8. The d and f Block Elements

Elements from 3rd group to 12th group in the Modern Periodic table are called d-block elements. In these elements their last electron enters in the penultimate d- sub shell. They are placed in between s-block and p-block elements. They show a regular transition from the highly electropositive metals of s-block elements to the less electropositive p-block elements. So they are called transition elements.

Transition elements can be defined as elements which contain partially filled d orbitals in their atomic state or in any of their oxidation state. This definition does not include Zn, Cd and Hg. So they are not regarded as transition elements. Or, they are called pseudo transition elements.

There are four series of transition elements.

1) 3d series [from Sc (z = 21) to Zn (z = 30)]
2) 4d series [from Y (z = 39) to Cd (z = 48)]
3) 5d series [from La (z =57), Hf (z = 72) to Hg (z=80)]
4) 6d series [from Ac (z=89), Rf (z=104) to Cp (z=112)]

Electronic Configuration

General outer electronic configuration of d-block elements is $(n-1) d^{1-10} ns^{1-2}$. There is only a small difference in energy between $(n-1)d$ orbital and ns orbital. So in some cases ns electrons are also transferred to $(n-1)d$ level.

The electronic configurations of Cr and Cu in the 3d series show some exceptions.

$_{24}Cr – [Ar] 3d^5 4s^1$

$29Cu – [Ar] 3d^{10} 4s^1$
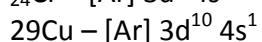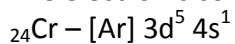
This is due to the extra stability of half-filled and completely-filled electronic configurations. (d^5 or d^{10})

The electronic configurations of Zn, Cd and Hg are represented by the general formula $(n-1)d^{10} ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. So they are not regarded as transition elements.

General characteristics of transition elements

1. Atomic and ionic radii

In a given transition series, the atomic and ionic radii first decreases, then become constant and increases towards the end of the series. This is because in transition elements the new electron enters in a d orbital. Initially since there is a few numbers of d electrons, the shielding effect is very poor. As the atomic number increases, the nuclear charge also increases, so the atomic radius decreases. Towards the middle of the series, the increase in nuclear charge is balanced by the shielding effect and so the atomic radius becomes constant. Towards the end of the series, as the e^- - e^- repulsion increases the atomic radius also increases

The atomic and ionic radii of 2nd and 3rd row transition metals are quite similar. This is due to the Lanthanide contraction. In between the 2nd and 3rd row transition elements, 4f electrons are present. The 4f electrons have very poor shielding effect and as a result the atomic and ionic radii of Lanthanides decrease from left to right (Lanthanide contraction).

2. Melting and boiling points

In a given transition series the melting and boiling points 1st increases up to the middle and then decreases. This can be explained in terms of metallic bond strength which depends on the number of unpaired electrons. As the number of unpaired electron increases, the metallic bond strength increases. Hence the melting point also increases.

In a given transition series, the number of unpaired electrons increases up to the middle and then decreases.

Another factor which affects the m.p is heat of atomization. Mn and Tc have low melting point even though they have d^5 configuration. This is because of their low heat of atomization.

The m.ps of second and third row transition series is higher than that of the first row due to their higher enthalpies of atomization.

3. Ionisation enthalpy

The ionisation enthalpy of transition elements generally increases from left to right. This is due to increase in nuclear charge. But the increase is not regular. This can be explained as follows.

After the removal of one electron, the relative energies of 4s and 3d orbitals get changed. Hence the remaining electron in the 4S level is transferred to 3d level. So the unipositive ions have d^n configuration with no 4s electrons. During this re-organisation of electrons, some energy is released and it is known as exchange energy. So the net energy required to remove the 1st electrons is equal to the sum of ionisation enthalpy and exchange energy.

The first ionisation enthalpies of Cr and Cu are low. This is because the removal of one electron does not change their d configuration. Similarly first ionisation enthalpy of Zn is high because after the removal of one electron there is no change in the d configuration

$$Zn \rightarrow Zn^+ + e^-$$
$$3d^{10}4s^2 \qquad 3d^{10}4s^1$$
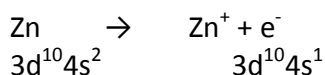
The 2nd I.E of Cr and Cu are very high. This is because the removal of one more e^- from these metals disrupted their stable configuration (d^5 or d^{10})

The 2nd I.Es of Mn and Zn are low, this is because after the removal of one more electron, they attain the stable half filled or completely filled electronic configuration.

4. Oxidation State

Transition metals show variable oxidation states. This is because in these elements d and s electrons have comparable energies. So in chemical reaction along with s-electrons, d-electrons also participate. In a given transition series, the maximum oxidation state increases up to the middle and then decreases. This is due to the half-filled or noble gas configuration. The common oxidation state of 1st row transition elements is +2. The maximum oxidation state increases from top to bottom in a group. In lower oxidation state, the transition element mainly forms ionic compounds.

Sc generally shows +3 oxidation state because after the removal of 3 electrons, it gets a stable noble gas configuration. The oxidation state of Zn is +2 because of the completely filled configuration of Zn^{2+}.

5. Electrode Potential

The electrode potential values of first row transition series generally increases from left to right with some exceptions. The $E^0(Cu^{2+}/Cu)$ is positive (+0.34V), while the E^0 values of all the other first row transition elements are –ve. This is because the high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy. So Cu does not easily reacts with acid and liberate H_2. Only oxidizing acids [HNO_3 and hot Conc. H_2SO_4] react with Cu and the acid get reduced.

Along the series the E^0 values become less –ve due to the increase in the sum of 1st and 2nd ionisation enthalpies. The E^0 values of Mn^{2+} and Zn^{2+} are more –ve, this is because of the half filled configuration of Mn^{2+} (d^5) and completely filled configuration of Zn^{2+} (d^{10}). $E^0(M^{3+}/M^{2+})$ value of Sc is very low and that for Zn is very high. This is because of their stable electronic configuration.

E^0 (Mn^{3+}/Mn^{2+}) is high because of the stable half filled configuration of Mn^{2+}. Similarly E^0 (Fe^{2+}/Fe^{3+}) is low, this is because after the removal of one electron from Fe^{2+}, it gets a stable electronic configuration.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$3d^6 \qquad 3d^5$$

Q. Explain why Cu^+ is not stable in aqueous solution?

This is due to the much more –ve hydration enthalpy of Cu^{2+} (aq) than Cu^+. In the case of Cu^{2+}, the hydration enthalpy is more compensated by ionisation enthalpy than in Cu^+.

6. Magnetic Properties

Transition metals show mainly two types of magnetic properties- paramagnetism and diamagnetism. Some transition metals also show ferromagnetism which is an extreme case of paramagnetism.

Paramagnetism arises from the presence of unpaired electrons. Each unpaired e- is associated with a spin magnetic moment and an orbital magnetic moment. For the compounds of 1st row transition elements, the contribution of orbital magnetic moment is effectively cancelled and so only spin magnetic moment is considered. It is determined by the no. of unpaired e⁻s and is calculated by the spin only formula:

$\mu_s = \sqrt{n(n+2)}$ where n is the no. of unpaired electrons and μ_s is the spin only magnetic moment in the unit of Bohr Magneton (B.M).

The magnetic moment increases with increase in no. of unpaired e⁻s. Thus the observed magnetic moment gives an idea about the no. of unpaired e⁻s present in the atom or ion.

7. Formation of coloured ions or compounds

Most of the Transition metals ions or compounds are coloured. This is because of the presence of partially filled d orbitals. When an electron from a lower energy d orbital is exited to higher d level, it absorbs energy and this is equal to the energy of certain colours in visible region. So the colour observed is the complementary colour of the light absorbed.

In aqueous solution most of the Transition metal ions are coloured since water molecules act as the ligands.

Among Ti^{2+} and Ti^{4+}, Ti^{2+} is coloured while Ti^{4+} is colourless. This is because Ti^{4+} has no partially filled d orbitals.

Ti^{2+} - [Ar] $3d^2$ $\qquad\qquad$ Ti^{4+} - [Ar] $3d^0$

Similarly among Cu^+ and Cu^{2+}, Cu^{2+} is coloured while Cu^+ is colourless. This is due to the lack (absence) of partially filled d orbitals in Cu^+.

8. Formation of Complexes

Transition metals form a large no. of complexes. This is due to:
1. Comparatively smaller size
2. High ionic charge
3. Presence of partially filled d orbitals
4. Ability to show variable oxidation state

Eg: $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Ni(CO)_4]$ etc.

9. Catalytic Property

Transition metals act as catalysts in a large no. of chemical reactions. This is due to their large surface area and their ability to show variable oxidation state.

10. Interstitial Compound Formation

These are formed when smaller atoms like H, N, C, B etc. are trapped inside the crystal lattice of the metal. They are usually non-stoichiometric and neither typically ionic nor covalent.

E.g.: Fe_3H, Mn_4N, TiC, $VH_{0.56}$, $TiH_{1.7}$ etc.

Some the properties of these compounds are:
1) They have high melting point.
2) They are very hard.
3) They retain metallic conductivity.
4) They are chemically inert.

11. Alloy Formation

Alloys are homogeneous solid solutions of elements in which at least one element is a metal. They are formed by atoms with metallic radii within about 15% of each other. Because of similar radii and other characteristics of Transition metals, they readily form alloys. The alloys formed are hard and have high m.p. e.g.: Bronze (Cu, Zn), Stainless steel (Fe, C, Ni, Mn and Cr).

Some Important Compounds of Transition Elements

1. Potassium dichromate ($K_2Cr_2O_7$)

Potassium dichromate is generally prepared from chromite ore ($FeCr_2O_4$). The preparation involves three steps.

1. *Conversion of chromite ore to sodium chromate*

   Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate.

   $4 FeCr_2O_4 + 8 Na_2CO_3 + 7 O_2 \rightarrow 8 Na_2CrO_4 + 2 Fe_2O_3 + 8 CO_2$
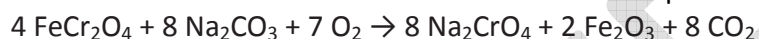
2. *Acidification of sodium chromate to sodium dichromate*

   The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.

   $2Na_2CrO_4 + 2 H^+ \rightarrow Na_2Cr_2O_7 + 2 Na^+ + H_2O$

3. *Conversion of sodium dichromate to potassium dichromate*

   The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.

   $Na_2Cr_2O_7 + 2 KCl \rightarrow K_2Cr_2O_7 + 2 NaCl$
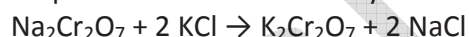
Properties

The chromate and dichromate are inter convertible in aqueous solution depending upon pH of the solution. Chromate on acidification gives dichromate and the dichromate on treating with alkali gives chromate.

$2 CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

$Cr_2O_7^{2-} + 2OH^- \rightarrow 2 CrO_4^{2-} + H_2O$
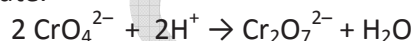
The oxidation state of chromium in chromate and dichromate is +6.

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.

Chromate ion   Dichromate ion
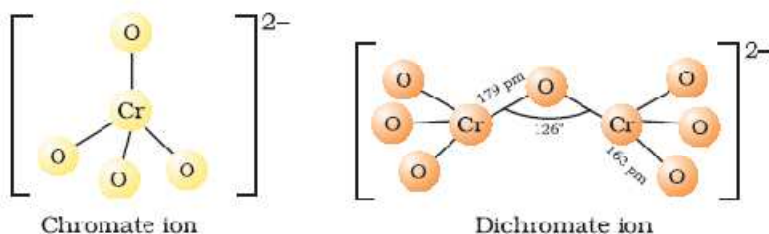
Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis.
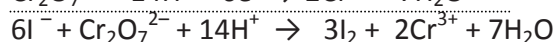
Oxidising Property

K$_2$Cr$_2$O$_7$ is a good oxidising agent in acidic medium. Its oxidising action can be represented as follows:
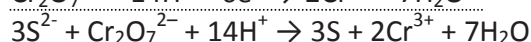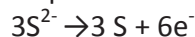
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Thus, acidified potassium dichromate will oxidise

1) Iodides to iodine
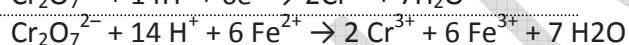$$6I^- \rightarrow 3I_2 + 6e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\overline{6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O}$$

2) Sulphides to sulphur
$$3S^{2-} \rightarrow 3S + 6e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\overline{3S^{2-} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3S + 2Cr^{3+} + 7H_2O}$$

3) Tin(II) to tin(IV)
$$3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\overline{3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O}$$
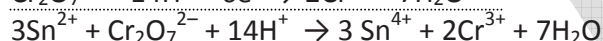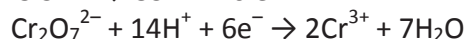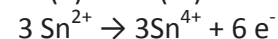
4) Iron(II) (ferrous) to iron(III) (ferric)
$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$\overline{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H2O}$$
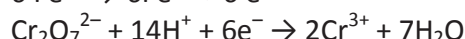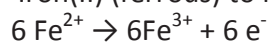
2. *Potassium permanganate (KMnO$_4$)*

Potassium permanganate is commercially prepared from Pyrolusite (MnO$_2$). The preparation involves two steps. In the first step MnO$_2$ is fused with KOH to form potassium manganate (K$_2$MnO$_4$). Then K$_2$MnO$_4$ is electrolytically oxidised to potassium permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
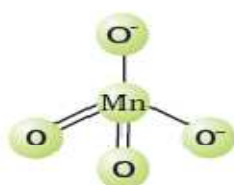$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$
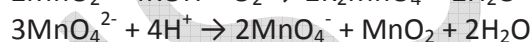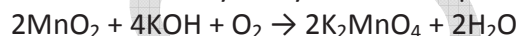
Properties

Potassium permanganate forms dark purple crystals which are iso-structural with those of KClO$_4$. When heated it decomposes and liberate O$_2$.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

The manganate and permanganate ions are tetrahedral

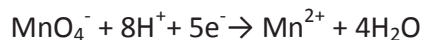Tetrahedral manganate (green) ion   Tetrahedral permanganate (purple) ion

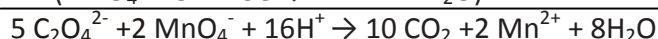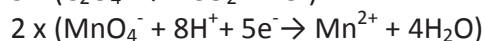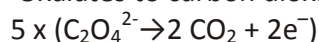The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

Oxidising Property

$KMnO_4$ is a good oxidizing agent in acidic, basic and neutral media. The oxidizing action in acidic medium is due to the reaction:
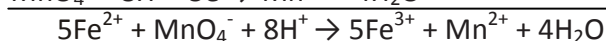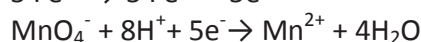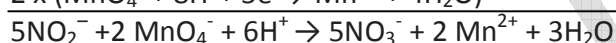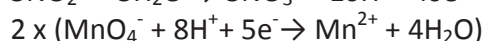
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Acidified permanganate solution oxidises:

1) Oxalates to carbon dioxide

$$5 \times (C_2O_4^{2-} \rightarrow 2\,CO_2 + 2e^-)$$
$$\underline{2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)}$$
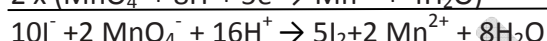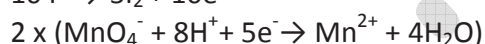$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8H_2O$$

2) Iron(II) to iron(III)

$$5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 5e^-$$
$$\underline{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$
$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

3) Nitrites to nitrates

$$5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + 10e^-$$
$$\underline{2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)}$$
$$5NO_2^- + 2\,MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2\,Mn^{2+} + 3H_2O$$

4) Iodides to free iodine.

$$10\,I^- \rightarrow 5I_2 + 10e^-$$
$$\underline{2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)}$$
$$10I^- + 2\,MnO_4^- + 16H^+ \rightarrow 5I_2 + 2\,Mn^{2+} + 8H_2O$$

5) Sulphite to sulphate

$$2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$$
$$\underline{5 \times (SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-)}$$
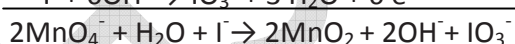$$5SO_3^{2-} + 2\,MnO_4^- + 6H^+ \rightarrow 5SO_4^{2-} + 2\,Mn^{2+} + 3H_2O$$
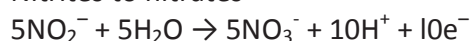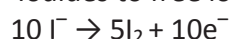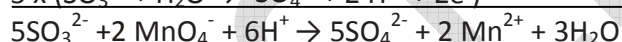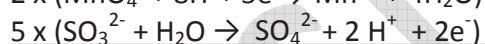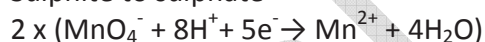
In alkaline or neutral medium, permanganate ion is reduced to MnO_2

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

In alkaline medium it oxidises

1) Iodide to iodate

$$(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-) \times 2$$
$$\underline{I^- + 6OH^- \rightarrow IO_3^- + 3H_2O + 6e^-}$$
$$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$$
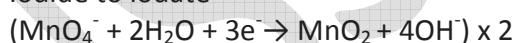
2) Thiosulphate to sulphate

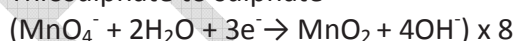$$(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-) \times 8$$
$$\underline{(S_2O_3^{2-} + 10OH^- \rightarrow 2SO_4^{2-} + 5H_2O + 8e^-) \times 3}$$
$$8MnO_4^- + H_2O + 3\,S_2O_3^{2-} \rightarrow 8MnO_2 + 2OH^- + 6SO_4^{2-}$$
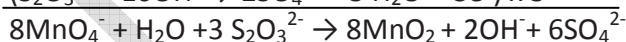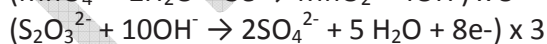
Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses: It is used as an oxidising agent in acidic, basic and neutral medium. It is used as a primary standard in volumetric analysis. It is used for the bleaching of wool, cotton, silk and other textile fibres and also for the decolourisation of oils.

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last electron enters in the anti-penultimate f-subshell are called f-block elements. They include lanthanides of the 6th period and actinides of the 7th period. They are also called *inner transition elements*. Since lanthanum ($_{57}La$) closely resembles lanthanides, it is also included along with them. Similarly, actinium ($_{89}Ac$) is included along with actinoids because of its close resemblance with them.

The Lanthanoids or lanthanides

The 14 elements after lanthanum of the 6th period are called lanthanides or lanthanoids or lanthanones or rare earths. They include elements from $_{58}Ce$ to $_{71}Lu$. They are generally represented as Ln.

Atomic and ionic radii - Lanthanide Contraction

In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanide series (though very slightly) is called *lanthanide contraction*.

Reason: In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and as a result the radii decreases.

Consequences:
1) Due to Lanthanide Contraction the 2nd and 3rd row transition series elements have similar radii.
   E.g. Zr – 160pm and Hf -159pm
2) Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.
3) The basic character of their hydroxides decreases from lanthanum to lutetium. i.e, $La(OH)_3$ is more basic than $Lu(OH)_3$.
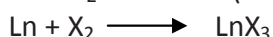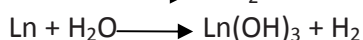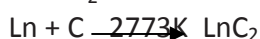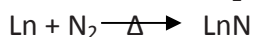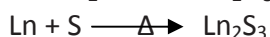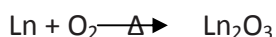
Oxidation number

In lanthanoids, the most common oxidation state is +3. However, +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filled or filled f subshells. Cerium shows the oxidation state +4 due to its noble gas configuration. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu and Yb shows +2 oxidation state because of the stable f^7 or f^{14} configuration. Sm shows +2 oxidation state also.

General properties of Lanthanoides

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. Their hardness increases with increasing atomic number. They have typical metallic structure and are good conductors of heat and electricity. Most of the lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions is due to the presence of f electrons. But La^{3+} or Lu^{3+} ion are colourless. The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

Chemical properties

Some of the chemical reactions of lanthanides are:

$Ln + O_2 \xrightarrow{\Delta} Ln_2O_3$

$Ln + S \xrightarrow{\Delta} Ln_2S_3$

$Ln + N_2 \xrightarrow{\Delta} LnN$

$Ln + C \xrightarrow{2773K} LnC_2$

$Ln + H_2O \longrightarrow Ln(OH)_3 + H_2$

$Ln + X_2 \longrightarrow LnX_3$

$$Ln + HCl \longrightarrow LnCl_3 + H_2$$

Uses of Lanthanides

The main use of the lanthanoids is for the production of alloy steels. An important alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A great deal of mischmetall is used in Magnesium based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

The Actinoids or Actinones

The 14 elements after actinium in the 7th period of modern periodic table are called actinides or actinoids or actinones. They include elements from $_{90}$Th to $_{103}$Lr. Most of them are artificially prepared and are short lived. They are radioactive. The elements after Uranium are artificially prepared and so they are called *trans-uranium elements or trans-uranic elements*.

Atomic and ionic radii

In actinoid series the atomic and ionic radii decreases regularly from left to right. This is known as Actinoid contraction.

Oxidation state

Common oxidation state of actinoids is +3. The elements in the first half of the series show higher oxidation states. The maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.

Comparison between lanthanoids and acinoids

1. Most of the actinoids are artificially prepared and are radioactive.
2. The first ionisation enthalpy of early actinoids is lower than those of lanthanoids.
3. Actinoid contraction is greater from elements to elements than lanthanoid contraction. This is due to greater shielding effect of 5f electrons.

¤   ¤   ¤   ¤   ¤   ¤   ¤   ¤   ¤   ¤   ¤