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Engineering Chemistry-I (BS-109)

Chemical Bonding

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How do atoms combine to form molecules?

Why do atoms form bonds?

A molecule will only be formed if it is more stable, and has a lower energy than the individual atoms. During chemical combination, the electron of the atoms rearrange to form a molecule.

Electrons in the outermost shell (valence electrons) are involved in the bond formation in order to achieve stable electronic configuration, which is achieved either by losing electrons or gaining electrons or sharing them.

Types of elements:

1. **Electropositive:** whose atoms give up one or more electrons such as alkali metals. (Cs is the most electropositive element)
2. **Electronegative:** acceptance of electrons. (F is the most electronegative element)
3. Elements which have little tendency to lose or gain electrons.

Types of bond formed based on the above character of element:

1. **Ionic bond:** Between an electropositive and an electronegative element
2. **Covalent bond:** Between two electronegative elements
3. **Metallic bond:** Between two electropositive elements

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Types of valencies based on electronic theory of valency:

1. Ionic valency or electrovalency:
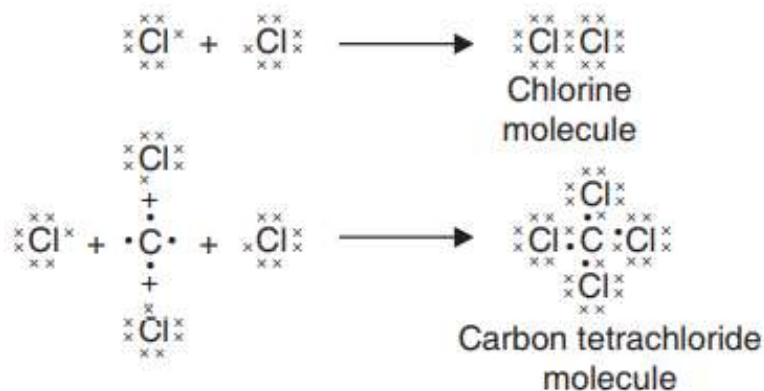
Electronic configuration of Na: 1s2 2s2 2p6 3s1 ➜ lose one electron from its outer shell to attain stable noble gas confgn
Electronic configuration of Cl: 1s2 2s2 2p6 3s2 3p5 ➜ gain one electron => it is electronegative

When Na and Cl react together, the outermost electrons of the Na is transferred to Cl atoms to produce Na^+ and Cl^- ions, which are held together in a crystal lattice through electrostatic attractions. This combination of two atoms by complete transfer of outermost electrons is known as electrovalency and this bond is known as ionic bond.

Electrovalency is seen in the case of atoms with a marked difference in their electronegativity values

2. Covalency: When atoms of similar electronegativity values combine to form molecules, they share their electrons to fill up their octets in the outermost shells. This combination is known as covalency and the bond formed is called covalent bond

Chlorine molecule

Carbon tetrachloride molecule

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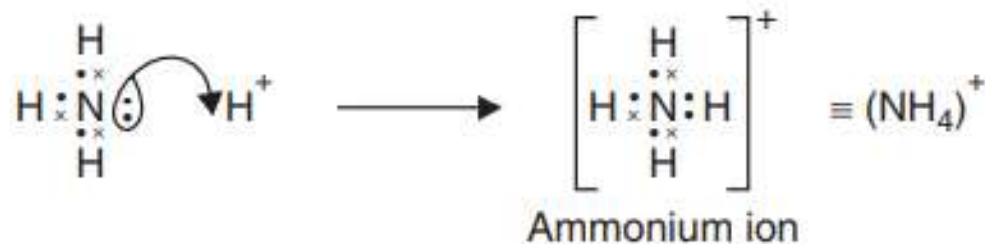
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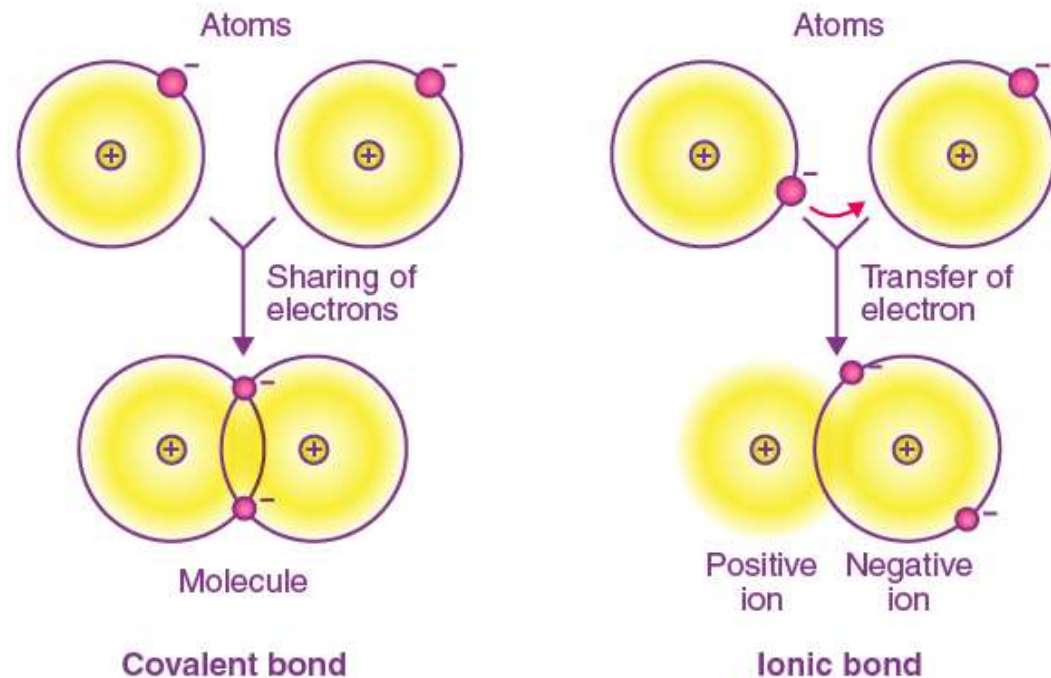UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

The main difference between valency and covalency is that valency is the number of electrons that an atom will lose or gain in order to stabilize itself whereas covalency is the maximum number of covalent bonds that an atom can form using its empty orbitals e.g. valency of N is 5 (1s2 2s2 2p3) whereas its covalency is 3 i.e. it forms three covalent bonds

3. Co-ordinate valency: Unlike equal contribution from both atoms in case of covalency, here, a pair of electrons is being contributed by a single atom while other atom contribute no electron towards the bond formation. After combination, the bond acts as purely covalent. This combination of atoms is called co-ordinate covalency and the bond is called coordinate bond.

The atom which donates the pair of electrons is known as 'donor' atom (should have a lone pair of electrons) and the atom which accepts the electron is known as 'acceptor' atom. It is indicated by the sign '→'

Ammonium ion

Covalent bond

Ionic bond

Electrovalent Compounds	Covalent Compounds
(i) They are Non-directional.	(i) They are directional in nature.
(ii) They cannot exhibit isomerism.	(ii) They can show isomerism.
(iii) m.p. and b.p. are high.	(iii) m.p. and b.p. are low.
(iv) They are conductors of electricity in solution or in their molten state.	(iv) They are nonconductors of electricity in solution or in molten state.
(v) They are soluble in polar solvents (H_2O) and insoluble in non-polar solvents (C_6H_6, CCl_4).	(v) They are soluble in organic solvents, generally insoluble in water.
(vi) They are polar in nature.	(vi) They are non-polar in nature.

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- The attraction and repulsive tendencies of atoms in a covalent bond arising due to their electronegativity difference impart partial ionic character to the covalent bond.
  - Case I: When electronegative values (x) of atoms A and B are equal, $x_A = x_B$, the bond A-B is 100% covalent.
  - Case II: When $x_A \neq x_B$, the bond gains partial ionic character and the molecule AB becomes polar e.g. HCl.

  - Greater the difference ($x_A - x_B$), greater is the ionic character of the bond.
  - The relation is represented as:

$$\% \text{ ionic character} = 100 \left[1 - \exp \left\{ 1 - \frac{1}{4}(x_A - x_B)^2 \right\} \right] \quad \textcolor{red}{\text{Pauling's equation}}$$

$$= 16(x_A - x_B) + 3.5 (x_A - x_B)^2 \quad \textcolor{red}{\text{Hannay-Smith equation}}$$
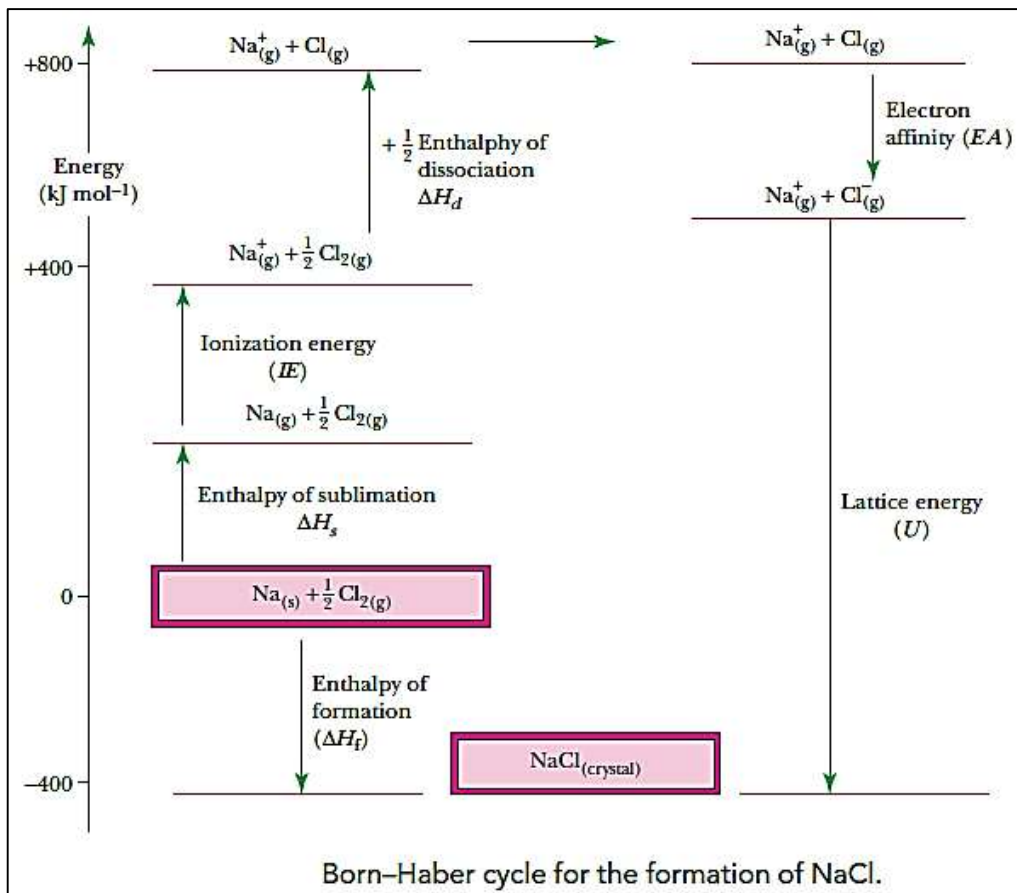
Calculation of partial ionic character of HF molecule:

$\% \text{ ionic character in HF molecule} \quad = 16(4.0 - 2.1) + 3.5(4.0 - 2.1)^2$

$$= 43\%.$$

- **Lattice Energy (U):** It is a type of potential energy that may be defined in two ways:
  (i) the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. (U is always positive)
  (ii) The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. (U is always negative)
- It is a measure of the cohesive forces that bind ions i.e. it estimates the strength of the bonds in an ionic compound (units: kJ/mol) (U_{NaCl}= -774 kJ/mol)
- Greater the lattice energy, more is the stability. The crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points.

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- **Born-Haber cycle:** Given by Born and Haber in 1919. It is a thermochemical cycle that can be used to

    (i)   calculate the lattice energy

    (ii) determine the electron affinity

    (iii) determine whether the bonding in a compound is truly ionic

- It is an application of **Hess's law** (overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step)

- It takes into account the **ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation**. The atoms in their standard state are first converted into gaseous atoms, then to ions and finally packed into crystal lattice

- **Ionization energy, sublimation energy and dissociation energy:** positive value (energy is required). **Dissociation energy** is the energy required to break apart a compound. **Sublimation energy** is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase.

- **Electron affinity and lattice energy:** negative value (energy is released)

- The **heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.

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Born–Haber cycle for the formation of NaCl.

Born-Haber cycle of $NaCl$:

Step-1: Sublimation energy (ΔH_S) of metal. $Na(s) \rightarrow Na(g)$

Step-2: Ionisation enthalpy (IE) of metal $Na(g) \longrightarrow Na^+_{(g)} + e^-$

Step-3: Dissociation energy (ΔH_d) of NON metal $\frac{1}{2} Cl_{2(g)} \longrightarrow Cl(g)$

Step-4: Electron Affinity (EA) of NON metal $Cl(g) + e^- \rightarrow Cl^-(g)$

Step-5: Lattice Enthalpy (U) of NaCl $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$.

Hence, Enthalpy of formation $(\Delta H_f) = \Delta H_S + IE + \frac{1}{2}\Delta H_d + EA + U$

As, except EA & U, all can be measured. Originally cycle was used to calculate electron affinity. By using known crystal structure, it was possible to calculate the lattice energy (U) & hence electron affinity (EA) was calculated.

Higher lattice energy then,

1. Higher is stability of ionic solids.   2. higher melting & boiling points.

2. lesser is the solubility.

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→ Covalent Bond - Energy changes:

→ Bond energies can be used to estimate the energy change of a chemical reaction.

→ When a bond is broken in the reactant, process is endothermic. $(\Delta H = +ve)$

→ When a bond is formed in the products, process is exothermic. $(\Delta H = -ve)$

So, we combine the positive energy change with the negative energy change to estimate the overall energy change. of the reaction.

Eg → $\qquad 2\,H-H + O-O \longrightarrow 2\,H-O-H$
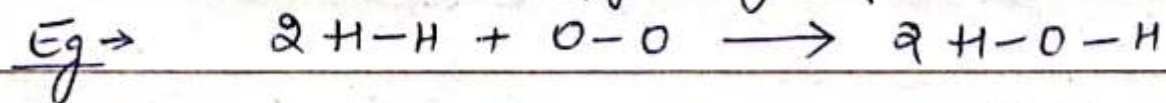
Energy required to break.

$2\,H-H = 2(+436\ KJ/mol)$
$1\,O-O = \quad (+498\ KJ/mol)$
_____
Total $= +1,370\ KJ/mol$

Energy required to form 4 O-H bonds.

$4(O-H) = 4(-463\ KJ/mol)$
_____
Total $= -1,852\ KJ/mol$

Net energy change $\Rightarrow (+1,370) + (-1,852) = -482\ KJ/mol$

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- **Potential energy curve for H_2 molecule:**

- When the H-atoms are separated by a large distance (infinity) we take this energy to be zero.

- Bringing the atoms closer to one another has an attractive potential and the bond has formed on reaching the lowest point on your curve. Lower the energy, more is the stability. At this point a covalent bond is formed and this distance is known as bond length. For H_2 molecule, the **bond length is 74 pm.**

- Moving the atoms closer together increases the potential energy because here we push electrons closer to one another and this energy increases rapidly with each small decrease in separation due to repulsion of similar charges.

Potential Engergy Vs Internuclear Distance Between Two Atoms
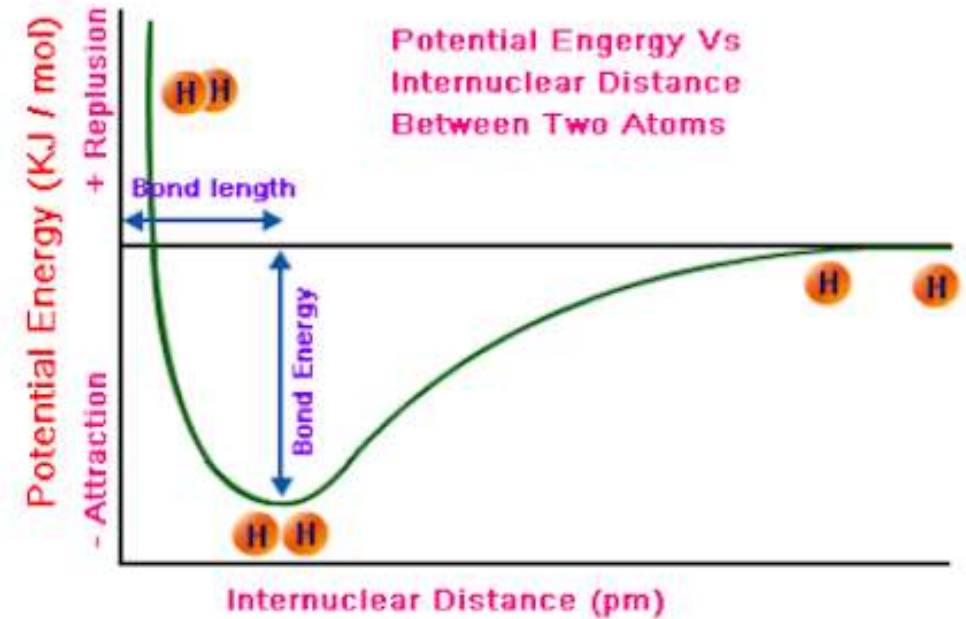
- **Properties of covalent bond:**

   (i) Covalent bonding does not result in the formation of new electrons. The bond only pairs them.

   (ii) They are very powerful chemical bonds that exist between atoms.

   (iii) Most compounds having covalent bonds exhibit relatively low melting points and boiling points.

   (iv) Compounds with covalent bonds usually have lower enthalpies of vaporization and fusion.

   (v) Compounds formed by covalent bonding don't conduct electricity due to the lack of free electrons.

   (vi) Covalent compounds are not soluble in water.

- **Bond parameters of covalent bond:**

Covalent bonds can be characterized on the basis of several bond parameters such as **bond length, bond angle, bond order, and bond energy** (also known as bond enthalpy). These bond parameters offer insight into the stability of a chemical compound and the strength of the chemical bonds holding its atoms together.

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- **Bond Order:** It is the total number of covalently bonded electron pairs between two atoms in a molecule.
  - Single bonds have a bond order of 1.
  - Double bonds have a bond order of 2.
  - Triple bonds have a bond order of 3.

  - Examples:
  (i)   The bond order of the carbon-hydrogen bond in C2H2 (ethene) is 1 and that of the carbon-carbon bond is 2.
  $$H2C=CH2$$

  (ii) The bond order of the oxygen-oxygen bond in an O2 molecule is 2.   O=O

  (iii) In a carbon monoxide molecule, the carbon-oxygen bond has a bond order of 3.   C ≡ O

- **Bond angle:** The angle formed between two covalent bonds that originate from the same atom. E.g. bond angle in a water molecule is 104.5°C

 ➤ bond angle increases with increase in s character: sp^3 (109.28) < sp^2 (120 °) < sp (180 °)

  ➤ bond angle decreases with decrease in electronegativity (less repulsions in bond pairs)

  H_2O (104.5) > H_2S (92.2) > H_2Se (91) > H_2Te (89.5)

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- **Bond length:** It is a measure of the distance between the nuclei of two chemically bonded atoms in a molecule. It is approximately equal to the sum of the covalent radii of the two bonded atoms.

r_1 r_2

Total bond length
$= r_1 + r_2$
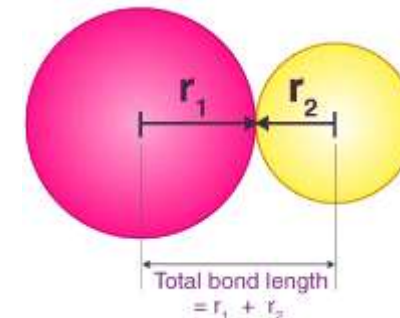
- For covalent bonds, the **bond length is inversely proportional to the bond order** – higher bond orders result in stronger bonds, which are accompanied by stronger forces of attraction holding the atoms together. Short bonds are a consequence of these strong forces of attraction.
- For a given molecule, bond length increases with the size of the other bonded atom   H-I > H-Br > H-Cl > H-F
- Bond length decreases with increase in s-character sp^3 (110 pm) > sp^2 (109 pm) > sp (108 pm)

- **Bond energy:** It is a measure of the strength of a chemical bond. It can be defined as the energy required to break all covalent bonds of a specific type in one mole of a chemical compound (which is in its gaseous state).
- The strength of a chemical bond is directly proportional to the amount of energy required to break it. Therefore, bond energy is:
    - Inversely proportional to the bond length, i.e. longer bonds have lower bond energies.
    - Directly proportional to the bond order, i.e. multiple bonds have high bond energies.
- Bond energy increases with increase in the electronegativity difference

        H-I < H-Br < H-Cl < H-F

Heat energy in   Bond-breaking
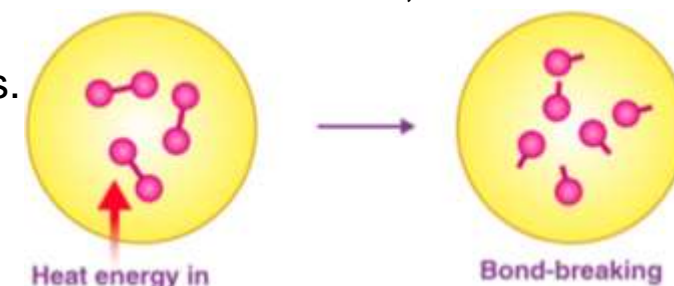
- Bond energy decreases with increase in number of lone pairs on bonded atoms due to l.p.- l.p. repulsions

        C-C > N-N > O-O > F-F

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- **Werner's theory of coordination compounds:** Put forward in 1893 in order to explain the structures, formation and nature of bonding in coordination compounds. He was the first inorganic chemist to win Nobel Prize and is also known as **Father of coordination chemistry**.
- Major postulates are: The central metal atom/ ion in a coordination compound exhibits two types of valencies - **primary and secondary.**
    - **Primary valency:**
        (i) It is the number of charges on the complex ion, which is matched (or neutralized) by the same number of charges from the negative ions) i.e. the **oxidation number** of the ion
        (ii) It is written outside the coordination sphere.
        (iii) These are non-directional and do not give any geometry to complex compound.
        (iv) e.g. $[Co(NH_3)_6]$ **Cl_3**, number of primary valencies 3, oxidation state +3
    - **Secondary valency:**
        i.   It is the number of ligand atoms coordinated to the metal i.e. the **coordination number** of the metal.
        ii.   They are satisfied by negative ion or by neutral molecules.
        iii. It is written inside the coordination sphere.
        iv.   e.g. $[Co$ **$(NH_3)_6$**$]Cl_3$, coordination number of Co is 6
        v.   They are always directed towards fixed position in space and this cause definite geometry of the coordinate compound. For Example: If a metal ion has six secondary valencies, these are arranged octahedrally around the central metal ion. If the metal ion has four secondary valencies, these are arranged in either tetrahedral or square planar arrangement around the central metal ion. The secondary valency thus determines the stereochemistry of the complex ion.

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- **Explanation of the structures of four complexes of Co (III) chloride with ammonia:** Werner treated a series of coordinate complexes with an excess of AgNO3, and weighed the AgCl precipitated.

  - CoCl3.6NH3 + Excess $Ag^+ \rightarrow$ 3AgCl =>(3Cl−ion get precipitated)

  - CoCl3.5NH3 + Excess $Ag^+ \rightarrow$ 2AgCl =>(2Cl−ion get precipitated)

  - CoCl3.4NH3 + Excess $Ag^+ \rightarrow$ AgCl =>(1Cl−ion get precipitated)

  - CoCl3.3NH3 + Excess $Ag^+ \rightarrow$ no ppt =>(0Cl−ion get precipitated)

- **Conclusions:**

- In $CoCl_3.6NH_3$, 3Cl− ions react with 3 silver ion form 3 silver chloride precipitates which act as primary valency and 6NH3 molecules act as secondary valency. Thus the compound is written as $[Co(NH3)_6] Cl_3$.

- Similarly, for $CoCl_3. 5NH_3$, 2Cl− ions act as primary valency, the remaining 1Cl− and 5NH$_3$ ions act as secondary valency. So the compound is $[Co(NH_3)_5 Cl] Cl_2$

- For $CoCl_3.4NH_3$, 1Cl− is primary valency, 2Cl− and 4NH3 is secondary valency. So the compound is $[Co(NH_3)_4 Cl_2] Cl$

- For $CoCl_3.3NH_3$, all 3Cl− and 3NH$_3$ ion act as secondary valency So the compound is $[Co(NH_3)_3 Cl_3]$

$[Co (NH_3)_6] Cl_3$ **I**

$[Co (NH_3)_5 Cl] Cl_2$ **II**

$[Co (NH_3)_4 Cl_2] Cl$
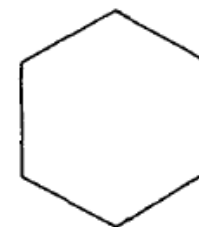
$[Co (NH_3)_3 Cl_3]$
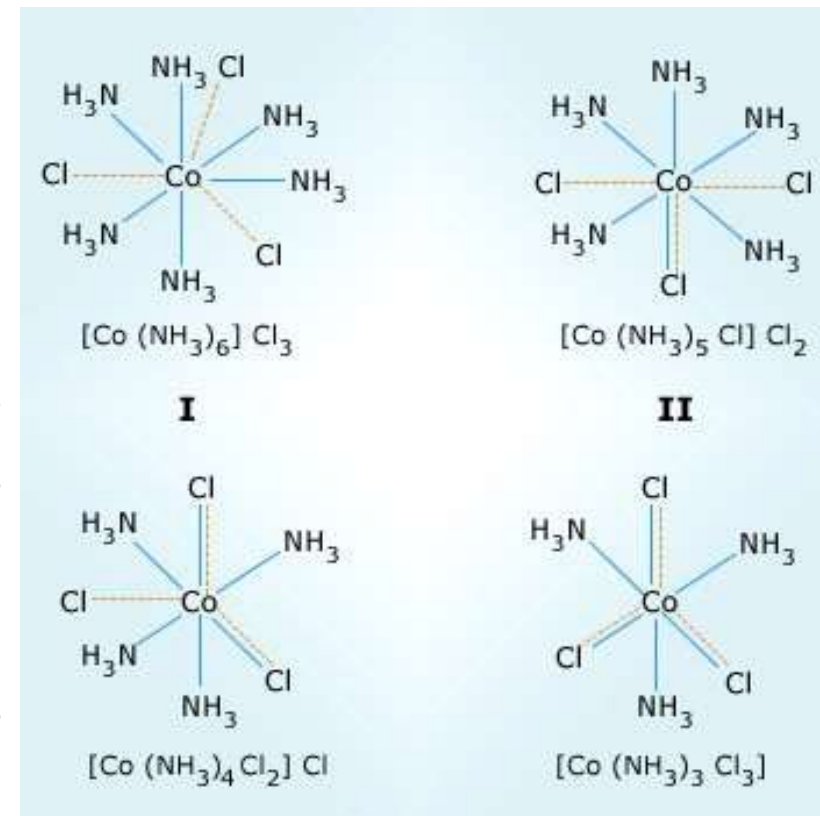
Dotted line represents the primary valency. Normal line represents the secondary valency.

Table 7.2 Number of isomers predicted and actually found
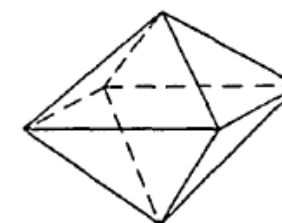
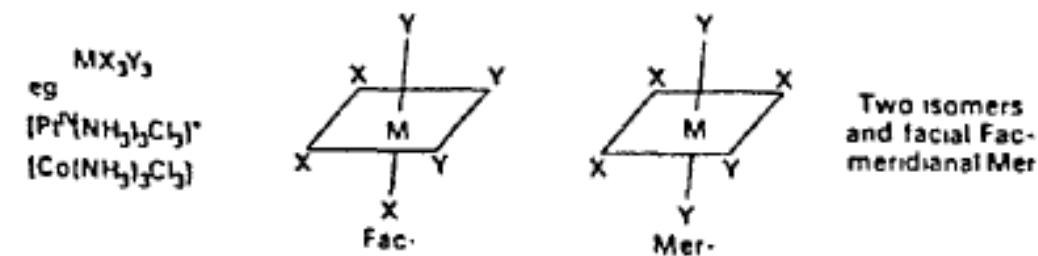| Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[MX_6]$	1	1	1	1
$[MX_5Y]$	1	1	1	1
$[MX_4Y_2]$	2	2	3	3
$[MX_3Y_3]$	2	2	3	3
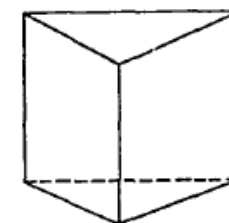
Planar hexagon   Trigonal prism   Octahedron

MX_6

eg

$[Co^{III}(NH_3)_6]^{3+}$

$[Fe^{III}(CN)_6]^{3-}$

Only one form

MX_5Y

eg

$[Pt^{IV}(NH_3)_5Cl]^{3+}$

$[Co^{III}(NH_3)_5Cl]^{2+}$

≡

Only one form as all six corners are equivalent

MX_4Y_2

eg

$[Pt^{IV}(NH_3)_4Cl_2]^{2+}$

$[Co^{III}(NH_3)_4Cl_2]^{+}$

$[Pt^{IV}(NH_3)_2Cl_4]$

Cis   Trans

Two isomers cis and trans

MX_3Y_3

eg

$[Pt^{IV}(NH_3)_3Cl_3]^{+}$

$[Co(NH_3)_3Cl_3]$

Fac·   Mer-

Two isomers and facial Fac-meridianal Mer

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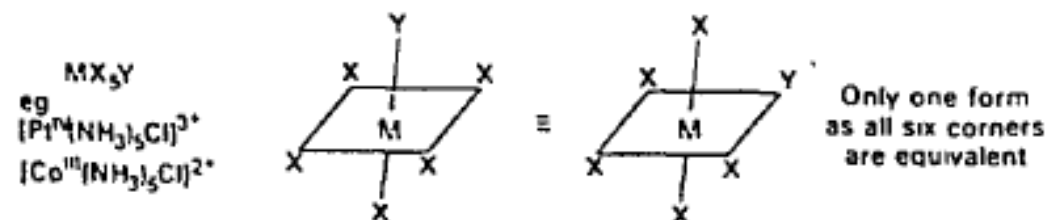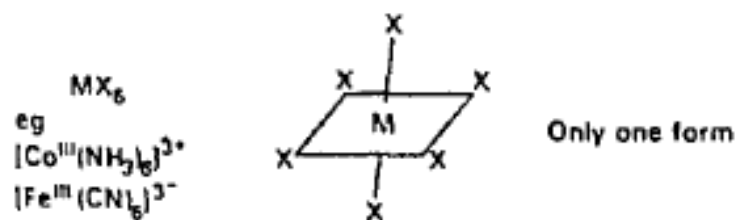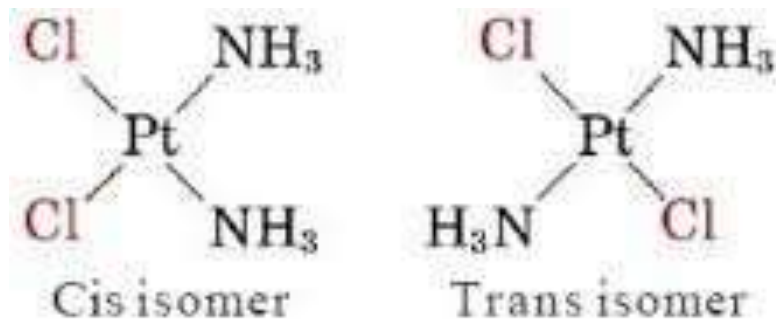
- He also studied the geometry of the complexes in which the **coordination number of the central metal atom is 4**. He proposed that there are two possible structure: Square Planar and Tetrahedral.

- $[PtCl_2(NH_3)_2]$ complex: In this complex the coordination number of the metal is 4, Werner found that it existed in two isomeric forms, cis and trans. This shows that all the four ligands lie in the same plane. Therefore the structure should be a square planar or tetrahedral.

Isomerism in square planar complexes

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- **Effective Atomic Number (EAN):** It represents the total number of electrons surrounding the nucleus of a metal atom in a metal complex. It is composed of the metal atom's electrons and the bonding electrons from the surrounding electron-donating atoms and molecules. This rule was given by English chemist Nevil V. Sidgwick

- In a number of metal complexes the metal atom tends to surround itself with sufficient ligands that the resulting effective atomic number is numerically equal to the atomic number of the noble-gas element found in the same period in which the metal is situated.

- EAN of the cobalt atom in the complex $[Co(NH_3)_6]^{3+}$ is 36, the sum of the number of electrons in the trivalent cobalt ion (24) and the number of bonding electrons from six surrounding ammonia molecules, each of which contributes an electron pair ($2 \times 6 = 12$).

- EAN of the iron atom in the complex $K_4[Fe(CN)_6]$ is 36, the sum of the number of electrons in the divalent iron ion (24) and the number of bonding electrons from six surrounding cyanide molecules, each of which contributes an electron pair ($2 \times 6 = 12$).

- EAN = Atomic number (Z) – Oxidation number (x) + 2 × Coordination number

    or, EAN= Z – x + 2nL, where n= Number of the ligands; L = Number of co-ordinate bonds formed by ligand

- e.g. $[Cu(NH_3)_4]^{2+}$: EAN = $29 – 2 + 2 (4) = 35$ (exception to the EAN rule due to presence of odd number of electrons)

    $[Ni(CO)_4]$: EAN = $28 – 0 + 2 (4) = 36$

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Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN	
Cr	24	$[Cr(CO)_6]$	0	12	36	
Fe	26	$[Fe(CN)_6]^{4-}$	2	12	36	
Fe	26	$[Fe(CO)_5]$	0	10	36	
Co	27	$[Co(NH_3)_6]^{3+}$	3	12	36	(Kr)
Ni	28	$[Ni(CO)_4]$	0	8	36	
Cu	29	$[Cu(CN)_4]^{3-}$	1	8	36	
Pd	46	$[Pd(NH_3)_6]^{4+}$	4	12	54	(Xe)
Pt	78	$[PtCl_6]^{2-}$	4	12	86	(Rn)
Fe	26	$[Fe(CN)_6]^{3-}$	3	12	35	
Ni	28	$[Ni(NH_3)_6]^{2+}$	2	12	38	
Pd	46	$[PdCl_4]^{2-}$	2	8	52	
Pt	78	$[Pt(NH_3)_4]^{2+}$	2	8	84	