Theory of Bonding in Complexes:

Sidgwick Theory:→ Electronic theory of valency was unknown when Werner had propounded his general theory of co-ordination. But with the advent of electronic theory of valency, it was considered necessary to make some modifications in it. Sidgwick accepted the Lewis concept of the two-electron covalent bond between two atoms in a molecule and introduced a new concept of co-ordinate bond.

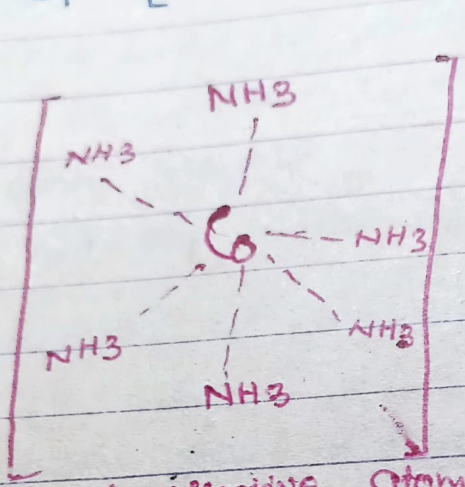
Sidgwick made a major contribution to bring Werner's theory into line with electronic theory of valency.

According to Sidgwick all the neutral molecules or anions which were capable of being co-ordinated to central metal ion ~~have~~ contain at least one unshared (lone) pair of electrons in their valency shell.

Sidgwick interpreted secondary valency of (i.e. non-ionisable valency) of central metal ion in terms of electron sharing. According to Sidgwick electron pair present on an atom in a ligand is donated to central metal ion. In this way ligand gets attached to central metal ion and the linkage so formed is called co-ordinate linkage or dative or semi polar bond. This bond is not very different from a covalent bond. The difference only lies in the mode of formation. It is represented as $M \leftarrow L$ i.e. the atom or ion furnishing the electron pair is called donor and the central metal ion is called acceptor.

The primary valencies of Werner were regarded as ionic valencies, this results by transfer of electron from one atom to other.

Hence in Cobalt-ammine Complex ($Co.6NH_3.Cl_3$)
i.e $(Co(NH_3)_6)^{+3}$
Cobaltic ion (Central ion) accepts 12 electrons from Six ammonia molecules (i.e. N-atom has one lone pair in NH_3, which is donated to central ion.)
Structure of $[Co(NH)3]^{+3}$ is Given below:—



Sidgwick Concept of effective atomic Number:→

Sidgwick Suggested that after the ligands have donated a certain number of electrons to the central metal ion through bonding. The total number of electrons on the central atom, including those gained from ligand in the bonding is called effective atomic Number.

i.e: Total number of electron possessed by central metal in the complex including those electron which is gained to the central metal ion from ligand in bonding. In many cases this total number of electrons (i.e E.A.N) surrounding the Co-ordinated metal ion is equal to the atomic number of the next gas.

Effective atomic Number = Atomic Number − Oxidation state + 2 × Co-

Example:— (E.A.N) of Co(III) in $[Co(NH_3)_6]^{3+}$ can be calcul as follows:—

Electrons in Co^0 atom = atomic number of Co = 27 electr

Electrons in Co^{3+} ion = 27 − 3 = : 24 electro

Electrons donated by six NH_3 molecule 6(:NH_3) = 2×6 = 12 electr

E.A.N of Co(III) in $[Co(NH_3)_6]^{3+}$ complex = 24 + 12 = 36

EAN (=36) of Co(III) is evidently equal to the atomic No. of

EAN rule as applied to Carbonyls:→

Metal Carbonyls and its derivatives frequently obey EAN rule By using this rule to metal Carbonyls it is possible to predict whether a given Carbonyl is a monomer.

Examples:→ The Effective Atomic Number of the Central me ion in the compounds i.e. $Ni^0(CO)_4$, $Fe^0(CO)_5$, $Cr^0(CO)_6$, $Fe^{+2}(CO)_4Cl_2$, $Mn^{+1}(CO)_5Br$, $Co^0(NO)(CO)_3$ and $Fe^0(NO)_2(CO)_2$ is 36.

To estimate the E.A.N in these Comp it has been assumed that CO, Cl^- and Br^- contribute two electrons and NO, three electrons to the Central metal i

$(CO)_6$ is the only monomeric Carbonyls which does not obey EAN

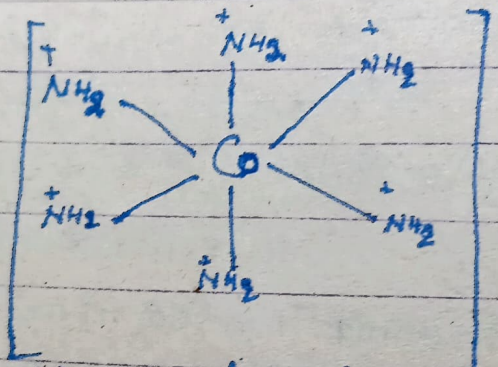
Metal Carbonyls of $M_x(CO)_y$ type also obey this rule, e.g. the E.A.N of Mn in $Mn_2(CO)_{10}$ is 36 as shown belo

This Compound has the formula $(CO)_5Mn-Mn\cdot(CO)_5$ which shows that each Mn atom donates one electron to the formation of Mn-Mn bond, and thus each me atom shares two electrons:—

Objection :→ Sidgwick's electronic interpretation of Co-ordination is not entirely satisfactory.

Following are main objections :—

(i) The donation of electron pair to central ion by ligands will produce an improbable accumulation of negative charge on central ion. In the case of $[Co(NH_3)_6]^{+3}$, the donation of electron pairs by ammonia molecules to Cobaltic ion will result in the accumulation of improbable negative charge on Cobaltic ion. In this way Cobaltic ion will result in Cobalt atom becoming negatively charged with molecules.



(2) Second main objection lies in the fact that electron donated by Neutral molecules (i.e. (NH_3), H_2O) to Central metal ion belonging to $2s^2$ pair, which has no bonding characteristic. To excite them for bonding much more energy is required. The required energy is greater than energy available in bonding

(3) It does not explain the directional Charecteristic of bond.

These are the draw-backs which Promoted Pauling to propose Valence bond Theory. based on Concept of hybridisation.