$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

Electrolytic oxidation

$$K_2 MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$
$$H_2 O \rightleftharpoons H^+ + OH^-$$

In this process manganate ions are converted to permanganate ions at anode.

 $MnO_4^{2-} - \rightarrow MnO_4^{-} + e^{-}$ Green Purple

Properties

- It is fairly soluble in hot water, but sparingly soluble in cold water.
- ➢ It exists in the form of purple crystals which melt at 250°C.



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- Uses of $KMnO_4$:
 - > As strong oxidising agent.
 - > It is used for bleaching of wool, cotton, silk and other textile fibres.
 - > As a disinfectant and germicide.

Illustration 2

What is the equivalent mass of $KMnO_4$ when it acts as an oxidising agent in acidic medium (molecular mass of $KMnO_4$ =158)?

Soln.: Oxidising action of KMnO₄ acidic medium is represented as:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

2 × 158 g
= 5 × 16
= 80 g

Eq. mass of KMnO₄ =
$$\frac{2 \times 1.58}{80} \times 8 = 31.6$$

or Eq. mass of KMnO₄

Molecular mass

Number of electrons gained per molecule

 $=\frac{158}{5}=31.6$

-

or $MnO_4^ \longrightarrow$ Mn^{2+} Oxidation state +7 +2

Eq. mass of KMnO₄

$$\frac{\text{Molecular mass}}{\text{Change in oxidation state per molecule}} = \frac{158}{5} = 31.6$$

The f-block elements are also called as **inner** transition
elements. Those elements in which the last electron or
differentiating electron enters the f-orbital are called
as f-block elements, since last electron enters inner to
penultimate shell *i.e.*
$$(n - 2)f$$
 shell. These elements were
also known as rare earths because of their rare occurrence.

Lanthanoids

• Electronic configuration : These are the inner transition elements in which the last electron enters into 4/-orbital.

Element	Symbol	Atomic	Electronic
		Number (Z)	Configuration
Lanthanum	La	57	[Xe] $5d^{1} 6s^{2}$
Cerium	Ce	58	[Xe] $4f^2 5d^0 6s^2$
Praseodymium	Pr	59	[Xe] $4f^3 5d^0 6s^2$
Neodymium	Nd	60	[Xe] $4f^4 5d^0 6s^2$
Promethium	Pm	61	[Xe] $4f^5 5d^0 6s^2$
Samarium	Sm	62	[Xe] 4f ⁶ 5d ⁶ 6s ²
Europium	Eu	63	[Xe] $4f^7 5d^0 6s^2$
Gadolinium	Gd	64	$[Xe] 4f^7 5d^1 6s^2$
Terbium	Тb	65	[Xe] 4f ⁹ 5d ⁰ 6s ²
Dysprosium	Dy	66	[Xe] $4f^{10} 5d^0 6s^2$
Holmium	Но	67	$[Xe] 4f^{11} 5d^0 6s^2$
Erbium	Er	68	[Xe] $4f^{12} 5d^0 6s^2$
Thulium	Tm	69	[Xe] $4f^{13} 5d^{\bullet} 6s^2$
Ytterbium	Yb	7●	$[Xe]4f^{14}5d^{0}6s^{2}$
Lutetium	Lu	71	[Xe] $4f^{14} 5d^1 6s^2$

• Oxidation states : The most stable oxidation state is +3 for all the lanthanoids. However lanthanoids exhibit different oxidation states also like +2, +3 and +4. Only those elements which attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation state. Example: Europium and ytterbium exhibit +2 oxidation states, cerium exhibits +4 oxidation state.

Each lanthanoid has a tendency to acquire most stable +3 oxidation state thus Sm^{2+} , Eu^{2+} and Yb^{2+} act as good reducing agents and Ce^{4+} and Tb^{4+} act as good oxidising agents in aqueous solution.

- Atomic and ionic radii (Lanthanoid contraction) : In lanthanides there is a regular decrease in atomic radii and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as lanthanoid contraction.
 - Causes : In lanthanoids, the nuclear charge increases by one unit at each successive element and a new electron enters the 4*f*-subshell. Due to the peculiar shape of *f*-orbitals, there is imperfect shielding of 4*f*-electron by other electrons from the nuclear attraction. As a result of this the size of lanthanoid atoms keep on decreasing from La to Lu. Although decrease in atomic radii is not very regular but ionic radii decreases steadily from La to Lu.
 - Consequences : The atomic radii of 5d-transition elements are very close to those of the corresponding 4d-transition elements so that the crystal structure and other properties of these elements are very similar. There is a difficulty in separation of lanthanoids due to their similar chemical properties. Ionic radii of M³⁺ decreases from La³⁺ to Lu³⁺ as a result covalent character in their oxides and hydroxides increases from La to Lu. Hence, their basic strength also increases from La(OH)₃ to Lu(OH)₃.
- Chemical reactivity : Representing the lanthanoids by the general symbol Ln, the general reactions may be shown as follows:



- Uses of lanthanoids : They are used in the form of their alloys such as misch metal or pyrophoric alloys.
 - Cerium salts are used for dyeing cotton and also as catalyst.
 - The compounds of lanthanoids are used in making magnetic and electronic devices.

Their oxides are used in glass industry. Recently lanthanoids have been used in lasers.

Actinoids

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- The elements in which the last electron enters one of the 5*f*-orbitals are called actinoids (or 5*f*-block elements). These are also called **second inner transition series** elements.
- Electronic configuration : The last electron enters into 5*f*-orbital in these elements. The general electronic configuration of these elements is $5f^{1-14} 6d \cdot 7s^2$.

Element	Symbol	Atomic Number	Electronic Configuration
Actinium	Ac	89	[Rn] 6d ¹ 7s ²
Thorium	Th	90	[Rn] 6 a ² 7s ²
Protactinium	Ра	91	[Rn] $5 f^2 6d^1 7s^2$
Uranium	U	92	[Rn] $5 f^3 6d^1 7s^2$
Neptunium	Np	93	[Rn] $5 f^4 6d^1 7s^2$
Plutonium	Pu	94	[Rn] 5 f^{6} 6 d^{0} 7 s^{2}
Americium	Am	95	[Rn] 5 $f^7 6d^0 7s^2$
Curium	Cm	96	[Rn] 5 $f^7 6d^1 7s^2$
Berkelium	Bk	97	[Rn] $5 f^9 6d^{\bullet} 7s^2$
Californium	Cf	98	[Rn] $5 f^{10} 6d^0 7s^2$
Einsteinium	Es	99	[Rn] $5f^{11} 6d^0 7s^2$
Fermium	Fm	100	[Rn] 5 f^{12} 6 d^0 7 s^2
Mendelevium	Md	101	[Rn] 5 f^{13} 6 d^0 7 s^2
Nobelium	No	102	[Rn] $5 f^{14} 6d^{\bullet} 7s^2$
Lawrencium	Lr	103	[Rn] $5f^{14} 6d^1 7s^2$

- Oxidation states : The most common and stable oxidation state of actinoids is +3. Actinoids also show oxidation state of +4 and even higher *i.e.*, +5, +6 and +7. Oxidation state first increases upto middle of series and then decreases.
- Atomic and ionic radii (Actinoid contraction) : There is a gradual decrease in the size of atoms or M^{3^+} ions across the series. This is known as actinoid contraction (very similar to lanthanoid contraction). The contraction is however greater from element to element in this series resulting from poor shielding by 5f-electrons.
- Chemical reactivity : Actinoids are highly reactive metals especially in the finely divided state. They reacts with boiling water to give a mixture of oxide and hydride.