

# CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED REVISION NOTES)

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## d – Block Elements

### 1. Atomic Volume and Densities:

- i) The atomic volume of the transition elements is much lower than those of their neighbouring s and p block elements. This is due to the fact that in d- block elements, the inner orbitals i. e. (n-1) d- orbitals are filled this leads to more nuclear pull resulting in decrease in volume.
- ii) Due to the decrease in atomic volume, the density of these elements increases. Therefore, the transition elements have quite high density. Following trends are observed among the densities of the transition elements.
  - a) In a given transition series, the density increases across the series and reaches a maximum value at the middle of the series.
  - b) The density increases down the group because the atomic size of the elements of second and third transition series is nearly the same , their atomic masses increases nearly two fold and the densities of the elements of the third series are generally twice those of the corresponding elements of the second transition series

### 2. Ionisational potential:

- i) Since atoms of transition elements are small in size, their ionisation energies are fairly high
- ii) The ionization potentials of the most of the d-block elements lie in between those of s and p –block elements. These are higher than those of s- block elements and are lower than those of p- block elements. This indicates that the d- block elements are less electropositive than the s- block elements.( alkali and alkaline earth metals).
- iii) The ionisation potential of d- block elements increases as we move across the series from left to right. However, the increase in the value is not as pronounced as in case of s and p – block elements of the same period. This is because in the transition elements, the effect of increasing nuclear charge is almost compensated by the extra screening effect provided by the increasing number of

(n-1)d electrons

### 3. Variable oxidation state:

All transition elements, except the first and the last members of each series exhibit variable oxidation state. The cause of showing different oxidation states is due to the fact that there is only a small difference between the energies of the electrons in the ns orbitals and (n-1)d –orbitals with the result that both ns as well as (n-1)d –electron may be used for compound formation. Therefore, the variable oxidation states of transition elements are related to their electronic configuration. This is clear from the following table of oxidation state of elements of first transition series.

Elements	Outer electronic Configuration	Oxidat ion
Sc	$3d^1 4s^2$	+2 ,+3
Ti	$3d^2 4s^2$	+2,+3,+4
V	$3d^3 4s^2$	+2,+3,+4,+5
Cr	$3d^4 4s^2$	+2,+3,+4,+5,+6,
Mn	$3d^5 4s^2$	+2,+3,+4,+5,+6,+7
Fe	$3d^6 4s^2$	+2,+3,+4,+5,+6
Co	$3d^7 4s^2$	+2,+3,+4
Ni	$3d^8 4s^2$	+2,+3,+4
Cu	$3d^{10} 4s^1$	+1,+2
Zn	$3d^{10} 4s^2$	+2

It must be noted that in some transition elements all of the (n-1)d –electrons are not involved during bond formation, e.g. iron ( $3d^6 4s^2$ ) should have +8 as its highest oxidation state, but actually it is only +6 which is also very rare( +2 and +3 are the common oxidation state of iron). The +6 (and not +8) as the highest oxidation state is explained on the basis that during bond formation only the unpaired electrons of the 3d- sub shell take part in bond formation. In iron there are 4 unpaired and 2 paired 3d- electron and hence the effective electrons for bond formation in 3d-orbitals are only four which may give +6 as the highest oxidation state.

**4. Complex Formation:** The cations of transition metals have a great tendency to

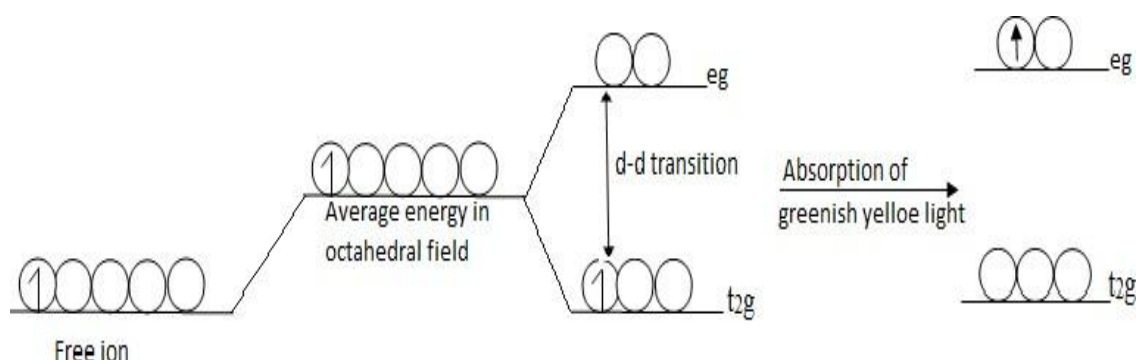
form complexes with several molecules or ions called ligands. The tendency of formation of complexes is due to the following two factors.

- i) The cations of these metals are very small in size and have a high effective nuclear charge. Thus they have a very high positive charge density which facilitates the acceptance of lone pairs of electrons from other molecules or ions.
- ii) The transition metal cations have vacant inner d-orbitals which are of appropriate energy to accept lone pair of electrons from the ligands. The bonds involved in the formation of complexes are coordinate hence the complexes are termed as coordinate complexes.

**5. Formation of Coloured Compound:** the transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one d-orbital to another i.e., intra d-d transition takes place. Thus, when light falls certain visible wavelength are absorbed. The transmitted (unabsorbed) or reflected light (or colour) appears coloured and gives the colour of compounds. The ions having no d-d transition are colourless.

To understand the cause of colour in transition metal complexes, consider complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , In this case, titanium is in +3 oxidation state.

The electronic configuration of  $\text{Ti}^{+3}$  :  $[\text{Ar}]3d^1$



During the formation of complex, as the six water molecules approach  $\text{Ti}^{+3}$  ion from different side these develop a negative field around it, as they donate lone pair present on oxygen to metal ion. There occurs repulsion between electrons of metal ion and ligand and energy of degenerate orbitals of metal ions increase and ultimately they split into two set of orbitals. The electron present in  $\text{Ti}^{+3}$ , prefers lower set of d-orbitals.

The energy gap between two set of d- orbitals is very less and the energy available in the visible light is sufficient to cause excitation of electron from lower set of d- orbitals to higher set of d –orbitals, called a d-d transitions.  $Ti^{+3}$  absorbs greenish yellow component of white light during excitation of electrons, hence its aqueous solution appears as purple. This is because purple is the complimentary colour of greenish yellow in white light.

- 6. Magnetic Properties:** Most of the transition elements show paramagnetism. Paramagnetism arises from the presence of unpaired electrons in atoms, ions or molecules. The magnetic character is comparable in terms of magnetic moment given by the expression  $\mu = \sqrt{n(n + 2)}$  Bohr Magneton, where  $n =$  the number of unpaired electrons. In general, greater the number of unpaired electrons, greater is the magnetic character. The maximum paramagnetism is noticed in  $d^5$  case which has maximum number of unpaired electrons.
- 7. Formation of alloys:** due to their almost equal atomic sizes, they can mutually substitute one another in the crystal lattice to form alloys.
- 8. Formation of non-stoichiometric compounds and interstitial compounds.** : transition metal can trap some of the small size atoms like hydrogen, boron, carbon, nitrogen etc., in the vacant spaces between the crystal lattice forming inter-orbital compounds. For example,  $FeC$  ,  $Fe_8N$ ,  $TiH_2$ . This property differentiates these metals from non-transition elements. The products obtained are hard and rigid. Non – stoichiometric compounds like i.e.  $Fe_{0.98}O$  ,  $Fe_{0.86}S$ ,  $VH_{0.56}$  ,  $TiH_{1.7}$  are often classified as interstitial compounds.
- 9. Catalytic properties:** Many transition metals and their compounds show catalytic properties, the most common being  $Fe$  ,  $Pt$  ,  $Ni$ ,  $V_2O_5$  etc. This property may be either due to their variable valency (incomplete  $d$ - orbitals) which enables them to form unstable intermediate compounds or due to the fact that they can provide a suitable reaction surface.

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