

20

The *d* and *f*-Block Elements

The ***d*-block** of the periodic table contains the elements of the groups 3-12 in which the *d*-orbitals are progressively filled. There are mainly three series of the elements, *3d*-series (Sc to Zn) *4d*-series (Y to Cd) and *5d*-series (La to Hg omitting Ce to Lu). The fourth *6d*-series which begins with Ac is still incomplete. The two series of the inner-transition metals, (*4f* and *5f*) are known as lanthanoids and actinoids respectively.

Transition Elements

Elements having partially filled *d*-orbitals in ground state or in excited state, are known as transition elements. They have been placed in the centre of the Periodic Table between *s*-block and *p*-block elements.

Iron is the most abundant and widely used transition metal.

General Electronic Configuration of Transition Elements

Transition elements have the electronic configuration $(n-1)d^{1-10} ns^{0-2}$. Zn, Cd, Hg, the end members of first three series have general electronic configuration $(n-1)d^{10} ns^2$. These elements do not show properties of transition elements to any extent and are called **non-typical transition elements**.

Electronic configuration of transition elements

3d-Series			4d-Series			5d-Series		
At. no.	Element	Electronic configuration	At. no.	Element	Electronic configuration	At. no.	Element	Electronic configuration
21	Sc	[Ar]3d ¹ 4s ²	39	Y	[Kr]4d ¹ 5s ²	57	La	[Xe]5d ¹ 6s ²
22	Ti	[Ar]3d ² 4s ²	40	Zr	[Kr]4d ² 5s ²	72	Hf	[Xe]4f ¹⁴ 5d ² 6s ²
23	V	[Ar]3d ³ 4s ²	41	Nb	[Kr]4d ⁴ 5s ¹	73	Ta	[Xe]4f ¹⁴ 5d ³ 6s ²
24	Cr	[Ar]3d ⁵ 4s ¹	42	Mo	[Kr]4d ⁵ 5s ¹	74	W	[Xe]4f ¹⁴ 5d ⁴ 6s ²
25	Mn	[Ar]3d ⁵ 4s ²	43	Tc	[Kr]4d ⁵ 5s ²	75	Re	[Xe]4f ¹⁴ 5d ⁵ 6s ²
26	Fe	[Ar]3d ⁶ 4s ²	44	Ru	[Kr]4d ⁷ 5s ¹	76	Os	[Xe]4f ¹⁴ 5d ⁶ 6s ²
27	Co	[Ar]3d ⁷ 4s ²	45	Rh	[Kr]4d ⁸ 5s ¹	77	Ir	[Xe]4f ¹⁴ 5d ⁷ 6s ²
28	Ni	[Ar]3d ⁸ 4s ²	46	Pd	[Kr]4d ¹⁰ 5s ⁰	78	Pt	[Xe]4f ¹⁴ 5d ⁹ 6s ¹
29	Cu	[Ar]3d ¹⁰ 4s ¹	47	Ag	[Kr]4d ¹⁰ 5s ¹	79	Au	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
30	Zn	[Ar]3d ¹⁰ 4s ²	48	Cd	[Kr]4d ¹⁰ 5s ²	80	Hg	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²

General Physical Properties of Transition Elements

- (i) **Atomic and ionic size** Ions of the same charge in a given series exhibit regular decrease in radius with increasing atomic number, because the new electron enters in a *d*-orbital and nuclear charge increases by unity.

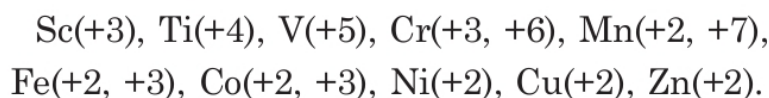
In last of the series, a small increase in size is observed due to electron-electron repulsion.

Atomic and ionic radii increase from 3*d*-series to 4*d*-series but the radii of the third (5*d*) series elements are virtually the same as those of the corresponding member of the second series. It can be explained on the basis of lanthanoid contraction [poor shielding of 4*f*].

- (ii) **Ionisation enthalpies** In a series as we move from left to right, ionization enthalpy increases due to increase in nuclear charge but not in regular trend.

The irregular trend in the first ionisation enthalpy of the 3*d* metals, though of little chemical significance, can be accounted by considering that the removal of one electron alters the relative energies of 4*s* and 3*d*-orbitals.

- (iii) **Oxidation states** Transition metals show variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are



The transition elements in their lower oxidation states (+2 and +3) usually form ionic compounds. In higher oxidation state, compounds are normally covalent.

Only Os and Ru show +8 oxidation states in fluorides and oxides.

Ni and Fe in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ show zero oxidation state.

(iv) **Enthalpy of atomisation** Transition elements exhibit higher enthalpies of atomisation. Because of the presence of a large number of unpaired electrons in their atoms, they have stronger interatomic interactions and hence, stronger bonds.

(v) **Trends in the M^{2+}/M standard electrode potentials**

$E_{M^{2+}/M}^\ominus$ is governed by three factors. Enthalpy of sublimation, enthalpy of ionisation and enthalpy of hydration.

The irregular trend of M^{2+}/M electrode potentials in 3d-series is due to irregular variation in ionisation enthalpy and heat of sublimation.

Except copper, 3d series elements are good reducing agents.

┌ If sum of the first and second ionisation enthalpies is greater than hydration enthalpy, standard potential ($E_{M^{2+}/M}^\ominus$) will be positive and reactivity will be lower and *vice-versa*. └

Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

An examination of the $E^\ominus(M^{3+}/M^{2+})$ values shows the varying trends. The low value for $\text{Sc}^{3+}/\text{Sc}^{2+}$ reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value for $\text{Zn}^{3+}/\text{Zn}^{2+}$ is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+} .

(vi) **Melting and boiling point** Due to strong metallic bond, they have high mp and bp. The mp of these elements become maximum in the middle and then decreases with the increase in atomic number. Manganese and technetium show abnormal values in the trend. Tungsten has the highest m.p. (3410°C).

Mercury is liquid at room temperature (mp – 38.9°C) due to absence of unpaired electrons, and weak metallic bonding.

(vii) **Density** d-block elements have high density because of their small atomic size and strong metallic bonding.

Densities of 3d series elements

Density	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
g/cm^3	3.0	4.54	6.12	7.19	7.40	7.87	8.74	8.90	8.92	7.13

Osmium has slightly lower density (22.52 g cm^{-3}) as compared to iridium (22.61 g cm^{-3}). Thus, iridium has the highest density among transition metals.

- (viii) **Atomic volume** Atomic volume decreases along the period due to decrease in atomic size.
- (ix) **Chemical reactivity** *d*-block elements are less reactive due to high ionisation energies. Some are almost inert and known as noble metals, e.g. Au, Pt, Os, Ir, etc.
- (x) **Complex formation** They are well known to form a large number of complex compounds mainly due to
- small atomic size and high nuclear charge
 - presence of partially filled or vacant *d*-orbitals, e.g. $\text{K}_4[\text{Fe}(\text{CN})_6]$
- (xi) **Magnetic properties**
- Paramagnetic** nature is due to the presence of unpaired electrons in *d*-orbitals. Paramagnetic character increases with increase in the number of unpaired electrons (*n*) and highest for Mn(II) [among 3*d*-series].
 - Diamagnetic substances are repelled by applied magnetic field and have no unpaired electron.
 - In ferromagnetism, permanent magnetic character is acquired by substance, e.g. Fe.

Magnetic moment (μ) is given by

$$\mu = \sqrt{n(n+2)} \text{ BM}, \quad (\text{Bohr magneton})$$

- (xii) **Coloured ions** Colour exhibited by transition metal ions is due to the presence of unpaired electrons in *d*-orbitals and is due to the *d-d* transitions of electrons. When visible light is incident on the ion, an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital.

Colour of a complex depends on the metal, its oxidation state and its ligands, e.g. $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ is pale blue while $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is dark blue. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour and anhydrous CuSO_4 is colourless.

Charge transfer also gives intense colour e.g. MnO_4^- ion does not contain any unpaired *d*-electron. Its purple colour is due to charge transfer from O to Mn, thus O^{2-} changes to O^- and Mn(VII) to Mn(VI). Charge transfer is possible only when the energy levels on the two different atoms involved are fairly close.

(xiii) **Catalytic properties** The transition metals and their compounds behave like catalyst due to

- the presence of partially filled *d*-orbitals resulting in variable oxidation states.
- formation of intermediate complex with reactants by lowering the energy of activation.
- their rough surface area, e.g. provides active sites for adsorption of reactant molecules.

Iron, in the preparation of NH_3 (Haber's process), finely divided nickel for hydrogenation, Pt in the preparation of nitric acid (Ostwald's process) etc.

Some important catalysts having transition metals are

- Zeigler Natta catalyst : $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$
- Lindlar's catalyst : Pd/BaSO_4
- Wilkinson's catalyst : $[\text{Ph}_3\text{P}]_3\text{RhCl}$
- Adam's catalyst : Pt/PtO
- Brown's catalyst or P-2 catalyst : Nickel boride

(xiv) **Formation of alloys** *d*-block elements have a strong tendency to form alloys, because their atomic sizes are very similar and in the crystal lattice, one metal can be readily replaced by another. Alloys so formed have high m.p. The metals Mo, W, Cr, Ni, and V are used for the production of stainless steel.

Amalgam is an alloy formed by mercury with other metals. Iron and platinum do not form any alloy with mercury.

List of Alloys

Alloy	Composition (%)	Uses
Stainless steel	Fe = 73, Cr = 18, Ni = 8, C (traces)	Cutlery, machine parts
Coinage alloy or Coinage silver	Ag = 92.5, Cu = 7.5	Coins, Jewellery
Dental alloy	Ag = 33, Hg = 52, Sn = 12.5, Cu = 2, Zn = 0.5	For filling teeth
Brass	Cu = 80, Zn = 20	Utensils, condenser tubes
Bronze	Cu = 80, Sn = 20	Utensils, statues, coins
Gun metal	Cu = 87, Sn = 10, Zn = 3	Gun, gears
Bell metal	Cu = 80, Sn = 20	Bells, Gongs
German silver	Cu = 60, Zn = 20, Ni = 20	Cutlery, resistant wires
Duralumin	Al = 95, Cu = 4, Mg and Mn = 1	Air ships
Misch metal	Ce(25%) + lanthanide metals + 5% Fe + traces of S, C, Si, Ca, Al	Lighter flints

- (xv) **Interstitial compounds** The vacant space present in a crystal lattice is known as interstitial site or void. The non-metal atoms (e.g. H, N, C, etc.) due to their small size when occupy such place, the resulting compound is known as interstitial compound. Such compounds are hard and rigid, e.g. cast iron and steel.
- (xvi) **Non-stoichiometric compounds** The compounds not having the elements in the exact ratio as in the ideal crystal are known as non-stoichiometric compounds, e.g. in $\text{Fe}_{0.94}\text{O}_1$, the Fe : O is approx 0.94 : 1 and not exactly 1 : 1. It is due to the variability of oxidation state in the transition metal.
- (xvii) **Spinel** These are the mixed oxides in which oxygen atoms constitute a fcc lattice, e.g. ZnFe_2O_4 . It is a normal spinel in which the trivalent ions occupy the octahedral holes and divalent ions occupy the tetrahedral holes.
- In inverse spinel, the trivalent ion occupy the tetrahedral holes and divalent ion occupy the octahedral holes. e.g. FeFe_2O_4 or Fe_3O_4 .

Some important reagents having transition metals

1. **Baeyer's reagent** Dilute alkaline KMnO_4 , used to test the presence of unsaturation.
2. **Tollen's reagent** Ammoniacal solution of AgNO_3 , i.e. $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, used to test the aldehyde group.
3. **Nessler's reagent** Alkaline solution of K_2HgI_4 is used to test $\text{NH}_3(g)$ and NH_4^+ .
4. **Benedict's solution** CuSO_4 solution + sodium citrate + Na_2CO_3 , used to test the aldehyde group.
5. **Lucas reagent** HCl (conc.) + anhydrous ZnCl_2 , used to distinguish between 1° , 2° and 3° alcohols.

Applications of Transition Elements

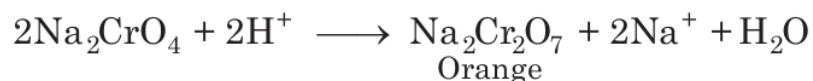
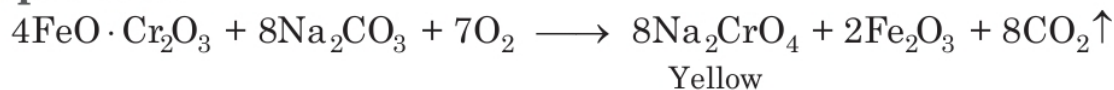
1. A mixture of TiO_2 and BaSO_4 is called titanox and a mixture of $\text{ZnS} + \text{BaSO}_4$ is called lithopone.
2. TiCl_2 and TiO_2 are used in smoke screens. TiO_2 is also used as white pigment of paints.
3. Tantalum is used in surgical venals and analytical weights.
4. Chromium is used in stainless steel and chrome plating.
5. Mo is used in X-rays tubes. Pt is used in resistance thermometers.
6. Cd is used for making joints in jewellery.
7. Ce is used as a scavenger of oxygen and sulphur in many metals.

Compounds of d-block Elements

1. Potassium Dichromate ($K_2Cr_2O_7$)

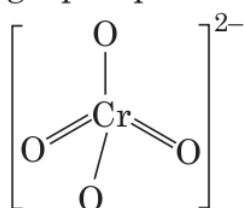
Ore Ferrochrome or chromite ($FeO \cdot Cr_2O_3$) or ($FeCr_2O_4$)

Preparation

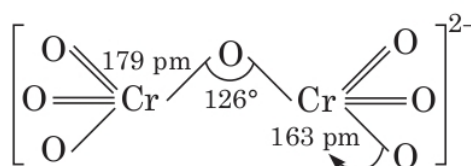


Sodium dichromate is more soluble than potassium dichromate.

Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

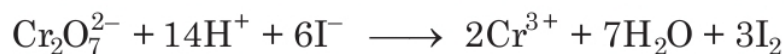


Chromate ion



Dichromate ion

Properties Sodium and potassium dichromates are strong oxidising agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).



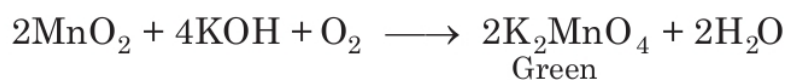
Uses

1. $K_2Cr_2O_7$ is used as an oxidising agent in volumetric analysis.
2. It is used in mordant dyes, leather industry, photography (for hardening of film).
3. It is used in chromyl chloride test.
4. It is used in cleaning glassware.

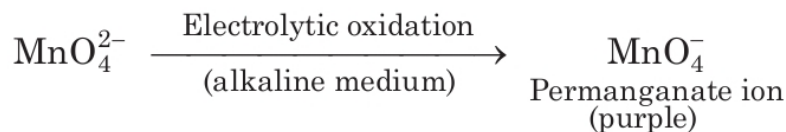
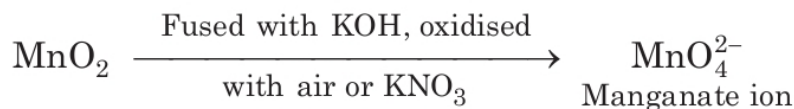
2. Potassium Permanganate ($KMnO_4$)

Ore Pyrolusite (MnO_2)

Preparation

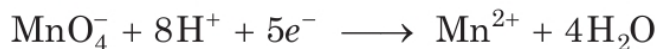


Commercial preparation

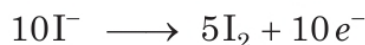
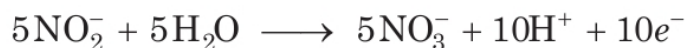
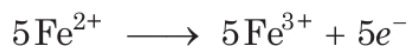
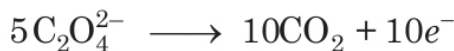


Properties KMnO_4 acts as strong oxidising agent.

1. In the presence of dilute H_2SO_4 , KMnO_4 is reduced to manganous salt.

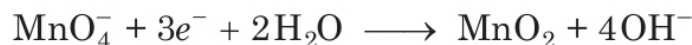


Acidic KMnO_4 solution oxidises oxalates to CO_2 , iron(II) to iron (III), nitrites to nitrates and iodides to iodine. The half-reactions of reductants are



To acidify KMnO_4 , only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with KMnO_4 and produce Cl_2 while HNO_3 , itself acts as oxidising agent.

2. In alkaline medium, KMnO_4 is reduced to insoluble MnO_2 .



Alkaline or neutral KMnO_4 solution oxidises I^- to IO_3^- , $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-} , Mn^{2+} to MnO_2 , etc.

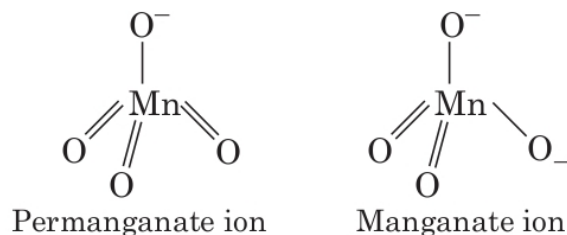
Aqueous KMnO_4 reacts with NH_3 to liberate N_2 gas.



Uses KMnO_4 is used

- (i) in laboratory preparation of Cl_2 .
- (ii) as an oxidising agent and disinfectant.
- (iii) in making Baeyer's reagent.
- (iv) for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

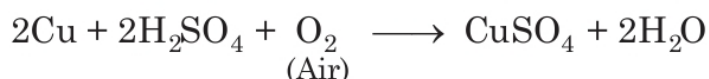
Structures



3. Copper Sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

It is also known as blue vitriol.

Method of preparation It is obtained by the action of dil H_2SO_4 on copper scrap in the presence of air.



Properties

1. On heating it turns white due to loss of water of crystallisation. At 1000 K, CuSO_4 decomposes into CuO and SO_3 .



2. It gives blue solution with NH_4OH and white ppt of Cu_2I_2 with KI .

Uses It is used in electroplating, as mordant in dyeing, in making bordeaux mixture [$(\text{Ca}(\text{OH})_2 + \text{CuSO}_4)$], etc.

4. Silver Nitrate (AgNO_3)

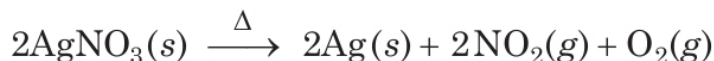
It is also called Lunar caustic.

Method of preparation It is prepared by heating silver with dilute nitric acid.



Properties

1. It is colourless, crystalline compound which blackens when comes in contact of organic substances (skin, cloth, etc.)
2. With potassium dichromate, it gives red ppt of Ag_2CrO_4 .
3. On strong heating, it decomposes to metallic silver.



4. Ammoniacal solution of silver nitrate is known as Tollen's reagent.

Uses It is used as laboratory reagent, in silvering of mirror, in the preparation of inks and hair dyes, etc.

Inner-Transition (f-block) Elements

The elements in which the filling of atomic orbitals by electrons in valence shell take place in *f*-subshells, two levels inside the outer subshell, are known as inner-transition elements. They are also known as *f*-block elements.

Classification of f-Block Elements

They have been classified into two series.

- (a) **4*f*-series** (first inner-transition series) The last electron enters in 4*f*-orbital. The elements belonging to this series are also known as **lanthanoids**.
- (b) **5*f*-series** (second inner-transition series) The last electron enters in 5*f*-orbital. The elements belonging to this series are also known as **actinoids**.

Lanthanides

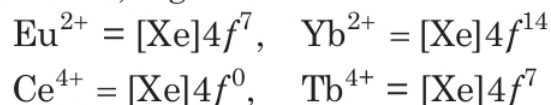
The fifteen elements from lanthanum (at. no. 57) to lutetium (at. no. 71) are known as **lanthanoids** or **rare earths**. Their properties are as follows :

Electronic Configuration

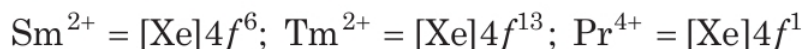
The general electronic configuration of these elements is $[\text{Xe}]4f^{0-14}5d^{0-1}6s^2$. The lanthanum, electronic configuration $[\text{Xe}]4f^05d^16s^2$ and lutetium, electronic configuration $[\text{Xe}]4f^{14}5d^16s^2$, have no partially filled 4*f*-orbital in their ground state, are considered as lanthanoids due to their properties close to these elements.

Oxidation State

The most common and most stable oxidation state of lanthanides is +3 but some elements also exhibit +2 and +4 oxidation states in which they leave behind stable ions, e.g.



An aqueous solution of Ce^{4+} is a good oxidising agent. The Eu^{2+} and Yb^{2+} can exist in aqueous solution and are good reducing agents. But there are exceptions also, e.g.



Magnetic Properties

Magnetic properties have spin and orbit contributions. Hence, magnetic moments are given by the formula,

$$\mu = \sqrt{4S(S + 1) + L(L + 1)}$$

Where, L = orbital quantum number, S = spin quantum number

All lanthanoid ions with the exception of La^{3+} , Lu^{3+} and Ce^{4+} , are paramagnetic in nature. For the first row transition elements, the orbital contribution is usually quenched out by interaction with the electric fields of the ligands in its environment. Thus, as a first approximation the magnetic moment can be calculated using the simple spin only formula.

$$\mu_s = \sqrt{n(n + 2)}$$

Lanthanoid Contraction

Steady decrease in the atomic and ionic (Ln^{3+}) radii as the atomic number of the lanthanoid elements increases is called lanthanoid contraction. This is because the additional electron goes to $4f$ -subshell. These $4f$ -orbitals being large and diffuse, have poor shielding effect. The effective nuclear charge increases which causes the contraction in the size of electron charge cloud. This contraction in size is quite regular and is known as lanthanoid contraction.

The f - f transitions are possible due to absorption of light from the visible region.

Consequences of Lanthanoid Contraction

- (i) Covalent character of cations increases.
- (ii) The electronegativity of trivalent ions increases slightly.
- (iii) There is decrease in basic strength of oxides and hydroxides from La to Lu.
- (iv) There is small increase in standard electrode potential values.
- (v) Sizes of Zr and Hf; Nb and Ta are similar, so they are called **chemical twins**.

Colour

The species containing unpaired electrons are coloured and so on in the case of lanthanoid ions.

Melting and Boiling Points

Lanthanoids have high melting and boiling points but there is no regular trend.

Density

Lanthanoids have densities varying from 6.67 to 9.7 g cm^{-3} , but there is no regular trend for these values.

Electronegativity

For lanthanoids, the electronegativity values are almost same as that of s -block elements. Lanthanoids form ionic compounds.

Ionisation Energies

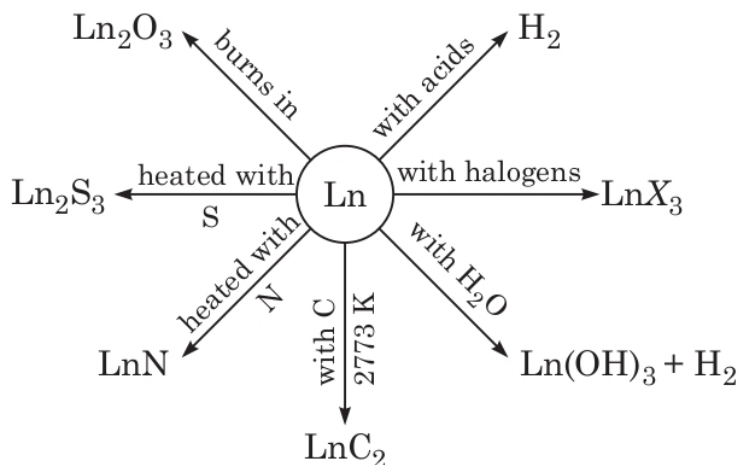
The ionisation energy values of lanthanoids are not very high due to their large size and comparable with those of alkaline earth metals.

Complex Compound

Due to their large ionic size, they have little tendency to form complexes.

Chemical Reactivity

Due to their low values of ionisation energies, the lanthanoids are very reactive.



Alloys

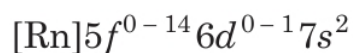
They form alloy especially with iron *e.g.* misch metal which consists of a lanthanoids metal 94 ~ 95%, iron ~ 5% and S, C, Ca and Al in traces. Mg mixed with 3% misch metal is used for making jet engine parts.

Actinoids

The fourteen elements from actinium (at. no. 89) onwards to lawrencium (at. no. 103) are known as actinoids and constitute the *5f*-series. From neptunium to onwards, the elements are man-made (artificially prepared) and also known as **transuranic elements**.

Electronic Configuration

The last electron in such elements enters in the *5f* atomic orbital. Their general electronic configuration is



There is not much difference between the energies of *5f* and *6d*, so it is difficult to predict whether the electron has entered in *5f* or *6d*.

Oxidation State

The common oxidation state is +3 but other oxidation states are also exhibited by actinoids upto the maximum being +7.

Magnetic Properties

The magnetic moments of actinoid ions are smaller than theoretical values. It is hard to interpret due to large spin orbit coupling.

Actinoid Contraction

It is similar to lanthanide contraction due to poor shielding of $5f$ -electrons. It is greater than lanthanoid contraction.

Melting and Boiling Points

They have high values for melting and boiling points but there is no regular trend.

Density

The value of density vary from 7.0 gcm^{-3} to 20 gcm^{-3} . Again there is no regular trend in density.

Reducing character

They are strong reducing agents as they have high E° values approximately 2.0 V.

Reactivity

Actinoids are very reactive in nature and combine with oxygen and halogens like lanthanoids.

Coloured Ions

Actinoid ions are coloured due to the presence of unpaired electrons and $f-f$ transitions.

Complex Formation

They have higher tendency to form complex compounds.