SIDGWICK THEORY (Electronic theory)

In the formation of complexes, saturated molecules or ions take par This suggests the operation of dative or co-ordinate covalency. In the formatio of the ammonium radical, a proton accepts and shares a pair of electron from the nitrogen atom of a saturated ammonia molecule. Similarly a cobalti ion

$$H^+ + :NH_3 \longrightarrow [H:NH_3] \text{ or } [NH_4]^+$$

Plays the role of an acceptor, which receives and shares 6 pairs o electrons from 6NH$_3$ molecules. A fresh shell of electrons is thus forme around the cobaltic ion. This shell now consists of 12 electrons. This is als a stable grouping.

The cobaltic ion (2,8,14), accepts these 12 electrons. So is attains structure 2,8,14 and 12. All the electrons in the last shell are shared. The total number of electrons now belonging to cobalt is 36. This is the numbe for the inert gas krypton.

The NH$_3$ molecules in the $[Co(NH_3)_6]^{3+}$ may be replaced one by one by H$_2$O molecules till a hexa hydrate $[Co(H_2O)_6]^{3+}$, is formed. Similarly the NH$_3$ molecules in, $[Co(NH_3)_6]^{3+}$ may be replaced partly by Cl$^-$ ions, e.g., $[Co(NH_3)_4Cl_2]^+$

The central metal atom may be Fe^{2+} or Fe^{3+} instead of Co^{3+}. The co-ordinating groups may be 6CN$^-$ ions. We get the complex ferrocyanide ions respectively.

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]$$

$$Fe(CN)_3 + 3KCN \longrightarrow K_3[Fe(CN)_6]$$

The original Fe^{2+} and Fe^{3+} ions with 2 and 3 positive charges respectively, after co-ordinating with 6 negatively charged CN$^-$ ions are converted into complex ferrocyanide ion and ferrocyanide ion with 4 and 3 negative charges respectively.

Fluoride ions may co-ordinate with a boron atom of BF$_3$ of a silicon atom of SiF$_4$ giving a borofluoride complex ion BF$_4$ or a silicofluoride complex ion SiF$_5^-$.

$$BF_3 + F \longrightarrow [BF_4]^-$$

Borofluroide ion

$$SiF_4 + F \longrightarrow [SiF_5]^-$$

Silicofluoride ion

In the case of salts containing several molecules of water of crystallisation, e.g., $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$ etc., both the cations and anions may be regarded as being co-ordinated with water molecule.

Effective atomic number:

Sidgwick suggested that metal ions would tend to accept electron pairs form donors until they have obtained a sufficient number of electrons such that the metal in the resulting complex ion has an effective atomic number of the next inert gas.

Definition

$$\left.\begin{array}{l}\text{The effective atomic}\\ \text{number (EAN) of a}\\ \text{metal in a complex}\end{array}\right\} = \left\{\begin{array}{l}\text{Atomic number of the metal - Electrons lost in ion}\\ \text{formation + number of electron}\\ \text{gained by Co-ordination}\end{array}\right.$$

In many cases the EAN of a metal in complex corresponds on the next heavier inert gas element.

Example:

i. In $K_4[Fe(CN)_6]$: Atomic number of Fe=26
Number of electrons lost during the formation of Fe^{2+} ion = 2
Number of electrons gained by co-ordination= 6 x 2 = 12
EAN of Fe = 26 - 2 + 12 = 36 = At. No of Kr.

ii. In $Ni(CO)_4$: Atomic number of Ni=28
It is in zero oxidation state. Therefore number of electron lost =0.
Number of electrons gained by co-ordination = 4 x 2 = 8
EAN of Ni = 28 + 8 = 36 = At. No. of Kr.

The EANs for various metals in complexes are given in table 2

TABLE 2

Metal ion	At. No. of Metal	C.N.	Elecrons ions in ion formation	Electrons added by Co-ordination	EAN
Fe^{2+}	26	6	2	12	36(Kr)
Co^{3+}	27	6	3	12	36(Kr)
Cu^{+}	29	4	1	8	36(Kr)
Pd^{4+}	46	6	4	12	54(Xe)
Ir^{3+}	77	6	3	12	86(Rn)
Pt^{4+}	78	6	4	12	86(Rn)

Note: There are certain metal ions, which do not obey the effective atomic number concept. E.g., In $[Fe(CN)_6]^{3-}$ EAN of Fe=26-3+12=35. Which is not the atomic number of the next inert gas viz Kr(36).