Unit 1

1. Define the Hard base and Soft acid
2. What is symbiosis?
3. Define ionic bond
4. Define lattice energy
5. State Radius ratio rule
6. Limiting radius ratio of tetrahedral and octahedral
7. How do you measure the strength of an acid or a base?
8. Give a brief account of classification of acid as hard and soft.
9. Comment on HSAB concept with suitable examples.
10. What do you know about acids-base strength and hardness- softness.
11. Write a critical note on applications and limitations of HSAB principle.
12. Discuss the therotical bases of hardness and softness.
13. Derive the Band lande equation
14. Give a brief account of Limiting of Radius ratio rule

Measure of acid – base strength:

All acids and bases do not ionize or dissociate to the same extent. This leads to the statement that acids and bases are not all of equal strength in producing H+ and OH- ions in solution. The acid and base dissociation constant is the measure of the strength of the acids and bases. The higher the dissociation constant the stronger the acid or base. Since electrolytes are created as ions are freed into solution there is a relationship between the strength of an acid, a base, and the electrolyte it produces. Strong acids and strong bases make strong electrolytes Acids and bases are measured.
using the pH scale.

HSAB Principle:

HSAB concept is an initialism for "hard and soft (Lewis) acids and base". Also known as the Pearson acid-base concept, HSAB is widely used in Chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge states and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable.
The theory is used in contexts where a qualitative, rather than quantitative, description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially so in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

HSAB theory is also useful in predicting the products of metathesis reactions. In 2005 it was shown that even the sensitivity and performance of explosive materials can be explained on basis of HSAB theory.
The Lewis concept failed to provide a definite and uniform scale to measure the relative strength of acids and bases.The Lewis definition recognizes acid and bases in terms of their ability to accept or donate electron pairs. The strength of an acid or a base can be determined by the very nature of the reaction involved in a particular electron transfer process.On the basis of phenomenological criteria, suggested by Lewis, one may predict that the displacement titrations can be made the basis for much determination.

For example in the reaction :

A+A'B = AB + A'

A'B is converted to AB one may predict that a is stronger than A'. It may be said that the relative stabilities of acid- base complexes are used to express the relative strengths .From above reaction.AB must be more stable than A'B. Attempts have been made to correlate the different factors governing strength , from enthalpies ($\Delta H= 0$) of acid – base reactions .One of the difficulties in such determination was, with different reference acids (or bases) different trends were observed in Kf, $\Delta G0$or ΔHThe complexing ability of the halide ions (Lewis bases)towards $Al3+$increases in the order $I-<Br-< CI-<F-$ But towards $Hg2+$the order is just reverse $I->Br->CI->F-$.

2. A similar reversal is seen in the heats of reaction of the acids I2 and C6H5OH with the bases (C2H5)2O and ((C2H5) 2S. Heat of reaction of I2 is greater with (C2H5) 2S than that with (C2H5) 2O. But the trend for phenol is just reverse. Inspite of such difficulties ,to deal with the interactions of acids and bases containing elements drawn from throughout the periodic table ,a qualitative correlation between various Lewis acids and bases has been achieved .Class – "a" and Class- " b" According to them the two categories of metal ions (Lewis acids)are as follows –I) Class (a) – The metal ions which prefer to from stable complexes with the ligands having donor atom of the first members of Gr.15 th(N),16 th(O), and 17 th(F) in the periodic table . Examples are – Alkali metals , Alkaline earth metals and the first row transition metals in high oxidation state (e.g.fe3+ ,Co3+.Etc. belong to class (a) acids) .ii)Class (b)- The other metal ions which prefer to from their most stable complexes with the ligands having donor atom of the lower members of Gr.15 th(P,As,Sb),16 th(S,Se,Te), and 17 th(Cl,Br,I) in the periodic table. Lighter transition elements in low oxidation state and heavier transition elements ,say Cu+,Ag+,Hg+,Pt2+,Pd2+ etc. act as class (b) acids.

CLASSIFICATION OF ACIDS AND BASES AS HARD AND SOFT:

AH:B1+ As+B2=AH :B2+As+B1

From above double displacement reaction it may be stated that B1 is softer than B2 when K1 > 1 .On this basis a list of hard and soft acids and bases may be obtained .See Table .1.1 The classification is not rigid and there occurs a gradation from hard acids to soft acids ,and hard bases to soft bases , including the borderline species.The criterion of hardness (or softness) is ascribed to the “hardness” of the electron cloud associated with a particular species .A firmly held electron – cloud having low polarizability makes the species “hard” while an easily polarizable electron clowdcharacterises the species as “soft”.The third category with intermediate characters will be a borderline .The details of distinguishing features of hard and soft acids and bases are summarized in table 1.1

Table 1.1 Classification of Lewis Acids and Bases

(A) Acids –

Hard	**Borderline**	**Soft**
H+, Li+,Na+, K+	Fe2+Co2+ Ni2+	Cu+,Ag+,Au+,TI+
Be2+,Mg2+,Ca2+	Cu2+ ,Zn2+,Pb2+	Hg+,Pd2+,Cd2+,
Cr2+,Cr3+,Al3+	SO2,BBr3	Pt2+,Hg2+,BH3,Br2
SO3,BF3,BCl3		Br+,HX
(H-bonding)		M0 and bulk metals

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Bases :

Hard	**Borderline**	**Soft**
F-,OH-,H2O,NH3	NO2,SO3,Br-	H-,R-,CN-,CO,I-,
CO32-,NO3-,O2-,	N3-,N2,C6H5N,	SCN-,R3P,C6H6,

SO42-, PO43-CIO4-,(Cl-)	SCN-	R2S

Theorotical basis of hardness and softness:

Several theories have been given to explain the stability of complexes Formed by hard-hard and soft-soft interactions. Some important theoriesare:

(a) **Ionic and covalent bond theory :**
(b) According to this theory ionic bond is formed by the interaction of hard acids and hard bases where as covalent bond is formed by the interaction of soft acids and soft bases. The electrostatic force of attraction between two oppositely charged ions is inversely proportional to the internuclear distance. The internuclear distance will be less in case of smaller ions. Therefore, the electrostatic attraction between two ions will be greater and consequently the resulting compound will be highly stable. Covalent bond is formed by the interaction of soft acids and soft bases. This is because the soft acids and soft bases have laege size. The polarization effects are, therefore important to explain their interactions. Soft acids are generally transition metal ions having six or more d-electrons. The d-sub shell is easily polarized. Therefore, the complexes formed by soft acids and soft bases have covalent bonding and are stable. In order to predict the hard and soft nature of given acid or base, Misons and his coworkers (1967) gave the following relation
(c) K=-logK=AX+BY+C

wher X and Y are the parameters for the acids, A and B are the parameters for the bases, C is a constant which adjust pK values in such a way that all of them lie on the same scale and K is the equilibrium constant for the dissociation of acid base complex.

Symbiosis:

The term was originally applied to describe the maximum flocking of either hard or soft ligands in the same complexes.

For hydrocarbon molecules, symbiosis implies that those containing a maximum number of C-H bonds (e.g. CH4) or C-C bonds (e.g. Me4C) are the most stable.

ionic bond:

The radius ratio is defined as the ratio of **the** radius of cation r+to that of anion in anions r- in an ionic crystal.

$$Rr = \frac{r+}{r-}$$

it is possible to predict the cation anion coordination number in any ionic crystal with the help of radius ratio. The radius ratio can be used to predict the shape of the ionic crystals.The effect of radius ratio in determining the coordination number and shape of ionic crystal is known as radius ratio effect.If increases more than number of anion can sit around the cation the coordination number (C.N) of cation will increase.The relation between various structure and radius ratio or show below.

C.N.	**Geometry**	**Radius ratio**
2	Linear	0 to 0.15
3	Triangular	0.15 to 0.22
4	Tetrahedral	0.22 to 0.414
5	Square planar.	0.414 to 0.732
6	Octahedral	0.414 to 0.732
8	Body centred cubic	0.732 to 1.00
12	Close packing	1

The anion repulsion is always greater for the higher coordination number resulting increase in the cation anion distance. The radius for coordination number eight r8 can be calculated from the radius of coordination number six r6 by the equation.

$r8/r6= [8A6/6A8]\ 1/(n-1)$

Where n is the bornExponent and A6 and A8 are the Madelungconstant of NaCl structure (C.N = 6) and CsCl structure (C.N = 8) respectively. The Madelung constants of the structures are almost the same.

$r8/r6 = (4/3)1/(n-1)$

and for n = 1 r8/r6 = [4/3] 1/9 = 1.032

Lattice energy:

It is defined as the energy released when gaseous ions come closer from infinite separation to from a crystal.

M+(g)+ X-(g) ----→MX(s)

It is denoted by the simbolU; it has a negative sign since the energy is released in the process.

Factors determining the lattice energy:

lattice energy depends upon the strong electrostatic attraction between oppositely charged ions present in the solid. As the Olympic force of attraction vary directly as the product of the charges it follows that the higher the valency of the ions,the greater would be the lattice energy of the ionic solid.

Ex: lattice energy of LiF = - 1033 kJ mol^{-1} lattice energy of CaF2 = - 2581 kJ mol^{-1}lattice energy of MgO = - 3932 kJ mol^{-1} .

Thus lattice energy increases as we move from Univalent lent ionic solids to Uni-bivalent ionic solids and to bi- bivalent ionic solids. The lattice energy is inversely proportional to inter- ionic distance.The smaller the inter -ionic distance the higher would be the magnitude of lattice energy and the greater would be the stability of ionic crystal.

Ex. LiF>LiCl>LiBr> LiI

The lattice energy depends upon the coordination number of each iron and the geometry pattern of the ions in the crystal lattice of the Crystal.

Born – Lande Equation:

For a pair of ions M+ and X- separated by a distance r; the electrostatic energy of attraction is given by the expression.

$$E = \frac{z+z-e2}{4\pi€r}$$

Z+ and z- are the charges on the ions; e- is the electronic Charge; r- is the distance between the ions; € - is permitted tave of the medium. Now in the crystal lattice there will be more interactions than the simple one in an Ion pair. In the sodium chloride lattice, thereare attractions by the 6 nearest neighbours of like charge.The summation of all these geometrical interactions is known as that Madelung constant. A the value of Madelung constant is determined only by the geometry of lattice and independent upon Ionic radius and charge. Therefore the energy of pair of ions in the Crystals.

$$E_c = \frac{Az^{+}z^{-}e^{2}}{4\pi\epsilon_{o}r}$$

Ions consist electron clouds, which repel each other at very close distances. It is negligible at largedistances but increases very rapidly as the ions approach Each Other closely.

The repulsive energy is givenby,

$$E_R = \frac{B}{r^{n}}$$

where B is the repulsion Coefficient and is the born exponent. The total energy for your mole of the crystal lattice

$$U = E_c + E_R = \frac{N\,A\,z^{+}\,z^{-}\,e^{2}.}{4\pi\epsilon_{o}r} + \frac{N\,B}{r^{n}}$$

At equilibrium distance,

$$\frac{dU}{dr} = \frac{N\,A\,z^{+}\,z^{-}\,e^{2}}{4\pi\epsilon_{o}r^{2}} - \frac{A\,N\,B}{r^{n+1}} = 0$$

$$N\,A\,z^{+}\,z^{-}\,e^{2}\,r^{n+1}$$

Therefore ,the value of B comes out to be $B = \frac{\quad}{4\pi€or}$

$$U_0 = \frac{N A z+ z- e2.}{4\pi€o r0} \left(1 - \frac{1}{n}\right)$$

This eqtuation is known as Bond land equation.

Solubility of ionic compounds:

The dissolution of an ionic compound in and solvent means rupturting of the lattice to give ions. The energy required forrupturtingthe lattice has to be supplied in order to dissolve the ionic compound. Polarsolvents which are capable of solvent in the ions provide this energy in the form of heat of solvation. As a result polar solvents are good solvents for ionic compounds. But, thenonpolar solvents because of their inability to solvate with the ions, cannot supply the required energy and as the result ionic compounds, are insoluble in nonpolar solvent. When we compareto the solubilities of Na2SO4 and CaSO4 in water CaSO4 is sparingly soluble as its dissolution requires larger amount of energy due to its larger lattice energy.

Radius Ratio Rule

In ideal ionic crystals, coordination numbers are determined largely by electrostatic considerations.

- Cations surround themselves with as many anions as possible and vice-versa.
- This can be related to the relative sizes of the ions. ⇒ radius ratio rule

Radius ratio rule states:

- As the size (ionic radius r) of a cation increases, more anions of a

particular size can pack around it.

- Thus, knowing the size of the ions, we should be able to predict a priori

which type of crystal packing will be observed.

- We can account for the relative size of both ions by using the RATIO of ionic radio.

–Limiting Radius Ratios

For a specific structure, we can calculate the limiting radius ratio, which is the minimum allowable value for the ratio of ionic radii (r+/r-) for the structure to be stable.

/r- range possible structures

8 (cubic) ≥ 0.732 CsCl, $CaF2$

6 (octahedral) 0.414 – 0.732 NaCl, $TiO2$, $CdCl2$

4 (tetrahedral) 0.225 – 0.414 antifluorite, ZnS

3 (triangular) 0.155 – 0.225

Examples:

The rotatable structure opposite shows the CsCl structure in which the Cs^+ ion is surrounded by 8 Cl^- ions.

To get as close to the cation as possible, the anions must touch along the edge of the cube, as shown in the figure below. Click the 'Directions In Which Anions Touch' button to see this view.

The side of the cube has a length, a, where:

$$a = 2r_-$$

Along the body diagonal, the Cs^+ is touching the two Cl^- ions on either end so its length, d, is:

$$d = r_- + 2r_+ + r_- = 2r_+ + 2r_-$$

Using Pythagoras’ theorem, the length of the side and the body diagonal of a cube are related:

$$d^2 = a^2 + a^2 + a^2 = 3a^2 = 3 \times 4r_-^2 = 12r_-^2$$

$$d = 2(3)^{1/2}r_-$$

So,

$2r_- + 2r_+ = 2r(3)^{1/2}r_-$

$r_+ / r_- = (3)^{1/2} – 1 = 0.732$

As long as the radius of the cation is *no smaller* than 73% that of the anion, the CsCl structure, with its high Madelung constant, is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch. If the cation is smaller than this, the cation and anion will not be in contact. A lower coordination number is then needed

The rotatable structure opposite shows the NaCl structure in which the Na^+ ion is surrounded by 6 Cl^- ions.

As shown in the figure below, along the cube edge, the Na^+ is touching two Cl^- ions so its length, a, is:

$a = r_- + 2r_+ + r_- = 2r_+ + 2r_-$

To get as close to the cation as possible, the anions must touch along the diagonal of a face of the cube. Click the 'Directions In Which Anions Touch' button to see this view. The diagonal has length, d, where:

$d = r_- + 2r_- + r_- = 4r_-$

Using Pythagoras’ theorem, the length of the side and face diagonal of a cube are related:

$d^2 = a^2 + a^2 = 2a^2$

$d = (2)^{1/2}a$

So,

$4r_- = (2)^{1/2}(2r_+ + 2r_-)$

$r_+ / r_- = (2)^{1/2} – 1 = 0.414$

As long as the radius of the cation is *no smaller* than 41% that of the anion, the NaCl structure is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch but the CsCl structure is even more stable when the cation radius reaches 73% that of the anion. If the cation radius is smaller than 41% that of the anion, the cation and anion will not be in contact. An even lower coordination number is then needed.

The rotatable structure opposite shows the ZnS (zinc blende) structure in which the Zn^{2+} ion is surrounded by 4 S^{2-} ions.

The distance from the centre of the tetrahedron to the corner, d, is:

$d = r_+ + r_-$

To get as close to the cation as possible, the anions must touch along the edge of the tetrahedron. Click the 'Directions In Which Anions Touch' button to see this view. This distance, a, is

$a = r_- + r_- = 2r$The tetrahedral angle, q, is 109.5° so. $\sin(q/2) = r_- / (r_+ + r_-)$

So,

$\sin(54.7°) = r_- / (r_+ + r_-)$

$r_+ / r_- = 0.225$

As long as the radius of the cation is no smaller than 23% that of the anion, the ZnS structure is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch but the NaCl structure is even more stable when the cation radius reaches 41% that of the anion.

UNIT – II

2 Mark questions

1. Define stepwise constants and overall stability constant.
2. What is mean by CFSE?
3. Define labile complex.
4. How deoes the charge of the ligand affect the stability of the complex?
5. What is meant by chealate effect?
6. Why $[Ti(H_2O)_6]^{3+}$ is coloured, $[Zn(H_2O)_6]^{2+}$ is colourless.
7. Give the Jorgenson's relation.
8. What is John -Teller effect?
9. Write any two limitation of CFT.
10. State Racah parameter.

5 Mark questions

1. Explain thermodynamic stability of complexes.
2. Draw and explain crystal field splitting pattern of square planar field.
3. Explain the factors that affect the magnitude of CFSE.
4. Explain spectrochemical series.
5. Write about Nephelauxetic effect.

10Mark questions

1. Discuss the different methods of determining stability constants of complexes.
2. How is over-all stability constant of a complex related to its step-wise stability constants?
3. Give an account of the various factors that affecting the stability of coordination complexes.

COORDINATION CHEMISTRY

STABILITY OF COMPLEXES:

The stability of coordination complex is an important factor that decides the stability and reactivity of a metal complex.The stability of metal complex generally means that it exists under favorable conditions without undergoing decomposition and has a considerable shelf life period. The term stability of metal complex cannot be generalized since the complex may be stable to one reagent/condition and may decompose in presence of another reagent/condition. The stability of metal complexes can be explained with the help of two different aspects, namely, thermodynamic stability and kinetic stability. Nevertheless, a metal complex is said to be stable if it does not react with water, which would lead to a decrease in the free energy of the system, i.e., thermodynamic stability. On the other hand, the complex is said to possess kinetic stability if it reacts with water to form a stable product and there is a known mechanism through which the reaction can proceed. For example, the system may not have sufficient energy available to break a strong bond, although once the existing bond is broken it could be replaced by new bond which is stronger than the older one. Stability of complex compound is assigned to be its existence in aqueous solution with respect to its bond dissociation energy, Gibbs free energy, standard electrode potential, pH of the solution, and rate constant or activation energy for substitution reactions.

Thermodynamic stability

Thermodynamic stability of a complex refers to its tendency to exist under equilibrium conditions. It determines the extent to which the complex will be formed or be converted into another complex at the point of equilibrium. In other words, thermodynamic stability of complexes is the measure of tendency of a metal ion to selectively form a specific metal complex and is directly related to the metal-ligand bond energies. The thermodynamic stability of complexes is represented by formation constant. The formation constant is also known as stability constant, which is the equilibrium constant obtained for the formation metal complex.

Stepwise and Overall Formation Constants

According to J. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex MLn may be supposed to take place by the following n consecutive steps.

where M = central metal cation

L = monodentate ligand

n = maximum co-ordination number for the metal ion M for the ligand

$$M + L \leftrightarrows ML \quad K_1 = \frac{(ML)}{[M][L]}$$

$$ML \leftrightarrows ML_2 \quad K_2 = \frac{(ML_2)}{[ML][L]}$$

$$ML_2 \leftrightarrows ML_3 \quad K_3 = \frac{(ML_3)}{[ML_2][L]}$$

Thus $$ML_{n-1} + L \leftrightarrows ML_n \quad K_n = \frac{(ML_n)}{[ML_{n-1}][L]}$$

The equilibrium constants, K_1, K_2, K_3, ...K_n are called **stepwise stability constants.**

The formation of the complex MLn may also be expressed by the following steps and equilibrium constants.

$$M + L \xrightarrow{B_1} ML, \ \beta = \frac{(ML)}{[M][L]}$$

$$M + 2L \xrightarrow{B_2} ML_2, \ \beta_2 = \frac{(ML_2)}{[M][L]^2}$$

Thus $$M + nL \xrightarrow{B_n} MLn, \ \beta_n = \frac{(MLn)}{[M][L]^n} \qquad ....(8.1)$$

The equilibrium constants, β_1, β_2, β_3, ...β_n are called overall formation or **overall stability constant**s. βn is called as n^th overall (or cumulative) formation constant or overall stability constants.

The higher the value of stability constant for a complex ion, the greater will be its stability. Alternatively 1/k values sometimes are called instability constant.

Stepwise and cumulative stability constants are also expressed as $\log_{10}K_1$, $\log_{10}K_2$................$\log_{10}K_n$ and $\log_{10}\beta_n$ respectively.

Relationship or Interaction Between βn and K_1, K_2, K_3, ...K_n

K's and β's are related to one another consider for example, the expression for β_3 is:-

$$\beta_3 = \frac{(ML_3)}{[M][L]3}$$

On multiplying both numerator and denominator by [ML] [ML_2] and on rearranging we get:

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$= \frac{[ML\ ]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]}$$

$$= K_1 \text{ x } K_2 \text{ x } K_3$$

$$\text{Thus } \beta_n = \frac{[ML\ ]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \ldots\ldots\ldots\ldots\ \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= K_1 \text{ x } K_2 \ldots\ldots\ldots\ldots K_n$$

$$\text{or } \beta_n = \sum_{n=1}^{n=n} K_n$$

From above relation, it is clear that the overall stability constant β_n is equal to the product of the successive (i.e. stepwise) stability constants, K_1, K_2, K_3, ...K_n. This in other words means that the value of stability constants for a given complex is actually made up of a number of stepwise stability constants.

Factors affecting the stability of metal complexes:

There are several factors that can affect the stability of the metal complexes, which include:

1. Nature of the central metal ion
2. Nature of the ligand
3. Chelating effect
4. Macrocyclic effect
5. Resonance effect

6. Steric effect or steric hindrance

1 Nature of central metal ion

1.1 Charge on metal cation

In metal cations, higher oxidation state forms more stable complex than lower oxidation states with ligands such as NH_3, H_2O, etc. Even few exceptions are there like CO, PMe_3, o-phenanthroline, bipyridyl, CN^-, which form more stable complex with lower oxidation state metals.

1.2 Size of central metal cation

The stability of metal complex increases with decrease in size of the metal cations. For M^{2+} ions, the general trend in stability for complexes is

Ba2+<Sr2+<Ca2+<Mg2+<Mn2+<Fe2+<Co2+<Ni2+<Cu2+>Zn2+Ba2+<Sr2+<Ca2+<Mg2+<Mn2+<Fe2+<Co2+<Ni2+<Cu2+>Zn2+

This trend in stability is known as Irving-Williams series.

This order of stability is also in good agreement with the charge to radius ratio concept because the radii decrease from Ba^{2+} to Cu^{2+} and then increased to Zn^{2+}. The order of size of dipositive ions is

Ba2+>Sr2+>Ca2+>Mg2+>Mn2+>Fe2+>Co2+>Ni2+>Cu2+<Zn2+Ba2+>Sr2+>Ca2+>Mg2+>Mn2+>Fe2+>Co2+>Ni2+>Cu2+<Zn2+

2 .Nature of ligands

Basic character of ligands: The greater is the basic character of ligand, the more easily it can donate its lone pair of electrons to the central metal ion and hence greater is the complex stability. In 3D-series metal ion, order of stability of complex with NH_3, H_2O, and F^- is:

NH3>H2O>F−NH3>H2O>F−

The nature of metal-ligand bond also affects the stability of metal complexes. The higher the covalent character, the greater will be the complex stability. For example, the stabilities of silver complexes have different halide ligands which are in the following order:

AgI2−>AgBr2−>AgCl2−>AgF2−AgI2−>AgBr2−>AgCl2−>AgF2−

Ligands having vacant p- or d-orbital tend to form π bond and hence form stable complexes with metals. Ligands that are capable of forming such π bond are CO, CN^-, alkene, phenanthroline, etc.

3. The chelate effect

The chelate effect is that the complexes resulting from coordination of metal ions with the chelating ligand are thermodynamically much more stable than the complexes with non-chelating ligands. Chelating ligands are molecules which can bind to single metal ion through several bonds and are also called as multidentate ligands. Simple (and common) examples include ethylenediamine and oxalate. Non-chelating ligands are ligands that bond to just one site, such as chloride, cyanide, and water.

The chelate effect can be understood by comparing the reaction of a metal ion, respectively, with a chelating ligand and with a monodentate ligand having similar/comparable donating groups. During the comparison study, the number of coordination should be maintained equal in both the cases, for example, the value obtained while adding a bidentate ligand is compared with the value obtained for two monodentate ligands. For example, coordination of metal ion with chelating ligand 2,2′-bipyridine can be compared with that of monodentate pyridine ligand. Another such comparison can be made between coordination behavior of chelating 1,2-diaminoethane (ethylenediamine = en) and monodentate ammonia. Such comparison studies revealed that the metal complex formed from chelating ligands are thermodynamically more stable than the complex formed from monodentate ligand. For example, formation of complexes from hydrated cadmium ion, $[Cd(H_2O)_4]^{2+}$ with methylamine (CH_3NH_2), ethylenediamine (en) and triethylenetetramine (trien), and their stability is in the following order:

[Cd(CH3NH2)4]2+<[Cd(en)]2+<[Cd(trien)]2+CdCH3NH242+<Cden2+<Cdtrien2+

4. Macrocyclic effect

A macrocyclic ligand is a cyclic molecule that contains nine or more atoms in the cyclic structure and has three or more potential donor atoms which can coordinate to the metal ion. It has been observed that the stability of metal complexes in the presence of macrocyclic ligand of appropriate size is higher than the stability of complexes coordinated to open-ended multidentate chelating ligands. Some notable examples of macrocyclic ligands include cyclic crown polyether, heme, etc. [12].

5. Resonance effect

Resonance increases the stability of the complexes. For example, acetylacetonate anion ligand shows resonance, and as a result it forms stable complexes upon reacting with metal ion (Figure 1). The ligand-metal π bonding increases the delocalization of electrons compared to free enolate as shown below and leads to increased stability (Figure 2).

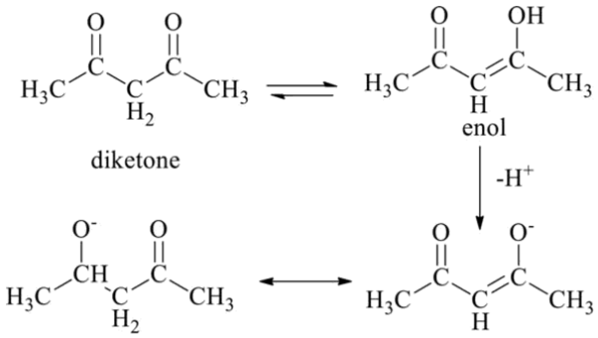


Figure 1.

Resonance structure of acetonylacetonate ligand.

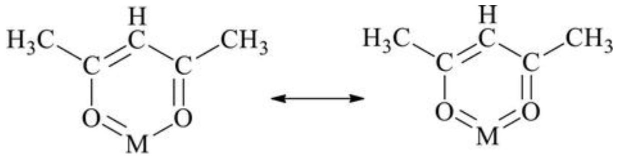


Figure 2.

Acetonylacetonate-metal complex.

6. Steric effect

The presence of bulky substituents in the ligands can affect the stability of the metal complex, and this type of destabilization of metal complex due to bulkiness of the substituent is called as steric effect [13]. For example, consider the ligand 8-hydroxy quinoline and its methyl substituted derivative 2-methyl-8-hydroxy quinolone. Both are bidentate ligands and form chelated complexes with Ni^{2+} ion as shown in Figure 3.

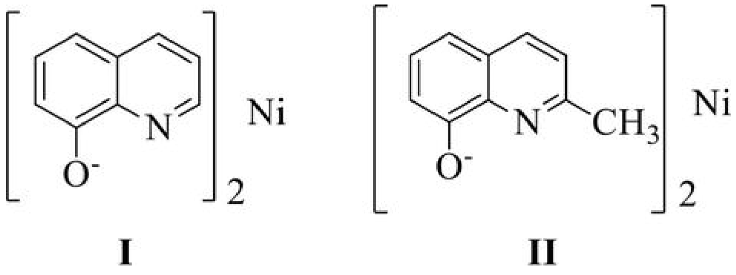


Figure 3.

Chelating complexes of Ni(II) ion showing steric effect.

The complex (II) is less stable than complex (I) because of bulky group attached to an atom adjacent to donor atom which cause a steric hindrance and lower the stability of the complex.

The Chelate Effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is much more thermodynamically stable. This can be seen by looking at the values for adding two monodentates compared with adding one bidentate, or adding four monodentates compared to two bidentates, or adding six monodentates compared to three bidentates.

The Chelate Effect is that complexes resulting from coordination with the chelating ligand is much more thermodynamically stable than complexes with non-chelating ligands.

Determination of stability constants

The determination of metal complexes involves several methods including spectroscopic and potentiometric methods. The determination of stability constant is very significant to understand the role and behavior of ligand(s) in stabilizing the metal complexes and found applications in the fields of biology, environmental study, metallurgy, food chemistry, and many other industrial processes. Some of the methods that are used for the determination of stability constants are given as follows.

Potentiometric method: Bjerrum's Method

It is a potentiometric method for determining the stability constant for complex formation. Although Bjerrum applied the method primarily to the binding of simple molecules or negative ions to positive metal ions. It may be used with equal success with chelating agents. The theoretical relationship outlined by Bjerrum are not restricted to complex formation but may be applied to any equilibrium process regardless of the nature of the interacting substances. Thus, it has been used with success on acid base, and redox equilibria. Although the reactions to be considered involve ions that are more or less completely hydrated, rather than the simple ions, but this fact does not affect the validity of the conclusions, provided the activity of the water is maintained constant.

Formation or dissociation of a complex ion for molecule in the solution always takes place in several steps, which can be easily determined by measuring pH in this method.

Experimental Determination of Stability Constant by Bjerrum's Method

This is a potentiometric method. When the lignad is a weak base or acid, competition between hydrogen ion and metal ions for ligand can be used to the determination of the formation constant.

Let us consider the equilibrium in which an acid and metal ions are added to a basic ligand in solution. Thus the following equation are obtained:

$$L + H^+ \xrightarrow{Ka} HL^+,\ Ka = \frac{[HL^+]}{[L][H^+]}$$

Basic Ligand Acid

$$L + M^+ \xrightarrow{KF} ML^+,\ KF = \frac{[ML^+]}{[L][M^+]}$$

Basic Ligand metal ion

Here Ka and KF are the acid association constant of the ligand and formation constant respectively.

Now if CH, Cm and CL are the total amounts in moles/litre of acid (H^+) , metal (m^+) and basic ligand (L), we have

$$C_H = [H^+] + [HL^+]$$

$$CL = [L] + [ML^+] + [HL^+]$$

$$Cm = [M^+] + [ML^+]$$

Solving the last three equations given above and using the acid association constant of the ligand, Ka. Then we get

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{Ka\,[H^+]}$$

$$[M^+] = C_m - [ML^+]$$

$$[L] = \frac{C_H - [H^+]}{Ka\,[H^+]}$$

Thus on putting the values of $[ML^+]$, $[M^+]$ and [L] from the above equation in

$$K_1 = \frac{[ML^+]}{[M^+][L]}$$

the value of K_1 can be calculated. For the determination of $[ML^+]$, $[M^+]$ and [L], the values of C_H, C_L, C_m, K_a and $[H^+]$, is generally determined potentiometrically using a P_H meter.

In order to get better results, the ligand must be a medium weak acid or base and the formation constant, K_1, should be within a factor of 10^5 of the value of the acid association constant of the ligand, K_a.

Spectrophotometric Method

Job's Method

From the knowledge of stoichiometry of the complex, the value of K (the stability constant) can be determined form the expression given below, if the value of m and n are known:

$$K = \frac{m^{n-1} \times n^{m-1} \times (P-1)^{m+n-1}[n-(m+n)x]}{C_1^{m+n-1} \times P^{n-1}[P(m+n)^{x-1}]^{m+n}}$$

where, K = Stability Constant

1/K = Dissociation Constant of the complex.

P = Ratio of the concentration of the ligand to the concentration of metal.

C_1 = Molar concentration of metal solution.

X = Concentration of ligand for which the concentration of complex is maximum.

m = The number of moles of a metal required to combine with "n" moles of ligand.

for (1:1) Metal ligand ratio in the complex

m = n = 1

$$K = \frac{(P-1)(1-2x)}{C_1 \times [(P+1)(x-1)]^2}$$

Vosburgh and Cooper as well as Katzin and Gebert have extended Job's treatment to systems in which two or more complexes are formed. The ratio of the concentration of metal should not be equal to 1 i.e. non-equimolecular solutions of ligand and metal should be used.

Polarographic method:

The half- wave potential($E_{1/2}$)for the polarographic reduction of a metal ion is altered when the metal complexed. Generally, the ($E_{1/2}$) for the reduction of a metal complex is more negative than that for the reduction of the corresponding simple metal Ion. This implies that the metal in the complexed state is less easily reduced than the free metal. Therefore, polarographic values can be used to determine the formation constants of complexes. This can be illustrated with a Pb(II) complex. For the reduction of simple Pb^{2+}, the equation is

$$Pb^{2+} + 2e^{-} \rightleftharpoons Pb$$

The Nernst equation for this reduction is

$$E = E^{o}_{Pb} - \frac{0.059}{n} \log \frac{[Pb]}{[Pb^{2+}]} \qquad (1)$$

Let the complex formation with lagand L be denoted as

$Pb^{2+} + x\,L \rightleftharpoons PbL_x$ (For simplicity the charge on L is ignored).

Then, the formation constant is given by

$$K = \beta_x = \frac{[\mathrm{PbL_x}]}{[\mathrm{Pb}^{2+}][\mathrm{L}]^x} \quad \text{or}$$

$$[\mathrm{Pb}^{2+}] = \frac{[\mathrm{PbLx}]}{K\,[\mathrm{L}]^x} \qquad (2)$$

The activity of [Pb^{2}+] decreases as the ligand concentration increases.The effect of complexation on $(E_{1/2})_c$, the half wave potential for the complex can be understood by combining equation (1) and (2) { substituting the value of [Pb^{2}+] from (2) in (1)}.

$$E = E^o_{Pb} - \frac{0.059}{n}\log\frac{[\mathrm{Pb}]}{[\mathrm{PbL_x}]} - \frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[\mathrm{L}]$$

Assuming that the complex is reversibly reduced, the values for [Pb] and [PbLx] can be obtained.

$$E = \left(E^o_{Pb} - \frac{0.059}{n}\log\frac{k}{k'}\right) - \left(\frac{0.059}{n}\log\frac{I}{I_d - I}\right) - \left(\frac{0.059}{n}\log K\right) - \left(\frac{0.059\,x}{n}\log[\mathrm{L}]\right)$$

$$E_{1/2} = E^o_{Pb} - \frac{0.059}{2}\log\frac{k}{k'}$$

For simplicity, let k be assumed to remain the same for the complex as for the simple ion.

Then,

$$E = E_{1/2} - \frac{0.059}{n}\log\frac{I}{I_d - I} - \frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[\mathrm{L}]$$

$E_{1/2}$ is the half wave potential for the simple metal Ion couple.

When I= I_d /2 for the complex, E=$(E_{1/2})$ç

$$\therefore \quad (E_{1/2})_c = E_{1/2} - \frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[\mathrm{L}]$$

The half - wave potential shift due to complexation is $\Delta E_{1/2}$.

$$\Delta E_{1/2} = (E_{1/2})_c - E_{1/2}$$

$$\therefore \quad \Delta E_{1/2} = -\frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[\mathrm{L}]$$

The equation indicates that a plot of $\Delta E_{1/2}$ versus log [L] will produce a straight line.

$$\text{slope} = -\frac{0.059\,x}{n}$$

Therefore, x the number of ligands bonded to the metal can be known.

$$\text{intercept} = -\frac{0.059}{n} \log K$$

Therefore, the simplicity constant K of the complex can be calculated.

2.2Crystal Field Theory (CFT)

Crystal field theory describes the net change in crystal energy resulting from the orientation of d orbitals of a transition metal cation inside a coordinating group of anions also called ligands.

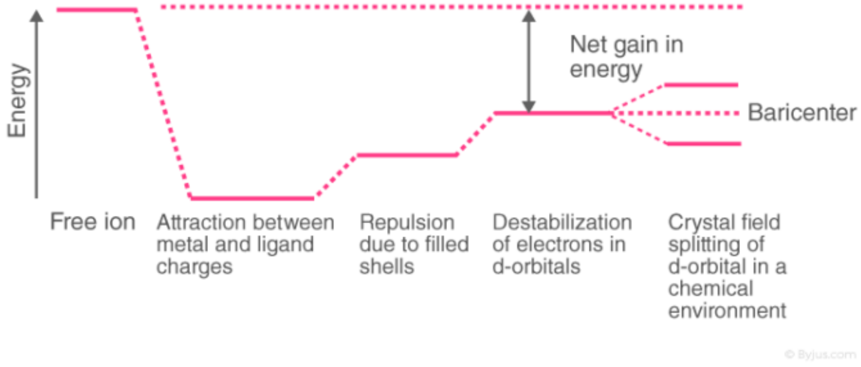
A major feature of transition metals is their tendency to form complexes. A complex may be considered as consisting of a central metal atom or ion surrounded by a number of ligands. The interaction between these ligands with the central metal atom or ion is subject to crystal field theory.

Crystal field theory was established in 1929 treats the interaction of metal ion and ligand as a purely electrostatic phenomenon where the ligands are considered as point charges in the vicinity of the atomic orbitals of the central atom. Development and extension of crystal field theory taken into account the partly covalent nature of bonds between the ligand and metal atom mainly through the application of molecular orbital theory. Crystal field theory often termed as ligand field theory.

Overview of Crystal Field Theory

In order to understand clearly the crystal field interactions in transition metal complexes, it is necessary to have knowledge of the geometrical or spatial disposition of d orbitals. The d-orbitals are fivefold degenerate in a free gaseous metal ion. If a spherically symmetric field of negative ligand filed charge is imposed on a central metal ion, the d-orbitals will remain degenerate but followed by some changes in the energy of free ion.

A summary of the interactions is given below.



Crystal Field Splitting

Crystal field theory was proposed which described the metal-ligand bond as an ionic bond arising purely from the electrostatic interactions between the metal ions and ligands. Crystal field theory considers anions as point charges and neutral molecules as dipoles.

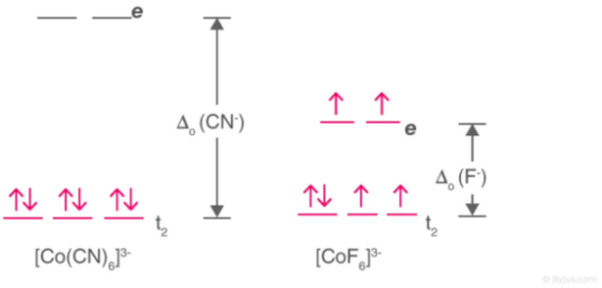
When transition metals are not bonded to any ligand, their d orbitals are degenerate that is they have the same energy. When they start bonding with other ligands, due to different symmetries of the d orbitals and the inductive effect of the ligands on the electrons, the d orbitals split apart and become non-degenerate.

High Spin and Low Spin

The complexion with the greater number of unpaired electrons is known as the high spin complex, the low spin complex contains the lesser number of unpaired electrons. High spin complexes are expected with weak field ligands whereas the crystal field splitting energy is small Δ. The opposite applies to the low spin complexes in which strong field ligands cause maximum pairing of electrons in the set of three t_2 atomic orbitals due to large Δ_o.

- **High spin –** Maximum number of unpaired electrons.
- **Low spin –** Minimum number of unpaired electrons.

Example: $[Co(CN)_6]^{3-}$ & $[CoF_6]^{3-}$



High Spin and Low Spin Complex

- $[Co(CN)_6]^{3-}$ – Low spin complex
- $[CoF_6]^{3-}$ – High spin complex

The pattern of the splitting of d orbitals depends on the nature of the crystal field. The splitting in various crystal fields is discussed below:

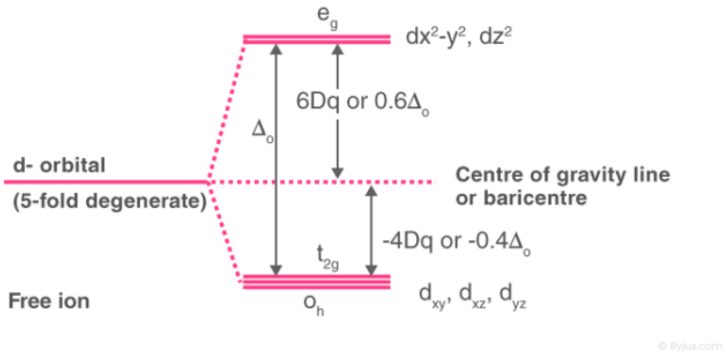
Crystal Field Splitting in Octahedral Complex

- In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
- This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.
- Hence, they have higher energy than average energy in the spherical crystal field.

- On the other hand, d_{xy}, $d_{yz,}$ and d_{xz} orbitals experience lower repulsions as they are directed between the axes.
- Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

Thus, the repulsions in octahedral coordination compound yield two energy levels:

- t_{2g}– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with lower energy
- e_g – set of two orbitals ($d_{x}{}^{2}-y^{2}$ and $d_{z}{}^{2}$) with higher energy



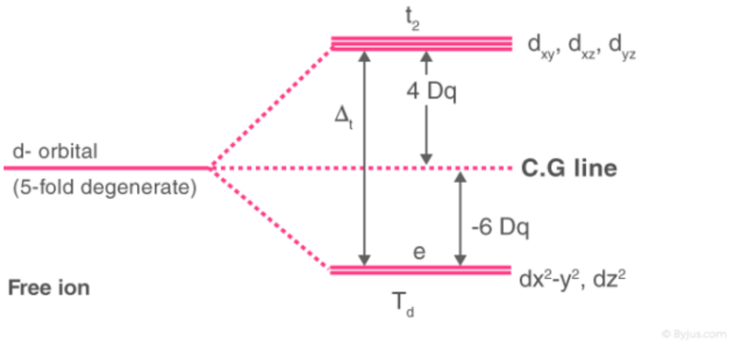
Crystal Field Splitting in Octahedral Complex

This splitting of degenerate level in the presence of ligand is known as crystal field splitting. The difference between the energy of t_{2g} and e_g level is denoted by "Δ_o" (subscript o stands for octahedral). Some ligands tend to produce strong fields thereby causing large crystal field splitting whereas some ligands tend to produce weak fields thereby causing small crystal field splitting.

Crystal Field Splitting in Tetrahedral Complex

The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d. The electrons in $d_{x}{}^{2}-y^{2}$ and $d_{z}{}^{2}$ orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals. As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbital set are raised while that os the $d_{x}{}^{2}-y^{2}$ and $d_{z}{}^{2}$ orbitals are lowered.

- There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.
- The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.



Crystal Field Splitting in Tetrahedral Complex

Thus, the repulsions in tetrahedral coordination compound yield two energy levels:

- t_2– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with higher energy
- e – set of two orbitals ($d_{x}{}^{2}$-y^2 and $d_z{}^2$) with lower energy

The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral filed because there are only two thirds as many ligands and they have a less direct effect of the d orbitals. The relative stabilizing effect of e set will be -6Dq and the destabilizing effect of t_2 set will be +4Dq

Square Planar Complexes

In a square planar, there are four ligands as well. However, the difference is that the electrons of the ligands are only attracted to the xyxy plane. Any orbital in the xy plane has a higher energy level. There are four different energy levels for the square planar (from the highest energy level to the lowest energy level): $d_{x^2-y^2}$, d_{xy}, $d_z{}^2$, and both d_{xz} and d_{yz}.

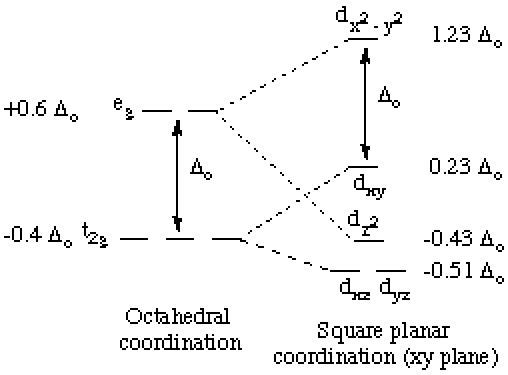


Figure : Splitting of the degenerate d-orbitals (without a ligand field) due to an square planar ligand field.

The splitting is affected by the following factors:

- the nature of the metal ion.
- the metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.

- the arrangement of the ligands around the metal ion.
- the coordination number of the metal (i.e. tetrahedral, octahedral...)
- the nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy *d* groups.

Crystal Field Stabilization Energy

In a chemical environment, the energy levels generally split as directed by the symmetry of the local field surrounding the metal ion. The energy difference between the eg and t_{2g} levels is given as or $10D_q$. It states that each electron that goes into the lower t_{2g} level stabilizes the system by an amount of $-4D_q$ and the electron that goes into e_g level destabilizes the system by $+6D_q$. That is the t_{2g} is lowered by $4D_q$ and the e_g level is raised by $+6D_q$.

For example, the net change in energy for d^5 and d^{10} systems will be zero as shown below.

d^5 :- $3(-4D_q) + 2(+6D_q) = -12D_q + 12D_q = 0$
d^{10} :- $6(-4D_q) + 4(+6D_q) = -24D_q + 24D_q = 0$

The decrease in energy caused by the splitting of the energy levels is called the “Ligand Field Stabilization Energy (LFSE)”.

Spectrochemical series
A **spectrochemical series** is a list of ligands ordered on ligand strength and a list of metal ions based on oxidation number, group and its identity. In crystal field theory, ligands modify the difference in energy between the d orbitals (**Δ**) called the **ligand-field splitting parameter** for ligands or the **crystal-field splitting parameter**, which is mainly reflected in differences in colour of similar metal-ligand complexes.

Spectrochemical series of ligands

The spectrochemical series was first proposed in 1938 based on the results of absorption spectra of cobalt complexes.
A partial spectrochemical series listing of ligands from small Δ to large Δ is given below.
$I^- < Br^- < S^{2-} <$ SCN− (S–bonded) < Cl− < N3− < F−< NCO− < OH− < C2O42− < O2−< H2O < acac− (acetylacetonate) < NCS− (N–bonded) < CH3CN < gly (glycine) < py (pyridine) < NH3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < NO_2^- (N–bonded) < $PPh_3 < CN^- <$ CO
Weak field ligands: H_2O, F^-, Cl^-, OH^-
Strong field ligands: CO, CN^-, NH_3, PPh_3
Ligands arranged on the left end of this spectrochemical series are generally regarded as weaker ligands and cannot cause forcible pairing of electrons within the 3d level, and thus form outer orbital octahedral complexes that are high spin. On the other hand, ligands lying at the right end are stronger ligands and form inner orbital

octahedral complexes after forcible pairing of electrons within 3d level and hence are called low spin ligands.

2.3 Spectrochemical series of metals

The metal ions can also be arranged in order of increasing Δ, and this order is largely independent of the identity of the ligand.

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$

In general, it is not possible to say whether a given ligand will exert a strong field or a weak field on a given metal ion. However, when we consider the metal ion, the following two useful trends are observed:

- Δ increases with increasing oxidation number, and
- Δ increases down a group.

Jorgenson's Relation

$$\Delta_0 = f.g$$

f- metal parameter

g- ligand parameter

John-Teller effect (Distortion in d^9 configuration): Any non linear molecule in a degenerate electronic state will be unstable and will undergo some kind of distortion while which lower its symmetry and split the the degenerate state. This is called John teller effect.

Let us consider Cu^{2+} ion which has 9 electrons in its 3d orbital, this ion when present at the centre of an octahedral complex. It will have one vacant orbital in eg level. According to John teller effect such a system cannot be e a perfect octahedron it will be distorted in some way.

significance: This effect helps us in understanding the the structure of some coordination complexes.

Magnetic Properties of Complexes

The complex in which central transition metal ion has unpaired electrons is Paramagnetic.

1. The complex in which central transition metal ion has no unpaired electrons is diamagnetic.
2. The magnetic moment of a complex is calculated by the spin only formula

$$M = \sqrt{[n(n+2)]}\ BM$$

BM = Bohr Magneton

The magnetic moment of complex compounds depends upon:

- Type of hybridization.
- The oxidation state of central transition metal ion.
- The number of unpaired electrons.

Colour of Complexes

Complexes in which central transition metal ion contains unpaired electrons shows colour. It is ‘d – d’ transition. The colour of complexes depends upon:

Number of unpaired electrons in transition metal ion

- Nature of ligands
- The oxidation state of central transition metal ion
- The wavelength of light absorbed and emitted
- The proportion of ligands in the coordination sphere

Example: [Ni(H2O)6]+2+en(aq)→[Ni(H2O)4en]$^{+2}$ – Green Pale blue

The Limitations Of Crystal Field Theory

The crystal field theory is highly useful and more significant as compared to the valence bond theory. Even after such useful properties, it has many limitations. The following points will clearly state the limitations of crystal field theory:

1. The assumption that the interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.
2. This theory takes only d-orbitals of a central atom into account. The s and p orbits are not considered for the study.
3. The theory fails to explain the behaviour of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H_2O is a stronger ligand as compared to OH^-.
4. The theory rules out the possibility of having p bonding. This is a serious drawback because is found in many complexes.
5. The theory gives no significance to the orbits of the ligands. Therefore, it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals.

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Nephelauxetic effect

The **nephelauxetic effect** is a term used in the inorganic chemistry of transition metals. It refers to a decrease in the Racah interelectronic repulsion parameter, given the symbol *B*, that occurs when a transition-metal free ion forms a complex with ligands. The name "nephelauxetic" comes from the Greek for cloudexpanding and was proposed by the Danish inorganic chemist C. K. Jorgensen. The presence of this effect brings out the disadvantages of crystal field theory, as this accounts for somewhat covalent character in the metal-ligand interaction.

Racah parameter

The decrease in the Racah parameter *B* indicates that in a complex there is less repulsion between the two electrons in a given doubly occupied metal d-orbital than there is in the respective M^{n+} gaseous metal ion, which in turn implies that the size of the orbital is larger in the complex. This electron cloud expansion effect may occur for one (or both) of two reasons. One is that the effective positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the *d*-orbitals can expand slightly. The second is the act of overlapping with ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals.

The reduction of *B* from its free ion value is normally reported in terms of the nephelauxetic parameter, β

$$\beta = B(\text{complex}) / B\ (\text{free ion})$$

Experimentally, it is observed that size of the nephelauxetic parameter always follows a certain trend with respect to the nature of the ligands present.

Ligands: The list shown below enlists some common ligands (showing increasing nephelauxetic effect , in order of increase of the amount of renormalization):
$F^- > H_2O > NH_3 > en > [NCS - N]^- > Cl^- > [CN]^- > Br^- > N_3^- > I^-$
Central metal ion: The nephelauxetic effect does not only depend upon the ligand type, but also upon the central metal ion. These too can be arranged in order of increasing nephelauxetic effect as follows:Mn(II) < Ni(II) ≈ Co(II) < Mo(II) < Re(IV) < Fe(III) < Ir(III) < Co(III) < Mn(IV)

Angular Overlap Model (AOM): This is a theory that estimates bonding strengths and energies according to the ability of frontier (ie valence) orbitals from ligands to overlap with the valence d-orbitals of the metal. The main consideration for orbital interactions is the directions/positions of d-orbitals and ligand orbitals in space. AOM is limited in that it only considers the metal d-orbitals (not the valence s- and p-). The advantage to this theory is that it is simple: it can be used well as an approximations to predict relative strengths of bonds in heteroleptic complexes and complexes with unique geometries.

TITLE: INORGANIC CHEMISTRY - I

CODE: 18KP1CH01

UNIT - III

2 MARK

1. What is Acid hydrolysis?
2. What is SN1 reaction ? Give example.
3. What is ligand substitution reaction?
4. Write down the definition of Trans effect?
5. What is means by redox reaction?
6. Give the example of inert and labile complexes?
7. State Marcus hush principle?
8. What is base hydrolysis?
9. Write down the Taube's reaction?
10. State VBT?

5 MARK

1. Explain inert and labile complex?
2. What is SN1 reaction? Explain with example.
3. Explain SN_{CB}mechanism?
4. Write short note on Marcus hush principle?
5. Briefly account on trans effect?

10 MARK

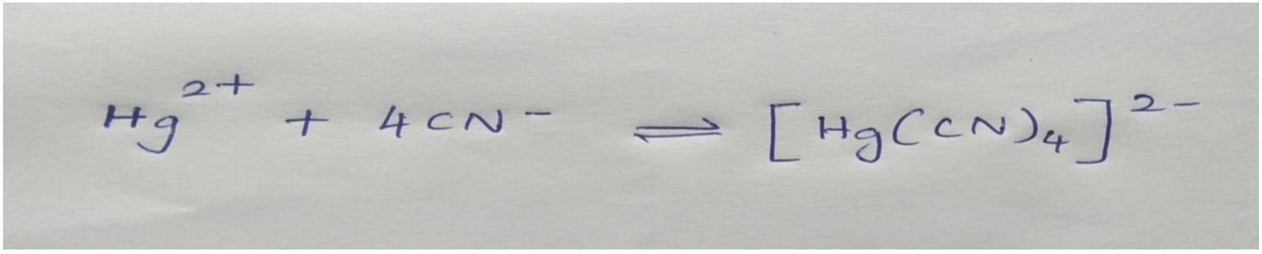
1. Explain the electron transfer mechanism?
2. What is acid hydrolysis? Explain the acid hydrolysis reactions of six coordinated complexes.
3. Explain ligand substitution reaction?
4. Explain inner and outer mechanism?

UNIT – III

REACTION MECHANISM OF TRANSITION METAL COMPLEX

1. **Inert and labile complex:**

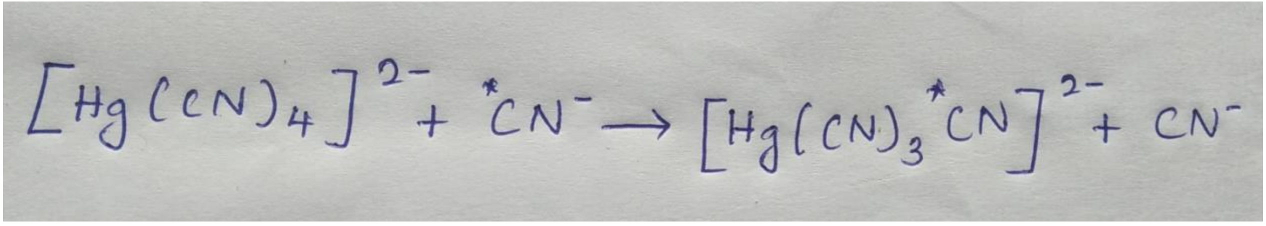
A complex which reacts rapidly is called a labile complex. A complex which reacts slowly is an inter complex. The word inert used here indicates only slowness of reaction but not inability to react , these two terms labile and inert relatively refer to rates of reactions and are not related to instability and stability. The term stability or instability refers to the thermodynamic character of the complex to exist under equilibrium conditions. For example, $[Hg(CN)_4]^{2-}$ is thermodynamically very stable. The thermodynamic stability of a complex is related is related to its formation constant higher is its formation constant (β), greater the stability. Thus for $[Hg(CN)_4]^{2-}$ formation constant is very high.



$$Hg^{2+} + 4CN^- \rightleftharpoons [Hg(CN)_4]^{2-}$$

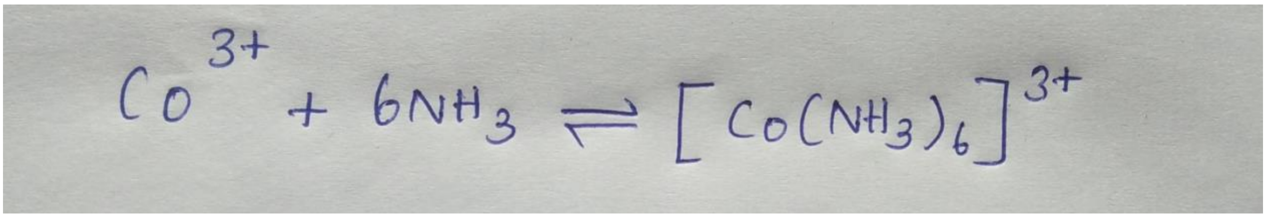
$$\beta = 1 \times 10^{42}$$

The kineticnature of this complex (lability or inertness) is not decided by its thermodynamic stability alone; it is influenced by other factors also such as the other reactant, temperature, solvent, etc. Though $[Hg(CN)_4]^{2-}$ is thermodynamic stable, it can react fast withsome reagents. For example its exchange reaction with isotopically labeled cyanide ion is extremely rapid;



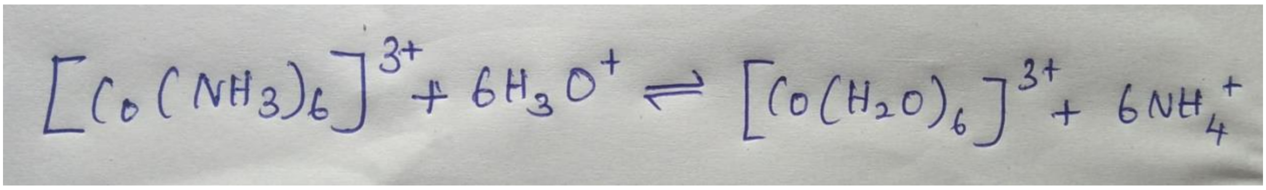
$$[Hg(CN)_4]^{2-} + {}^{*}CN^- \rightarrow [Hg(CN)_3{}^{*}CN]^{2-} + CN^-$$

On the other hand $[Co(NH^3)_6]^{3+}$ is thermodynamically unstable it has a low β value.



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

However $[Co(NH_3)_6]Cl_3$ can be prepared form aqueous medium and stored in the laboratory. This is possible because its reaction with H_2O in acid medium is very slow.
Thus, $[Hg(CN)_4]^{2-}$ is stable, $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable, but inert unlike these two complex ions, $[Fe(CN)_6]^{3-}$ is stable and inert.



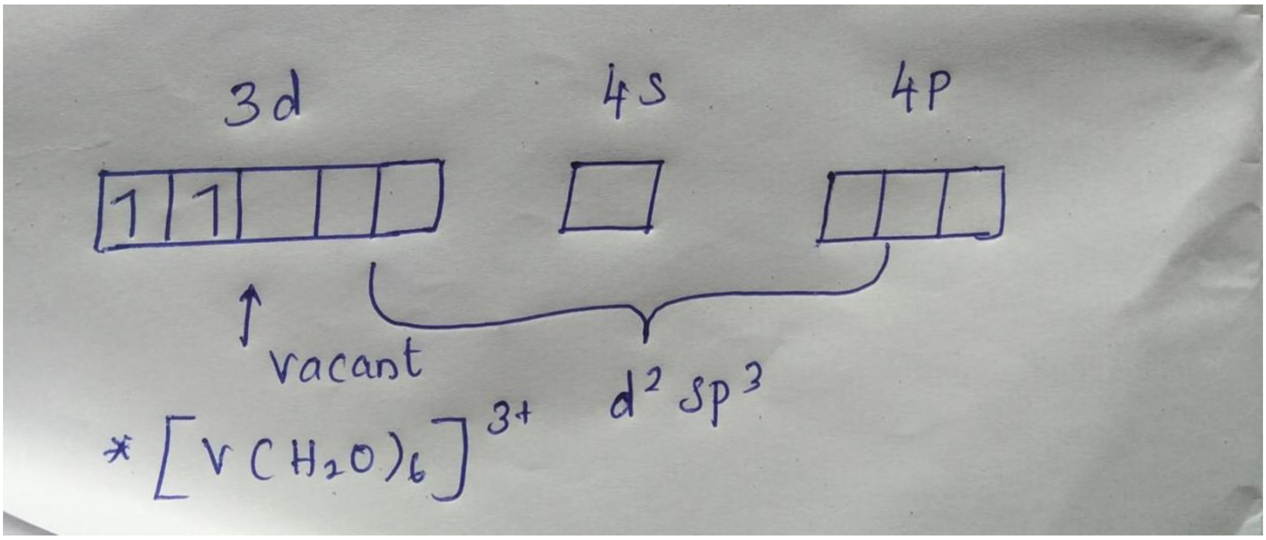
$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightleftharpoons [Co(H_2O)_6]^{3+} + 6NH_4^+$$

2. VBT explanation of lability and inertness:

According to the VBT, the octahedral complexes are types, namely 1. Outer orbital complexes which use sp3d2 hybridizationand 2. Inner orbital complexes which use d2 sp3 hybridization. Outer orbital complexes are generally labile. This lability is correlated with the weakness of the bonds of sp3d2 type as compared with d2 sp3 bonds. For example, mn^{2+} (d), fe^{3+} (d6), fe^{3+} (d5) and co^{2+} (d7) all high spin complex (outer orbital complexes), exchanging their ligands rapidly and hence are labile.

In the inner orbital complexes, if all the three t2g levels are filled either singly or doubly, then they are inter kinetically. If an inner orbital complex contains one or two electronsin the t2g set then at least one level will be vacant. For example, $[v(H_2O)_6]^{3+}$ contains two electrons in the 3d level.

Two of the three t2g levels are singly occupied. Hence the third level can be used to accept the electron pair donated by the incoming ligands to form a 7 coordinated intermediate which is less stable, Tg get itself stabilized one of the original six ligands is expelled leading to a substitution product . This means that this complex,$[v(H_2O)_6]^{3+}$ is labile.



* $[V(H_2O)_6]^{3+}$

But in, $[Cr(H_2O)_6]^{3+}$, there is no d level vacant to accept the electron pair donated by the incoming ligands, hence this complex is inert.

3. **LIGAND SUBTITUTION REACTIONS**

The substitution of one or more ligands in a complex by another ligands is a ligand substitution reaction. This can be denoted as

$$[ML_5X]^{n+} + Y^- \longrightarrow [ML_5Y]^{3+} + X^-$$

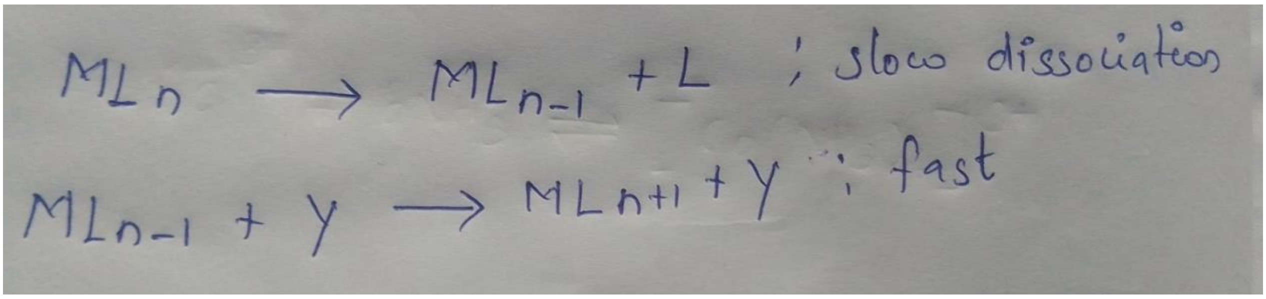
In this reaction, the ligand x in the complex is substituted by another ligand y-

$$[Cr(H_2O)_6]^{3+} + CN^- \rightleftharpoons [Cr(H_2O)_5CN]^{2+} + H_2O$$

A ligand substation react ion may proceed through SN_1or SN_2 mechanism.

4. **SN_1 Mechanism:**

In this mechanism first the reactant metal complex dissociated the ligands to be replaced is lost from the complex. Then, the vacancy created in the coordination sphere is taken by the new ligand. This mechanism is depicted generally as



$ML_n \longrightarrow ML_{n-1} + L$; slow dissociation

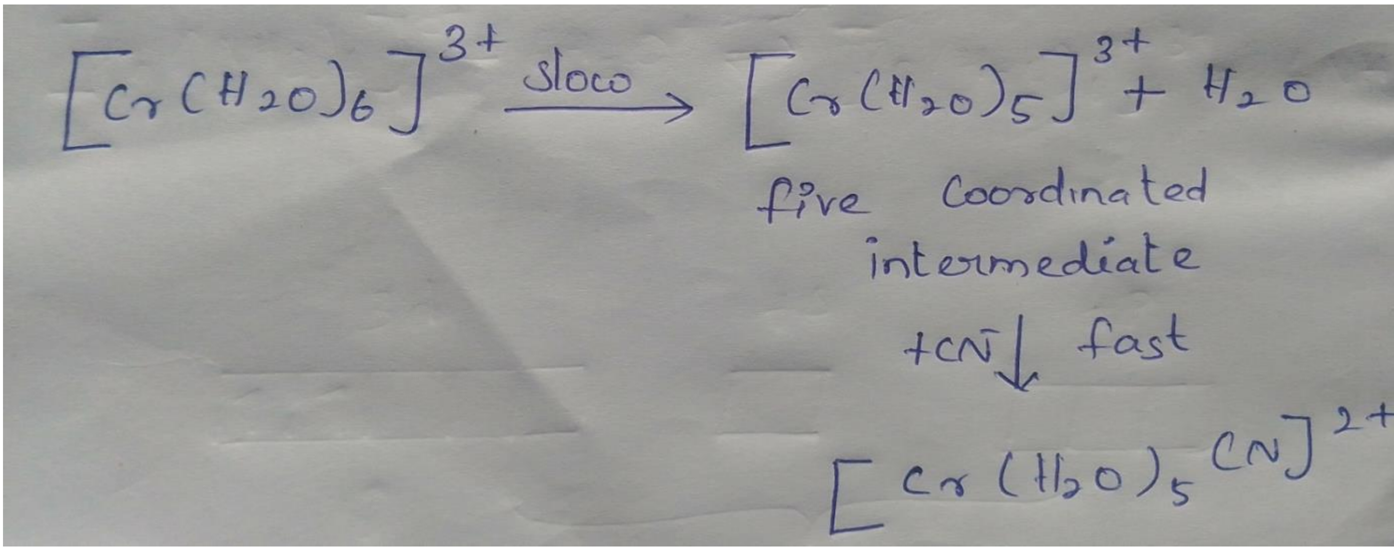
$ML_{n-1} + Y \longrightarrow ML_{n+1} + Y$; fast

Characteristics

1) Only one species (ML) is involved in the formation of the activated species the slow step1.
2) In the second step, the activated species undergoes fast reaction with the incoming ligand Y.
3) The activation energy for the first step is high and that for the second step is low.
4) The rate of the over all reactiondepends upon [MLn], not upon[Y].
5) The reaction is first order with respect to MLn; it is zero order with respect to Y.
6) In the formation of the activated complex in an SN_1 reaction, the coordination number of the metal is decreased by one (n to n-1).
7) The rate law for this substitution is

$$\nu = k_1[MLn]$$

where ν is the rate and k1 is the first order rate constant.



$$[Cr(H_2O)_6]^{3+} \xrightarrow{slow} [Cr(H_2O)_5]^{3+} + H_2O$$

five coordinated intermediate

$$\Big\downarrow {+CN^-} \quad fast$$

$$[Cr(H_2O)_5CN]^{2+}$$

The rate law for this reaction is

$$\nu = k\ \{[Cr(H_2O)_6]^{3+}\}$$

According to this mechanism, the rate of the reaction is directly proportion to the concentration of $[Cr(H_2O)_6]^{3+}$; it is independent of the concentration of CN^-.

5. **SN_2 mechanism:**

This mechanism is depicted in the general form as

$$MLn + Y \longrightarrow MLnY \ : \ \text{slow association}$$

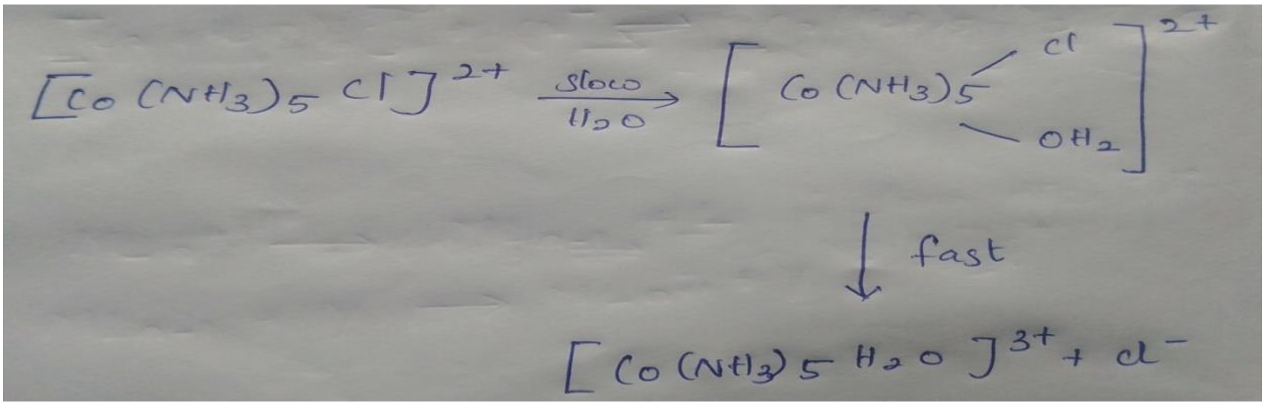
$$MLnY \longrightarrow ML_{n-1}Y + L \ : \ \text{fast}$$

Characteristics

1) In this reaction, two species (MLn and Y) are involved in the formation of the activated species; Y is added to the reactant complex to form the activated species.
2) In this second fast step, the activated complex loses a ligand (L) and the new ligand Ybecomes a permanent part of the molecule.
3) The rate of the overall reaction depends upon [MLn] and [Y].
4) The reaction is first order with respect to MLn and first order with respect to Y, it is over all second order.
5) In this formation of the activated species, the coordination number of the metal is increases (n to n+1).
6) The general ate law for this reaction is

$$\nu = k_2\ [MLn]\ [Y]$$

This mechanism may be illustrated with the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$



$$[Co(NH_3)_5Cl]^{2+} \xrightarrow[H_2O]{\text{slow}} \left[Co(NH_3)_5 \begin{matrix} Cl \\ OH_2 \end{matrix}\right]^{2+} \xrightarrow{\text{fast}} [Co(NH_3)_5H_2O]^{3+} + Cl^-$$

The rate of this reaction is proportional to the product of the concentrations of the two reactants:

$$v = k_2 [Co(NH_3)_5Cl]^{2+} [H_2O]$$

The expectation that a reaction would occur exclusively either by the SN_1 mechanism or by the SN_2 mechanism is not realize. In a reaction, the attachment of YtoM and the release of L from M can be simultaneous, In addition the activated species cannot be directly detected.

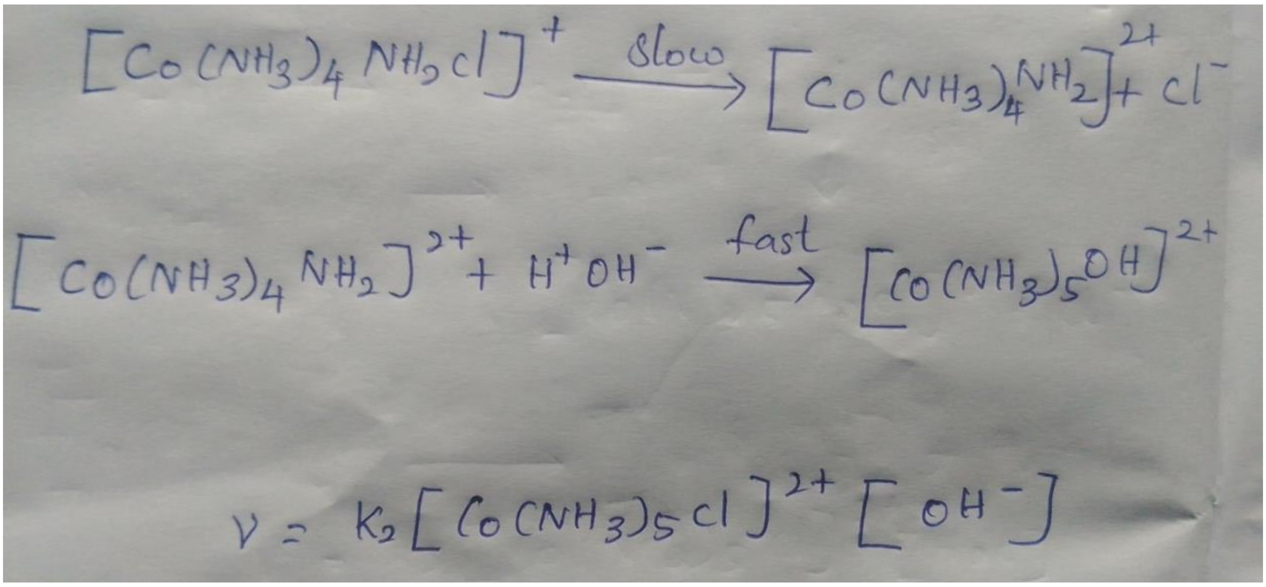
6. **SN_1CB mechanism:**
    1) In this mechanism, one of the ligands in the complex is converted into its conjugatebase (CB) by the action of the base normally OH^-. This first step is fast.
    2) Then in the second step, which is rate determining the conjugate base dissociates releasing the ligand to be replaced.
    3) Subsequently the new ligand is added to the remaining part the complex species, leading to the product.
    4) This mechanism is called unimolecular because in the slow step only one molecule (ion as shown in the mechanism) is involved.
    5) But the kinetics is second is second order because the concentration of thecomplex and concentration of the base (OH-) are involved up to the slow step.
    6) The rate of this reaction is denoted as

$$\nu = k_2[MLn]\,[OH-]$$

For this mechanism the react complex should have at least one proton hydrogen ion on the ion leaving ligand. This mechanism may be illustrated with the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4NH_2Cl]^{+} H_2O$$

Conjugate Base



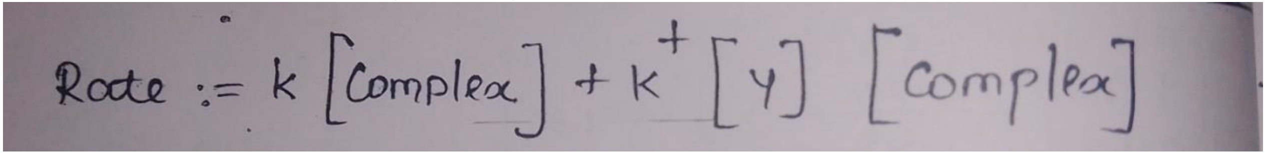
$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow{slow} [Co(NH_3)_4NH_2]^{2+} + Cl^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H^+OH^- \xrightarrow{fast} [Co(NH_3)_5OH]^{2+}$$

$$v = k_2[Co(NH_3)_5Cl]^{2+}[OH^-]$$

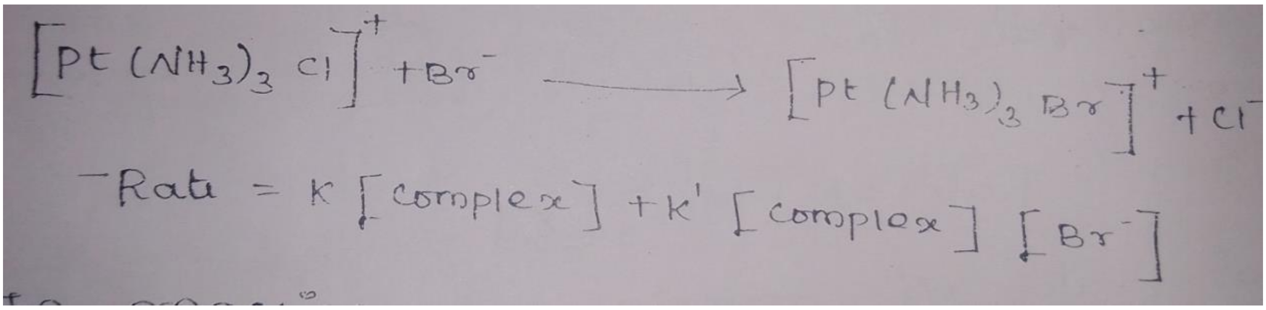
It is actually a hydrolysis reaction, Cl^- getting replaced by $OH^-$for the hydrolysis of cobalt animines the reaction rates ate about million times faster with base compared to acid hydrolysis.

7. **Substitution reaction in square planar complex:**
   In general these complexes proceed by molecular displacement SN_2 mechanism. The rate law is given is general form as



$$\text{Rate} := k[\text{Complex}] + k^{+}[Y][\text{Complex}]$$

Here k is first order rate constant for SN_2 reaction between complex and solvent k_1 is the second rate constant for the reaction with Y. Thus rx of legend displacement may be proceed by two paths. Both supporting associate mechanism. The first path involves solvent and the second involves the entering of ligand Y.



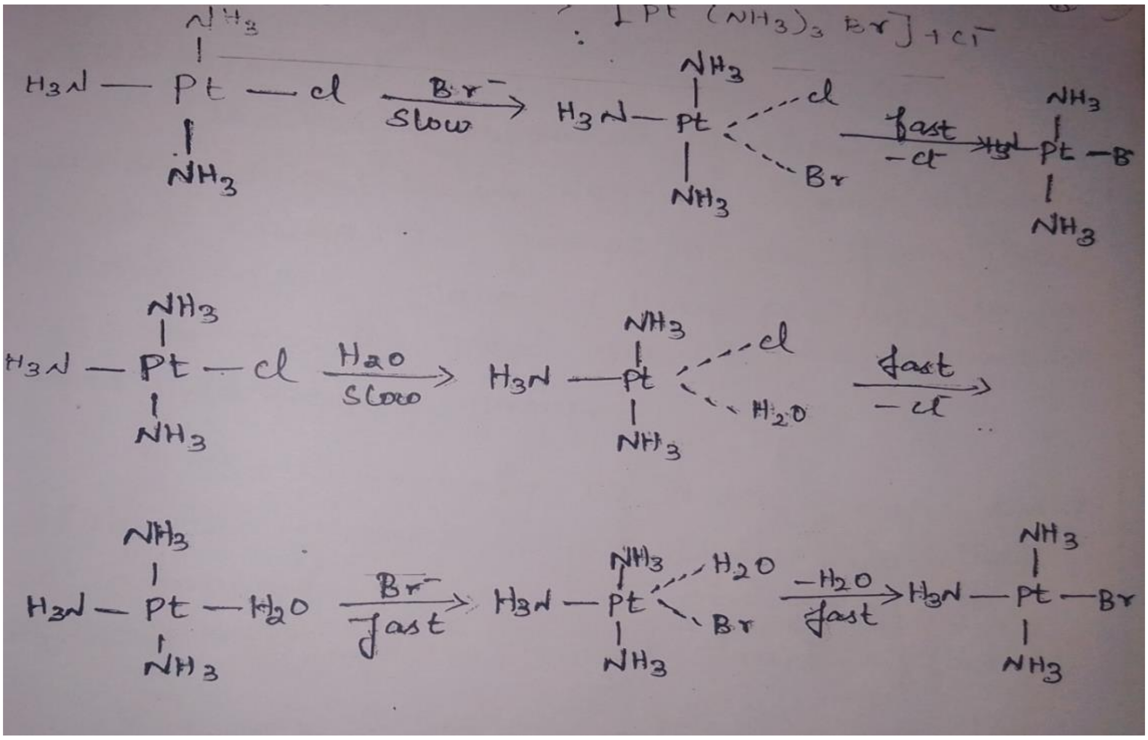
$$[Pt(NH_3)_3Cl]^+ + Br^- \longrightarrow [Pt(NH_3)_3Br]^+ + Cl^-$$

$$-\text{Rate} = k[\text{complex}] + k'[\text{complex}][Br^-]$$

The reaction occurs by two paths. In the pathway H_2O replaces X^- in a slow step and its subsequently by Y^- in a rapid step. The solvent path gives pseudo first order kinetics . The second is direct path or reagent path when gives a second order kinetics.

The two paths are shown in the following scheme.

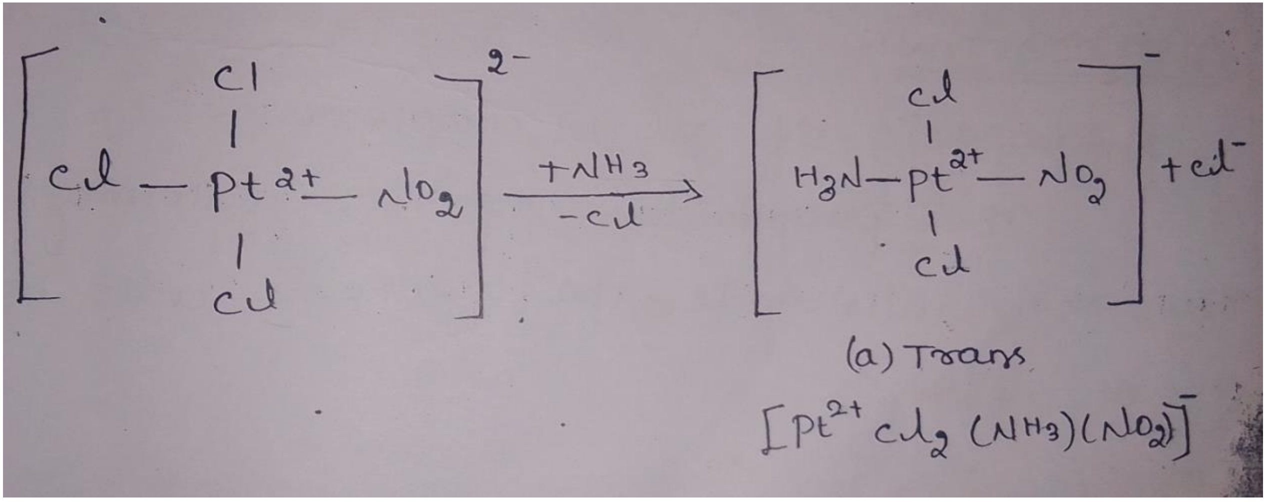
$$[Pt(NH_3)_3Cl] + Br^- \longrightarrow [Pt(NH_3)_3Br] + Cl^-$$

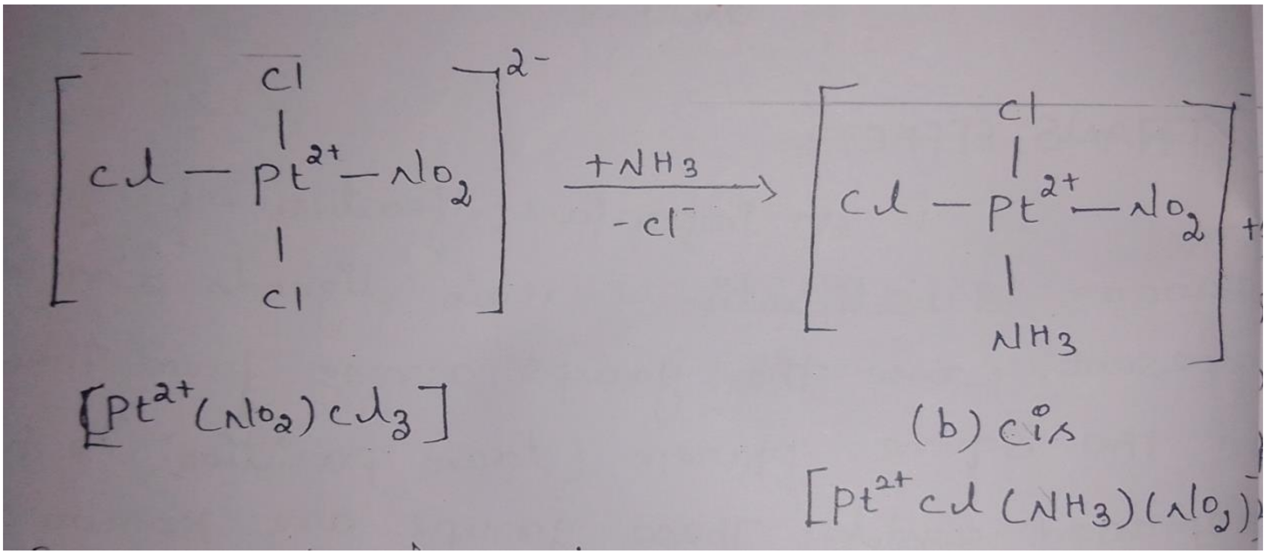


8. **TRANS EFFECT:**
   It is an important feature of square planar substitution. Certain ligands already present. Cause the groups across from then in the square planer (trans position) to be replaced easily. These groups are known as trans directing groups.

   The property of these groups due to which the group lying Transto them are replaced fare, more easily by the entering ligand is called Trans effect.

   Consider the substitution reaction in Pt (II) square planar complex [Pt (No_2) $Cl_3]^{2-}$ with NH_3 to yield [Pt (No_2) Cl_3 $(NH_3)]^-$theoretically there are two possible traction products.





Experiment have however, shown that it only (a) which is formed.[a] is formed by the replacement of Cl^- lying Trans to No^{2-} in Pt (No_2) $Cl_3]^{2-}$ by NH_3. The formation of (a) is explained by saying that Cl^- ion lying Trans to No_2 in Pt (No_2) $Cl_3]$ is for more easily replaced by NH_3. Then either of the two Cl^- joins lying to NO_2 ion. Then phenomena of such type of replacement are called Trans effect.

9. Electron Transfer reactions (REDOX REACTION):

In an electron – transferreaction, an electron is transformed fromonecomplex to another.

$$[Cr(H_2O)_6]^{2+} + [IrCl_6]^{2-} \longrightarrow [Cr(H_2O)_6]^{3+} + [IrCl_6]^{3-}$$

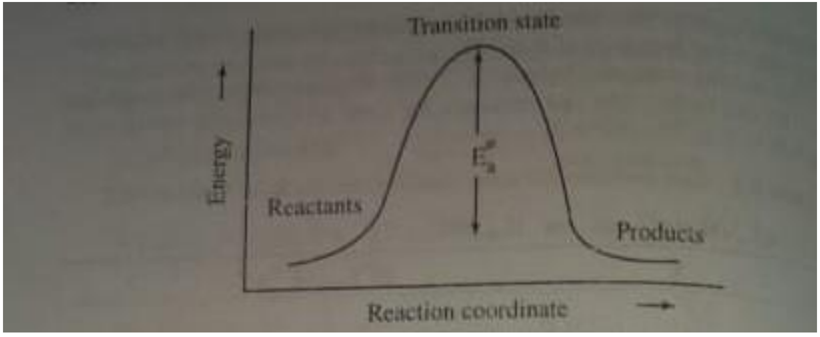
In the reaction given above, an electron has been transferred from the chromium complex to the iridium complex. Thus the chromium complex gets oxidized and the iridium complex gets reduced. This is a simple redox reaction. An electron transfer occursbetween two complex reactants.

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

No net c change in the stoichiometry occurs in a such an electron transfer as all the concentration apparently remain unchanged there is no net chemical change. But this reaction involving electron transfer can be proved by labeling one of the reactants. For example, if labeled iron (II) is used then after the reaction, the labeled iron will be found in Fe (III) startalso.

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

The kinetics of this reaction canbe followed by estimation of Fe*either as Fe (III) or Fe (II). The energy of activation, for this reaction is 33KJ mol-1. An electrontransfer with no net chemical change is called an electron exchange reaction. No net free energy change occurs in this reaction.

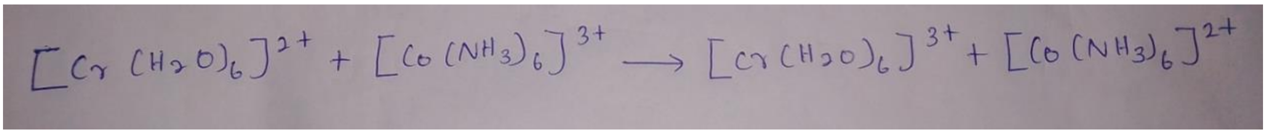


The two o types mechanism as known as for electron transfer reaction.

1) The outer sphere mechanism
2) The inner sphere mechanism

I. Outer sphere mechanism(OSM)or(tunneling mechanism):

1. In this mechanism the electrons hops across from the reduction to the oxidant. The coordination sphere remains unaffected. The ligands in the tow reactants remain as such and bonds, are neither made nor broken. The electron is set to *tunnel through* the medium from the reductant to the oxidant.



$$[Cr(H_2O)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Cr(H_2O)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

2. As there is not movement of any ligand, the Franck-Condon activated barrier for this process is small.

The energy Ea* is a constituted by three portions.

a) The electrostatic energy arising from repulsion between the species of like charge.
b) The energy required to distort and reorient the tow coordination sphere for easy flow of electron and
c) The energy needed to modify the solvent structure about each reactant species.

3.This mechanism is expected of reactants which are not labile complexes. The ligands in the tow reactants are so firmly attached that one complex does not form and bond with other involving its ligands even if one of the reactants of labile, the other would not offer a suitable site for attachment of the metal ion of the labile complex; hence only OSM is possible.

4.Outer sphere reaction are first order in each reactant, the over all order being two.

1.The oxidant (O) andthe reductant (R) interact and form a precursor complex.

$$O+R \rightarrow O\text{---}R$$

2.In second step the precursor complex is activated which is a prerequisite for reaction.

$$O\text{----}R \rightarrow (O\text{----}R)^*$$

The energy of activation can be acquired by O---R from other O and R molecules or from the solvent molecules.

3.Then changes in metal ligands bond length occur the molecule framework remaining intact.

$$(O----R)^* \rightarrow (O^{-}------R^{+})$$

4. In this step the electron from the reductant is displaced is displaced towards the oxidant producing an ion pair.

5.In the final step, the ion pair breaks into product ions.

$$(O^{-}------R^{+}) \rightarrow O^{-} + R^{+}$$

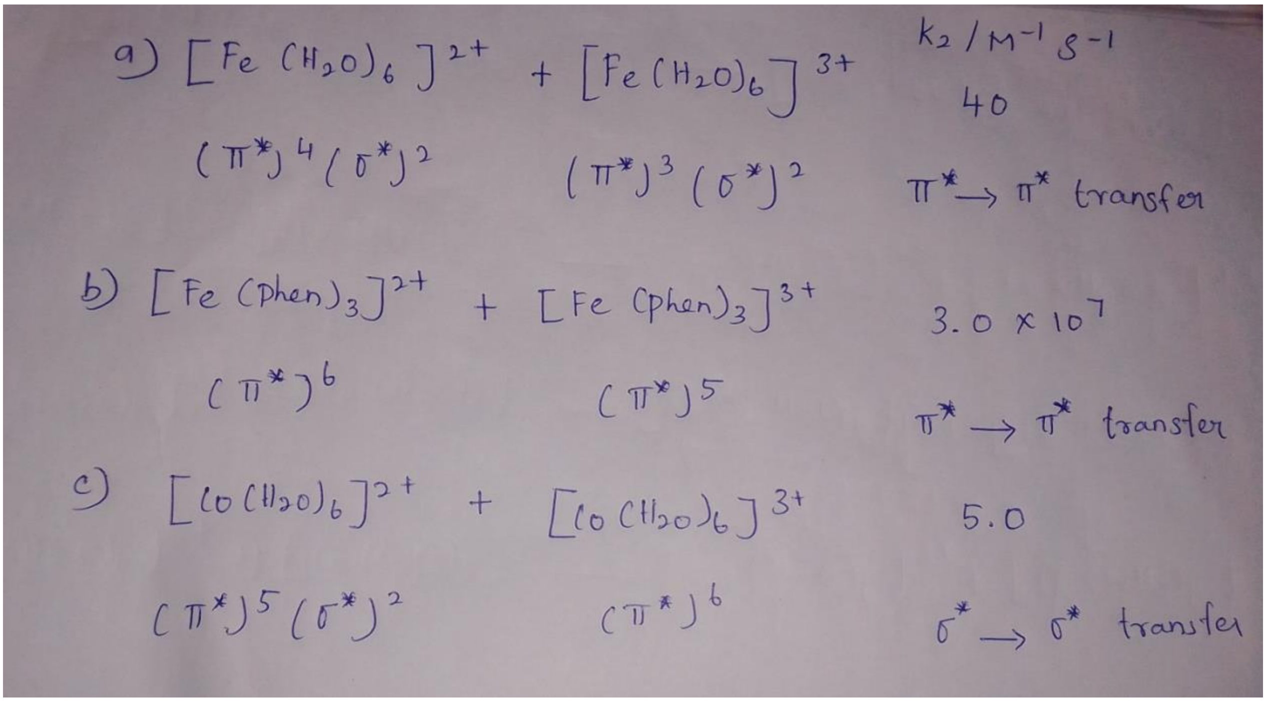
Essential requisite for electron – transfer

For easy electron transfer, the reductant and oxidant should have similar structures. The Franck Condon principle assumes than an electron moves very quickly compared to an atom; therefore during the electron transfer no prescribe equal energies for the participating electronic orbital.

If electron transfer occurs as such without any energy input then the productFe (II) complex would have bond lengthscharacteristic Fe (III) and Fe (II) complex product would have bond lengths characteristics of Fe (II). Since such as situation is unacceptable, energy input justprecede electron transfer. This energy input causes shortcoming of the bonds in Fe (II) reactant complex so that the participating orbitals are modified to have the same energy. After these readjustments of the bonds lengths the electron jumpoccurs. The energy involved readjustments of the bond lengths is small because the geometries of the tow reactants are similar. Thus the bond length adjustments are critical for ease of electron transfer in OSM.

Electron transfer and M.O. symmetry

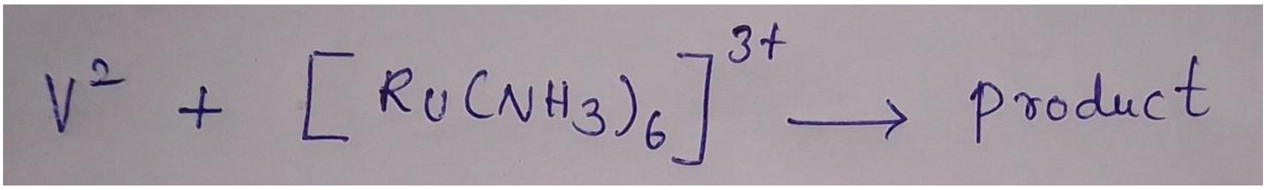
The highest occupied molecular orbital (HOMO) of the reductant is the donor orbital and the lowest unoccupied molecular orbital (LUMO) of the oxidant is the receptor orbital. If either of these molecular orbital does not meet the symmetry requirements for effective electron transfer, then higher chemical activation involving strong deformation and electron configuration change is necessary for reaction. This factor is a qualitative guide to guess the speed of electron transfer reaction. Each of the following OS electron transfers involves symmetry molecular orbitals.



		$k_2/M^{-1}s^{-1}$
a) $[Fe(H_2O)_6]^{2+}$	+ $[Fe(H_2O)_6]^{3+}$	40
$(\pi^*)^4(\sigma^*)^2$	$(\pi^*)^3(\sigma^*)^2$	$\pi^* \rightarrow \pi^*$ transfer
b) $[Fe(phen)_3]^{2+}$	+ $[Fe(phen)_3]^{3+}$	3.0×10^7
$(\pi^*)^6$	$(\pi^*)^5$	$\pi^* \rightarrow \pi^*$ transfer
c) $[Co(H_2O)_6]^{2+}$	+ $[Co(H_2O)_6]^{3+}$	5.0
$(\pi^*)^5(\sigma^*)^2$	$(\pi^*)^6$	$\sigma^* \rightarrow \sigma^*$ transfer

Marcus Hush principle:

Reaction between two completelydifferent complex ions or molecules is a cross reaction.

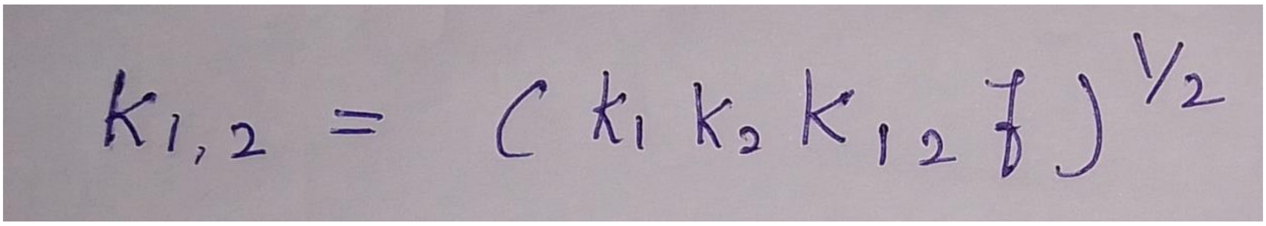


$$V^{2} + [Ru(NH_3)_6]^{3+} \longrightarrow \text{product}$$

Example

A cross reaction involves large chemicals activation; however it is fast because the large Ea* requirement is partly compensated by an attendant negative free energy exchange. For cross reaction, $\Delta G\# < 0$; the products is more stable than reactants. The rate is maximum when the electron is transformed from a ∏* to ∏* orbital. The rate constant of a cross reaction involving the OSM can be predicted by anequation proposed by Marcus hush.

$k_{1,2}$is the rate constant for the reaction.



$$k_{1,2} = (k_1 k_2 K_{12} f)^{1/2}$$

$k_1$and k_2 each is the rate constant for electron exchange same total.

$K_{1,2}$ is equilibrium constant for cross reaction. The term *f* close to I and is given by

$$\log f = (\log k_{1,2})^2 / 4 \log \frac{k_1 k_2}{Z^2}$$

Z=measure of collision frequency

The equation calledMarcus hush equation can now be applied to an example.

The rate constant for the cross electron transfer.

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \xrightarrow{k_{1,2}} [Fe(CN)_6]^{8-} + [Mo(CN)_8]^{4-}$$

Can be predicted from the rate constant of the reaction

$$[Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \xrightarrow{k_1} [Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

$$[Mo(CN)_8]^{4-} + [Mo(CN)_8]^{3-} \xrightarrow{k_2} [Mo(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$

Substituting the experiment measured $k_1$and k_2 value in the Marcus- Hush.

Good agreement between the calculated $k_{1,2}$ values and the experimentally determined $k_{1,2}$ is $1.6 \times 10^{-3}\ M^{-1}s^{-1}$ and the experimental $k_{1,2}$ is $1.0 \times 10^{-3}\ M^{-1}s^{-1}$ for the reaction.

$$Cr^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow \text{Product}$$

Such agreements substantiate the validity of the Marcus hush principle.

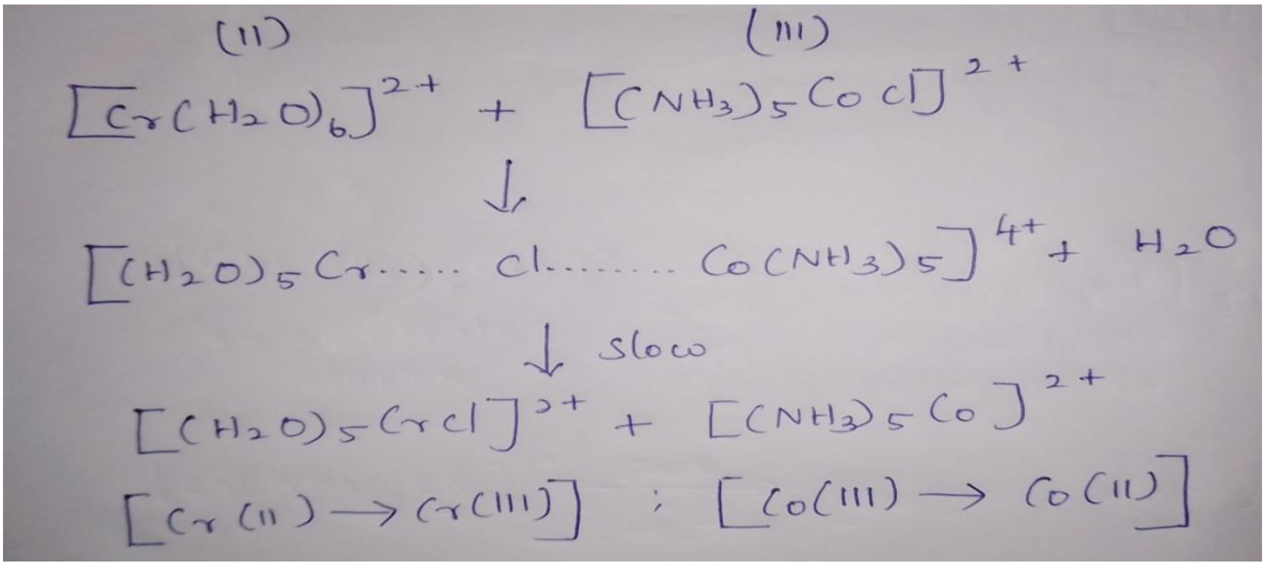
II. Inner sphere mechanism(ISM):

Characteristic:

1. In this mechanism, the oxidant and the reductant attach themselves to the another at some stage of the reaction. (in the OSM, at no stage of the reaction the tow reactants are attached to one another).
2. Activation is required for the two reactant molecules to orient themselves in proper configuration for reaction.
3. There should be at least one ligand (in one reactant) capable of binding simultaneously to two metals however transiently.
4. The attachment between O and R occurs through a bridging ligand (molecule, atom or iron).
5. In this mechanism, a ligand is shaped between the reductant and oxidant and their inner (primary) coordination sphere.
6. This bridge helps the transfer of electron from the R to O, the electron presumably passing through the bridging ligand.
7. The intermediate formed in this reaction is binuclear.
8. Unlike with the OSM, here bonds are broken and made during reaction, therefore, this mechanism is more complicated than OSM.
9. The rate determined step is the electron-transfer step and not the complex formation step.
10. One ligand of one reactant (usually the reductant) must be substitutionally labile; that is, it should be capable of getting replaced by a bridging ligand in an easy substitution process.

    Example Taube’s Reaction

    Taube’s reaction is the IS redox reaction



Proof for ISM the two important aspects of ISM are:

1. The transfer of a particular ligand from one coordination sphere to another.
2. The formation of a binuclear intermediate.

Therefore, the proof for this mechanism must prove these two facts.

At the end of the Cr (II) – Co (III) reaction, all the Cr (III) is found as [Cr (H_2O) 5Clp2+ and the Co (II) species without any C^- attached to it. This proves the transfer of Cl^- from the reactant Co (III) species to reactant Cr (II) species. The formation of the bridged transition state is in accord with the following facts;

the reactant Co(III) complex is not labile and therefore, the transfer of Cl^- is independent of bridge formation and electron transfer is unlikely when an electron is transferred from Cr(II) to Co(III), the Co-l bond becomes labile while the Cr-Cl bond becomes non labile.

When the reaction is noticed in the presence of added radioactive Cl^- in solution, no radioactivity is incorporated in the product chromium complex. If Cl^- had dissociated from $[Co(NH_3)_5Cl]^{2+}$ and the the sphere Cl^-migrated to $[Cr(H_2o)_6]^{2+}$ through the solvent, then some added radioactive Cl^- would have been incorporated in the Cr(III) product. The absence of radioactivity in Cr (III) species proves that the chlorine is transferred direct from from Co to Cr through the bridge in the redox reaction and not though the solvent.

Though the reaction pathwayindicates the formation of the pentamminecobalt (II) complex, actually [Cr (H2O) 6]2+ is formed because the d2-Co (II) complex is so labile that it gets hydrolysed quickly to the aqua complex in an acidic medium.

The rate-accelerating role of the bridging ligand sis obvious as in its absence the complex [Co (NH3)6]3+ undergoes a very slow (OSM) reaction.

The rates of electron transfer from Fe (II) to various FeX2+ complexes (where X = F-, Cl- , Br- , I-) do not differ much.

As the rates do not differ much, the bridges mechanism is riles out. The reactions are likely to follow OSM in which the X- ligands do not play any significant role so as to affect the reaction rate.

Rationalize the following observation For the reaction,

$$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{H^+} [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5X]^{2+} + 5NH_4$$

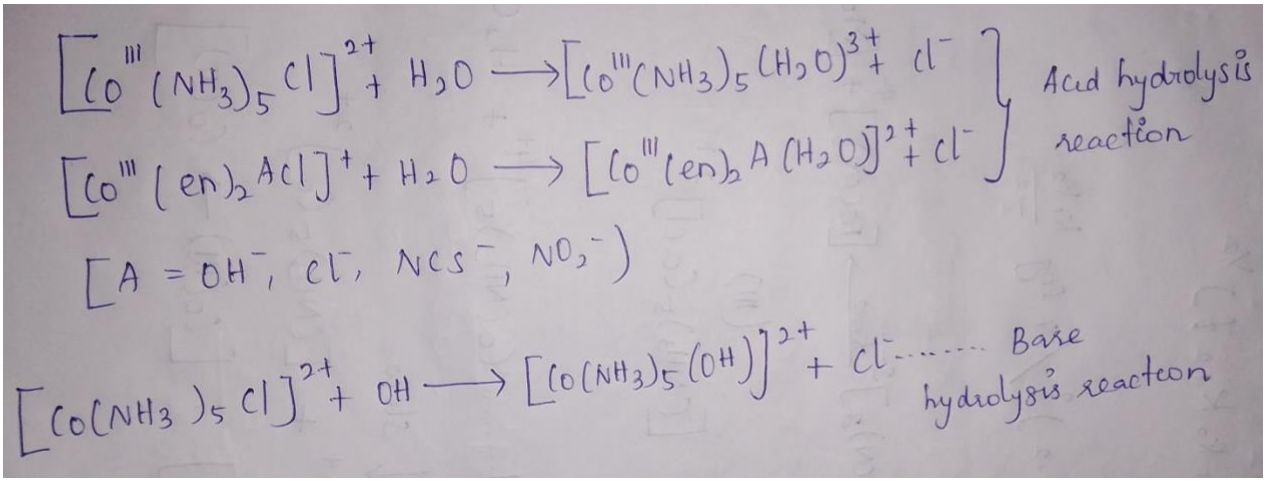
Both OS and IS mechanism operate simultaneously however,

$$\frac{k_{OS}(N_3^-)}{k_{OS}(NCS^-)} = 1 \quad \text{and} \quad \frac{k_{IS}(N_3^-)}{k_{IS}(NCS^-)} >> 1$$

The nature of the ligand X on Co does not matter for the OSM as the electron presumably tunnels to the oxidants; X has to role to play in this process. In the ISM on the contrary,X forms a bridge between the reactants and promotes the electron transfer. Therefore, the nature of X does matter in this mechanisms. A conjugated ligand enables faster reaction than a non conjugated one, as in the former conduction of electron over the conjugated system is easy.

Hydrolysis reactions:

These are substitution reaction in which a ligand is replaced by a water molecule or by OH- groups. The reaction in which an aqua complex is formed as a result of the replacement of a ligand by H2o molecules are called **acid hydrolysis or aquations reactions** while those in which a hydroxo complex is formed by the replacement of a ligand by OH- group are called **base hydrolysis**reactions. Acid hydrolysis reaction occur in neutral and acid solution (pH<3) while base hydrolysis reactions occurs in acid solutions (pH>10). For intermediate pH ranges the reaction is referred to just as hydrolysis reaction.Examples of this reaction are given below.



$$[Co^{III}(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co^{III}(NH_3)_5(H_2O)]^{3+} + Cl^-$$

$$[Co^{III}(en)_2ACl]^{+} + H_2O \longrightarrow [Co^{III}(en)_2A(H_2O)]^{2+} + Cl^-$$

Acid hydrolysis reaction

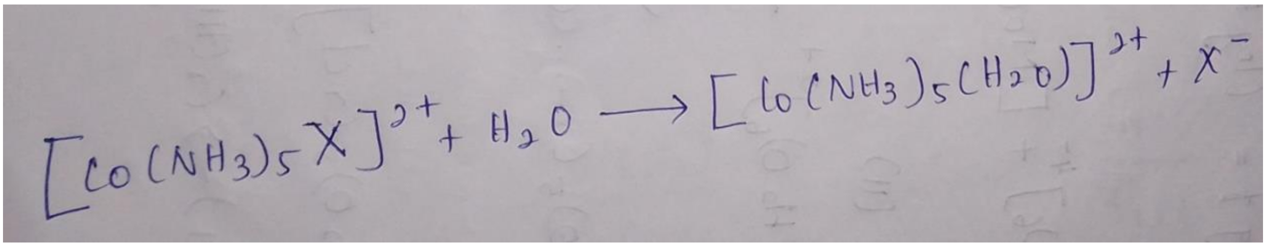
$[A = OH^-, Cl^-, NCS^-, NO_2^-)$

$$[Co(NH_3)_5Cl]^{2+} + OH \longrightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$$ ...... Base hydrolysis reacton

Aquation or acid hydrolysis reactions of six-coordinatedCo (III) amminecomplexes

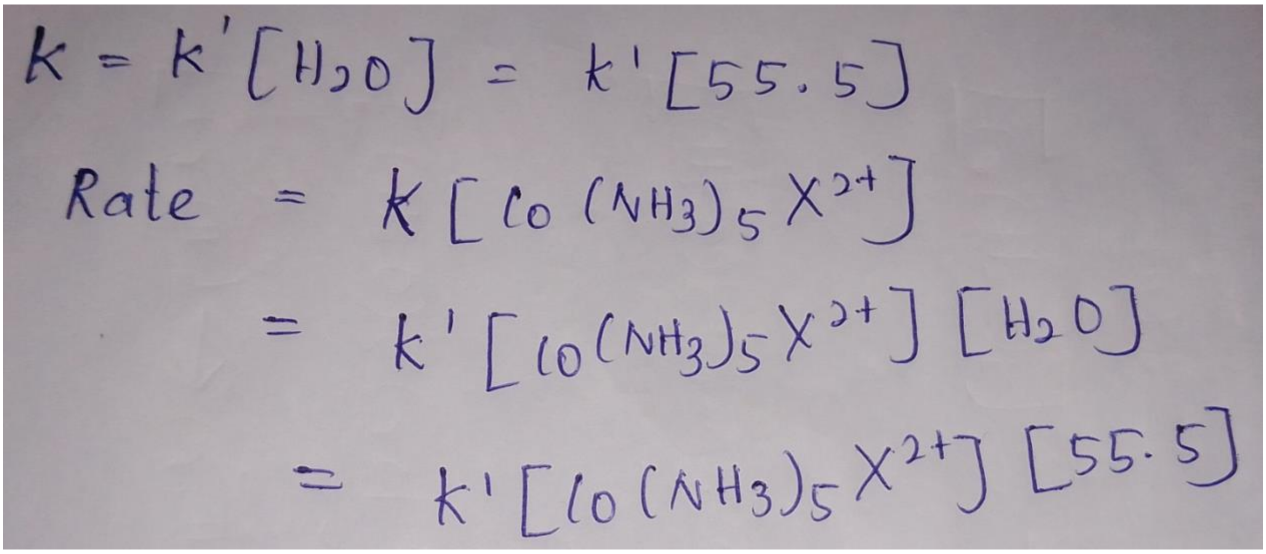
Ammine complexes of Co (III) have been most widely studied. Since work on these complexes has been done exclusively in water, the reaction of complexes with solvent water had to be considered first. In general it has been observed that NH3 of ammines like ethylene diamine or its derivatives coordinated to Co(III) are replaced very slowly by H2O molecules and hence in acid hydrolysis only the replacement of ligands other than amines is usually considered.

The rates of hydrolysis of reaction of the type



$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{2+} + X^-$$

Rate laws given below are experimentally indisguishable in aqueous solution, since



$$k = k'[H_2O] = k'[55.5]$$

$$\text{Rate} = k[Co(NH_3)_5X^{2+}]$$

$$= k'[Co(NH_3)_5X^{2+}][H_2O]$$

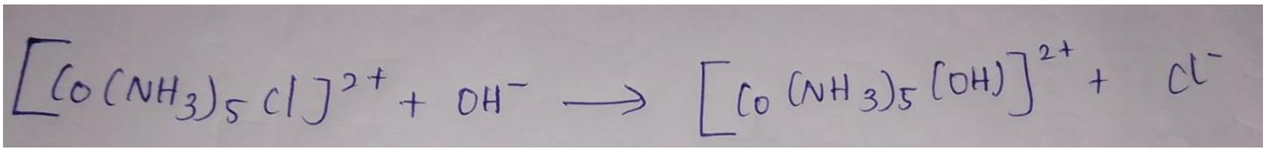
$$= k'[Co(NH_3)_5X^{2+}][55.5]$$

Thus rate law does not tell us whether H2O is involved in the rate determining step.

The rate law given above does not indicate whethertheseraactionsproceed by an SN2 displacement of X- by H2O or by an SN1 dissociation followed by addition of HO. However a study as to how the following factors affect the rate constant of these reaction can give us information about the nature of mechanism by which these reaction proceeds.

Base hydrolysis reactions of six-coordinated Co (III) ammine complexes

Most of the kinetic work has been done on six coordinated Co (III) ammines complexes. For ammine complexes of Co (III) containing N—H bonds it has been seem that the rate of base hydrolysis is often as much 10-4 times faster than the corresponding rate of the acid hydrolysis. Here we shall discuss the mechanism of the base hydrolysis reaction of [Co (NH3)5Cl] 2+ only. The base hydrolysis reaction represented by



$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

Can proceed by any of the following two mechanisms

1. **S_N2 Displacement mechanism**

According to this mechanism the reaction proceeds as

$$[Co(NH_3)_5Cl]^{2+} \xrightarrow[\text{Rate determining step}]{\text{slow }(+OH^-)} [Co(NH_3)_5(OH)(Cl)]^{+} \xrightarrow{\text{fast }(-Cl^-)} [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

$$CN = 6$$

The slow step which is a rate determining step is a second order reaction first order with respect to the complex and first order with respect of the base.

$$\text{Rate of Reaction} = k\,[\text{complex}][\text{base}]$$
$$= k\,[Co(NH_3)_5Cl^{2+}][OH^-]$$

2. **S_N1 dissociation mechanism**

This has been suggested by Garrick (1937). Before mechanism could be applied, the complexes which acts as a bronsted acid is converted into its conjugate base (abbreviated as CB) $[Co(NH_3)_4(NH_2)Cl]^+$ which is obtained by removing a proton(H^+) from the amino group present in the complex. CB is an amido complex, since it contains as amido group: NH2-, OH- which is a base converted into its conjugated acid, H_2O.

$$\mathbf{[Co(NH_3)_5Cl]^{3+} + OH^- \leftrightarrow [Co(NH_3)_4(NH_2)Cl]^+ + H_2O}$$

UNIT – IV

2marks

1. Define : Nuclear mass
2. What is radio active decay
3. What is mean by stellar energy

4. Define : Nuclear density
5. What is electron capture? Give an example
6. Define : Chain reaction
7. What is nuclear fission reaction?
8. What is nuclear fusion reaction?
9. What is mean by α particle decay?
10. Define : Nuclear charge.

5 Marks

11. Explain about nuclear fission reaction.
12. Write the activation of neutron analysis
13. Discuss the isotopic dilution analysis.
14. Write a short note on nuclear fusion reaction.
15. Explain : Radio active decay.

10 Marks

16. Discuss the main compartments of nuclear reactors.
17. How will you detect and measurement of radioactivity.
18. Explain about properties of nuclei.
19. Discuss the types of nuclear reaction.

Nuclear Properties

Nuclear Structure

From the scattering of alpha particles, Rutherford concluded that the atom of any element consists of central core called nucleus and electron moves around it. The entire mass of atom and positive charge is concentrated inside the nucleus. The mass of the electron is insignificantly small. The nucleus is consists of two particles, proton and neutron. Their masses are nearly same

Mass of proton (m_p) $= 1.67161 \text{ X } 10^{-27}$ Kg

The proton is positively charged particle while neutron is neutral particle. Both the neutron and proton in a nucleus together are called nucleons. The number of proton in a nucleus is called atomic number and the sum of proton and neutron number is called mass number. The stability of nucleus depends upon the relative number of protons and neutrons. The n/p ratio for stable nuclei is always greater than 1.

Static Properties of Nucleus

Nuclear Size (Radius)

From the scattering of alpha particles, Rutherford showed that the mean radius of an atomic nucleus is of the order of 10^{-14} to 10^{-15} meter.As the volume of the nucleus is proportional to number of nucleons (A);

$$\text{Volume } \alpha \text{ A}$$

$$\frac{4}{3}\pi R^3 \alpha A$$

$$R^3 = c\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} A^{\frac{1}{3}}$$

$$R^3 = R_o A^{\frac{1}{3}}$$

R_o is a constant and has an average vale of $1.4 \text{ X } 10^{-15}$ m.

Nuclear Mass

Nucleus is consist of neutron and proton i.e., nucleons therefore, nuclear mass will be the sum of mass of nucleons

Nuclear mass $(M_N) = Z\, m_p + (A-Z)\, m_n$

As the mass of proton is approximately equal to mass of neutron therefore,

$M_N = A\, m_p$

Nuclear Density

All nuclei have same density.

$$Density(\rho) = \frac{Mass}{Volume}$$
$$\rho = \frac{M_N}{V_N}$$
$$\rho = \frac{Am_p}{\frac{4}{3}\pi R^3}$$
$$\rho = \frac{Am_p}{\frac{4}{3}\pi (R_o A^{\frac{1}{3}})^3}$$
$$\rho = \frac{m_p}{\frac{4}{3}\pi (R_o)^3}$$
$$\rho = \frac{3 \times 1.67 \times 10^{-27}}{4 \times 3.14 \times (1.4 \times 10^{-15})^3}$$
$$\rho = 1.48 \times 10^{17} Kg/m^3$$

Nuclear Charge

The proton is positively charged particle while neutron is neutral particle, therefore the charge of nucleus is positive, while the atom whole is neutra.

Therefore nuclear charge = $+Ze$

Where e is charge of electron

Nuclear Spin

Spin quantum number = ½

Spin angular momentum

$$S = \sqrt{S(S+1)}\frac{h}{2\pi}$$

$$S = \frac{\sqrt{3}}{4\pi}$$

Nuclear Magnetic Momentum

$$\mu_N = \frac{e}{2m_p}\frac{h}{2\pi} = 3.152 \times 10^{-8} eV/T$$

Radioactive decay

Many nuclei are radioactive; that is, they decompose by emitting particles and in doing so, become a different nucleus. In our studies up to this point, atoms of one element were unable to change into different elements. That is because in all other types of changes we have talked about only the electrons were changing. In these changes, the nucleus, which contains the protons which dictate which element an atom is, is changing. All nuclei with 84 or more protons are radioactive and elements with less than 84 protons have both stable and unstable isotopes. All of these elements can go through nuclear changes and turn into different elements.

In natural radioactive decay, three common emissions occur. When these emissions were originally observed, scientists were unable to identify them as some already known particles and so named them

1. alpha particles (α)
2. beta particles, (β)
3. gamma rays (γ)

using the first three letters of the Greek alphabet. Some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays except much higher in energy and even more dangerous to living systems.

Alpha Decay

The nuclear disintegration process that emits alpha particles is called alpha decay. An example of a nucleus that undergoes alpha decay is uranium-238. The alpha decay of UU-238 is

$$^{238}U_{92} \rightarrow {}^{4}He_{2} + {}^{234}Th_{90}$$

In this nuclear change, the uranium atom ($^{238}U_{92}$)transmuted into an atom of thorium ($^{234}Th_{90}$) and, in the process, gave off an alpha particle. Look at the symbol for the alpha particle: He24He24. Where does an alpha particle get this symbol? The bottom number in a nuclear symbol is the number of protons. That means that the alpha particle has two protons in it which were lost by the uranium atom. The two protons also have a charge of +2+2. The top number, 4, is the mass number or the total of the protons and neutrons in the particle. Because it has 2 protons, and a total of 4 protons and neutrons, alpha particles must also have two neutrons. Alpha particles always have this same composition: two protons and two neutrons.
Another alpha particle producer is thorium-230.

$$^{230}Th_{90} \rightarrow {}^{4}He_{2} + {}^{226}Ra_{88}$$

These types of equations are called nuclear equations and are similar to the chemical equivalent discussed through the previous chapters.

Beta Decay

Another common decay process is beta particle emission, or beta decay. A beta particle is simply a high energy electron that is emitted from the nucleus. It may occur to you that we have a logically difficult situation here. Nuclei do not contain electrons and yet during beta decay, an electron is emitted from a nucleus. At the same time that the electron is being ejected from the nucleus, a neutron is becoming a proton. It is tempting to picture this as a neutron breaking into two pieces with the pieces being a proton and an electron. That would be convenient for simplicity, but unfortunately that is not what happens; more about this at the end of this section. For convenience sake, though, we will treat beta decay as a neutron splitting into a proton and an electron.

The proton stays in the nucleus, increasing the atomic number of the atom by one. The electron is ejected from the nucleus and is the particle of radiation called beta.

To insert an electron into a nuclear equation and have the numbers add up properly, an atomic number and a mass number had to be assigned to an electron. The mass number assigned to an electron is zero (0) which is reasonable since the mass number is the number of protons plus neutrons and an electron contains no protons and no neutrons. The atomic number assigned to an electron is negative one (-1), because that allows a nuclear equation containing an electron to balance atomic numbers. Therefore, the nuclear symbol representing an electron (beta particle) is

e−10e−10 or β−10β−10

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay.

$$^{234}\mathrm{Th}_{90}\rightarrow \mathrm{e}-10+{}^{234}\mathrm{Pa}_{91}$$

Gamma Radiation

Frequently, gamma ray production accompanies nuclear reactions of all types. In the alpha decay of UU-238, two gamma rays of different energies are emitted in addition to the alpha particle.

$$^{238}\mathrm{U}_{92}\rightarrow {}^{4}\mathrm{He}_{2}+{}^{234}\mathrm{Th}_{90}+2\gamma 00$$

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown. Nuclear reactions produce a great deal more energy than chemical reactions. Chemical reactions release the difference between the chemical bond energy of the reactants and products, and the energies released have an order of magnitude of 1×103kJ/mol1×103kJ/mol. Nuclear reactions release some of the binding energy and may convert tiny amounts of matter into energy. The energy released in a nuclear reaction has an order of magnitude of 1×1018kJ/mol1×1018kJ/mol.

Electron Capture

Electron capture is one form of **radioactivity**. A parent nucleus may capture one of its orbital electrons and emit a neutrino. This is a process which competes with **positron emission** and has the same effect on the atomic number. Most commonly, it is a K-shell electron which is captured, and this is referred to as K-capture.This is a schematic that grossly distorts the picture relative to a **scale model** of the atom. The electron orbit radii are tens of thousands of times the diameter of the nucleus.

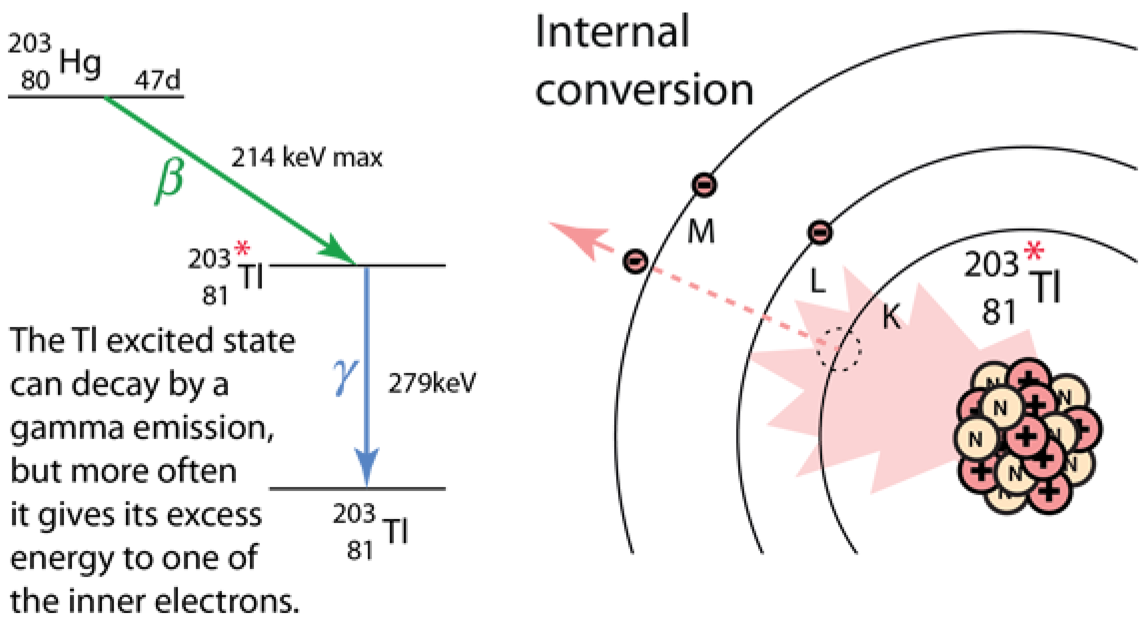
A typical example is the decay of **beryllium**

$$^{7}_{4}\mathrm{Be} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{7}_{3}\mathrm{Li} + \nu$$

The capture of the electron by a proton in the nucleus is accompanied by the emission of a neutrino. The process leaves a vacancy in the electron energy level from which the electron came, and that vacancy is either filled by the dropping down of a higher-level electron with the emission of an **X-ray** or by the ejection of an outer electron in a process called the **Auger effect.**

Internal Conversion

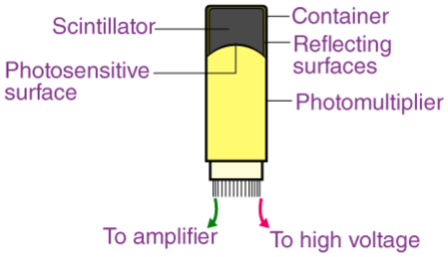
Internal conversion is another electromagnetic process which can occur in the nucleus and which competes with gamma emission. Sometimes the multipole electric fields of the nucleus interact with orbital electrons with enough energy to eject them from the atom. This process is not the same as emitting a **gamma ray** which knocks an electron out of the atom. It is also not the same as **beta** decay, since the emitted electron was previously one of the orbital electrons, whereas the electron in beta decay is produced by the decay of a neutron.



An example used by Krane is that of ^{203}Hg, which decays to ^{203}Tl by beta emission, leaving the ^{203}Tl in an electromagnetically excited state. It can proceed to the ground state by emitting a 279.190 keV gamma ray, or by internal conversion. In this case the internal conversion is more probable. Since the internal conversion process can interact with any of the orbital electrons, the result is a spectrum of internal conversion electrons which will be seen as superimposed upon the electron energy spectrum of the beta emission. The energy yield of this electromagnetic transition can be taken as 279.190 keV, so the ejected electrons will have that energy minus their binding energy in the ^{203}Tl daughter atom.

Scintillation Counter

Scintillation Counter is an instrument that is used for measuring ionizing radiation. “It comprises the scintillator that generates photons in response to incident radiation”, a PMT tube is used to convert an electronics and electric signal to process the signal.



A scintillation counter is used to detect gamma rays and the presence of a particle. It can also measure the radiation in the scintillating medium, the energy loss, or the energy gain. The medium can either be gaseous, liquid, or a solid. The scintillator counter is generally comprised of transparent crystalline material such as glasses, liquids, or plastics. One sector of the scintillators is placed (optical contact) with the pin code.

A charged particle loses energy when passing through the scintillator thus leaving the trail of excited molecules and atoms. A rapid interatomic transfer of electronic excitation energy follows, which leads to the burst of scintillator material luminescence characteristics. The scintillation response, when a particle stops leading to the light output. The energy loss of a particle is measured when a particle passes completely through a scintillator.

Applications of Scintillation Counter

1. Scintillation Counters are widely used in radioactive contamination, radiation survey meters, radiometric assay, nuclear plant safety, and medical imaging, that are used to measure radiation.
2. There are several counters of mounted on helicopters and some pickup trucks for rapid response in case of a security situation due to radioactive waste or dirty bombs.
3. Scintillation counters designed for weighbridge applications, freight terminals, scrap metal yards, border security, contamination monitoring of nuclear waste, and ports.

4. It is widely used in screening technologies, In vivo and ELISA alternative technologies, cancer research, epigenetics, and Cellular research.
5. It also has its applications in Protein interaction and detection, academic research, and Pharmaceutical.
6. Liquid Scintillation Counter is a type of scintillation counter that is used for measuring the beta emission from the nuclides.

Geiger Muller Counter

Geiger counter is a device which is used to detect and measure particles in the ionized gases. It is widely used in applications like radiological protection, radiation dosimetry, and experimental physics. It is made up of the metallic tube, filled with gas and a high voltage range of multiples of 100V is applied to this gas. It detects alpha, beta, and gamma particles.

When radioactive isotopes are used in medical research work on humans, it is important to make sure that the amount of radioactive material administered to human subjects is as little as possible. In order to achieve this, a very sensitive instrument is necessary to measure the radioactivity of materials. A ‘particle detector’ to measure the ionizing radiation was developed by Geiger and Muller in the year 1928 and they called it a ‘Geiger Muller Counter’ which in short is known as the ‘GM counter.’ In the large and dominant use as a hand-held radiation survey instrument, it would be one of the planet’s renowned radiation detection instruments.

Principle of Geiger Counter

The Geiger counter would contain Geiger-Müller tube, the element of sense that detects the radiation and the electronics that processes that would provide the result.The Geiger-Müller tube is filled with a gas such as helium, neon, or argon at the pressure being the lowest, where there is an application of high voltage. There would be the conduction of the electrical charge on the tube when a particle or photon of incident radiation would turn the gas conductive by the means of ionization.

Types of Geiger Counter

The Geiger counter is dictated entirely by the design of the tube, can be generally categorised into two types:

- **End Window**
- **Windowless**

End Window

This style of the tube would have a small window at one of its ends. This window would be helpful in ionizing particles that could travel easily.

Windowless

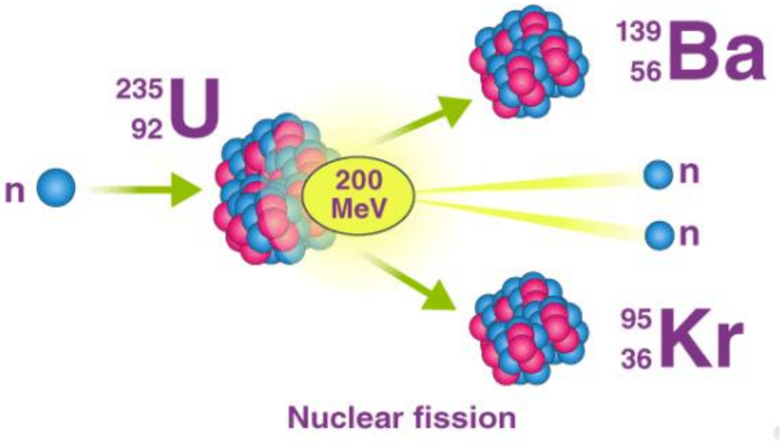
As the name suggests, this type of tube would not have any windows and the thickness would be in the range of one to two mm. This type of tube is used for detecting high penetrating radiations.

Geiger Counter Units

The measurement of particles would be in different units, the widely used one of them is the Counts Per Minute (CPM). The measurement of radioactivity would be in micro-(µSv/hr) – Sieverts per hour and (mR/hr)milli-Roentgens per hour.

Nuclear Fission

Nuclear fission refers to the splitting of an atomic nucleus into two or lighter nuclei. This process can occur through a nuclear reaction or through radioactive decay. Nuclear fission reactions often release a large amount of energy, which is accompanied by the emission of neutrons and gamma rays (photons holding huge amounts of energy, enough to knock electrons out of atoms).



Nuclear fission was first discovered by the German chemists Otto Hahn and Fritz Strassmann in the year 1938. The energy produced from fission reactions is converted into electricity in nuclear power plants. This is done by using the heat produced from the nuclear reaction to convert water into steam. The steam is used to rotate turbines in order to generate electricity.

Examples

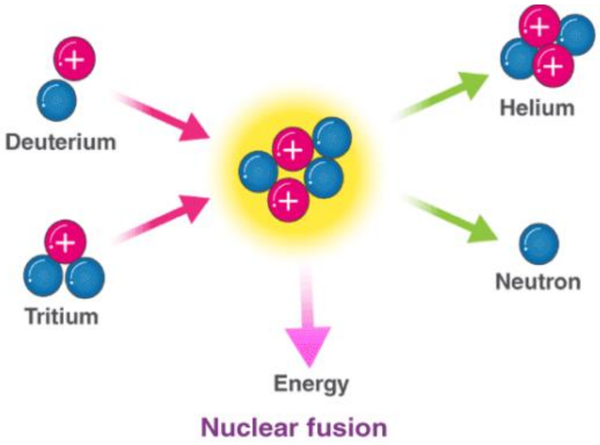
An important example of nuclear fission is the splitting of the uranium-235 nucleus when it is bombarded with neutrons. Various products can be formed from this nuclear reaction, as described in the equations below.

- $^{235}U + {}^{1}n \rightarrow {}^{141}Ba + {}^{92}Kr + 3\,{}^{1}n$
- $^{235}U + {}^{1}n \rightarrow {}^{144}Xe + {}^{90}Sr + 2\,{}^{1}n$
- $^{235}U + {}^{1}n \rightarrow {}^{146}La + {}^{87}Br + 3\,{}^{1}n$
- $^{235}U + {}^{1}n \rightarrow {}^{137}Te + {}^{97}Zr + 2\,{}^{1}n$
- $^{235}U + {}^{1}n \rightarrow {}^{137}Cs + {}^{96}Rb + 3\,{}^{1}n$

Another important example of nuclear fission is the splitting of the plutonium-239 nucleus.

Nuclear Fusion

In nuclear fusion reactions, at least two atomic nuclei combine/fuse into a single nucleus. Subatomic particles such as neutrons or protons are also formed as products in these nuclear reactions.



An illustration of the nuclear fusion reaction between deuterium (^2H) and tritium (^3H) that yields helium (^4He) and a neutron (^1n) is provided above. Such fusion reactions occur at the core of the sun and other stars. The fusion of deuterium and tritium nuclei is accompanied by a loss of approximately 0.0188 amu of mass (which is completely converted into energy). Approximately $1.69*10^9$ kilojoules of energy are generated for every mole of helium formed.

Nuclear Cross Section

The nuclear cross section of a nucleus is used to describe the probability that a nuclear reaction will occur. The concept of a nuclear cross section can be quantified physically in terms of "characteristic area" where a larger area means a larger probability of interaction. The standard unit for measuring a nuclear cross section (denoted as σ) is the barn, which is equal to 10^{-28} m^2 or 10^{-24} cm^2. Cross sections can be measured for all possible interaction processes together, in which case they are called total cross sections, or for specific processes, distinguishing elastic scattering and inelastic scattering; of the latter, amongst neutron cross sections the absorption cross sections are of particular interest.

In nuclear physics it is conventional to consider the impinging particles as point particles having negligible diameter. Cross sections can be computed for any sort of process, such as capture scattering, production of neutrons, etc. In many cases, the number of particles emitted or scattered in nuclear processes is not measured directly; one merely measures the attenuation produced in a parallel beam of incident particles by the interposition of a known thickness of a particular material. The cross section obtained in this way is called the total cross section and is usually denoted by a σ or σ_T.

Typical nuclear radii are of the order 10^{-14} m. Assuming spherical shape, we therefore expect the cross sections for nuclear reactions to be of the order of πr^2 or 10^{-28} m^2 (i.e. 1 barn). Observed cross sections vary enormously - for example, slow neutrons absorbed by the (n,) reaction show a cross section much higher than 1,000 barns in some cases (boron-10, cadmium-113, and xenon-135), while the cross sections for transmutations by gamma-ray absorption are in the region of 0.001 barn.

Q - Value

In writing down the reaction equation, in a way analogous to a chemical equation, one may in addition give the reaction energy on the right side:

Target nucleus + projectile → Final nucleus + ejectile + Q.

For the particular case discussed above, the reaction energy has already been calculated as $Q = 22.2$ MeV. Hence:

$${}_3\mathrm{Li}^6 + {}_1\mathrm{H}^2 \rightarrow 2\,{}_2\mathrm{He}^4 + 22.2\ \mathrm{MeV}.$$

The reaction energy (the "Q-value") is positive for exothermal reactions and negative for endothermal reactions, opposite to the similar expression in chemistry. On the one hand, it is the difference between the sums of kinetic energies on the final side and on the initial side. But on the other hand, it is also the difference between the nuclear rest masses on the initial side and on the final side.

Compound nuclear reaction

Either a low-energy projectile is absorbed or a higher energy particle transfers energy to the nucleus, leaving it with too much energy to be fully bound together. On a time scale of about 10^{-19} seconds, particles, usually neutrons, are "boiled" off. That is, it remains together until enough energy happens to be concentrated in one neutron to escape the mutual attraction. The excited quasi-bound nucleus is called a compound nucleus.Low energy (e, e' xn), (γ, xn) (the xn indicating one or more neutrons), where the gamma or virtual gamma energy is near the giant dipole resonance. These increase the need for radiation shielding around electron accelerators.

Stellar energy

It was soon realised that the energy of the stars was produced by nuclear fusion, the temperatures required in the stars being lower than those needed in the laboratory because of the enormous pressures in the stellar interiors. One such reaction that occurs in the Sun is the so called PP chain shown below.

$$^{1}_{1}H \quad + \quad ^{1}_{1}H \quad \text{Giving} \quad ^{2}_{1}H \quad + \quad e^{+} \quad + \quad \text{energy}$$

Part of the energy in the first reaction is high-speed neutrinos and these can be detected on the Earth.

Other reactions may then occur such as:

$$^{3}_{2}He + ^{4}_{2}He \longrightarrow ^{7}_{4}Be + \gamma$$

Heavier and heavier nuclei can be produced by successive fusion reactions. The types of reaction taking place in the Sun are shown below:

${}^{12}_{6}C$ + ${}^{1}_{1}H$ giving ${}^{13}_{7}N$ + energy

${}^{13}_{7}N$ giving ${}^{13}_{6}C$ + e^{+}

${}^{13}_{6}C$ + ${}^{1}_{1}H$ giving ${}^{14}_{7}N$ + energy

${}^{14}_{7}N$ + ${}^{1}_{1}H$ giving ${}^{15}_{8}O$ + energy

${}^{15}_{8}O$ giving ${}^{15}_{7}N$ + e^{+}

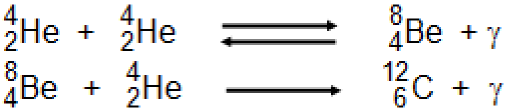
${}^{15}_{7}N$ + ${}^{1}_{1}H$ giving ${}^{14}_{6}C$ + ${}^{4}_{2}He$

The net result of this series of reactions is:

$4{}^{1}_{1}H$ giving $4{}^{4}_{2}He$ + $2e^{+}$ energy

In other words, 564 million tonnes of hydrogen are being converted into 560 million tonnes of helium every second, producing a staggering output of 3.90×10^{20} MW - equivalent to some million million million large power stations! Although the Sun is converting four million tonnes of mass into energy every second it is thought that it will continue to last for a further 10^{9} years. At higher temperatures (around 10^{8} K) the fusion of helium starts the building of heavier elements.

The reaction is:



$$\begin{aligned} {}^{4}_{2}He + {}^{4}_{2}He &\rightleftharpoons {}^{8}_{4}Be + \gamma \\ {}^{8}_{4}Be + {}^{4}_{2}He &\longrightarrow {}^{12}_{6}C + \gamma \end{aligned}$$

This is known as the triple alpha process and is the first stage of 'helium burning'. Beryllium 8 is very unstable and so can revert to two alpha particles but eventually an equilibrium is set up and maintained.

Nuclear reactor

A nuclear reactor is a system used to initiate and contain a nuclear chain reaction, and they have many useful applications. These nuclear reactions produce thermal energy through either nuclear fission or nuclear fusion. Nuclear reactors are primarily used for the generation of electricity, however they can be used for propulsion in vehicles such as submarines or naval vessels, for production of useful isotopes or neutrons, and for research and training.

Fuel

Nuclear reactors require the use of nuclear fuels, elements that can be readily altered and will release thermal energy. Uranium is the most common element used as a nuclear fuel, although thorium is also possible. The naturally occurring isotopes are found in countries such as Kazakhstan, Canada and Australia. The uranium fuel is manufactured into small fuel pellets and are packed into fuel rods and surrounded by cladding to avoid leaking into the coolant. These fuel rods are assembled into a fuel bundle, as seen below. There can be hundreds of fuel bundles in a nuclear reactor, meaning there can be tens of thousands of fuel rods.

Fuel enrichment

Not all nuclei of a given element are built exactly the same. An element is defined by the number of protons within the nucleus, and varying numbers of neutrons in the nucleus can cause it to behave differently. Natural uranium is mostly made up of uranium-238 (99.3%), with uranium-235 (0.7%) and very small amount of uranium-234 (0.0055%).[8] Most reactors require a higher percentage of uranium-235 in order to sustain nuclear fission reactions, which can be done through uranium enrichment processes.

Moderator

Moderators are used to slow down the neutrons produced from fission. This is necessary because many nuclear fuels (uranium-235, for instance) require neutrons to be slow-moving in order to absorb them. Nuclei with low mass numbers are most effective at doing so, therefore materials like water or graphite are often used.

Most reactors use light water as a moderator, such as pressurized water reactors and boiling water reactors. Carbon works similarly and is used in reactors such as the RBMK. A third type of moderator used in CANDU reactors is heavy water, which is water composed of heavy hydrogen, called deuterium, rather than normal hydrogen.

The simulation below should help in visualizing how a moderator does its job: neutrons that are going too fast are absorbed by uranium-238 and do not yield fission (green) and the moderated neutrons are absorbed by uranium-235 which splits into smaller atoms and produces excess neutrons to continue the reaction (red).

Coolant

The coolant, as its name implies, is used to remove heat from the core and move it to somewhere that it is useful. This keeps the fuel from overheating and melting down, at the same time as transferring the heat to water to make steam. Light water, heavy water, and various gases are the most common coolants for nuclear reactors. Coolants may also serve as the moderator, as is the case in many water-moderated reactors.

Control rods

Control rods can be inserted into the reactor core to reduce the amount of fuel which undergoes fission reactions. The rods contain neutron absorbing atoms such as gadolinium or cadmium. By absorbing neutrons within the core, it prevents those neutrons from reacting with the fuel. Control rod movement can be used to adjust the number of reactions occurring at the core, or fully inserted to shut down the reactor completely.

Safety systems

Safety systems are those in place to shut down the reactor and prevent radioactive material from being released. Some systems are passive, such as the dropping the control rods into the reactor core in CANDU reactors. The control rods are suspended above the core and held there by an electromagnet (a magnet which requires a constant supply of electricity to operate). In the event that a loss of power occurs, the control rods work to stop the reactions in the core. Strong containment buildings must also surround the reactor to prevent any radioactive leaks or external damage to the reactor.

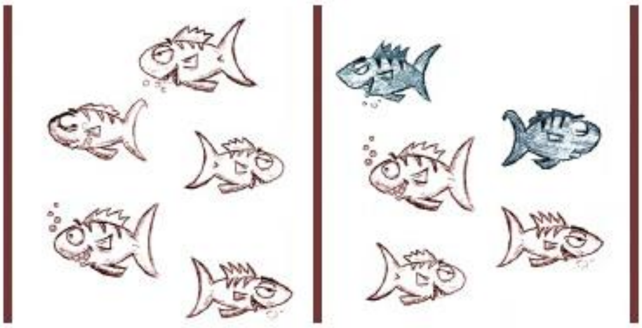
Economics

The building of nuclear reactors is economically intensive. The initial capital costs are high compared to fossil fuel plants with similar output. Nuclear power requires a high amount of additional safety, and is completely responsible for all possible nuclear waste. What makes nuclear power economically feasible is the large amount of energy that comes from a small volume of fuel. This relationship is known as energy density, and provides a cost advantage to using nuclear fuels. The cost of fuel is relatively lower for a nuclear power plant compared to fossil fuels. This is what makes nuclear reactors competitive despite high initial capital costs.

Isotope dilution analysis

Isotope dilution analysis is a method of determining the quantity of chemical substances. In its most simple conception, the method of isotope dilution comprises the addition of known amounts of isotopically-enriched substance to the analyzed sample. Mixing of the isotopic standard with the sample effectively "dilutes" the isotopic enrichment of the standard and this forms the basis for the isotope dilution method. Isotope dilution is classified as a method of internal standardisation, because the standard (isotopically-enriched form of analyte) is added directly to the sample. In addition, unlike traditional analytical methods which rely on signal intensity, isotope dilution employs signal ratios. Owing to both of these advantages, the method of isotope dilution is regarded among chemistry measurement methods of the highest metrological standing.

Isotopes are variants of a particular chemical element which differ in neutron number. All isotopes of a given element have the same number of protons in each atom. The term *isotope* is formed from the Greek roots *isos* ("equal") and *topos* ("place"), meaning "the same place"; thus, the meaning behind the name is that different isotopes of a single element occupy the same position on the periodic table.



Isotope dilution can be effectively explained using mark and recapture method from biology - a method commonly used in ecology to estimate the population size of fish.Isotope dilution can be likened to Lincoln-Petersen method. Assume that the number of fish in a pond is to be determined. Five labeled fish are added to the pond during the first visit ($n_B = 5$). On the second visit, a number of fish is captured and one observes that the ratio of native-to-labeled is 10:1. From here, we can estimate the original number of fish in the pond, n_A:

$$n_A = n_B \times 10/1 = 50$$

This is a simplified view of isotope dilution yet it illustrates the salient features of isotope dilution. A more complex situation arises when the distinction between labeled and unlabeled fish becomes fuzzy. This can occur, for example, when the lake already contains a small number of labeled fish from the previous field experiments. In such situation, the following expression can be employed:

$$n_A = n_B \times R_B \; R_{AB} / R_{AB} - R_A \times 1 + R_A / 1 + R_B$$

where R_A is the ratio of the native-to-labeled fish in the lake, R_B is the ratio of the native-to-labeled fish in the lot of n_B marked fish which are added to the pond, and R_{AB} is the ratio of the native-to-labeled fish captured during the second visit.

Applications

Isotope dilution is almost exclusively employed with mass spectrometry in applications where high-accuracy is demanded. For example, all National Metrology Institutes rely significantly on isotope dilution when producing certified reference materials. In addition to high-precision analysis, isotope dilution is applied when low recovery of the analyte is encountered. In addition to the use of stable isotopes, radioactive isotopes can be employed in isotope dilution which is often encountered in biomedical applications, for example, in estimating the volume of blood.

UNIT – V

2 Mark questions

1. What is metal cluster?
2. State capping rule.

3. What are isopoly anions?
4. What are heteropoly anions?
5. What are higher boranes?
6. How many types of boranes are there?
7. What is nido boranes? Give example.
8. What is closo boranes? Give example.
9. What is arachno boranes? Give example.
10. What are metalboranes.

5 Mark questions

1. Explain the wade model of metal clusters?
2. Discuss the metal-meal multiple bondsinvolving metal clusters.
3. Write note on poly anion of molybdate.
4. Write note about metallocarboranes.
5. Explain the structure and type of carborane.

10 Mark questions

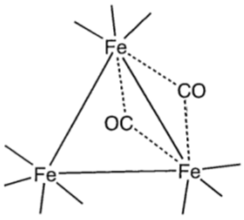
1. Justify the applications of organometals C-C and C-N cross coupling reaction.
2. Explain. Isopoly anions and its structure.
3. Write the preparation and properties of higher boranes.

METAL CLUSTERS & INORGANIC POLYMERS

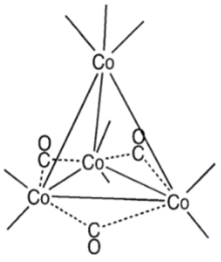
METAL CLUSTERS:

Analysis of the structures of newly prepared polynuclear complexes that contain two or more metals was, until recently, very difficult. However, with the progress of single crystal X-ray structural analysis, our understanding of the chemistry of polynuclear complexes is progressing quickly. Metal-cluster complexes are polynuclear complexes built by three or more transition-metal atoms with bonds between the metals coordinated by ligands to form polyhedral frames, such as a triangle, a regular tetrahedron, a regular octahedron, and an icosahedron. Even if there is no strong bond between metals, as long as there is some bonding interaction, they may be included as cluster compounds.

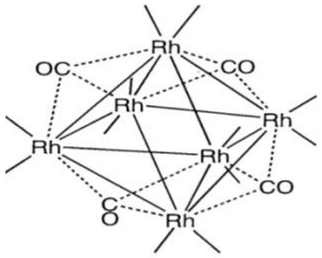
Example:



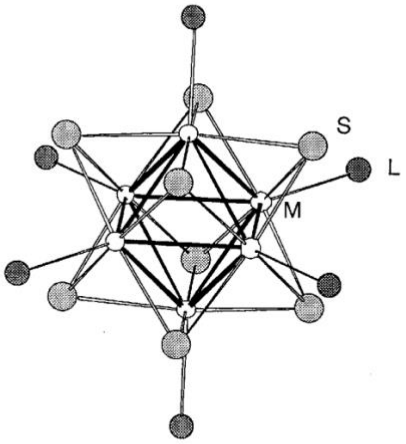
$Fe_3(CO)_{12}$

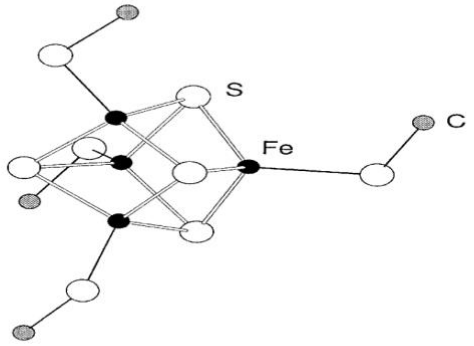


$Co_4(CO)_{12}$



$Rh_6(CO)_{16}$





$[Mo_6S_8L_6]$.

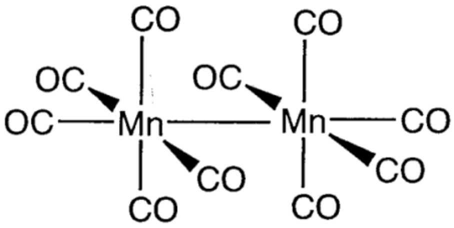
$[Fe_4S_4(SR)_4]^{2-}$.

COMPOUNDS WITH METAL-METAL BONDS:

The concept of the formation of a coordinate bond between ligands and a central metal proposed by A. Werner was the basis for the development of the chemistry of complexes. The bonding mode and structures of known complexes have become the guidepost of the preparation of a much larger number of new complexes. For most of the dinuclear or polynuclear complexes that contain two or more metals in a complex, it was sufficient to take into consideration only the bonds between the metal and ligands.

The concept of direct bonds between metals was born of the necessity of explaining the structural chemistry of the dinuclear metal carbonyls that have a partial structure with an odd number of electrons. Two $Mn(CO)_5$ units in $Mn_2(CO)_{10}$ are connected by a direct Mn-Mn bond without the help of bridge ligands. According to X-ray structural analysis (1963), the Mn-Mn distance of 292 pm was significantly longer than twice that of the metal radius of 127 pm but a Mn-Mn direct bond was envisaged in the absence of a bridge carbonyl ligand. This compound's diamagnetism indicates a structure with an even number of electrons (18 electrons) by sharing electrons between two d^7-Mn (17 electrons) moieties, each with five carbonyl ligands.

Similarly, it can be concluded that $Co_2(CO)_8$, with two bridging carbonyl ligands, should have a direct Co-Co bond to be compatible with its diamagnetism.

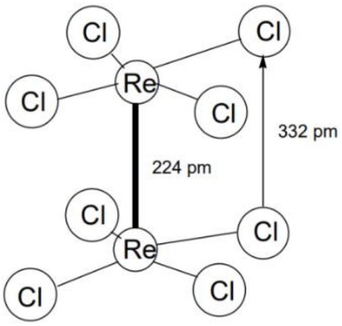


Structure of $Mn_2(CO)_{10}$.

The concept of the single bond between metals introduced for dinuclear metal carbonyl compounds is also very useful in explaining the structure of cluster carbonyl compounds containing two or more metals. However, even if the bond distance between metals analyzed by X-ray is sufficiently short, this does not prove the existence of a bond between metals unless the orbital conditions to account for such bonds are also fulfilled.

M-M multiple bonds

There are many dinuclear compounds in which the metal atoms are bound by multiple bonds with bond orders of 2 to 4. The M-M quadrupole bond was proposed first for $Re_2Cl_8^{2-}$, and this remains the best-known example $Re_2Cl_8^{2-}$. The Re-Re distance in this compound is only 224 pm, which is unusually short compared with the Re-Re distance of 275 pm in rhenium metal. Another unusual feature is that the $ReCl_4$ units assume an **eclipsed** configuration (chlorine atoms overlap along the direction of the Re-Re bond) even though the **staggard** configuration (in which chlorine atoms do not overlap along the Re-Re bond direction) should be more stable because the distance between $ReCl_4$ units is very short, resulting in the distances between the chlorine atoms being very short (experimental value of 332 pm). As a result, the repulsive interaction between the chlorine atoms becomes strong.



Structure of $Re_2Cl_8^{2-}$.

Polyhedral skeletal electron pair theory
In chemistry the polyhedral skeletal electron pair theory (PSEPT) provides electron counting rules useful for predicting the structures of clusters such as borane and carborane clusters. They are sometimes known as Wade's rules or the Wade–Mingos rules. The rules are based on a molecular orbital treatment of the bonding. These rules have been extended and unified in the form of the Jemmis mno rules.

Predicting structures of cluster compounds

Different rules ($4n$, $5n$, or $6n$) are invoked depending on the number of electrons per vertex.

The 4*n* rules are reasonably accurate in predicting the structures of clusters having about 4 electrons per vertex, as is the case for many boranes and carboranes. For such clusters, the structures are based on deltahedra, which are polyhedra in which every face is triangular. The 4*n* clusters are classified as *closo*-, *nido*-, *arachno*- or *hypho*-, based on whether they represent a complete (*closo*-) deltahedron, or a deltahedron that is missing one (*nido*-), two (*arachno*-) or three (*hypho*-) vertices.

However, hypho clusters are relatively uncommon due to the fact that the electron count is high enough to start to fill antibonding orbitals and destabilize the 4*n* structure. If the electron count is close to 5 electrons per vertex, the structure often changes to one governed by the 5n rules, which are based on 3-connected polyhedra.

As the electron count increases further, the structures of clusters with 5n electron counts become unstable, so the 6*n* rules can be implemented. The 6*n* clusters have structures that are based on rings.

A molecular orbital treatment can be used to rationalize the bonding of cluster compounds of the 4*n*, 5*n*, and 6*n* types.

4*n* rules

The following polyhedra are *closo* polyhedra, and are the basis for the 4*n* rules; each of these have triangular faces. The number of vertices in the cluster determines what polyhedron the structure is based on.

Number of vertices	Polyhedron
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron
7	Pentagonal bipyramid
8	D_{2d} (trigonal) dodecahedron (snub disphenoid)
9	Tricapped trigonal prism
10	Bicapped square antiprism
11	Edge-contracted icosahedron (octadecahedron)
12	Icosahedron (bicapped pentagonal antiprism)

Using the electron count, the predicted structure can be found. *n* is the number of vertices in the cluster. The 4*n* rules are enumerated in the following table.

Electron count	Name	Predicted structure

$4n - 2$	Bicapped *closo*	$n - 2$ vertex *closo* polyhedron with 2 capped (augmented) faces
$4n$	Capped *closo*	$n - 1$ vertex *closo* polyhedron with 1 face capped
$4n + 2$	*Closo*	*closo* polyhedron with n vertices
$4n + 4$	*Nido*	$n + 1$ vertex *closo* polyhedron with 1 missing vertex
4n + 6	*Arachno*	$n + 2$ vertex *closo* polyhedron with 2 missing vertices
4n + 8	*Hypho*	$n + 3$ vertex *closo* polyhedron with 3 missing vertices
4n + 10	*Klado*	$n + 4$ vertex *closo* polyhedron with 4 missing vertices

For example, in $Rh_6(CO)_{16}$ the total number of electrons would be $6 \times 9 + 16 \times 2 - 6 \times 10 = 86 - 60 = 26$. Therefore, the cluster is a *closo* polyhedron because $n = 6$, with $4n + 2 = 26$.

Other rules may be considered when predicting the structure of clusters:

1. For clusters consisting mostly of transition metals, any main group elements present are often best counted as ligands or interstitial atoms, rather than vertices.
2. Larger and more electropositive atoms tend to occupy vertices of high connectivity and smaller more electronegative atoms tend to occupy vertices of low connectivity.
3. In the special case of boron hydride clusters, each boron atom connected to 3 or more vertices has one terminal hydride, while a boron atom connected to two other vertices has two terminal hydrogen atoms. If more hydrogen atoms are present, they are placed in open face positions to even out the coordination number of the vertices.
4. For the special case of transition metal clusters, ligands are added to the metal centers to give the metals reasonable coordination numbers, and if any hydrogen atoms are present they are placed in bridging positions to even out the coordination numbers of the vertices.

Example: $Os_6(CO)_{18}$

Electron count: 6 × Os + 18 × CO – 60 (for 6 osmium atoms) = $6 \times 8 + 18 \times 2 - 60 = 24$

Since $n = 6$, $4n = 24$, so the cluster is capped *closo*.

5*n* rules

As discussed previously, the 4*n* rule mainly deals with clusters with electron counts of $4n + k$, in which approximately 4 electrons are on each vertex. As more electrons are added per vertex, the number of the electrons per vertex approaches 5. Rather than adopting structures based on deltahedra, the 5n-type clusters have structures based on a different series of polyhedra known as the 3-connected polyhedra, in which each vertex is connected to 3 other vertices. The 3-connected polyhedra are the duals of the deltahedra. The common types of 3-connected polyhedra are listed below.

Number of vertices	**Type of 3-connected polyhedron**
4	Tetrahedron
6	Trigonal prism
8	Cube
10	Pentagonal prism
12	D_{2d} pseudo-octahedron (dual of snub disphenoid)
14	Dual of triaugmented triangular prism (K_5 associahedron)
16	Square truncated trapezohedron
18	Dual of edge-contracted icosahedron
20	Dodecahedron

The $5n$ rules are as follows.

Total electron count	**Predicted structure**
$5n$	n-vertex 3-connected polyhedron
$5n + 1$	$n – 1$ vertex 3-connected polyhedron with one vertex inserted into an edge
$5n + 2$	$n – 2$ vertex 3-connected polyhedron with two vertices inserted into edges
$5n + k$	$n − k$ vertex 3-connected polyhedron with k vertices inserted into edges

Example: P_4

Electron count: 4 × P = 4 × 5 = 20

It is a $5n$ structure with $n = 4$, so it is tetrahedral

Example: P_4S_3

Electron count 4 × P + 3 × S = 4 × 5 + 3 × 6 = 38

It is a $5n + 3$ structure with $n = 7$. Three vertices are inserted into edges

Example: P_4O_6

Electron count $4 \times P + 6 \times O = 4 \times 5 + 6 \times 6 = 56$

It is a $5n + 6$ structure with $n = 10$. Six vertices are inserted into edges

6*n* rules

As more electrons are added to a $5n$ cluster, the number of electrons per vertex approaches 6. Instead of adopting structures based on $4n$ or $5n$ rules, the clusters tend to have structures governed by the $6n$ rules, which are based on rings. The rules for the $6n$ structures are as follows.

Total electron count	**Predicted structure**
$6n - k$	n-membered ring with $k/2$ transannular bonds
$6n - 4$	n-membered ring with 2 transannular bonds
$6n - 2$	n-membered ring with 1 transannular bond
$6n$	n-membered ring
$6n + 2$	n-membered chain (n-membered ring with 1 broken bond)

Example: S_8

Electron count $= 8 \times S = 8 \times 6 = 48$ electrons.

Since $n = 8$, $6n = 48$, so the cluster is an 8-membered ring.

Hexane (C_6H_{14})

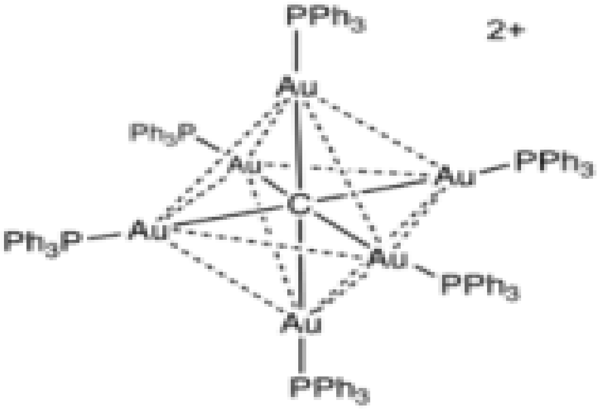
Electron count $= 6 \times C + 14 \times H = 6 \times 4 + 14 \times 1 = 38$

Since $n = 6$, $6n = 36$ and $6n + 2 = 38$, so the cluster is a 6-membered chain..

Capping and Decapping Series of Boranes

Whereas many of the capped series of carbonyl clusters of transition metals are known, those of corresponding borane series are unknown. These include the monocapped, bicapped, tricapped, tetracapped and so on. This paper attempts to correlate selected capped series of the carbonyl series with the hypothetical corresponding ones of boranes using 14n and 4n rules. Some selected examples of capped and decapped borane series have been generated and tabulated. The borane clusters are found to follow a precise numerical algorithm. A comparison of selected examples of carbonyl cluster of lower series such as closo, nido and arachno with the corresponding borane clusters has been made. The popularly cited Rudolph system of deducing shapes of clusters is also discussed in terms of decapping series. The use of fragments and their corresponding fragment series enormously simplifies the categorization of molecular formulas into series from which their shapes can be predicted with or without the use of the cluster number (k value). The fragment series vindicates the vital Hoffmann’s isolobal concept very well.

CARBIDE CLUSTER



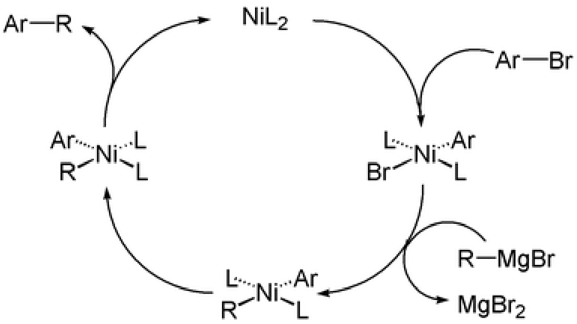
The complex $[Au_6C(PPh_3)_6]^{2+}$, containing a carbon-gold core.

Metal complexes containing C are known as metal carbido complexes. Most common are carbon-centered octahedral clusters, such as $[Au_6C(PPh_3)_6]^{2+}$ and $[Fe_6C(CO)_6]^{2-}$. Similar species are known for the metal carbonyls and the early metal halides. A few terminal carbides have been isolated, e.g., $[CRuCl_2\{P(C_6H_{11})_3\}_2]$.

Metallocarbohedrynes (or "met-cars") are stable clusters with the general formula M_8C_{12} where M is a transition metal (Ti, Zr, V, etc.).

Cross-coupling reaction:A **cross-coupling reaction** in organic chemistry is a reaction where two fragments are joined together with the aid of a metal catalyst. In one important reaction type, a main group organometallic compound of the type R-M (R = organic fragment, M = main group center) reacts with an organic halide of the type R'-X with formation of a new carbon–carbon bond in the product R-R'. Cross-coupling reaction are a subset of coupling reactions. It is often used in arylations.

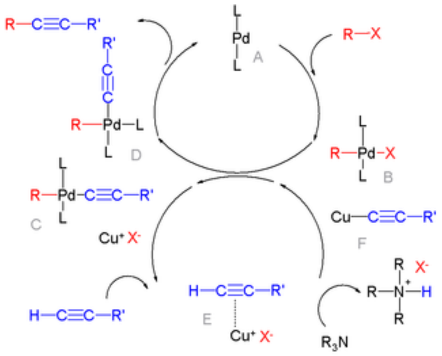
Mechanism:



Mechanism proposed for Kumada coupling (L = Ligand, Ar = Aryl).

The mechanism generally involves reductive elimination of the organic substituents R and R' on a metal complex of the type $L_nMR(R')$ (where L is some arbitrary spectator ligand). The crucial intermediate $L_nMR(R')$ is formed in a two step process from a low valence precursor L_n. The oxidative addition of an organic halide (RX) to L_nM gives $L_nMR(X)$. Subsequently, the second partner undergoes transmetallation with a source of R'^-. The final step is reductive elimination of the two coupling fragments to regenerate the catalyst and give the organic product. Unsaturated organic groups couple more easily in part because they add readily. The intermediates are also less prone to beta-hydride elimination.

Catalysts:



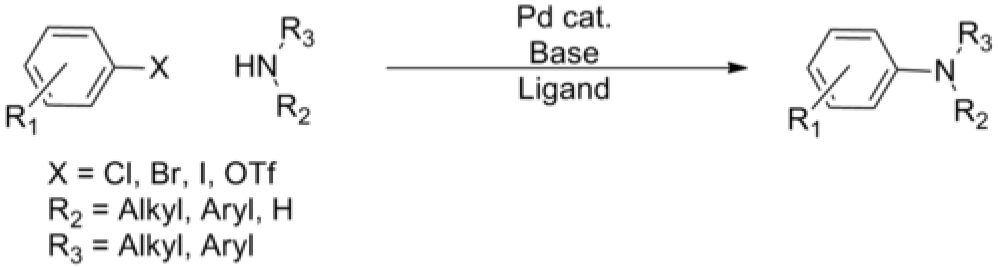
Mechanism proposed for the Sonogashira coupling.

Catalysts are often based on palladium, which is frequently selected due to high functional group tolerance. Organopalladium compounds are generally stable towards water and air. industry, which faces extensive regulation regarding heavy metals. Many pharmaceutical chemists attempt to use coupling reactions early in production to minimize metal traces in the product. Heterogeneous catalysts based on Pd are also well developed.

Applications: Aromatic substitutions are a very important class of reaction for both the fine chemical and pharmaceutical industries. The use of palladium as a catalyst for these types of reactions is common during the research stages of product development. Its desirable criteria include high selectivity, being compatible with many types of functional groups, typical use without protection groups and strong bases, and introduction at relatively late stages of the total synthesis. However, its use is less common in large-scale manufacture due to their cost and availability of aromatic halides at scale. In addition, palladium contamination of pharmaceutical products has to be 10 ppm or less that is difficult to achieve without strenuous and typically wastefully remediation strategies in place. In this contribution, we aim to give an overview of the use of a range of greener methodologies and catalysts trends in C-C couplings at industrial scale, with selected examples of current compounds industrially produced via such reactions.

Carbon–heteroatom coupling

Many cross-couplings entail forming carbon–heteroatom bonds (heteroatom = S, N, O). A popular method is the Buchwald–Hartwig reaction:



Applications of Palladium-Catalyzed C–N Cross-Coupling Reactions

Pd-catalyzed cross-coupling reactions that form C–N bonds have become useful methods to synthesize anilines and aniline derivatives, an important class of compounds throughout chemical research. A key factor in the widespread adoption of these methods has been the continued development of reliable and versatile catalysts that function under operationally simple, user-friendly conditions. This review provides an overview of Pd-catalyzed N-arylation reactions found in both basic and applied chemical research from 2008 to the present. Selected examples of C–N cross-coupling reactions between nine classes of nitrogen-based coupling partners and (pseudo)aryl halides are described for the synthesis of heterocycles, medicinally relevant compounds, natural products, organic materials, and catalysts.

ISOPOLY & HETEROPOLY ANIONS

The polymerization of simple monomeric oxide anions of Cr, Mo, W,V, Nb& Ta occurs when their alkaline solutions are gradually acidified. If from any oxyacid, the O atoms are replaced by radicals of the same acid . The acids which are obtained as a result of the apparent condensation of number of simple O containing acid molecules to give compounds containing more than a single molecule of acid anhydride is called **poly acid.** The ions of the polyacids are similarly derived from those of the simple acids by the elimination of O^{2-} ions are known as **poly anions**

The anions of the weak acids derived from the metals of group V A & VI A and particularly vanadium, molybdenum & tungsten have the property of condensing reversibly as the p H of their solutions is lowered to give a series of larger anions known as poly anions & the corresponding acids are called poly acids . Mo(VI), W(VI), V(V), Nb(V), Ta(V)etc have the tendency to form polymeric oxoanions containing MO_6 octahedra. In general, the acidification of basic solutions of vanadate$(VO_4)^{3-}$, niobate $(NbO_4)^{3-}$, molybdate $(Mo\ O_4)^{2-}$, tungstate (WO_4) etc leads to their polymerization yielding poly acids & poly anions.

The polyacids can be divided into two groups

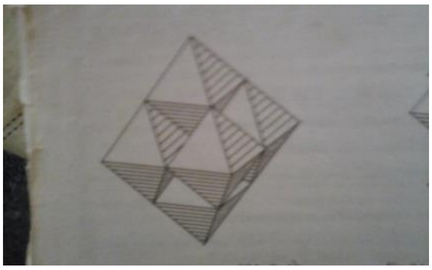
Isopolyacids : where the acids/anions which condense together are all of the same type. ie, all $Mo\ O_6$ groups or all WO_6 groups.

Hetropolyacids : where two or more different types of anions condense together ie, molybdate or tungstate groups with phosphate $(PO_4)^{3-}$, silicate $(Si\ O_4)^{4-}$ or borate groups.

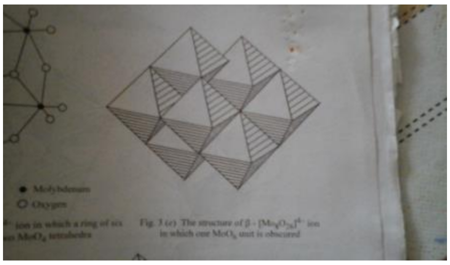
Isopolymolybdate

When the trioxide of molybdate is dissolved in aqueous alkali, the resulting solution contain tetrahedral $[Mo\ O_4]^{2-}$. If these solutions are made strongly acidic, precipitates of yellow molybdic acid $Mo\ O_3 . 2H_2O$ is obtained which convert into the monohydrate if warmed. At the pH between these two extremes, polymeric anions made up of $Mo\ O_6$ octahedra are formed & their salts can be crystallized.

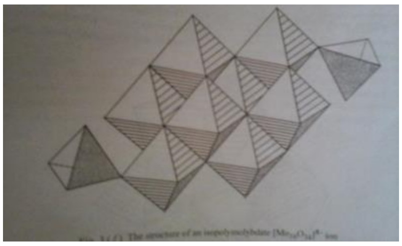
Examples:



$[Mo_6\ O_{19}]^{2-}$



$[Mo_8\ O_{26}]^{4-}$



$[Mo_{10}\ O_{34}]^{8-}$

The sharing of edges between MO_6 octahedra causes repulsion between the metal ions . This repulsion is reduced partially by displacement of M from the exact centre of the octahedra . For O atom bonded only to one metal atom , the M–O bond length ~ 1.70 A^0 , while the M-O-M bond length is 1.90 A^0. Repulsion should increase with increase in the ionic radius. V^{5+}(68pm) < Mo^{6+} (73pm) < W^{6+}(73pm) < Nb^{5+}(78pm) < Ta^{5+}(78pm) and is in agreement with the degree of distortion observed. The most common edge shared polyanions are $(V_{10}O_{28})^{6-}$, $(Mo_7\ O_{24}]^{6-}$, $(Mo_8\ O_{26}]^{4-}$, $(W_6\ O_{19}]^{2-}$,$(W_7\ O_{24}]^{6-}$, $(Ta_6\ O_{19}]^{8-}$. To form larger polyanions such as $(W_{12}\ O_{42}]^{12-}$or $(H_2\ W_{12}\ O_{40}]^{6-}$, the edge sharing must give way to apex sharing ie, larger aggregates require some extent of apex sharing in order to reduce cation – cation repulsion.

Isopolytungstate: The formation of isopolytungstate $[WO_4]^{2-}$ is similar to that of molybdates. But its chemistry is even more difficult. There are three types of polytungstates. (1)Normal tungstates (2)Paratungstates (3)Metatungstates

Normal tungstates: general formula **,** $M_m\ (WO_4)_n$. eg: Na_2WO_4 & $Na_2W_2\ O_7$

paratungstate A , $(W_6O_{21})^{6-}$, metatungstates$(H_2\ W_{12}O_{40})^{6-}$

There is greater incidence of corner sharing in the higher poly tungstates than in the poly molybdates. The metatungstate ion $(H_2\ W_{12}O_{40})^{6-}$ is composed of 4 identical tritungstate groups .Each of these tritungstate group is made up of $3WO_6$ octahedra. The 4 tritungstate groups are then attached to each other by corner sharing resulting in a cavity in the centre of the ion.

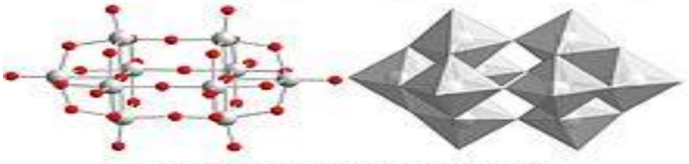
The isopolytungstate system differs from isopolymolybdate system in that, the equilibrium of the molybdenum species is complete within a matter of minutes, whereas for tungsten, this may take several weeks.

Isopolyvanadate

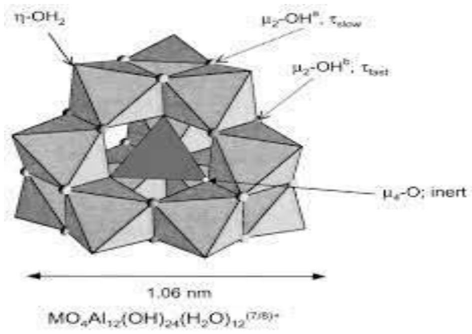
In strongly alkaline solution the ion present is VO_4^{3-} or $[VO_3(OH)]^{2-}$. As the pH is reduced from 13 to 8 condensation to $[V_2O_7]^{4-}$ takes place. Further reduction pH to 7.2 gives the so called metavanadate. In the solid metavanadate the anion consists of chains of VO_4 tetrahedra linked by sharing corners & the species in solution is almost a trimer $[V_3O_9]^{3-}$ or tetramer $[V_4O_{12}]^{4-}$. As the pH is still reduced further orange decavanadate is produced at about p H =6 $[V_{10}O_{28}]^{6-}$. The ion is protonated to $[HV_{10}O_{28}]^{5-}$ & $[[H_2V_{10}O_{28}]^{4-}$ as the p H is lowered to 3.5 . Many salts of decavanadate ions, for example $[Ca_3V_{10}O_{28}]$ occur as minerals . $[V_{10}O_{28}]^{6-}$ are found to be made up of 10 VO_6 octahedra fused together joined by sharing edges.

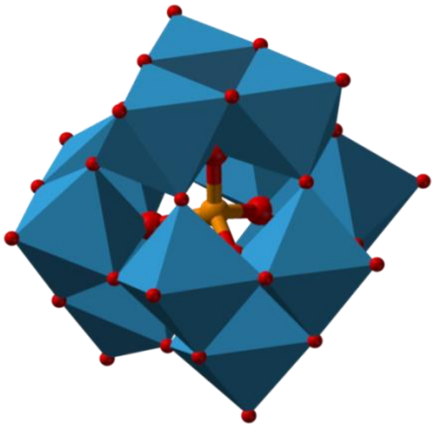
Structures of heteropoly acids

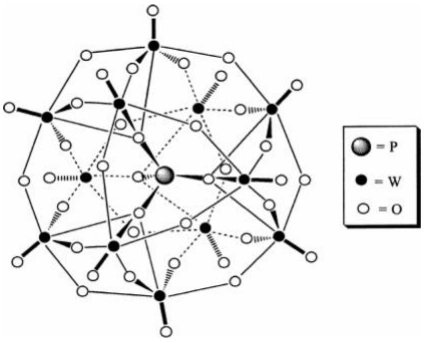
Decacoltanate ($[M_{10}O_{28}]^{6-}$ (M = Nb, Ta)



Decatungstate ($[W_{10}O_{32}]^{4-}$







Structure of the phosphotungstate anion Keggin structure, $XM_{12}O_{40}^{n-}$

Primary structure of $PW_{12}O_{40}$ 3 − Keggin ion.

12 – heteropoly acids : The structure of $[X^n\ Mo_{12}\ O_{40}]^{8-n}$ or $[PW_{12}\ O_{40}]^{3-}$ (12polyacids) is often called **Keggins structure** . The first structural study was made on 12 phospho tungstic acid. The central PO_4 group is surrounded by 12 WO_6 octahedra . Each corner O atom of the PO_4 group is shared with 4 octahedra, each of which also shares one O atom with its two neighbours. The octahedra are further linked together by sharing corners. The same structure is found in a number of hetero polyacids based on elements other than phosphorus (eg: silico tungstates, borotungstates, silico molybdates).

6 – heteropoly acids: In 6 – heteropoly acids the central atom is larger (I , Te or Rh) & capable of coordinating with 6 atoms of oxygen. Six MO_6 octahedra are arranged in a hexagonal annulus so as to share two corners with each of two neighbouring octahedral. The central cavity of the resulting $[M_6\ O_{24}]^{12}$ structure is found to be just large enough to accommodate an octahedron corresponding with that of hetero atom. This structure was identified in potassium & ammonium molybdo tellurates which contain $[Te\ Mo_{6}\text{-}O_{24}]^{6-}$ ion.

18– heteropoly acids: The structure of $[X_2\ M_{18}\ O_{62}]^{6-}$ or $[P_2\ W_{18}\ O_{62}]^{6-}$ sometimes called the **Dawson structure** .

BORANES

Boranes are compounds consisting of boron and hydrogen. They were investigated systematically by the german scientist Alfred Stock at the beginning of the 19th century. The most basic example is diborane ($B_2H_6B_2H_6$), all boranes are electron-deficient compounds. For $B_2H_6B_2H_6$ usually 14 electrons are needed to form 2c,2e-bonds, but only 12 valence electrons are present. Because of this there are two B-H-B bonds, which have three centers, but only two electrons (3c, 2e bond). This can be interpreted as a molecular orbital that is formed by combining the contributed atomic orbitals of the three atoms. In more complicated boranes not only B-H-B bonds but also B-B-B 3c, 2e-bonds occur. In such a bond the three B-atoms lie at the corners of an equilateral triangle with their sp^3 hybrid orbitals overlapping at its center. One of the common properties of boranes is, that they are flammable or react spontaneously with air. They burn with a characteristic green flame. And they are colorless, diamagnetic substances.

Nomenclature

In neutral boranes the number of boron atoms is given by a prefix and the number of Hydrogen-atoms is given in parentheses behind the name.

example: $B_5H_{11}B_5H_{11}$ → pentaborane(11), $B_4H_{10}B_4H_{10}$ → tetraborane(10)

For ions primarily the number of hydrogen-atoms and than the number of boron-atoms is given, behind the name the charge is given in parentheses.

example: $[B_6H_6]^{2-}[B_6H_6]^{2-}$ → hexahydrohexaborat(2-)

Wades rule, Structures of boranes

Wades rule helps to predict the general shape of a borane from its formula.

- count the number of B-H units
- every B-H unit contains 4 valence electrons, but two of them are needed to establish the bond between B and H, thus every B-H unit contributes two electrons to the skeletal electrons.
- every further H-Atom contributes a further electron to the skeletal electrons and
- charge contributes electrons
- the resulting number of electrons has to be divided by two to get the number of skeletal electron pairs within the borane. The general structure is defined by the number of skeletal electron pairs

Formula Skeletal	Skeletal electron pairs	Type
$[B_nH_n]^{2-}[B_nH_n]^{2-}$	n+1	Closo
$B_nH_n+4B_nH_n+4$	n+2	Nido
$B_nH_n+6B_nH_n+6$	n+3	Arachno
$B_nH_n+8B_nH_n+8$	n+4	Hype

The polyhedra are always made up of triangular faces, so they are called **deltahedra**. Usually there are three possible structure types:

Closo-boranes: closed deltahedra without B-H-B 3c,2e-bonds

- thermally stable and moderately reactive.

example: $B_6H_6^{2-}$ is closo-type and the 6 B's lie on the corners of a octahedron

Nido-boranes

- closo borane with one corner less and addition of two hydrogen-atoms instead
- B-H-B-bonds and B-B-bonds are possible.
- thermally stability lies between closo- and arachno-boranes.

example: B_5H_9 is nido-type and the 5 B's lie on the corners of a square pyramid where one corner is removed

Arachno-boranes

- closo borane deltahedron but with two BH-units removed and two H-atoms added.

it has to have B-H-B 3c, 2e-bonds.thermally unstable at room temperature and highly reactive.Example: B_4H_{10} is arachno type and the 4 B's lie on the corners of an octahedron where two corners are removed.

Bonding in boranes

Boranes are nonclassically–bonded compounds, that is, there are not enough electrons to form 2-centre, 2-electron bonds between all pairs of adjacent atoms in the molecule. A description of the bonding in the larger boranes was formulated by William Lipscomb. It involved:

- 3-center 2-electron B-H-B hydrogen bridges
- 3-center 2-electron B-B-B bonds
- 2-center 2-electron bonds (in B-B, B-H and BH_2)

Lipscomb's methodology has largely been superseded by a molecular orbital approach. This allows the concept of multi-centre bonding to be extended. For example, in the icosahedral ion $[B_{12}H_{12}]^{2-}$, the totally symmetric (A_g symmetry) molecular orbital is equally distributed among all 12 boron atoms.

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Reactivity of boranes

The lowest borane, BH_3, is a very strong Lewis acid. The molecule itself exists only transiently, dimerizing instantly to form diborane, B_2H_6, but its adducts BH_3.THF and BH_3.DMSO are stable enough to be used in hydroboration reactions. Other boranes are electrophilic and react vigorously with reagents that can supply electron pairs. With an alkali metal hydride, for example,

$$B_2H_6 + 2\ H^- \rightarrow 2\ BH_4^-$$

Further demonstrating that they are *not* in general "electron-deficient" (see above), boranes can also function as *electron donors* owing to the relative basic character of the low-polarity $B\text{-}H_{\text{terminal}}$ groups, as in reactions with halogens to form haloboranes.

The reaction of some lower boranes with air is strongly exothermic; those of B_2H_6 and B_5H_9, for example, occur explosively except in very low concentration. This does not result from any inherent instability in the boranes. Rather, it is a consequence of the fact that a combustion product, boron trioxide, is a solid. For example

$B_2H_6(g) + 3\ O_2(g) \rightarrow B_2O_3(s) + 3\ H_2O(g)$

The formation of the solid releases additional energy to what is released by the oxidation reaction. By contrast, many *closo*-borane anions, such as $B_{12}H_{12}^{2-}$, do not react with air; salts of these anions are metastable because the *closo*- structure creates a very high activation energy barrier to oxidation.

The higher boranes can be deprotonated when treated with a very strong base. For example,

$B_5H_9 + NaH \rightarrow Na(B_5H_8) + H_2$

They can also act as weak acids. For example, pentaborane(9) reacts with trimethylphosphine

$B_5H_9 + 2\ PMe_3 \rightarrow B_5H_9(PMe_3)_2$

producing what can be regarded as a derivative of the unknown *hypho*-borane B_5H_{13}. Acidity increases with the size of the borane.[10] $B_{10}H_{14}$ has a pK value of 2.7 temperature not stated.

$B_5H_9 < B_6H_{10} < B_{10}H_{14} < B_{16}H_{20} < B_{18}H_{22}$

Reaction of a borane with the transient BH_3, produced by dissociation of B_2H_6, can lead to the formation of a *conjuncto*-borane species in which two small borane sub-units are joined by the sharing of boron atoms.[11]

$B_6H_{10} + (BH_3) \rightarrow B_7H_{11} + H_2$

$B_7H_{11} + B_6H_{10} \rightarrow B_{13}H_{19} + H_2$

Other *conjuncto*-boranes, where the sub-units are joined by a B-B bond, can be made by ultra violet irradiation of *nido*-boranes. Some B-B coupled *conjuncto*-boranes can be produced using $PtBr_2$ as catalyst.

Reaction of a borane with an alkyne can produce a carborane; the icosahedral closo-carboranes $C_2B_{10}H_{12}$, are particularly stable.

Example of Boranes:

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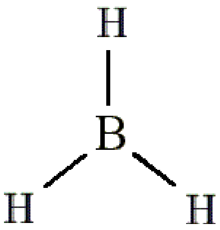
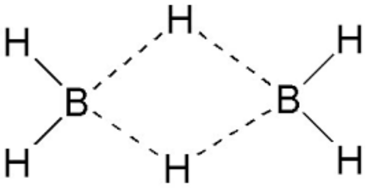
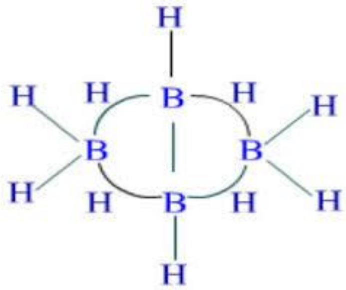
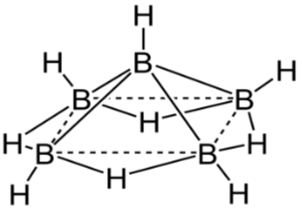
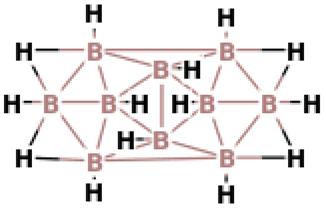


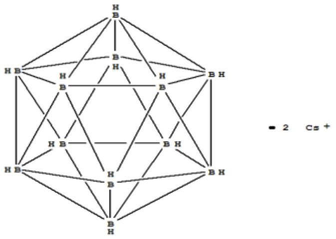




Borane BH_3 Diborane(6) B_2H_6 Tetraborane(10) B_4H_{10}

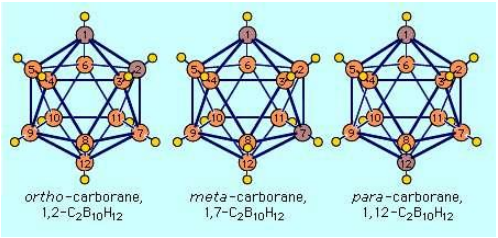




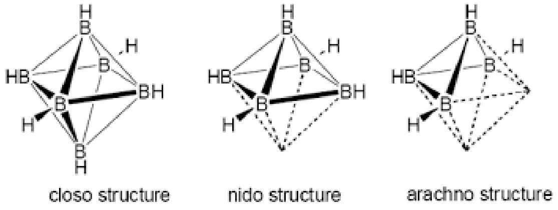


Pentaborane(9) B_5H_9 Decaborane(14) $B_{10}H_{14}$ Dodecaborate(12) $B_{12}H_{12}^{2-}$

Carboranes are electron-delocalized (non-classically bonded) clusters composed of boron, carbon and hydrogen atoms that may also contain other metallic and nonmetallic elements in the cluster framework. Like many of the related boron hydrides, these clusters are polyhedra or fragments of polyhedra, and are similarly classified as *closo*-, *nido*-, *arachno*-, *hypho*-, etc. based on whether they represent a complete (*closo*-) polyhedron, or a polyhedron that is missing one (*nido*-), two (*arachno*-), three (*hypho*-), or more vertices. Carboranes are a notable example of heteroboranes.



ortho-carborane, 1,2-$C_2B_{10}H_{12}$ *meta*-carborane, 1,7-$C_2B_{10}H_{12}$ *para*-carborane, 1,12-$C_2B_{10}H_{12}$



closo structure nido structure arachno structure

Preparation

Carboranes have been prepared by many different routes, the most common being addition of alkynyl reagents to boron hydride clusters to form dicarbon carboranes. For example, the high-temperature reaction of pentaborane with acetylene affords several closo-carboranes as well as other products:

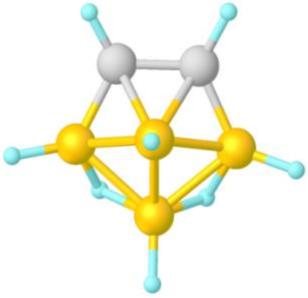
$$\textit{nido}\text{-}B_5H_9 + C_2H_2 \rightarrow \quad \textit{closo}\text{-}1,5\text{-}C_2B_3H_5,\ \textit{closo}\text{-}1,6\text{-}C_2B_4H_6,\ 2,4\text{-}C_2B_5H_7$$

When the reaction is conducted at lower temperatures, an open-cage carborane is obtained:

nido-B_5H_9 + C_2H_2 → *nido*-2,4-$C_2B_4H_8$

Other procedures generate carboranes containing three or four cage carbon atoms.
Monocarba derivatives:*Mono*carboranes are clusters with B_nC cages. The 12-vertex derivative is best studied, but several are known.Typically they are prepared by the addition of one-carbon reagents to boron hydride clusters. One-carbon reagents include cyanide, isocyanides, and formaldehyde. For example, monocarbadodecaborate ($[CB_{11}H_{12}]^-$) is produced from decaborane and formaldehyde, followed by addition of borane dimethylsulfide.

Dicarba cluster: Dicarbaboranes can be prepared from boron hydrides using alkynes as the source of the two carbon centers. In addition to the *closo*-$C_2B_nH_{n+2}$ series mentioned above, several open-cage dicarbon species are known including *nido*-$C_2B_3H_7$ (isostructural and isoelectronic with B_5H_9) and *arachno*-$C_2B_7H_{13}$.



Structure of nido-$C_2B_4H_8$, highlighting some trends: carbon at the low connectivity sites, bridging hydrogen between B centers on open face.

Syntheses of icosahedral *closo*-dicarbadodecaborane derivatives ($R_2C_2B_{10}H_{10}$) employ alkynes as the R_2C_2 source and decaborane ($B_{10}H_{14}$) to supply the B_{10} unit.
Tricarba, tetracarba, pentacarba, and hexacarba clusters: Carboranes having more than two carbon atoms in the skeletal framework, obtained in a variety of ways, include derivatives of *nido*-$C_3B_3H_7$, *nido*-$C_3B_8H_{11}$, *nido*-$C_4B_2H_6$, *nido*-$C_4B_4H_8$, *nido*-$C_5BH_6^+$, and *arachno*-$H_6C_6B_6Et_6$.
Reactions: Carboranes undergo a wide variety of reactions. Deprotonation of *closo*-dicarbadodecaboranes using organolithium reagents gives the dilithio derivatives.

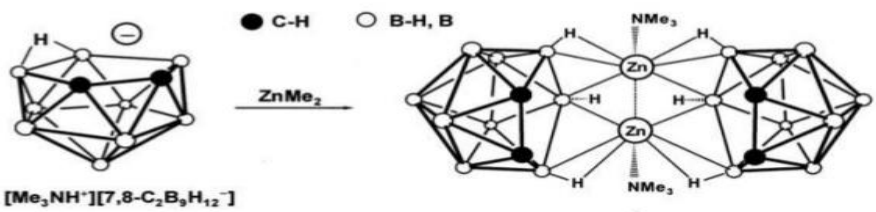
$C_2B_{10}H_{12}$ + 2 BuLi → $Li_2C_2B_{10}H_{10}$ + 2 BuH
These dilithiated compounds react with a variety of electrophiles, e.g. chlorophosphines, chlorosilanes, and sulfur.

METAL BORANES: The intensive research focus on metal borohydrides in the early 21st century has recently broadened to encompass higher metal boranes such as metal–$B_{10}H_{10}$'s and $B_{12}H_{12}$'s. This review summarizes the recent breakthroughs in the area of higher metal boranes in these last few years, in addition to highlighting core research from the mid-20th century.

Metallocarborane:

Base-induced degradation of carboranes give anionic nido derivatives, which can be employed as ligands for transition metals, generating **metallacarboranes**, which are carboranes containing one or more transition metal or main group metal atoms in the cage framework, discovered in 1965. The bulk of the work on metallacarboranes has centered on 12-vertex MC_2B_9 and $M_2C_2B_8$ clusters and 7-vertex MC_2B_4 and $M_2C_2B_3$ (triple-decker and multidecker sandwich) clusters, but metallacarboranes of 6 to 15 vertices have also been prepared, as have clusters with varying numbers of carbon, boron, and metal. Diborolyl-metal complexes featuring MC_3B_2 and $M_2C_3B_2$ cages, representing another type of metallacarborane, have also been extensively studied.

Structure of some Metallocarborane:



$[Me_3NH^+][7,8\text{-}C_2B_9H_{12}^-]$

1

Highly planar, Zn_2B_2 diamond-like structure, weak Zn-Zn bond.

Chemical structures of the anionic metallacarboranes [3,3 0-Fe(1,2-closo-C 2 B 9 H 11) 2] À (a) and [3,3 0-Fe(8,9,12-Cl 3-1,2-closo-C 2 B 9 H 8) 2] À (b) with their cluster vertex numbering; neutral ferrocene (c).