

II B.Sc
III SEMESTER
INORGANIC CHEMISTRY
UNIT I
CHEMISTRY OF d BLOCK ELEMENTS PART 2

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Magnetic property:

Most of the d block elements shows paramagnetic and ferromagnetic character in its atomic state and also in ionic state. we know that an unpaired electron produces electric field around it due to its spin motion and there exist a magnetic field around the spinning electron. we know that electrons spinning itself and also moves in orbital around the nucleus. Thus the magnetic moment of electron is due to the combination of both spin angular momentum and orbital angular momentum.

Therefore the magnetic moment of an electron is calculated as

$$\mu = (4S(S+1))^{\frac{1}{2}} + (L(L+1))^{\frac{1}{2}}.$$

we know that a metal ion is surrounded by ligands and other orbitals due to this it is difficult to observe the orbital angular momentum of an electron in orbital.

Hence the magnetic moment due to orbital motion is neglected.

Therefore the magnetic moment is calculated as

$$\mu = (4S(S+1))^{\frac{1}{2}}$$

If a metal containing n number of electrons then the spin quantum number is $S=n/2$.

Therefore the equation becomes

$$\mu = (4n/2(n/2+1))^{\frac{1}{2}}$$

$$\mu = (n(n+2))^{\frac{1}{2}} \text{ B.M}$$

By using above equation we can calculate magnetic moment of a metal in its free state or ionic state.

As the number of electrons in d orbital increases then the magnetic character of d block elements is also increases. If any element does not containing unpaired electrons it shows diamagnetic character. I.e, Sc^{+3} , Ti^{+4} , V^{+3} , Cu^{+1} , Zn^{+2} etc; are diamagnetic in nature due to absence of unpaired electron. While Ti^{+3} , Fe^{+3} , Cr^{+3} , Cu^{+3} etc, are paramagnetic nature due to presence of unpaired electron.

in metal complexes, the magnetic character is depends on the strength of the ligand also. In presence of strong ligand the magnetic character of a metal complexe is decreases.

Ability to form complexes / complex formation:

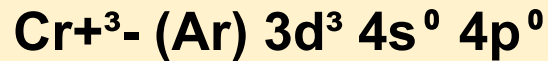
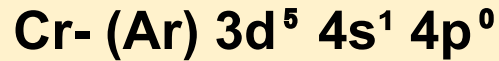
Most of the d block elements forms complex compounds with ligands.

Any atom or group or molecule is able to donate electron pair to the empty orbital of a metal atom is called as ligand.

the tendency of formation of complex of a metal is due to the following two factors.

- A transition metal cations are relatively very small in size and have positive charge density which facilitates the acceptance of lone pair of electrons donated by ligands.
- The transition metal cations have vacant d orbitals and have appropriate energy to accept lone pair of electrons donated by ligands.

In $(\text{Cr}(\text{NH}_3)_6)\text{Cl}_3$ complex Cr is in the + 3 oxidation State.



here Cr^{+3} have 6 vacant orbitals so that 6 NH_3 molecules donates 6 lone pairs to these vacant orbitals. the bonds involved in the formation of complexes are co-ordinate covalent bonds. Hence the compounds formed are also known as coordination compounds. The stability of a complex at a given temperature is increases with the atomic number of metal. if a metal have different oxidation State then in a higher oxidation state it forms more stable compounds. depending upon this the transition metals are classified into two types:

Class A and class B acceptors:

some of the metal ions forms more stable complexes with ligands like ammonia, H₂O, Py etc, these elements are called as class A acceptors.

Generally the first half of transition series are belong to this category.

The other transition elements forms less stable complexes with ligands like F, Cl etc, these are called as class B accepted.

some of the metals having completely filled d orbitals hence sometimes the electrons present in these orbitals are donated to the ligands having vacant orbitals and forms a $d\pi-p\pi$ back bonding.

Catalytic property:

A number of transition metals and their compounds are known to be catalyse various reactions of industrial importance.

Generally, the catalysis is based on principle of adsorption. since most of the transition elements have number of incompletely filled d orbital and provides larger surface area for the process of adsorption of reactants on the surface(catalyst). so the concentration of reactants on the catalyst surface increases and the bonds on the reactants are weaker then the reaction takes place at lower energy. thus we can say that transition metal catalyst forms unstable intermediate state with the reactant and they can provide suitable reaction surface.

Examples:

- TiCl_4 is used as zeigler-knatta catalyst in polymerization process of polyethylene
- Nickel is used as a good catalyst in hydrogenation of oils into fat.
- Iron is used as catalyst in the manufacture of ammonia by haber's process.
- Pt, Pd are used as catalyst in the reduction of so many organic compounds.
- Cr, Mn and V compounds are used as a good oxidizing agents.

Stability of various oxidation States:

In the block elements the oxidation state for heavier elements is more stable as the core of these elements is unstable and hence can lose one or more electrons from the unstable core giving higher oxidation States.

Higher oxidation states are shown by chromium, manganese and Cobalt.

In case of halides, manganese does not exhibit +7 oxidation State, however MnO_3F is known. $\text{Cu}^{+2}(\text{aq})$ is known to be more stable than $\text{Cu}^{+}(\text{aq})$ as the ΔH of Cu^{+2} is more than Cu^{+} , which compensates for the second enthalpy of Cu. Mn exhibits high oxidation states in the oxides.

For example: In Mn_2O_7 the oxidation state Mn is +7. As oxygen is able to form multiple bonds with metals. Hence Mn_2O_7 show higher oxidation State than MnF_4 . In Mn_2O_7 , Mn is tetrahedrally surrounded by oxygens including a Mn-O-Mn bridge.

However other elements of the group exhibit +3 oxidation State such as Fe_2O_3 and +4 oxidation state such as V_2O_4 .

In p block elements we have seen lower oxidation states as favoured by the heavier members where as we acknowledge an opposite trend in d block. As in group 6, Mo(VI) is found to have higher stability in comparison to Cr(VI).