Acid & Bases

① Arrhenius concept :- (1887)

An acid is a substance which dissociates in aqueous solⁿ to give hydrogen ions

e.g.

$$HCl \xrightarrow{H_2O} H^+_{(aq.)} + Cl^-_{(aq.)}$$

$$HNO_3 \xrightarrow{H_2O} H^+_{(aq.)} + NO_3^-{}_{(aq.)}$$

$$CH_3COOH \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

General,

$$HA \overset{H_2O}{\rightleftharpoons} H^+_{(aq)} + A^-_{(aq.)}$$

Base :- Base is substance which dissociates in aq. solⁿ to give hydroxyl ion

e.g.

$$NaOH \xrightarrow{H_2O} Na^+_{(aq.)} + {}^-OH_{(aq.)}$$

$$NH_4OH \xrightarrow{H_2O} NH_4^+{}_{(aq.)} + {}^-OH_{(aq.)}$$

$$Ca(OH)_2 \xrightarrow{H_2O} Ca^{++}_{(aq.)} + 2\,{}^-OH_{(aq.)}$$

gives fast H^+

In General $BOH \rightleftharpoons B^+_{(aq.)} + {}^-OH_{(aq.)}$

Thus, According to Arrhenius concept,

Acid gives H^+ ions in water, bases gives ${}^-OH$ in water

The strength of the acid & bases depends upon its capacity of ionisation to H^+ or ${}^-OH$ ion respectively.

HCl, HNO_3, H_2SO_4 – ionised completely in water – strong acid.

CH_3COOH, HCN – weak acid.

IIly, ~~NH_4~~, $NaOH$, KOH – strong base, NH_4OH, $Ca(OH)_2$ – weak base

② Bronsted - Lowry concept :-

The Arrhenius concept of acids & bases was exten further by Bronsted & Lowry (1923)

According to Bronsted - Lowry concept

Acid → An Acid is a substance which can donate Proton (H^+

Base → A base is substance which can accept a proton (H^+)

e.g. 1) $HCl + NH_3 \rightleftharpoons \overset{+}{NH_4} + \overset{-}{Cl}$

A B.

$\overset{-}{Cl} \xrightarrow{H^+} HCl.$

Base

2) $\overset{+}{NH_4}{}_{(aq.)} + H_2O \rightleftharpoons \overset{+}{H_3O} + NH_3$

Acid Base

$NH_3 \xrightarrow{H^+} \overset{⊕}{NH_4}$

Base.

Neutralis^n : 3) $NaOH + HCl \rightleftharpoons NaCl + H_2O$

The acid-base reac^n is known as Proton transfer reac^n.

There are certain substances such as H_2O, HCO_3^-, HSO_4^- etc which are capable of donating as well as accepting the Proton. These substance are called amphoteric substance.

e.g.:- $HCl + H_2O \rightleftharpoons \overset{+}{H_3O}{}_{(aq.)} + \overset{-}{Cl}{}_{(aq.)}$

Acid base

$H_2O_{(l)} + NH_3 \rightleftharpoons \overset{+}{NH_4}{}_{(aq.)} + \overset{-}{OH}{}_{(aq.)}$

Acid Base.

H.W.,

$\overset{-}{HCO_3} + NH_3 \rightleftharpoons \overset{+}{NH_4}{}_{(aq.)} + \overset{2-}{CO_3}{}_{(aq.)}$

Acid.

$HCl + H\bar{CO_3} \rightleftharpoons H_2CO_3{}_{(aq.)} + \bar{Cl}_{(aq.)}$

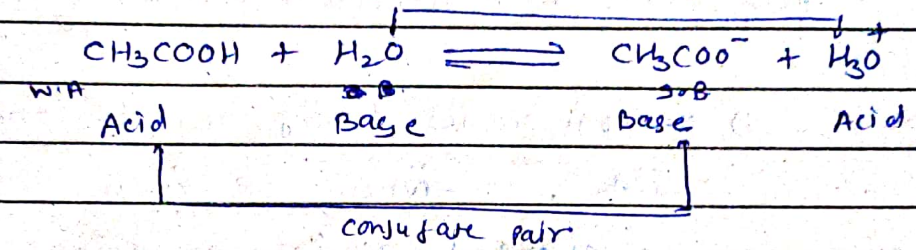
Base.

- It is noted that all Arrhenius acids are also Bronsted acids but Arrhenius bases are not Bronsted bases.
- When an acid loses a proton, the residual part of it has a tendancy to regain the Proton. ∴ it behaves as a base.

$$Acid \rightleftharpoons \overset{+}{H} + Base.$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

consider ionisation of acetic acid in water.



$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

- In above reac^h acetic acid donates a proton to water & thus acts as acid. - Water accepts a proton & therefore acts as a base.
- In the reverse reac^h hydronium ion donates a proton to the acetate ion & therefore acts as an acid. The acetate ion accepts a proton & therefore behaves as a base.

⇒ ∴ "such pair of substances which can be formed from one another by the gain or loss of proton are known as conjugate acid-base pairs".

Advantages of B-L concept over Arrhenius :-

1) It can explain basic character of substances like Na_2CO_3, NH_3 etc. which donot contain ^-OH group.

2) This concept is not limited to molecules but also covers even the ionic species to act as acid or bases

3) It explain the acid-base reac^h in the non-aqueous medium also

* All Bronsted ~~acid~~ bases are also Lewis bases but all Bro acids are not Lewis acid.

③ **Lewis concept of acids & Bases:-**

G.N. Lewis (1923)

According to this concept. "Acid is substance which can accept pair of $\bar{e}$" While Base is substance which can donate a pair of $\bar{e}$.

$$A + :B \longrightarrow A-B$$

Lewis Acid Lewis Base

∴ Acid are $\bar{e}$ pair acceptors. Base are $\bar{e}$ pair donors.

Lewis Base :- 1) Neutral species having at least one pair of $\bar{e}$.

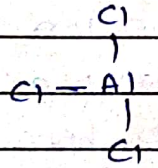
$\ddot{N}H_3$, $-\ddot{N}H_2$, $R-\ddot{O}-H$

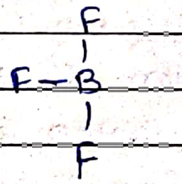
2) Negatively charged species or anions : (Nucleophiles)

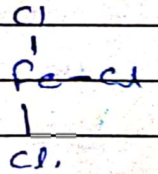
$C\bar{N}$, $\bar{C}l$, $\bar{O}H$ etc - are lewis base.

Lewis Acids :- 1) molecules in which the central atom has incomplete octet

e.g.







2) simple cations can acts as Lewis acid because they are deficient in $\bar{e}$s. (electrophiles).

e.g. $Ag^+ + \ddot{N}H_3 \longrightarrow [H_3N \longrightarrow Ag \longleftarrow NH_3]^+$

L. Acid L. Base

3) molecules in which the central atom has empty d-orbitals

Eg SiF_4, $SnCl_4$, PF_5 etc $AlCl_3$, AsF_6, SbF_5 etc

$$SiF_4 + 2\bar{F} \longrightarrow [SiF_6]^{2-}$$

Acid base

4) molecules in which atom of disimillar electro-vities are joined by multiple bonds.

$O=S=O$ 2.5 3.5 3.5

e.g. $O=C=O + \bar{O}H \longrightarrow \bar{O}-\overset{\overset{OH}{|}}{C}=O$ or HCO_3

L-Acid L. Base Bicarbonate

e-g

$$\ddot{N}H_3 + H^+ \longrightarrow \overset{\oplus}{N}H_4$$

Base   Acid

Limitations of Lewis concept:-

① Lewis concept is too general & includes all co-ordin comp & co-ordn reacn.

② It does not explain the behaviour of well known protonic acids like HCl, H_2SO_4 etc which donot form coordinate bonds with bases. ∴ these are not regarded as acids according to Lewis concept.

3) It does not explain the relative strengths of acid & bases.

4) Acid-base reacn are usually fast but the formn of co-ordn comp. is slow. Hence it do not fit in the acid-base concept

5) The catalytic activity of acids is due to $H^+_{(aq.)}$ ion. ∵ Lewis acid need not contain hydrogen, ∴ many Lewis acid will not possess catalytic property.

* Lux-Flood concept:- This concept was proposed by Lux & extended by Flood. [It describe A-B behaviour in terms of oxide ion].

Lux 1939 & Flood 1947

According to this concept acid is substance which accepts the oxide ion & a base is a substance which donate th oxide ion. In other word.

Acid is an oxide ion-acceptor

Base is an oxide ion-donor

(4n+2)π = 6π

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
Base Acid.

$$PbO + SO_3 \longrightarrow PbSO_4.$$
Base Acid.

$$MgO + CO_2 \longrightarrow MgCO_3$$

Cady-Elsey 1928

★ The Solvent - system concept (Autoionisation)

It is put forth by Franklin, an acid is a substance which, in a solvent, increases the concentratn of a cation characteristic of that solvent.

Base is substance which, in a solvent increases the conc. of an anion characteristic of that solvent.

e.g. 1) $2H_2O \rightleftharpoons \overset{+}{H_3O} + \bar{O}H$
solvent cation solvent anion

In water substance giving H_3O^+ - Acids
those giving $\bar{O}H$ - Base

2) $2NH_3 \rightleftharpoons \underset{Acid}{\overset{+}{NH_4}} + \underset{base.}{\bar{N}H_2}$

According to solvent-system concept, in liq NH_3 substance which give ammonium ion ($\overset{+}{N}H_4$) acts as acids. While those giving amide ions ($\bar{N}H_2$) acts as a base.

$$NH_4Cl \xrightleftharpoons{liq.NH_3} \overset{+}{NH_4} + \bar{Cl}$$
Acid

$$KNH_2 \xrightleftharpoons[NH_3]{liq.} \overset{+}{K} + \bar{N}H_2$$

The acid-base neutralisation reacn of NH_4Cl & KNH_2 in liq. NH_3 is analogous to that of HCl & NaOH in H_2O

$$NH_4Cl + KNH_2 \longrightarrow KCl + 2NH_3$$
$$HCl + NaOH \longrightarrow NaCl + H_2O$$

(117)

$2H_2SO_4 \rightarrow \overset{+}{H_3SO_4} + \bar{H}SO_4$
Acid Base

Consider the autoionization of liq. nitrogen tetraoxide.

$$N_2O_4 \rightleftharpoons \underset{A}{NO^+} + \underset{B}{NO_3^-}$$

According to solvent-system concept, In liq. N_2O_4, the substances which furnish nitrosyl ions (NO^+) behaves as acid & which furnish NO_3^- as base

eg: NOCl → Acid $NOCl \xrightleftharpoons{liq\,N_2O_4} NO^+ + Cl^-$
$NaNO_3$ → Base $NaNO_3 \xrightarrow[liq.]{N_2O_4} Na^+ + NO_3^-$

Usanovich concept :- (1938)

Acid :- Any chemical species which reacts with bases, gives up cations, or accepts anion or $\bar{e}$. ~~Combines with cation~~

Base :- Any chemical species which react with acids, gives up anion or $\bar{e}$ or combines with cation.

e.g. 1) $Na_2O + SO_3 \longrightarrow 2Na^+ + SO_4^{--}$

base acid (exchange anion

2) $3\,(NH_4)_2S + Sb_2S_5 \longrightarrow 6NH_4^+ + 2SbS_4^{3-}$

base. (acid)

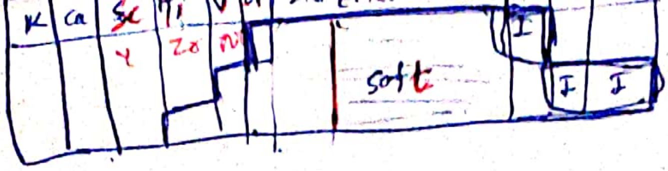
3) $2Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^-$ (exchang g $\bar{e}$)

Hard & soft acids & Bases:

The coord^n chemist found that while certain ligand prefer to form stable complexes with heavier ions such as Ag^+, Hg^{2+}, Pd^{2+}, Pt^{2+} etc some other ligands prefer to form stable complexes with lighter ions such as Li^{2+}, Be^{2+} Al^{3+}, Sc^{3+} etc.

Based on this preferential tendency to form stable complexes, the ions as well as ligands have been classified into two categories each.

The cations (i.e. Lewis acid) are categorised as hard & soft acids, the anion & neutral ligands are categorised as hard & soft bases



Hard - Small
high charge
weak Polarisible

HARD AND SOFT ACIDS AND BASES.

Hard and soft acids and bases concept play an important to explain the Formation of complex compound.

Definition and classification.

HARD ACIDS: The cation (Lewis acid) which having small size, high oxidation state and low polarisability. Such cations are said to be HARD ACIDS.

FOR EXAMPLE:

- Alkali metals, Li^{+}, Na^{+}, K^{+}
- Alkaline earth metals Be^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}
- Light transition metal with higher oxidation state Ti^{4+}, Cr^{3+}, Fe^{3+} (First transition series elements) ~~Co^{++}, Ni^{++}, Cu^{++}, Zn^{++}~~
- Hydrogen H^{+}

Characterstics of Hard Acids:

- ✓ Small size
- ✓ Higher oxidation state.
- ✓ Low polarisability.

SOFT ACIDS: The cation (Lewis acids) which having large size, low oxidation state and high polarisability. Such cations are said to be SOFT ACIDS.

FOR EXAMPLE:

Heavier transition metal with lower oxidation state Cu (Cu^{+}), Hg^{2+}, Pd^{2+}, Ag^{+}, Pt^{2+} (Second and third transition series elements.)

Characterstics of soft acids:

- Large size
- Lower oxidation state.
- High polarisability.

HARD BASES. (Ligand)...

The anion or neutral molecule which havin small size, high oxidation state and low polarisability ~~ar~~ such anion or neutral molecule are said to be HARD BASES.

FOR EXAMPLES

The ligands contain N, O donor atoms such as NH_3, RNH_2, H_2O as well as O^{2-} F^-, Cl^-, SO_4^{--}, PO_4^{--} ~~etc.~~ O_2^-, ROH etc.

characteristics: small size, high o.s., low polarisability, high electronegativity

SOFT BASES (Ligand)

The anion or neutral molecule which having large size, low oxidation state and high polarisability. such anion or neutral molecule are said to be SOFT BASES.

FOR EXAMPLE

The ligand contain P, S, As, Se as donor atom. such as R_3P, $S_2O_3^{2-}$, SCN^-, R_3As as well as H^-, C_6H_6, CN^-, SCN^-, I^- etc.

characteristics

1. large size,
2. low ~~High~~ o.s. Low o.s.
3. high ~~Low~~ polarisability High Polarisability.
4. Low electronegativity.

Borderlines acids and bases

Lewis acid which show some characteristics of hard acid and some characteristics of soft acids called Borderline acids.

FOR EX: Fe^{2+}, Cu^{2+}, Zn^{2+}, Sn^{3+}, Sb^{3+} ~~etc~~ Bi^{3+}, SO_2, $B(CH_3)_3$ etc

Lewis bases which show some characteristics of hard bases & some characteristics of soft bases called Borderline bases.

FOR EX:

N_3^-, Br^-, NO_2^-, C_6H_5N etc. Cl^-, nitrate, Sulfate, aniline etc

BONDING IN HARD-HARD & SOFT-SOFT COMBINATION. (Pearson HSAB concept)

According to Hard and soft acid & bases concept, Hard and soft acids are metal ions and Hard & soft bases are ligands.

In the formation of coordination compound hard acid prefer to bond to hard bases & soft acid prefer to to bond soft bases. This is known as HSAB principle. This concept was put by the scientist R.G. Pearson.

Application of HSAB principle.

1. Stability of complex:

According to pearson, stability of complexes can be explain on the basis of HSAB principle. The complexes are formed by the combination of hard acids and hard bases or soft acids & soft bases are highly stable.

$$\underset{\text{Hard Acid}}{A} + \underset{\text{Hard Base}}{B} \longrightarrow \underset{\text{stable complex}}{A:B}$$

FOR EX.

AgI_2^- exist as a stable compound but AgF_2^- not. The reason is Ag^+ is a soft acid & interact with soft base I^- & gives stable complex AgI_2^-. Where as F^- ion is hard base & gives unstable complex.

$$\underset{SA}{Ag^+} + \underset{SB}{2I^-} \longrightarrow \underset{\text{stable complex}}{AgI_2^-}$$

$$\underset{SA}{Ag^+} + \underset{HB}{2F^-} \longrightarrow \underset{\text{Unstable}}{AgF_2}$$

②

$$\underset{HA}{Co^{3+}} + \underset{HB}{6F^-} \rightleftharpoons \underset{\text{stable}}{[CoF_6]^{3-}}$$

$$\underset{HA}{Co^{3+}} + \underset{SB}{6I^-} \rightleftharpoons \underset{\text{unstable}}{[CoI_6]^{3-}}$$

Following reaⁿ proceed or not (feasibility) of chemical Reacⁿ:-

$$\underbrace{\underset{(H\cdot S)}{LiI} + \underset{(S-H)}{CsF}}_{\text{unstable}} \longrightarrow \underset{(H-H)}{LiF} + \underset{(S-S)}{CsI} \quad \text{(proceed)}$$

$$\underset{(H-S)}{CaS} + \underset{(H-H)}{H_2O} \longrightarrow \underset{(H-H)}{CaO} + \underset{soft}{H_2S} \quad (proceed)$$

$$\underset{(S-H)}{HgF_2} + \underset{(H-S)}{BeI_2} \longrightarrow \underset{(H-H)}{BeF_2} + \underset{(S-S)}{HgI_2} \quad (proceed)$$

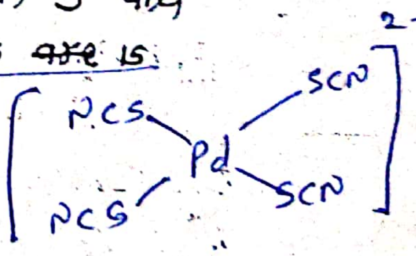
2. prediction of coordination (1) complexes of ambidentate ligand.

According to pearson, prediction of complex of ambidentate ligand can be explain on the basis of HSAB principle.

An ambidentate ligand is a monodentate ligand, which having two donor group but coordinate through one.

FOR EX:

SCN^- is a ambidentate ligand. it coordinate through either sulphur or nitrogen atom. It form stable complex of ~~with~~ Co, ~~Ni, Cu, Zn~~ through N atom and represent as $[Co(NCS)_4]^{-2}$. the reason is ~~these~~ Co metals ~~are~~ is hard acids & N is hard base. In other hand Pd, ~~Rh, Ir, pt~~ form stable complex with S and represent as $[Pd(SCN)_4]^{-2}$. The reason is these Pd metals ~~are~~ is soft acids & sulphur is soft base.



3. Prediction of hardness and softness.

In following reaction predict the hardness or softness of base B.

$$[BH]^+ + \underset{\text{soft acid}}{[CH_3Mg]^+} \longrightarrow \underset{SA-SB}{[CH_3MgB]} + \underset{H.A.}{H^+}$$

In this reaction if B is shifted to right, it is base ~~while~~ ~~left it is~~ (SA-SB) while left, it is hard ~~acid~~ base and interact with Hard acid H^+.

- Pearson's Principle
- Theories g hardness & softness such as electronic theory, π-bonding theory & Pitzer's th
- Applicat^{n} g SHAB. - stability.
  - feasibility g chem. reac
- Limitation g SHAB.

① Electronic Theory : (electrostatic interaction)

- Hard acid & hard bases form purely ionic compounds. These hard-hard interaction are purely ionic or electrostatic.

e.g. Hard acid such as Li^{+}, Na^{+}, K^{+}

Hard bases as $\bar{O}H$, F^{-}, O^{2-} forms ionic compounds

- The electrostatic energy bet^{n} a +ve ion & -ve ion is inversely proportional to interatomic distance.
- smaller the ions, smaller would be internuclear distance & greater would be electrostatic attractions bet^{n} ions resulting in the release g energy.

∴ The resulted complex formed is highly stable.

② π-bonding Theory :- (π-bonding contributions)

- This theory can be applied to explain the bonding bet^{n} the soft - soft complexes.
- The soft acids are generally metals in low oxid^{n} states containing loosely held outer d-$\bar{e}$s
- These can be easily donated to ligands

many soft base are π-bond acceptors & soft acid are π-bond donors. e.g. Ligands g P, As, CO.

HASB + SAHB ✗

HAHB + SASB ✓

Theories g Hardness & softness. (SHAB Principle)

1) Electronic Theory (electrostatic interaction)

- H.A. & H.B forms purely ionic compounds. These hard-hard interactions are purely ionic or electrostatic

e.g. Hard acid such as Li^+, Na^+, K^+ & Hard bases $\bar{O}H$, F^-, O^{2-} form ionic compounds.

- The electrostatic energy betn a +ve ion & a -ve ion is inversely proportional to interatomic distance.
- Smaller the ions, smaller would be internuclear distance & greater would be electrostatic attractions betn ions resulting in the release g energy

∴ The resulted complex formed is highly stable.

2) π-bonding theory :-

- This theory can be applied to explain the bonding betn soft-soft complexes.
- The soft acids are generally metals in low oxidn state containing loosely held outer d-$\bar{e}$
- These can be easily donated to ligands.
- many soft base are π-bond acceptors & soft acids are π bond donars. e.g. Ligands g P, As, CO

3) Pitzer's Theory :-

- This theory g London & vander waal's forces explains that the interacting soft-soft groups depends on the products g Polarizibilities g the interacting groups
- Both soft acids & soft bases have larges value g Polarizibilities.
- most g soft acid have large number g d-$\bar{e}$ & have greater Polarising Power & soft bases such as I^-, S^- are easily Polarizable

∴ Bonding betn soft ~~bond~~ acid & soft base are largely covalent.

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Limitations of SHAB Concept :-

1) It does not involve any quantitative scale of measurement

2) It is assumed that hard - soft factors do not depend on acidic or basic Character of the ~~Complex~~. Compound.

3) Due to Soft - soft ($\overset{+}{CH_3} - \overset{+}{H}$) interactions above reac^n proce

$$\overset{+}{CH_3}{}_{(g)} + H_{2\,(g)} \longrightarrow CH_4 + \overset{+}{H}_{(g)}$$

Actually, this reac^n not proceed at all. Because unfavourable entropy Change.