

## The d and f-Block Elements Top 15 Concepts

1. **d -Block elements:** The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as d – block elements. Their general electronic configuration is  $(n - 1)d_{1-10} ns_{1-2}$  where  $(n - 1)$  stands for penultimate (last but one) shell.

2. **Transition element:** A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states.

3. **Zinc, cadmium, mercury** are not regarded as transition metals due to completely filled *d* – orbital.

4. **f-Block elements:** The elements constituting the *f* -block are those in which the 4 *f* and 5 *f* orbitals are progressively filled in the latter two long periods.

5. **Lanthanoids:** The 14 elements immediately following lanthanum, i.e., Cerium (58) to Lutetium (71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties. Therefore, it is studied along with lanthanoids.

6. **Actinoids:** The 14 elements immediately following actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They belong to second inner transition series. Actinium (89) has similar properties. Therefore, it is studied along with actinoids.

7. **Four transition series:**

a. 3d – transition series. The transition elements with atomic number 21(Sc) to 30(Zn) and having incomplete 3d orbitals is called the first transition series.

b. 4d – transition series. It consists of elements with atomic number 39(Y) to 48 (Cd) and having incomplete 4d orbitals. It is called second transition series.

c. 5d – transition series. It consists of elements with atomic number 57(La), 72(Hf) to 80(Hg) having incomplete 5d orbitals. It is called third transition series.

d. 6d – transition series. It consists of elements with atomic number 89(Ac), 104(Rf) to 112(Uub) having incomplete 6d orbitals. It is called fourth transition series.

8. **General Characteristics of transition elements:**

a. **Metallic character:** All transition elements are metallic in nature, i.e. they have strong metallic bonds. This is because of presence of unpaired electrons. This gives rise to properties like high density, high enthalpies of atomization, and high melting and boiling points.

b. **Atomic radii:** The atomic radii decrease from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding effect increases and electron electron repulsions repulsion increases.

c. **Lanthanoid Contraction:** The steady decrease in the atomic and ionic radii of the transition metals as the atomic number increases. This is because of filling of

4f orbitals before the 5d orbitals. This contraction in size is quite regular. This is called lanthanoid contraction. It is because of lanthanoid contraction that the atomic radii of the second row of transition elements are almost similar to those of the third row of transition elements.

d. **Ionisation enthalpy:** There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 3d and 4d transition series because of Lanthanoid Contraction.

e. **Oxidation state:** Transition metals show variable oxidation states due to tendency of (n-1)d as well as ns electrons to take part in bond formation.

f. **Magnetic properties:** Most of transition metals are paramagnetic in nature due to presence of unpaired electrons. It increases from Sc to Cr and then decreases because number of unpaired electrons increases from Sc to Cr and then decreases.

g. **Catalytic properties:** Most of transition metals are used as catalyst because of (i) presence of incomplete or empty d – orbitals, (ii) large surface area, (iii) variable oxidation state, (iv) ability to form complexes, e.g., Fe, Ni, V<sub>2</sub>O<sub>3</sub>, Pt, Mo, Co and used as catalyst.

h. **Formation of coloured compounds:** They form coloured ions due to presence of incompletely filled d – orbitals and unpaired electrons, they can undergo d – d transition by absorbing colour from visible region and radiating complementary colour.

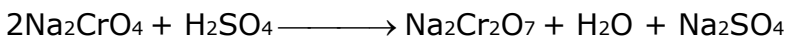
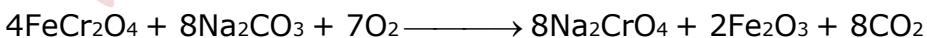
i. **Formation of complexes:** Transition metals form complexes due to (i) presence of vacant d – orbitals of suitable energy (ii) smaller size (iii) higher charge on cations.

j. **Interstitial compounds:** Transition metals have voids or interstitials in which C, H, N, B etc. can fit into resulting in formation of interstitial compounds. They are non – stoichiometric, i.e., their composition is not fixed, e.g., steel. They are harder and less malleable and ductile.

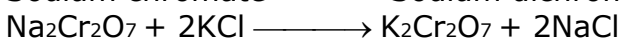
k. **Alloys formation:** They form alloys due to similar ionic size. Metals can replace each other in crystal lattice, e.g., brass, bronze, steel etc.

### 9. Preparation of Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>):

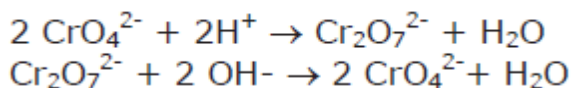
It is prepared by fusion of chromate ore (FeCr<sub>2</sub>O<sub>4</sub>) with sodium carbonate in excess of air.



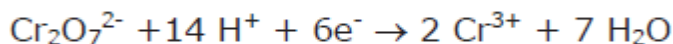
Sodium chromate                      Sodium dichromate



10. **Effect of pH on chromate and dichromate ions:** The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

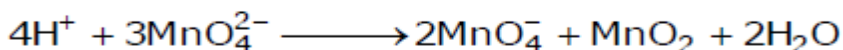
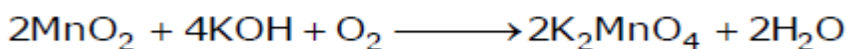


11. Potassium dichromate acts as a strong oxidizing agent in acidic medium.



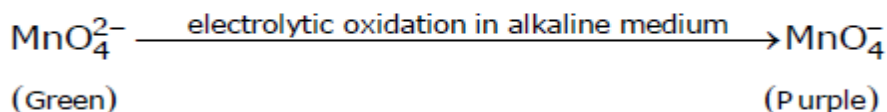
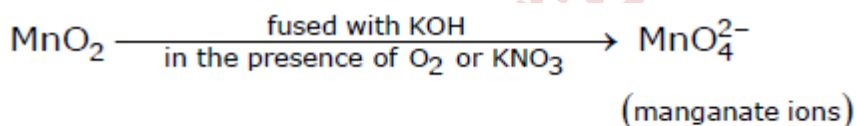
12. Preparation of **Potassium permanganate** ( $\text{KMnO}_4$ ):

- a. Potassium permanganate is prepared by fusion of  $\text{MnO}_2$  with alkali metal hydroxide ( $\text{KOH}$ ) in presence of  $\text{O}_2$  or oxidising agent like  $\text{KNO}_3$ . It produces dark green  $\text{K}_2\text{MnO}_4$  which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

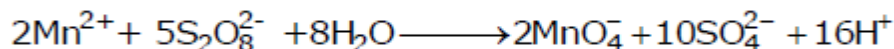


Or

- b. Commercially it is prepared by the alkaline oxidative fusion of  $\text{MnO}_2$  followed by the electrolytic oxidation of manganate (VI).

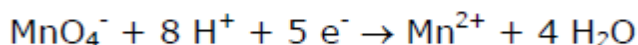


- c. In laboratory,  $\text{Mn}^{2+}$  salt can be oxidized by peroxodisulphate ion to permanganate ion.

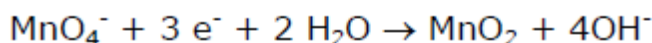


13. Potassium permanganate acts as a strong oxidizing agent in acidic, neutral or faintly basic medium.

In acidic medium.



In neutral or faintly basic medium,



14. Properties of Lanthanoids and Actinoids.

Lanthanoids	Actinoids
+3 oxidation state is most common along with +2 and +4	Actinoids also show higher oxidation states such as +4, +5, +6 and +7.  They are more reactive
Except Promethium, they are non - radioactive.	They are radioactive
The magnetic properties of lanthanoids are less complex than actinoids.	The magnetic properties of the actinoids are more complex than those of the lanthanoids

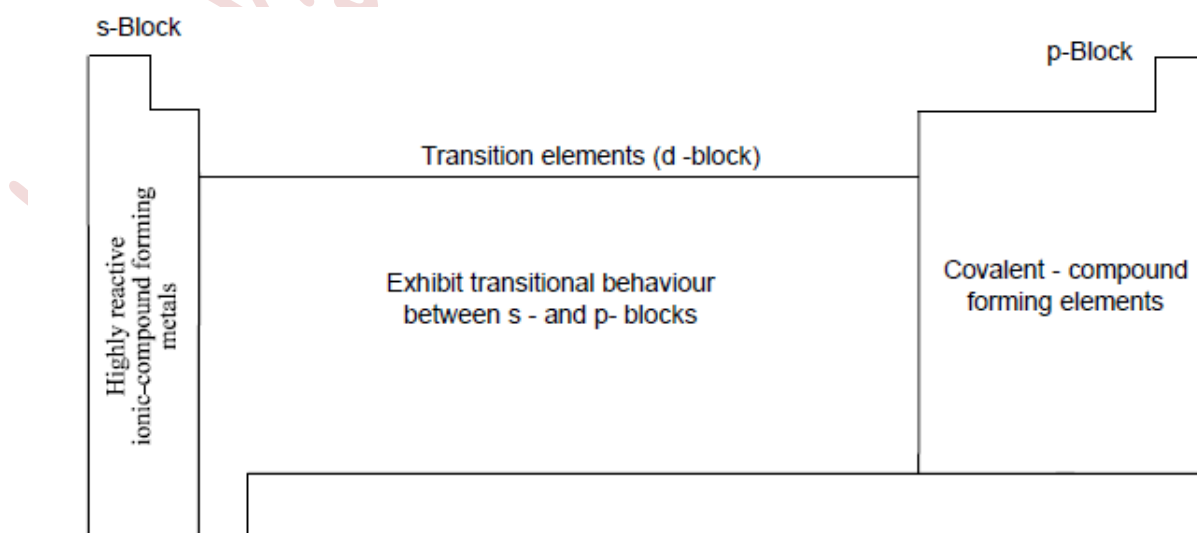
15. Mischmetall - It is a well known alloy which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

## NOTES

### Transition Elements

The elements lying in the middle of the periodic table between group-2 and group-13 are known as **d-block elements**. These d-block elements are called **transition elements** because they exhibit transitional behaviour between s-block and p-block elements

Transition elements may be defined as the elements whose atoms or simple ions have partially filled d-orbitals. Zinc, Cadmium and mercury are not considered as transition elements because their atom as well as ion does not have partially filled orbitals



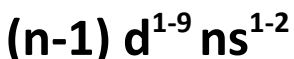
## Electronic Configuration

Depending upon the subshell ( 3d, 4d, 5d) involved, transition elements are mainly classified into three series:

- 1. First transition series or 3d series :** Elements of this series involves the filling of 3d orbitals.
- 2. Second transition series or 4d series :** Elements of this series involves the filling of the 4d orbitals
- 3. Third transition series or 5d series :** It consists of elements which involve the filling of 5d orbitals

There is also an incomplete fourth series starting with actinium.

### General Electronic Configuration :



(n-1) stands for the penultimate shell and the d-orbital may have *one to nine* electrons and the s-orbital of the ultimate shell (n) may *two* (or in some cases one) electrons.

## Physicochemical Properties

### 1. Metallic Character :

All the transition elements are metallic in nature and nearly all of them have simple hcp, ccp or bcc lattices. Due to their greater effective nuclear charge and the large no. of valence electrons, the metallic bond is quite strong and hence they are hard, possess *high densities* and *high enthalpies of atomisation*.

### 2. Oxidation States :

Transition elements exhibit variable oxidation state *due to the participation of ns as well as (n-1)d electrons*.

i) Except scandium, the most common oxidation state of the first row transition elements is +2 which arises from the loss of two 4s electrons, which means that after scandium, d-orbital become more stable than the s-orbital.

- ii) In the +2 and +3 oxidation states, bonds formed are generally ionic while in higher oxidation states, the bond formed are essentially covalent. For example in  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$  etc. the bonds formed between metal and oxygen are covalent.
- iii) The highest oxidation state shown by transition elements is +8.

## 2. Ionization Energy :

The ionization energies of transition elements are higher than those of s - block elements but lower than p - block elements. In a particular transition series, ionization energy increases gradually as we move from left to right, and it is due to the increase in nuclear charge.

It may be noted that *the first ionization energies of 5d elements lie higher than those of 3d and 4d elements* because of the weak shielding of the nucleus by 4f electrons.

Further the magnitudes of ionization energies provide an indication of the energy needed to raise the metal to a particular oxidation state in a compound. From the knowledge of values of ionization energies of the metal it is possible to rationalize the relative stabilities of various oxidation state.

*Ni(II) Compounds are thermodynamically more stable than Pt(II) compounds, on the other hand Pt (IV) compounds are more stable than Ni (IV) compounds.* It is due to that sum of first four ionization energies is less for platinum whereas sum of the first two ionization energies is less for nickel. Hence  $\text{K}_2\text{PtCl}_6$  is a well known compound.

## 3. Complex formation (Complexation) :

Transition metal ions form variety of complexes due to the following reasons:

- i) *Small size and high nuclear charge.*
- ii) *Availability of vacant d-orbitals of suitable energy, which can accept lone pair of electrons donated by the molecule or ion (ligand).*

## 4. Coloured Complexes :

Compounds of transition elements are usually coloured due to the promotion of an electron from one d-orbital to another by the absorption of visible light. It can be clearly explained as follows:

The d-orbital in the transition elements do not have same energy in their complexes. Under the influence of the ligand attached, the d-orbital split into two sets of orbital of slightly different energies. In the transition elements which have partly filled d-orbitals, the transition of electron can take place from one of the lower d-orbitals to some higher d-orbital within the same subshell. The energy required for this transition falls in the visible region. So when white light falls on these complexes they absorb a particular colour from the radiation for the promotion of electron and the remaining colours are emitted. The colour of the complex is due to this emitted radiation.

A few of the transition metal ions such as  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Sc}^{3+}$  are colourless. In these ions, the d-orbital are either completely filled or empty. Other transition metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  are coloured, the d-orbitals in these ions contain unpaired electron.

#### 5. Catalytic properties :

Transition metals and their compounds are known to act as good catalyst due to the following reasons:

- i) Due to their variable oxidation state, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (*Intermediate compound formation theory*)
- ii) In some cases the finely divided metals or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact (*Adsorption theory*)

#### 6. Magnetic properties :

Two types of magnetic behaviour are found in substances *diamagnetism* and *paramagnetism*. Paramagnetic substances are attracted by the magnetic field and weigh more while the diamagnetic substances are slightly repelled by the magnetic field and weigh less.

As the transition metal ions generally contain one or more unpaired electrons in them and hence their complexes are generally paramagnetic. Paramagnetic character increases with increase in no. of unpaired electrons. Further paramagnetism is expressed in terms of magnetic moment, which is related to the no. of unpaired electrons as follows:

$$m = \sqrt{n(n+2)} \text{ B.M.}$$

n - no. of unpaired electrons

B.M. - Bohr magneton, a unit of magnetic moment

*More the magnetic moment, more will be the paramagnetic character.*

### 8. Formation of Alloys:

As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and have often high melting point.

### 9. Interstitial Compound:

Transition metals form no. of interstitial compounds, in which they take up atoms of small size e.g. H, C and N in the vacant spaces in their lattices. The presence of these atoms results in decrease in malleability and ductility of the metals but increases their tensile strength.

### INNER TRANSITION ELEMENTS :

The f- block elements are known as *inner transition elements* because they involve the filling of inner sub-shells (4f or 5f).

1. **Lanthanides:** It consists of elements that follow *lanthanum* and involve the filling of 4f subshell.
2. **Actinides:** It consists of elements that follow *Actinium* and involve the filling of 5f subshell.

### Some Important Properties Of Lanthanides

#### 1. Electronic Configuration :



Where x = 1 to 13

#### 2. Oxidation State :

Lanthanides exhibit the oxidation state of +3. Some of them also exhibit the oxidation state of +2 and +4.



### 3. Colouration :

Many of the lanthanides ions are coloured in solid state as well as in solutions. The colour is due to the *f - f transition* since they have partly filled f - orbitals.

### 4. Lanthanide Contraction :

The steady decrease in the size of lanthanide ions ( $M^{3+}$ ) with the increase in atomic no. is called lanthanide contraction.

**Causes:** As we move down the group from left to right in a lanthanide series, the atomic no. increases and for every proton in the nucleus the extra electron goes to 4f orbital. The 4f orbital is too diffuse to shield the nucleus effectively, thus there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently, the attraction of the nucleus for the electrons in the outermost shell increases with the increase of atomic no., thus size decreases.

## Consequences of Lanthanide Contraction

### 1. Separation of Lanthanides :

Due to the similar sizes of the lanthanides, it is difficult to separate them but due to lanthanide contraction their properties slightly vary (such as ability to form complexes). The variation in the properties is utilized to separate them.

### 2. Basic Strength of Hydroxide :

Due to the lanthanide contraction, size of  $M^{3+}$  ions decreases and there is increase in covalent character in M-OH and hence basic character decreases.

### 3. Similarity of second and third transition series:

The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to the lanthanide contraction.

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