

# CHEMISTRY STUDY MATERIALS FOR CLASS 12

## ( NCERT BASED NOTES OF CHAPTER -8 )

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### The d & f - Block Elements

#### **Introduction:**

Periodic table is the systematic arrangement of elements in the order of increasing atomic numbers of the elements. On the basis of electronic

#### **d – Block Elements**

configuration the periodic table has been divided into four blocks known as s , p, d and f block

**Defination:** The elements in which last electrons enters the ‘ d ’ orbital of the penultimate shell i.e. (n-1) d orbital are called as d-block elements.

The d –block elements are called transition elements and consist of elements lying between s and p –blocks starting from fourth period onwards. These elements have properties which are transitional between those of s and p block elements. All these elements are metal.

The transition elements may be defined as elements whose atoms or simple ions in their common oxidation state contain partially filled d- subshell. The general electronic configuration of these metals is  $(n-1)d^{1-10}ns^{1-2}$

**Classification of d –block elements :** These are divided into three transition series.

- (i) The first transition series. (3d-series) involves the filling of 3d- orbitals and has 10 elements from scandium ( Z = 21 ) to zinc ( Z = 30 ) in the fourth period.
- (ii) The second transition series ( 4d-series) involves the filling of 4d orbitals and has 10 elements from yttrium ( Z= 39) to cadmium ( Z= 48 ) in the fifth period.
- (iii) The third transition series ( 5d-series) involves the filling of 5d-orbitals and has 10 elements. The first element of this series is lanthanum ( Z= 57 ) . it is followed by 14 elements ( lanthanides or lanthanons involving filling of 4f- orbitals). The next nine elements are from hafnium ( Z =72)to mercury ( Z = 80).

- (iv) The fourth transition series ( 6d-series) involves the filling of 6d- orbitals and is incomplete starting from Actinium ( Z= 89 ) and extended upto element with atomic number 104

### **General Characteristics of Transition Elements:**

The members of given transition series do not differ so much from one another as those of non-transition elements (representative elements) of the same period. The reason is that the electronic configuration of transition elements differ only in the number of electrons in ( n-1) d- sub shell i.e., the number of electrons in the outermost shell ( n) remains the same. The outermost configuration is  $ns^2$  where n is the number of the period to which the given transition elements belong some important properties of transition elements are as follows.

**1. Metallic Character.** : d- Block elements have low ionisation energy and hence easily lose electrons to form cations. Furthermore these elements have only one or two electrons in their outermost energy shell i.e., they have a large number of vacant orbitals in the outermost shell which make them form metallic bond. Because of this all the transition elements are metal.

They are generally (i) malleable and ductile (ii) forms alloys with several other metals. ( iii) they are good conductors of heat and electricity. However, they differ from non-transition metals in being hard and brittle in certain cases. (Mercury has an exceptional behaviour. It is a liquid at room temperature). It is due to the presence of unpaired electrons in d-orbitals of their atoms which has a tendency for covalent bonding involving d-d overlapping. In a particular series the hardness increases upto the middle with increasing number of unpaired d- electrons. Thus, Cr, Mn and W having maximum number of unpaired d- electrons are very hard metals, while Zn , Cd and Hg are not hard metals due to the absence of unpaired electrons.

**2. Melting and Boiling Points:** The melting and boiling points of the transition elements are generally very high. This is due to the presence of covalent bonding by the unpaired d- orbital electrons.

**3. Atomic Radii:** The Variation in atomic radii across each transition series is not as simple as that observed in s and p- block elements. However, following overall trends in the variation of atomic radii across the period are observed.

i) The atomic radii of the d-block elements of a given series generally decrease with increases in the atomic number. This is due to the fact that with an increase in atomic number the nuclear charge increases which in turn increasingly tend to attract the electron cloud inward resulting in decrease in size. However, the decrease in the radii across a period is not uniform. The decrease in radii of transition metals is small as compared to the decrease in the radii of s and p block elements for the same periods. For ex. The radii of the elements from Cr. To Cu are very close to one another. This may be explained on the basis of screening effect In d- block elements electrons are added to an (n-1) d- sub shell which adds to the primary screening effect. The additional electrons effectively screen the outer ns- electrons from the inward pull of the nucleus. As a result, the size of the atom does not change much from Cr to Cu.

ii) In a given series the atomic radius decreases from group 3 elements upto the group 10 elements and then increases again towards the end of the series. This anomalous increase in atomic radius towards the end of the series is because of the increased force of repulsion among the added electrons .also the d- orbitals get completely filled in group 11 and 12 elements which also causes a decrease in force of attraction.

iii) Atomic radius increases on descending down the groups although the increase is not as significant as in case of s and p block elements. The very close similarity between the radii of the elements of second and third transition series, ( Ex. Zr and Hf , Nb and Ta , Mo and W , Tc and Re etc.) is the consequence of the filling of 4f sub shell.

#### **4. Atomic Volume and Densities:**

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.

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 increase 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

### **5. Ionisational potential:**

Since atoms of transition elements are small in size, their ionisation energies are fairly high

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).

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

### **6. 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	Oxidation
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- subshell take part in bond formation. In iron there are 4 unpaired and 2 paired 3d- electrons and hence the effective electrons for bond formation in 3d- orbitals are only four which may give +6 as the highest oxidation state.

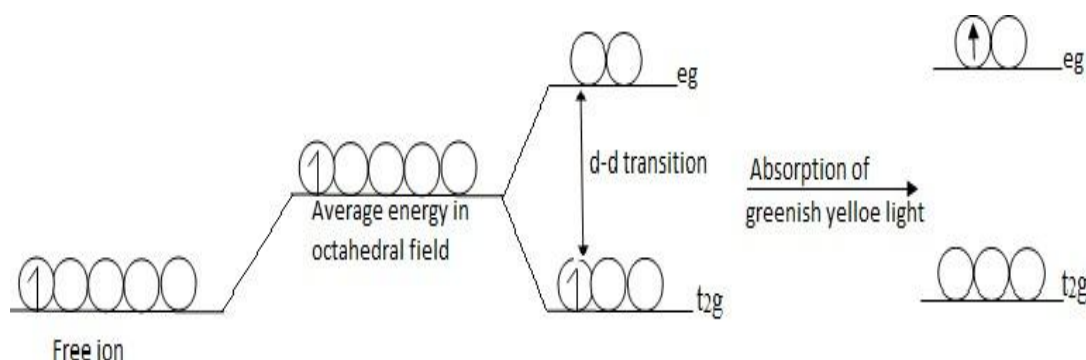
**7. Complex Formation :** The cations of transition metals have a great tendency to form complexes with several molecules or ions called ligands. The tendency of formation of complexes is due to the following two factors.

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.

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.

**8. 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.  $\text{Ti}^{+3}$  absorbs greenish yellow component of white light during excitation of electrons, hence it's aqueous solution appears as purple. This is because purple is the complimentary colour of greenish yellow in white light.

**9. 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.

**10. Formation of alloys :** due to their almost equal atomic sizes, they can mutually substitute one another in the crystal lattice to form alloys.

**11. 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 interstitial compounds. For example, FeC , Fe<sub>8</sub>N, TiH<sub>2</sub>. This property differentiates these metals from non-transition elements. The products obtained are hard and rigid. Non – stoichiometric compounds like i.e. Fe<sub>0.98</sub>O ,Fe<sub>0.86</sub>S. VH<sub>0.56</sub> , TiH<sub>1.7</sub> are often classified as interstitial compounds.

**12. Catalytic properties:** Many transition metals and their compounds show catalytic properties, the most common being Fe , Pt ,Ni, V<sub>2</sub>O<sub>5</sub> 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.

**13. Reactivity :** The  $d$ - block elements are unreactive due to the following factors:

**High ionisation energies :** on account of small size of their atoms, ionisation energies of  $d$ - block elements are fairly high

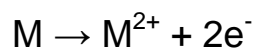
**High heats of sublimation:** Due to presence of covalent bonding, these have high heats of sublimation.

The tendency to remain unreactive is more pronounced in platinum and gold in the third transition series.

**14. Standard Electrode Potential:** The standard reduction potential of all the transition elements (except Cu and Hg in 3d-series etc.) is lower ( negative ) than that of hydrogen(taken as Zero ) . Thus all the transition elements, with negative reduction potential, liberate hydrogen from dilute acids

However, some metals evolve hydrogen very slowly because they are protected from the attack of acids by the formation of an impervious layer of an inert oxide. For example, chromium is so unreactive that it can be used as protective non-oxidising metals.

**15. Reducing Properties:** Transition metals with sufficiently negative standard reduction potential should be good reducing agents i.e, they should be oxidised easily to their ions.



However they are not good reducing agents as compared to elements of Group 1 , 2 and 13 . This is because the transition metals have less tendency to form ions due to their low reactivity.

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