vs $AlMe_3$

Sol^n:

Now let us consider the relative Lewis acidity of BMe_3 and $AlMe_3$ towards Me_3N. Here $AlMe_3$ forms a stronger adduct. In BMe_3, to remove the electron deficiency on B-centre, hyperconjugation occurs.



This makes BMe_3 an weaker Lewis acid. Besides this, in the adduct of BMe_3 the steric hindrance is also much larger compared to that ~~of~~ in the adduct of $AlMe_3$. It is due to the smaller size of B compared to that of Al.

Here it would be mentioned that $AlMe_3$ remains as a dimer Al_2Me_3 through the 3c−2e Al—C—Al bridge. This weak 3c—2e bond is replaced by strong 2c—2e bond during the adduct formation

$$Al_2Me_6 + 2NMe_3 \longrightarrow 2\,Me_3Al \leftarrow NMe_3.$$

Prob: Compared the acid strength of R_3COH Vs R_3SiOH.

Sol^n:

R_3SiOH is a stronger Bronsted acid than R_3COH because of the O—Si π-bonding. In fact, the conjugate base R_3SiO^- is stabilised through the π-bonding. The higher the acid strength of R_3SiOH compared to that of $R_3C{-}OH$ arises mainly from the resonance stabilisation of the conjugate base $R_3Si{-}O^\ominus$ in which the vacant d-orbital of silicon participate in pi-bonding to delocalise the negative charge. In other words, the

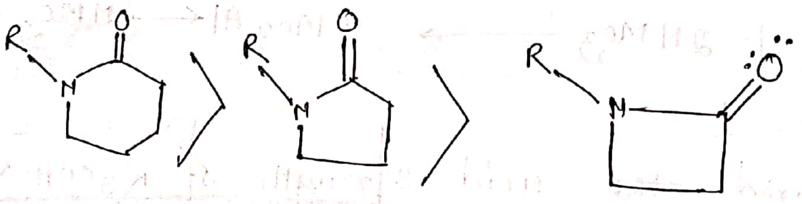
The said O(2P) ⟶ Si(3d) π- bonding in the undissociated R_3SiOH places a +ve charge on the oxygen site to favour the deprotonation process

$$R_3\overset{\ominus}{Si}=\overset{\oplus}{O}-H \longleftrightarrow R_3Si=O]^{\ominus}+H^{\oplus}$$

. This is ~~not~~ absent in R_3COH.

Prob: Basicity of exocyclic oxygen centre in lactams and lactones.

Sol: The basicity of the exocyclic oxygen centre in the lactams and lactones is noticed. As the ring size decreases, the internal bond angle decreases and the p-characters are gradually enriched in the cyclic bonds and consequently the s-character is getting concentrated towards the exocyclic bond. Thus the basicity (which decreases with the increase ~~the~~ s-character projected by carbon towards the exocyclic oxygen) of the excocyclic carbonyl oxygen runs in the lactums as indicated.



STERIC FACTORS :

F-strain and B- strain.

The steric factor (more correctly, F- strain) for simple protonation and deprotonation equilibria is not very much important, but in the aduct formation involving the bulkier Lewis acids and bases, the steric factors becomes very much important. There are two types of steric hindrances i.e front strain (F- strain and B- strain)

1. F – strain :

When lewis acid and base are having the bulkier substituents, in the adduct there will be a steric interaction among the substituents on the acid and base. This phenomenon is simply referred to as steric hindrance in older literature. In such cases, the protonation and deprotonation equilibria are not much effected because of the very tiny size of H.

Example:

ⓐ $(CH_3CH_2CH_2C)_3N: \longrightarrow B(CH_2CH_3)_3$: Here the n-Propyl groups on the base are free to rotate around the single bonds in space. Similarly, the ethyl groups on the acid are also free to rotate in space. Thus in the adduct, the substituents on the acid and base will mutually experience a steric crowding.

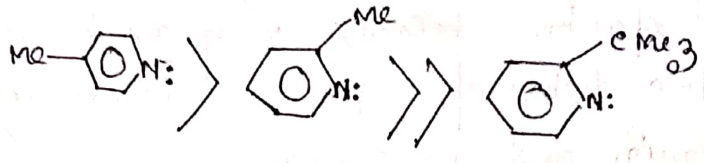
ⓑ Lewis base strength of Pyridine and its substitute derivatives towards BMe_3.

The stability sequence of the adducts formed

ⓑ Lewis base strength of pyridine and its substituted derivaties towards BMe_3.

Soln: The stability sequence of the adducts formed with the lewis acid BMe_3 by the different bases runs as indicated.

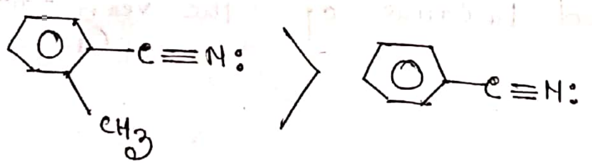
$Me_3N > Et_3N$;



The enhance the stability of the adduct for the base 4-Picoline may be accounted for its enhanced basicity due to electron releasing effect of the methyl group. The decrease stability for 2-Picoline and 2-(t-butyl)-Pyridine arises definitely due to the F-strain.

Note:

2-Me(C_6H_4)CN forms a stabler adduct than (C_6H_4)CN with BMe_3.



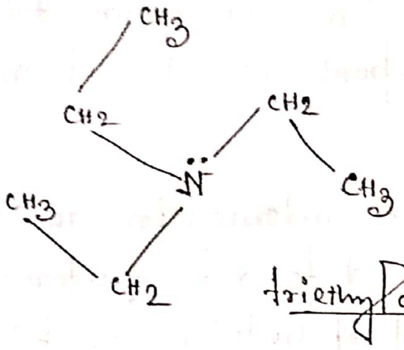
Here the donar site 'N' of the 'CN' group is far away from the methyl group. Thus the F-strain is not important in the adduct due to the Me group, but the electron pushing inductive effect of the Me-group favours the Lewis basic character of the CN group.

ⓒ Basicity of Triethylamine and bicyclic amine, quinuclidine (a bridged piperidine):

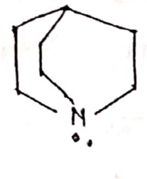
Soln:

Compared to $N(C_2H_5)_3$, quinuclidine forms a stabler adduct with BMe_3. Here $N(C_2H_5)_3$ is also suffering from the B- strain. ~~which will be~~ ~~discuss latter~~.

However, as the methyl groups in quinuclidine are folded back behind the nitrogen, the F- strain in the adduct is less compared to that existing in the adduct formed by $N(C_2H_5)_3$ in which the ethyl groups can freely rotate in space.



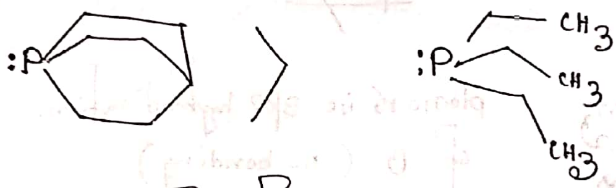
triethylamine.



Quinuclidine.

Similarly:

bicyclic phosphine $:P(C_2H_4)_3CH$ is more basic than $:P(C_2H_5)_3$.



Note: It is to interesting to note that in terms of Bronsted basicity (Protonation) where steric crowding is not important, ~~the free base~~ triethylamine, piperidine and quinuclidine — a bridged piperidine are almost equally base.

2. B-strain :

In attaining the structure of the adduct, sometimes, some sort of configurational change in the acid or base or the both may be required. Their will be require the reorganisation energy. If the substituents of the free acid or base favours a particular configuration for its stability, but this configuration may not be suitable for the adduct formation then the B-strain is highly important to determine the acid-base strength.

The configuration adopted in the free species may be governed by different factors such as, steric factor (i.e effect of bulkier groups), π-bonding interaction and cost of hybridisation.

	Free species	Configuration in free species	Required configuration in the adduct.
i)	BF_3, BCl_3, BBr_3 Lewis acids	planar i.e sp^2-hybridisation of B (π-bonding)	Tetrahedral sp^3-arrangement.
(ii)	PH_3 (Lewis base)	($H-\hat{P}-H \simeq 90^\circ$ (i.e almost pure p-orbitals in bonding lone pair housed in almost pure p-orbital))	($H-\hat{P}-H \simeq 109^\circ$ sp^3 almost hybridisation of P)
(iii)	$(SiH_3)_3N$ (Lewis base)	sp^2-hybridisation of N, (π-bonding)	sp^3-hybridisation of N,
(iv)	$N(C_2H_5)_3$ [Lewis base]	N-tends to have sp^2-hybridisation to relux the steric crowding.	N-tends to adopt sp^3-hybridisation.
(v)	Trimesityl borane and BR_3 (Lewis acid)	sp^2-hybridisation of B to relive the steric crowding,	sp^3-hybridisation of B.

Here it is important to mention that though the F-strain has nothing to do with the protonation and deprotonation equilibria, the B- strain is important in all type of lewis acid base adducts including $H^{\oplus}$ as the lewis acid.