

A POLARIZATION

→ We know that, anions are larger in size than cations. In ionic molecules, when cations and anions are approaches, then electron ~~cloud~~ cloud of anion is attracted by cation, ^{due to electrostatic force of attraction} at the same time nucleus of anion is repelled by cation. As a result of this the shape of anion get distorted. This distortion in the shape of anion by the cation is called as Polarization.

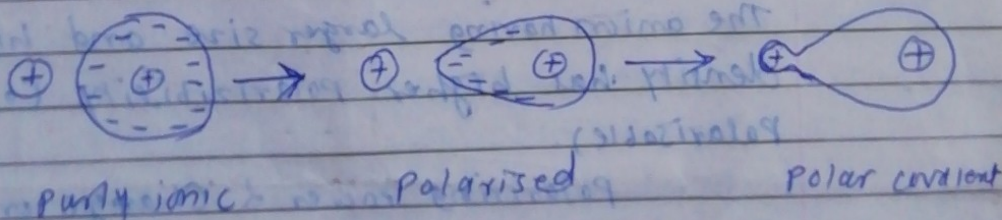
→ When the extent of polarization is large, ~~then~~ then, cations and anions overlap each other to some extent. This overlapping gives covalent character to the ionic bond called polar covalent bond.

→ The polar ~~covalent~~ covalent bond is more stable than pure ionic and covalent bond.

✓ → The ionic nature of covalent bond depends upon polarizing power of cation and polarizability of anion.

Def → The power of cation to polarise (distort) the anion is called as polarizing power.

Def → and The tendency of anion to get polarised (distort) by the cation is called as polarizability eg. LiI, LiBr, AlCl₃, FeCl₃ etc.



Effect of Polarisation on Nature of Bond (Covalent character in ionic compounds)

→ The nature of bond formed between cation and anion in the ~~molecule~~ ionic molecule depends upon effect of polarization of one ion upon other.

→ If degree of polarisation is small, then bond ~~becomes~~ ^{remain} ionic.

→ If degree of polarisation is large, then electron cloud of anion is attracted toward cation due to electrostatic force of attraction, and gives covalent character to ionic bond.

→ The greater is the polarisation, greater is the covalent character induced in the ionic bond.

Fajjan's Rule of Polarization

This rule gives information about partial covalent ~~character~~ character in ionic bond.

Fajjan's Rules is ~~can be~~ given as follows

Rule - 1:-

The cation having small size and higher charge has higher polarising power.

i.e. smaller is the size of cation, higher is the polarising power.

~~Polarising~~ Polarizing power $\propto \frac{1}{\text{size of cation}}$

OR Polarising power \propto Charge on cation

Rule - 2

The anion having larger size and higher charge density has higher polarizability (or easily polarisable).

Polarising power \propto Charge on anion

OR Polarising power \propto size of anion.

Rule - 3

The cation with pseudo-inert gas configuration ($ns^2 np^6 nd^0$) have higher polarizing power than cation with ~~actual~~ inert gas configuration ($ns^2 np^6$)

Explanation

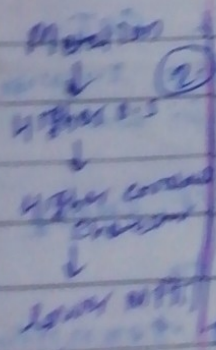
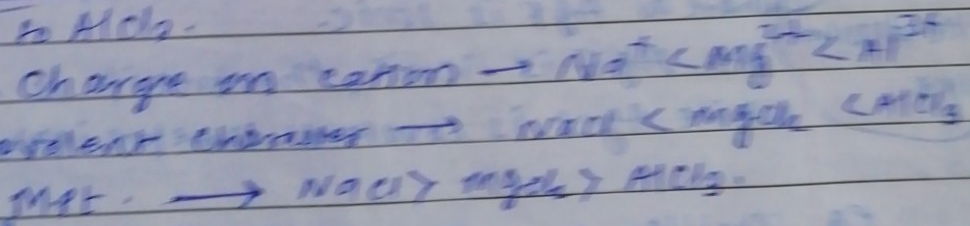
This is because d-electrons of pseudo inert gas configuration shield nuclear charge to extent less effectively (less) than s & p electrons of inert gas configuration. Therefore nucleus of the pseudo inert gas configuration exerts more positive charge than nucleus of inert gas configuration. Therefore higher polarizing power.

Applications of Fajan's Rule or Applications of concept of Polarization or Consequences of Fajan's Rule

① As charge on the cation increases, polarizing power increases.

② The change in the compound's mass, molar mass increases, the polarizing power increases in the order of $Na^+ < Mg^{2+} < Al^{3+}$. Therefore $AlCl_3$ has highest covalent character among the three.

③ As covalent character increases, the melting point decreases. Therefore M.P.T. decreases from $NaCl$ to $AlCl_3$.



② IF metallic character is same but oxidation state (charge) is different then the molecule with higher oxidation state has higher covalent character. Therefore lower M.P.T.
 eg. consider $SnCl_2$ (Sn^{2+}) and $SnCl_4$ (Sn^{4+}), it is observed that $SnCl_4$ has more covalent character therefore lower M.P.T.

Polarising power $\propto \frac{\text{covalent character}}{\text{ionic character}}$

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Charge on cation \rightarrow $\text{Sn}^{4+} > \text{Sn}^{2+}$, $\text{Pb}^{4+} > \text{Pb}^{2+}$, $\text{Tl}^{3+} > \text{Tl}^{+}$
 Covalent character \rightarrow $\text{SnCl}_4 > \text{SnCl}_2$, $\text{PbCl}_4 > \text{PbCl}_2$, $\text{TlCl}_3 > \text{TlCl}$
 M.P. \rightarrow $\text{SnCl}_4 < \text{SnCl}_2$, $\text{PbCl}_4 < \text{PbCl}_2$, $\text{TlCl}_3 < \text{TlCl}$

③ The halides of alkali and alkaline earth metals are ionic. But as we go top to bottom in the group, size increase therefore polarising power decreases therefore covalent character decreases therefore ionic character increases.
 Thus LiCl has maximum covalent character while CsCl has maximum ionic character.
 Size of cation $\rightarrow \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$
 Covalent character $\rightarrow \text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$

③ Solubility of salts

AgF is soluble in water whereas AgCl is not. because F^- anion has smaller size while Cl^- ion has larger size. As we know that larger is the size of anion, greater is the polarisability. Therefore Cl^- ion is more polarised by Ag^+ than F^- ion. therefore AgCl has more covalent than AgF . That means AgCl is covalent whereas AgF is ionic.

like-dissolved like

As AgF is ionic, therefore it is soluble in water while AgCl is covalent, therefore insoluble in water.

eg similar examples. AlF_3 & AlCl_3 | CaF_2 CaI_2
 \downarrow \downarrow \downarrow \downarrow
 soluble insoluble soluble insoluble
 in water in water in water in water

④ The halides of transition metals like AgCl , CuCl_2 have covalent character as compared to alkali metals like NaCl , KCl , because transition metals have pseudo inert gas configuration $(ns^2 np^6 nd^x)$ and causes more polarisation and covalent character, but alkali metals have inert gas configuration $(ns^2 np^6)$.

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OR Applications of Concept of Polarization [Fajan's rule]

The concept of polarization is useful in determining

- ① degree of covalent character in an ionic compound.
- ② The tendency of cation to form complexes
- ③ The tendency of cation toward solvation
- ④ solubility of salts
- ⑤ M.P. of salts.
- ⑥ Nature of oxides.
- ⑦ Thermal stability of carbonates
- ⑧ Bond energy etc.

(B) Covalent Bonding

The bond formed by the sharing of electrons is called an covalent bond.

Covalent bond is directional in nature that means atoms are bonded in specific direction (orientation)

with respect ~~to~~ to one another.

Directional Nature of covalent bond

The covalent bond is directional in nature that means atoms are bonded in specific direction

with respect to one another. ~~The covalent bond~~

~~possesses direction when non-spherical orbitals~~

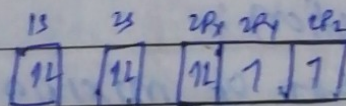
eg. ~~When~~ ^{When} ~~p-orbitals~~ ^{p-orbitals} are involved in the formation of covalent bond, ~~in such orbital~~, the electron density is concentrated in particular direction and molecule possess definite geometrical shapes.

eg. Formation of H₂O molecule.

H (1)



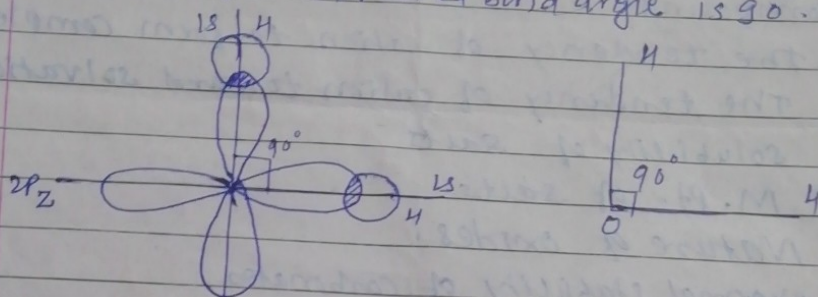
O (8)



H (1)

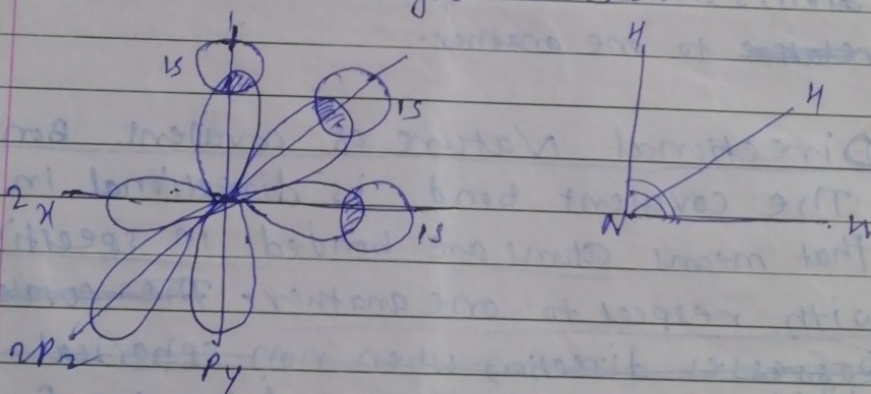


Now, $2p_y$ and $2p_z$ orbitals of oxygen atom are mutually perpendicular and two O-H bonds formed in H_2O are also mutually perpendicular and therefore expected bond angle is 90° .



eg. 02 Formation of NH_3 molecule.

The $2p_x$, $2p_y$ & $2p_z$ orbitals of nitrogen atom mutually perpendicular and three N-H bonds formed in NH_3 molecule are also mutually perpendicular and therefore expected bond angle is 90° .



Structure of H_2O & NH_3 molecule

The actual bond angle in H_2O (105.5°) and NH_3 (107.5°) are greater than 90° which can be explain on the basis of Hybridization and VSEPR theory.

Def

Hybridization :-

The process of mixing and recasting of atomic orbitals having near about same energy to form new equivalent orbitals having same shape, size energy and orientation is called hybridization.

* Need of Hybridization

The need of hybridization is

- (i) to explain observed valency of element.
- (ii) to explain equivalence of bonds (ie to explain equivalence of bond length, bond angle, bond energy).
- (iii) to explain the geometry ~~shape~~ of molecule.

* Steps involved in hybridization

The steps involved in hybridization are

(1) Formation of excited state:-

The atoms in ground state absorb some energy and goes to excited state. In this process, electron pair in lower energy orbital is split up and one electron from this pair is promoted to higher energy orbital. This step is necessary when atom has less no. of ~~electron~~ unpaired electrons than required.

(2) Mixing and Recasting of atomic orbitals:-

- The atomic orbitals in the excited state mix up and forms new hybride orbitals of equal energy.
- The total no. of hybride orbitals formed is equal to the no. atomic orbitals mixed.

(3) Reorientation of hybrid orbitals

The hybride orbitals are arranged in the space around central atom and oriented in ~~a space~~ such way that there is minimum repulsion between them.

* Conditions for Hybridization

- (1) Atomic orbitals of same atom can take part in hybridization.

- ② The atomic orbitals which take part in hybridization should have nearabout same energy.
- ③ The atomic orbitals like vacant, half filled or completely filled can take part in the process of hybridization. The electrons present in them do not take part in this process.

Characteristics of Hybridization

- ① The atomic orbitals of same atom have nearabout same energy.
- ② The no. of hybrid orbitals formed is equal to the no. of atomic orbitals used for hybridization.
- ③ The hybrid orbitals have same shape, size, energy and orientation.
- ④ The hybrid orbitals are more directional than atomic orbitals.
- ⑤ The hybrid orbitals can form stronger covalent bond than atomic orbitals.
- ⑥ The hybrid orbitals have same characters as that of parent atomic orbitals.
- ⑦ The distribution of electrons in hybrid orbitals is according to Hund's Rule, Aufbau principle and Pauli's exclusion principles.

Types of Hybridization

S.No.	Type of Hybridization	Geometry	Example
1	sp hybridization	Linear / Diagonal	BeCl ₂
2	sp ² hybridization	Trigonal planar	BF ₃ , BCl ₃
3	sp ³ — u —	Tetrahedral	CH ₄ , NH ₄ ⁺
4	sp ³ d — u —	Trigonal bipyramidal	PCl ₅
5	sp ³ d ² — u —	Octahedral	SF ₆
6	sp ³ d ³ — u —	Pentagonal bipyramidal	IF ₇

① sp³ Hybridization

The process of mixing and re-creating of one s-orbital and three p-orbitals having near about same energy to form four hybrid orbitals with same shape, size, energy and orientation is called as sp³ hybridization.

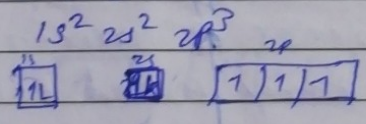
The bond angle in sp³ hybridization is 109°28'. The sp³ hybridization is also called as tetrahedral hybridization.

on the basis of sp³ hybridization we can explain geometry of CH₄, CCl₄, NH₃, NH₄⁺ ion etc. ---

Formation of NH₄⁺ ion

① In NH₄⁺ ion, ~~There is one Nitrogen atom and four hydrogen atoms~~ is central atom and it undergoes sp³ hybridization.

② The electronic configuration of Nitrogen atom is ${}_{7}N \rightarrow 2, 5$

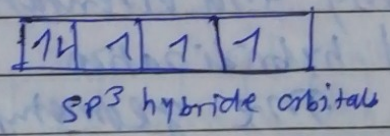


③ The electronic configuration of Hydrogen atom is ${}_{1}H \rightarrow 1s^1$

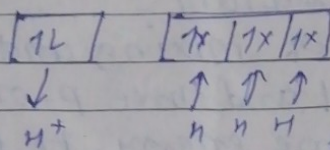
↑

~~④ In the formation of NH₄⁺ ion, Nitrogen atom gained 3 electrons from 3 hydrogen atoms and donate one electron pair from 2s orbital~~

④ In ground state Nitrogen atom undergoes sp³ hybridization and form four sp³ hybrid orbitals.



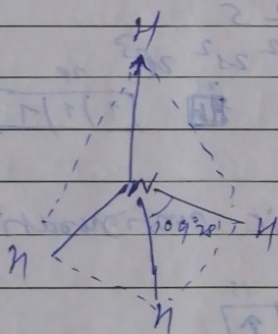
⑤ In the formation of NH₄⁺ ion, The nitrogen atom gain 3 electrons from 3-hydrogen atoms and donate one electron pair to H⁺ ion.



} sp^3 hybridization.

The half filled sp^3 hybrid orbitals of nitrogen atom overlap axially with ^{three} 1s orbitals of hydrogen atom and forms three N-H sigma bonds. While one lone pair on nitrogen atom is donated to H^+ ion and forms coordinate bond and thus NH_4^+ ion is formed. Actually, H^+ ~~the covalent bond is~~ ion has empty 1s orbital which overlaps with sp^3 hybrid orbital of nitrogen containing lone pair of electron and forms coordinate covalent bond in NH_4^+ ion.

The geometry of NH_4^+ ion is tetrahedral with bond angle $109^\circ 28'$.



② sp^3d Hybridization:-

The process of mixing and recasting of one s, three p and one d orbitals having near about same energy to form five hybrid orbitals with same shape, size energy and orientation is called as sp^3d hybridization.

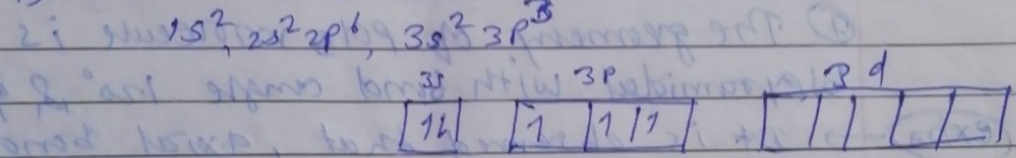
The geometry of sp^3d hybridization is trigonal bipyramidal with bond angle 120° & 90° . Out of these five orbitals, three orbitals are

in one plane called as equatorial orbitals and two orbitals are perpendicular to the plane called as axial orbitals.

Formation of PCl₅ molecule

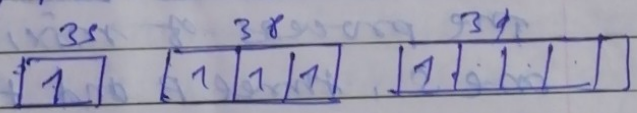
- ① In PCl₅ molecule, there ~~are~~ is one phosphorus atom and five chlorine atoms. Phosphorus atom is central atom. Therefore it undergoes hybridization.
- ② The electronic configuration of phosphorus atom is

$_{15}P \rightarrow 2, 8, 5$

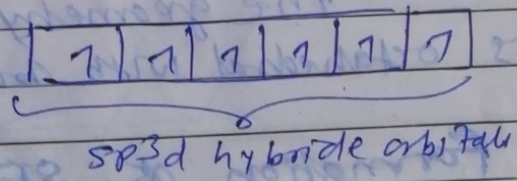


③ formation of excited state

In the excited state, one electron from 3s orbital is transfer to 3d orbital. Therefore Electronic configuration of phosphorus atom in excited state is

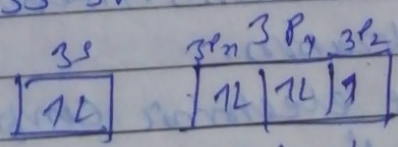


④ The excited state, phosphorus atom undergoes ~~the~~ sp³d hybridization and forms five hybrid orbitals.



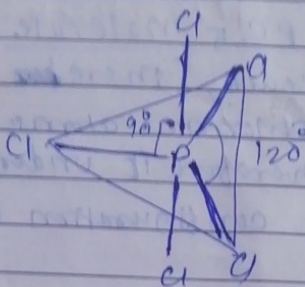
⑤ Electronic configuration of chlorine atom is

$_{17}Cl \rightarrow 2, 8, 7$
 $3s^2 3p^5$



3p_z orbital contain unpaired electron.

② In the formation of PCl_5 molecule, sp^3d hybrid orbitals of phosphorus atom overlap with $3p^2$ orbitals of chlorine atom and forms 5 $P-Cl$ σ bonds.



④ The geometry of PCl_5 molecule is trigonal bipyramidal with bond angle 120° & 90° .

(exn) → It is observed that, axial bonds are longer than equatorial bonds. Therefore axial bonds are weaker and more reactive than equatorial bonds.

③ sp^3d^2 Hybridization

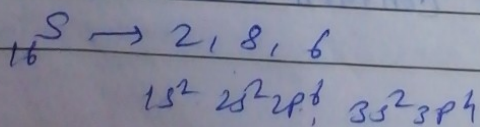
The process of mixing and recasting of one s , three p and two d -orbitals having near about same energy to form six hybrid orbitals with same size, shape, energy and orientation is called as sp^3d^2 hybridization.

The geometry of sp^3d^2 hybridization is octahedral with bond angle 90° .

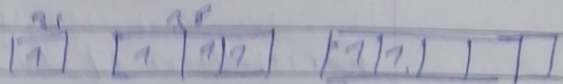
Formation of SF_6 molecule

① In SF_6 molecule, there is one sulphur atom and six fluorine atoms. Sulphur atom is central atom. Therefore it undergoes hybridization.

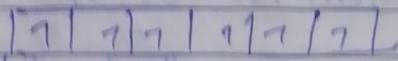
② The electronic configuration of sulphur atom is



① In the excited state, one electron from $3s$ and $3p_x$ orbitals transfer to $3d$ orbital. Therefore electronic configuration of Sulphur in excited state is

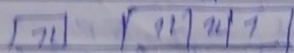
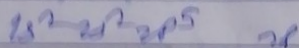
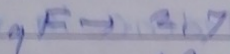


② In the excited state, Sulphur atom undergoes sp^3d^2 hybridization and form six hybrid orbitals with same shape, size, energy and orientation.

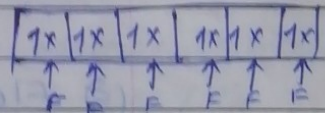
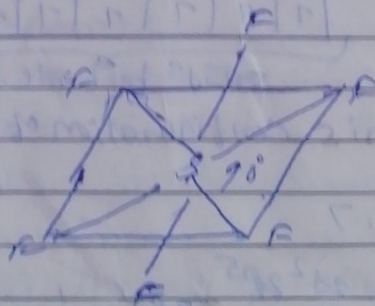


sp^3d^2 hybrid orbitals

③ The electronic configuration of Fluorine atom is



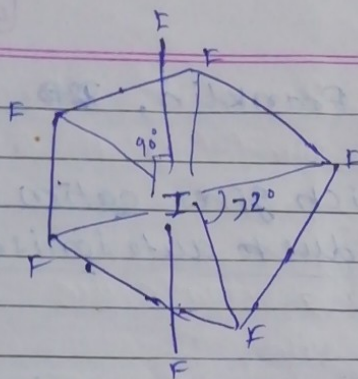
④ In the formation of SF_6 molecule, each sp^3d^2 hybrid orbitals of Sulphur atom overlap with $2p$ orbital of six Fluorine atoms and forms six $S-F$ sigma bond.



The geometry of SF_6 molecule is octahedral with bond angle 90° .

⑤ sp^3d^3 Hybridization

The process of mixing and recasting of one s , three p and three d -orbitals having near about same energy ~~with~~ to form new hybrid orbitals with same shape, size, energy and orientation is called sp^3d^3 hybridization.



The geometry of PF_7 molecule is pentagonal bipyramidal with bond angle 72° and 90° .

(c) Acids and Bases

The concept of acids and bases can be explained on the basis of various theories like:

(1) Arrhenius concept: The H^+ and OH^- ion system in water.

(2) Lowry-Bronsted concept of acids and bases: The proton donor-acceptor system.

(3) Lewis theory: The electron pair donor-acceptor theory.

(4) Franklin Theory: The general theory of solvent system.

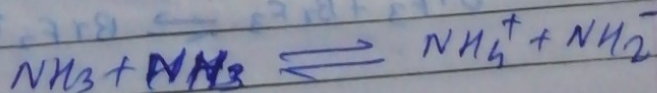
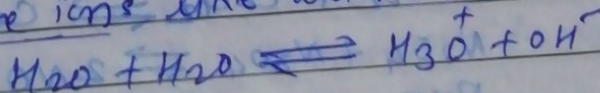
(5) Usanovich concept: Like a synthesis of previous acid-base theories.

(6) Lux-Flood Concept: An oxide ion acceptor-donor system.

Here we shall discuss, Franklin theory of solvent system and Lux-Flood concept only.

* Franklin Theory of solvent system or Solvent system of acid-base concept

According to Franklin, the non-aqueous solvent molecules dissociate into ~~the~~ positive and negative ions like water.



According to Franklin, ~~DE~~

Acid:

The substance which gives cation by the dissociation of solvent itself due to auto ionisation is called as acid.

Base:

The substance which gives anion by the dissociation of solvent itself due to auto-ionisation is called base.

The solvent system of acid base concept to non-protic solvent (eg SO_2 , COCl_2 , N_2O_4 etc) was applied by eady and Elsey.

According to them:

* Acid:

The substance which gives cations on dissolution or direct reaction with solvent is called as acid.

* Base:

The substance which gives anion on dissolution or direct reaction with solvent is called as base.

eg:

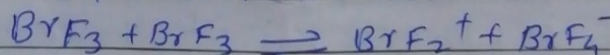
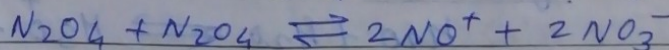
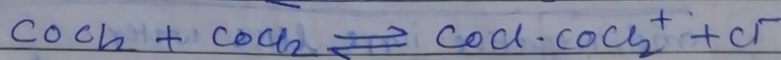
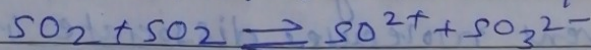
① - The substance such as SOCl_2 gives SO^{2+} ions in liquid SO_2 as a solvent acts as acid while

the substance ~~is~~ such as Na_2SO_3 gives SO_3^{2-} ions in liquid SO_2 as a solvent acts as base.

② - The substance NOCl gives NO^+ ions in N_2O_4 as solvent acts as acid while

the substance NaNO_3 gives NO_3^- ions in N_2O_4 as solvent acts as base.

③ - The autoionisation of some non protionic solvents



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✓ Success of Franklin Theory

- ① This theory is applicable to proton and non-proton system.
- ② This theory is applicable in aqueous as well as non-aqueous solvents.
- ③ There are the most general definitions of acids and bases.

* Limitations or Drawbacks of Franklin theory

- ① This theory explain acid-base phenomenon only in solvent. (Processes)
- ② This theory can not explain neutralization reaction in absence of solvent.
- ③ It can not explain existence of ions in low dielectric constant solvents.
- ④ This theory considered the chemical properties of solvents rather than physical properties.
- ⑤ This theory gives stress mainly on ionization of solvent rather than dielectric const.

LUX-Flood concept of acids and bases or oxide ion-donor acceptor concept.

According to this concept,

Acid:

The substance which accept oxide ion is called as acid. or

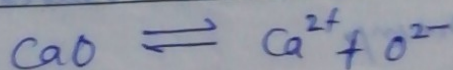
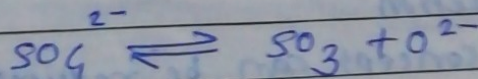
Acid is a oxide ion acceptor.

Base:

The substance which donate oxide ion is called as base or.

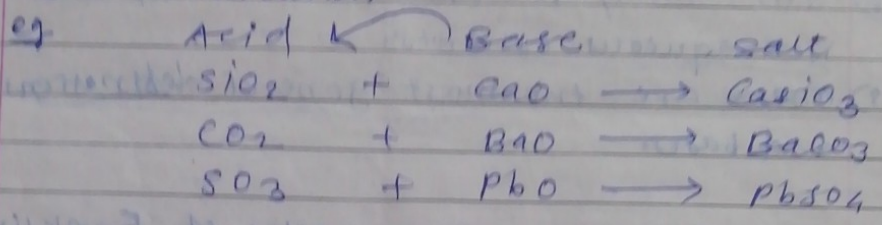
Base is a oxide ion donor.

eg $\text{Base} \rightleftharpoons \text{Acid} + \text{oxide ion}$



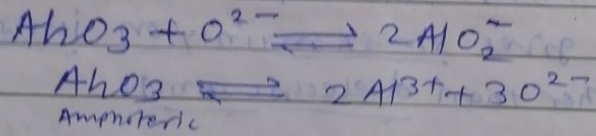
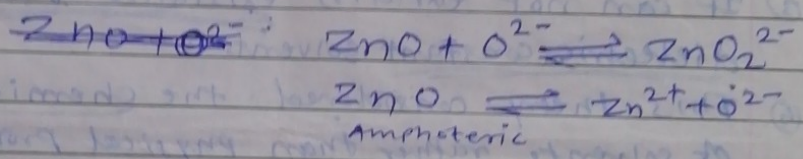
Neutralisation:

The process of transfer of oxide ion from base to the acid and forms a salt is called as neutralization



Amphoteric substance

The substance which donate as well as accept oxide ions depending upon the reaction conditions is called as amphoteric substance.



Advantages or Merits of Lux-Flood concepts

- ① This theory is use to explain acid-base behaviour of non-protonic ~~substance~~ substances
- ② This theory is used to explain oxide ion transfer reactions at higher temperature.
eg In ceramics and metallurgy.
- ③ This theory is also applicable to the transfer of negative ions like halides or sulphides

Limitations

- ① According to this theory, acid base reactions involving oxide ion transfer are also only acid base reaction
- ② This concept can be reduced to one part of Lewis theory.

Imp

Concept of Hard and soft acid and base

According to Lewis theory, Acid is a substance which accept electron pair while base donate electron pair.

In 1963, R.G. Pearson classified Lewis acid (particularly metal cation) and Lewis bases into two types

- (i) Hard and soft acids
- (ii) Hard and soft bases

(i) Hard and soft acids

(a) Hard acid:

The substance which has strong tendency to accept electrons is called as Hard acid.

Salient features of Hard acids

- (i) They have small size
- (ii) They have high positive oxidation state.
- (iii) They have high polarizing power
- (iv) Their outermost electrons are not easily removed.

(v) They have high Ionisation potential.

eg Alkali & Alkaline earth metals, and transition metal ions like Ti^{4+} , Fe^{3+} , Co^{3+} , Al^{3+} are hard acids.

(b) Soft acid:

The substance which has weak tendency to accept electrons ^{is} called as soft acid.

Salient features of soft acids

- (i) They have large size.
- (ii) They have low or zero oxidation state.
- (iii) They have low polarizing power.
- (iv) Their outermost electrons are easily removed.
- (v) They have low ionisation potential.

eg Heavier Transition metals like Hg^{2+} , Ag^+ , Pt^{2+} , Cu^{2+} and metal ions in metal carbonyl are soft acids.

Alkali	
Z	II
H	
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	Ra

2 Hard and soft Bases

(a) Hard Base

The substance which cannot donate valence electron easily is called as hard base.

eg. NH_3 , H_2O , OH^- , F^- are hard bases.

ex) H_2O , OH^-

Salient features of Hard bases

- ① they cannot donate electrons easily.
- ② they are hard to oxidised.
- ③ they have low polarizability.
- ④ they have high electronegativity.
- ⑤ they do not have empty low energy orbitals.
- ⑥ they can form strong bond with proton.

(b) Soft Base

The substance which donate valence electron easily is called as soft base.

eg. I^- , RS^- , H^- , R_3P , R_2S are soft bases

Salient features of soft base

- ① they donate valence electron easily.
- ② they are easy to oxidised.
- ③ they have high polarizability.
- ④ they have low electronegativity.
- ⑤ they have empty low energy orbitals.
- ⑥ they can form weak bond with proton.

mem

SHAB principle OR

Pearson's principle OR

Principles of soft and hard acids and bases

This concept explain stability of complexes formed between acids and bases.

According to this concept,

"The complex is most stable when both acid and base are either soft OR hard."

That means, hard acid is prefer to combine with hard base while soft acid is prefer to combine with soft base, and most stable complex ~~was~~ is formed.

Applications of SHAB principle

- ① In predicting the stability of complexes:
 eg ① The complex AgI_2^+ is stable but AgF_2^- does not exist. because in AgI_2^+ , both Ag^+ and I^- are soft acid and base respectively, but in AgF_2^- , Ag^+ is soft acid but F^- is hard base.
 eg ② CoF_6^{3-} is more stable than CoI_6^{3-} because in CoF_6^{3-} , Co^{3+} and F^- are hard acids/base resp. ~~while~~ but in CoI_6^{3-} , Co^{3+} is hard and I^- is soft.

- ② In predicting solubility of compounds:
 $Hg(OH)_2$ dissolves readily in ^{acidic} aqueous solution while HgS or CuS does not. Because $Hg(OH)_2$ is formed by the combination of Hg^{2+} (soft acid) and OH^- (hard bases) therefore $Hg(OH)_2$ is less stable. on the other hand HgS is formed by the combination of Hg^{2+} (soft acid) and S^{2-} (soft base) therefore HgS is stable. Therefore $Hg(OH)_2$ is soluble in acidic solution while HgS does not.

- ③ In predicting the existence of metallic ores
 The metal like Mg, Ca, Al exist in a nature in the form of carbonates and oxides whereas the metals like Cu, Hg, Ag exist in the nature in the form of sulphides.
 The metal ions Mg^{2+} , Ca^{2+} , Al^{3+} are hard acids and CO_3^{2-} and O^{2-} are hard bases therefore

Therefore carbonate and oxide ores of Mg, Ca, Al are hard-hard combination therefore they are stable. But Cu^{2+} , Hg^{2+} , Ag^{+} ions are very soft acids and S^{2-} ion is very soft base. Therefore sulphides of Cu, Hg & Ag are soft-soft combination. Therefore they are very stable.

END

② In predicting solubility of compounds:

Hg^{2+} dissolves readily in aqueous solution

while Hg_2^{2+} does not. Because Hg^{2+} is

formed by the combination of Hg^{2+} (soft acid) and

OH^{-} (hard base) therefore Hg^{2+} is more stable.

On the other hand Hg_2^{2+} is formed by the combination

of Hg^{2+} (soft acid) and S^{2-} (soft base) therefore

Hg_2^{2+} is stable.

Therefore Hg^{2+} is soluble in acidic solution

while Hg_2^{2+} does not.

③ In predicting the existence of metallic ores

the metal like Mg, Ca, Al exist in nature

in the form of carbonates and oxides whereas

the metals like Cu, Hg, Ag exist in the form

of sulphides.