

SUBJECT - CHEMISTRY
CLASS - BSc(Hons) PART-II
PAPER - III
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TOPIC - Sidgwick rule of effective atomic number in co-ordination complexes.

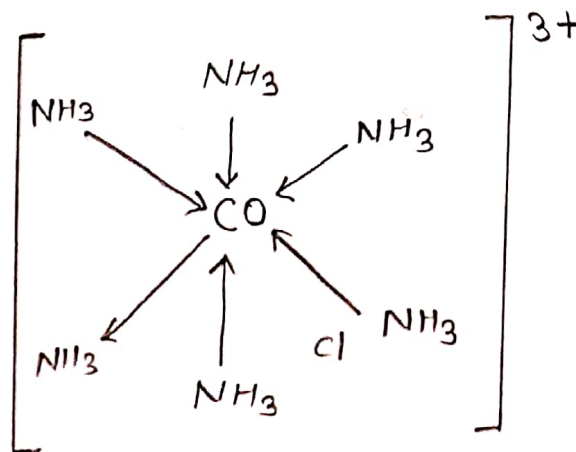
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Sidgwick rule: Sidgwick gave an electronic interpretation of Werner's Theory.

According to Sidgwick Werner's primary valencies were regarded as amounting to electron transfer and his Secondary or nonionic valencies to electron pair sharing.

We know that, all neutral molecules or anions which were capable of being co-ordinated to central metal ion have atoms with at least one unshared lone pair of electrons in their valency shells.

Thus the linkage of these co-ordinating groups to metal ion by Secondary valencies arises due to the donation of the electron pairs to the central metal by these groups. Bonds of this type are termed as co-ordinate bonds. These bonds have been indicated by arrows for example the structure of $[Co(NH_3)_6]^{3+}$ ion may be written as shown below:



Sidwick's Concepts of Effective Atomic Number (EAN Concept or Noble gas Rule): Sidwick 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 ligands in the bonding is called The effective atomic number (EAN) of the central metal ion and in many cases this total number of electrons i.e (EAN) surrounding the Co-ordinated metal ion is equal to the atomic number of the next gas

Example: EAN of Co(III) in $[Co(NH_3)_6]^{3+}$

- Electrons in Co atom = atomic number of Co = 27 electrons
- Electrons in Co^{3+} ion = $27 - 3$ = 24 electrons
- Electrons donated by Six (NH_3) = 2×6 = 12 electrons
- EAN of Co(III) in $[Co(NH_3)_6]^{3+}$ = $24 + 12 = 36$

EAN = 36, of Co(III) is evidently equal to the atomic number of Kr (next gas)

Exceptions to EAN Rule: Though in many cases the EAN is the same as the atomic number of the next gas, yet it is not always so this total number of electron i.e EAN may be a few units more or less than the atomic number of the next inert gas.

Complexes of Ni(II) Co(II) Ag(I) etc which have more than one CO-ordination number depending on the nature of the ligand. generally do not follow the EAN rule. Some metal atoms such as Fe(III) which has its CO-ordination number equal to 4 in $[Fe^{III}Cl_4]^-$ and equal to 6 in $[Fe^{III}(CN)_6]^{3-}$ never follow this rule.

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by Co-ordination	E.A.N	Atomic number of next inert gas
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	$26 - 2 + 12 = 36$	36 Kr.
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	$27 - 3 + 12 = 36$	36 Kr
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	$28 - 0 + 8 = 36$	36 Kr
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	$29 - 1 + 8 = 36$	36 Kr
Cr	24	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	3	12	$24 - 3 + 12 = 33$	36 Kr
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	$78 - 2 + 8 = 84$	84 Rn
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	$46 - 4 + 12 = 54$	54 Xe
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	$46 - 2 + 8 = 52$	54 Xe

From the above it is evident that tendency to attain an inert gas Configuration is a significant factor but not a necessary condition for complex formation. Some complexes of Chromium and platinum are equally stable. Yet the EAN is short of inert gas Configuration for complex formation, it is essential to produce symmetrical structure i.e. tetrahedral, square planar, octahedral, without any consideration of the number of electrons involved.