d & f-block elements & their important compounds

Section (A) : Electronic configuration, atomic and ionic size, density, melting and boiling points

Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^2 4s^0$	$3d^3 4s^0$	$3d^4 4s^0$	$3d^5$	$3d^6 4s^0$	$3d^7 4s^0$	$3d^8 4s^0$	$3d^9 4s^0$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_a H^{\oplus}$ / kJ mol^{-1}											
		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy / $\Delta_i H^{-}$ / kJ mol^{-1}											
$\Delta_i H^{\oplus}$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^{\oplus}$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^{\oplus}$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic radii/pm	M	164	147	135	129	137	126	125	125	128	137
	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard electrode		–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76
Potential $E^{\oplus}$ / V	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–

d-block Elements		
Last electron enters in (n – 1)d subshell. d-block elements lie in middle of periodic table.		
General Introduction		
1.	**Occurrence**	Three of transition metals are very abundant in the earth's crust.
		Fe → 4th most abundant elements in earth's crust by weight. Ti → 5th most abundant elements in earth's crust by weight. Mn → 12th most abundant elements in earth's crust by weight.
	First row	Element with even atomic no. are in general more abundant than their neighbours with odd atomic no. except for Mn (Z = 25) but still 12th most abundant element by weight.
	2nd and 3rd row	Less abundant than 1st d- series elements. Tc → does not occur in nature. Last six members of 2nd and 3rd row occur less than 0.16 ppm in earth's crust.
	Coinage metals	Cu, Ag and Au are called coinage metals.
	Noble metals	Cu, Ag, Au, Hg and Pt.
2.	**No. of elements**	Total d-block elements – (40) Total transition elements – (36). If 112 elements are included in periodic table. (Except Zn, Cd, Hg and Uub)
3.	**Groups**	IIIB to VIIB, VIII, IB, IIB or group 3 to 12 (IUPAC).

4.	**Period**	4th to 7th

4_{th} period	3d- series (Sc - Zn)
5_{th} period	4d- series (Y - Cd)
6_{th} period	5d- series (La - Hg)
7_{th} period	6d- series (Ac - Uub)

Section (B) : Ionization enthalpy, oxidation state, Electrode potential and chemical reactivity

Periodic trends and chemical properties

S.N.	Properties	DISCRIPTION
1	**Metallic character**	All the transition elements are metals, therefore they are showing all the metallicproperties. Good conductor of heat and electricity. Metallic lustre, strong and ductile. With the exception of Zn, Cd, Hg, Mn all the transition metals have one or more regular metallic structure. The transition metals are hard and have low volatility (except Zn, Cd and Hg).
2	**Electronic configuration**	$(n-1)d^{1-10}\,ns^{1\text{ or }2}$

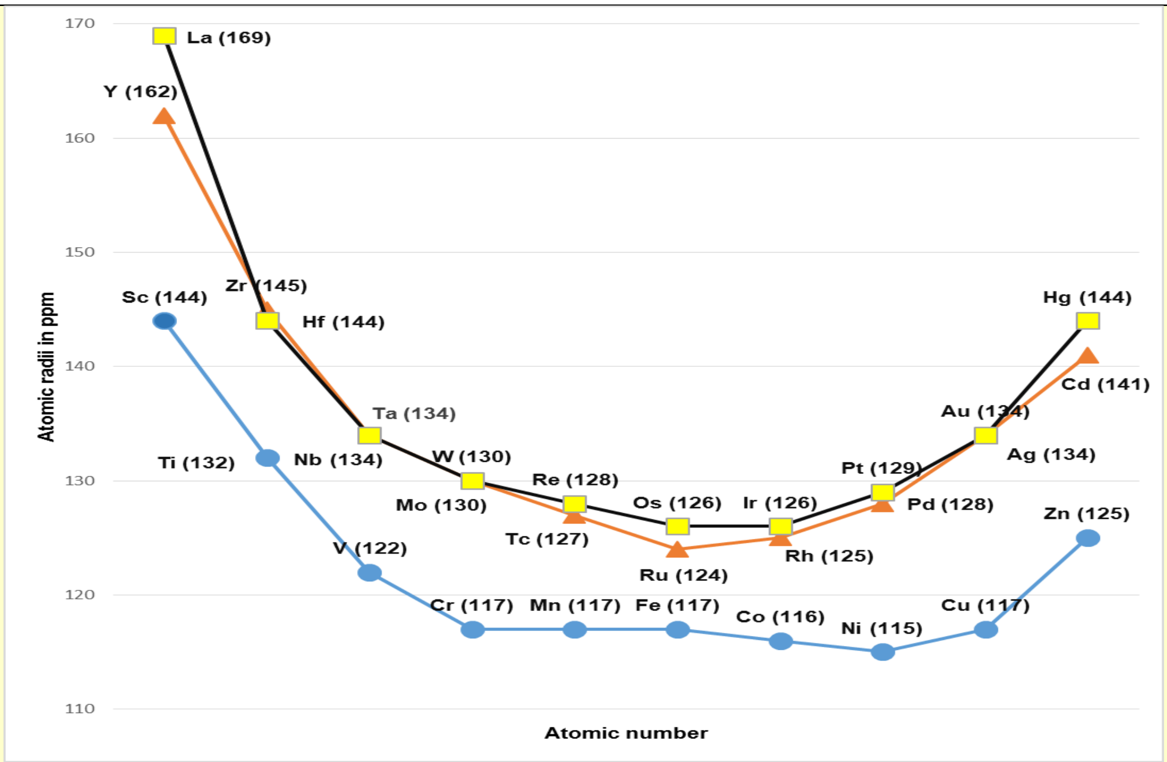
	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9	10	11 IB	12 IIB
3d Series	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$
4d Series	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 4s^1$	48 Cd $4d^{10} 4s^2$
5d Series	57 La* $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$
6d Series	89 Ac** $6d^1 7s^1$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

		Electrons are being filled penultimate shells, thus outer electronic configuration remains same , with exception in some cases, e.g.Cr and Cu.
		Cr and Cu attain extra stability of half-filled and full-filled electronic configuration by changing the expected pattern of electronic configuration.
		The electronic structure of 2nd and 3rd rows do not always follow the pattern of the first row, e.g. Group 10

Ni	$3d^8 4s^2$
Pd	$4d^{10} 5s^0$
Pt	$5d^9 6s^1$

<table>
<tr><td></td><td></td><td>d-orbitals are complete at Cu, Pd, Ag, Au.
<table><tr><td>Ni ($3d^8\ 4s^2$)</td><td>Cu($3d^{10}4s^1$)</td><td>Zn($3d^{10}4s^2$)</td></tr><tr><td>Pd($4d^{10}5s^0$)</td><td>Ag($4d^{10}5s^1$)</td><td>Cd($4d^{10}5s^2$)</td></tr></table>Even though ground state of the atom has a d^{10} configuration Pd and coinage metals behaves as typical transition elements, as in their most common oxidation states they have incomplete d-orbital.</td></tr>
<tr><td></td><td>Transition elements</td><td>A transition element is defined as the one which has incompletely filled <i>d</i> orbitals in its ground state or in any one of its oxidation states.
Zinc, Cadmium and Mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, they are some times not regarded as transition metals.
All transition elements are d-block elements but all d-block elements are not transition elements. (as per NCERT)</td></tr>
<tr><td>3</td><td>Size of atoms and ions</td><td>In the transition series (e.g. in the first transition series), the covalent radii of the elements decrease from left to right across a row until near the end when the size increases slightly.</td></tr>
<tr><td></td><td>d-orbital contraction</td><td>On moving from left to right, extra protons are placed in the nucleus and the extra electron are added. The orbital electron shield the nuclear charge incompletely. Thus the nuclear charge attracts all the electrons more strongly, hence a contraction in size occurs. The radii of the elements from Cr to Cu, are very close to one another because the extra electron being added increases the repulsion between the electrons and counter balances the increased nuclear charge on the outer electrons (4s). As a result of this, the size of the atom does not change much in moving from Cr to Cu and for zinc this repulsion even dominates the nuclear charge so size slightly increases.
<table><tr><td>Element</td><td>Sc</td><td>Ti</td><td>V</td><td>Cr</td><td>Mn</td><td>Fe</td><td>Co</td><td>Ni</td><td>Cu</td><td>Zn</td></tr><tr><td>Atomic radius (pm)</td><td>144</td><td>132</td><td>122</td><td>117</td><td>117</td><td>117</td><td>116</td><td>115</td><td>117</td><td>125</td></tr></table></td></tr>
<tr><td></td><td>Lanthanide Contraction</td><td>As we move along the lanthanide series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these f-orbitals. This imperfect shielding in unable to counter balance the effect of the increased nuclear charge. Hence, the net result is a contraction in the size though the decrease is very small.
Thus covalent and ionic radii of Nb (5th period) and Ta (6th period) are almost same due to poor shielding of f-orbitals electrons.</td></tr>
</table>

<table>
<tr><td></td><td colspan="2">

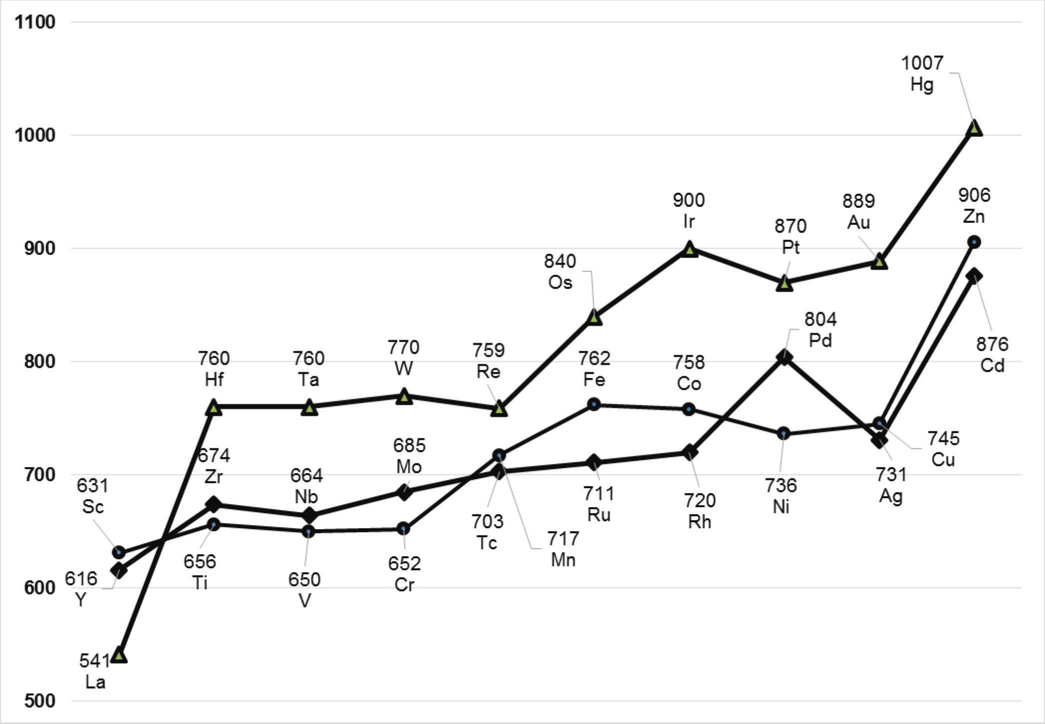


Ti < Zr ≈ Hf (Lanthanide Contraction)

Sc < Y < La

Due to Lanthanide contraction elements of 4d and 5d series belong to a particular group have almost same atomic radii. Ex. Zr ≈ Hf, Tc≈Re, Nb≈ Ta, Ru ≈Os etc.

</td></tr>
<tr><td rowspan="2">**4**</td><td>**Ionization energies of transition metals**</td><td>Ionization energy normally increases from left to right in the period.
Ionization energy values of third transition series is greater than ionization energy values of first and second transition series.</td></tr>
<tr><td colspan="2">Memory warning : Need not memorise the graph.</td></tr>
</table>



First ionization energies of the d-block elements (Numerical values are given in kJ mol^{-1}).

(i)The first ionisation potential for the first four 3d-block elements (Sc,Ti,V & Cr) differ only slightly from one another.

(ii) Similarly the value first ionisation energy of Fe, Co, Ni & Cu also are fairly close to one another.

(iii) The value of first ionisation energy for Zn is considerably higher due to the extra stability of $3d^{10}4s^2$ level which is completely filled in Zn atom.

(iv) The first ionization energy of Mn is slightly higher than adjacent elements in 3d series due to half-filled stable configuration.

(v) Second ionisation energy value for Cr & Cu are higher as the Cr^+& Cu^+ ion are extra stable due to $3d^5$ and $3d^{10}$ Configuration.

(vi) In vertical columns, the ionisation energy decrease from first member to the second member.

(vii) However the third member (5d series) has higher value than second member
(4d-series) due to lanthanide contraction. I.E. (3rdT.S.) > I.E. (2ndT.S.) > I.E. (1stT.S.)

5 **Oxidation-State** They show variable oxidation–state.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					**+1**	
	+2	**+2**	**+2**	+2 (a)	+2	+2	+2	+2	+2
+3	+3	+3	+3	**+3**	**+3**	**+3**	**+3**		
	+4	**+4**	**+4**	+4(b)	**+4**	**+4**	**+4**		
		+5	**+5**	**+5**					
			+6	**+6**	**+6**				
				+7					

(a) Acidic medium (b) Basic medium

* Shaded states are popular ones.

* Underlined states are the most stable ones.

The oxidation states change in units of 1, unlike that in p-block elements, where generally oxidation state differs by units of 2.

Trends of Oxidation state

Highest oxidation state of 3d-series elements can be calculated by n + 2

(where n = number of unpaired electrons) **It is not applied for Cr and Cu.**
The transition metal ions having stable configuration like d^0, d^5 or d^{10} are more stable. **Ex.** Sc^{+3}, Ti^{+4}, V^{+5} Fe^{+3}, Mn^{+2}, Zn^{+2} etc.
Most common oxidation state among the transition elements is +2.
Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).
The highest oxidation states (+4, +5, +6, +7, +8) are found in compounds of oxide and oxyfluoride because fluorine and oxygen are most electronegative elements and good oxidants.

e.g. $\overset{+7}{Mn}O_4^-, \overset{+6}{Cr_2}O_7^{2-}, \overset{+6}{Cr}O_4^{2-}, \overset{+4}{Mn}O_2, \overset{+6}{Mn}O_4^{2-}, \overset{+6}{Cr}O_2F_2$

Lower oxidation states even negative (-2, -1, 0, +1) is stabilised by π-bonding ligands such as carbon monoxide and dipyridine due to phenomena of synergic bonding $Ni(CO)_4$ and $Fe(CO)_5$, oxidation state of Ni and Fe is zero.
They form ionic compounds in low oxidation states and covalent compounds in Higher oxidation state.

Formulas of Oxides of 3d Metals (* mixed oxides)

OXIDATION NUMBER	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4	CrO_2	MnO_2					
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					Mn_3O_4*	Fe_3O_4*	Co_3O_4*			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
									Cu_2O	

6 **Colour**

Ionic and covalent compounds of many transition elements are coloured.
They form different coloured compounds. The compounds in which metal ion has an unpaired electron that compound may be coloured. When an electron from a lower energy d-orbital is exited to a higher energy d-orbital, if the energy of excitation lies in visible range, complimentary colour is observed.
MnO_4^- is coloured inspite of d^0 configuration of Mn. It is not due to d-d transition but it occurs due to charge transfer between Mn and O.

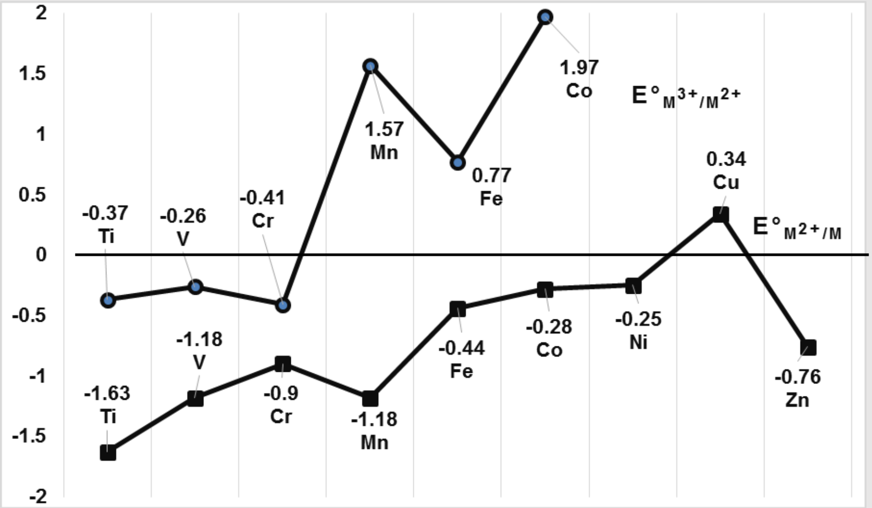
Memory warning : Memorize the table completely**.**

Oxidation State	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
(I)									**Colurless**	
(II)				**Blue**	**Pink**	**Green**	**Pink**	**Green**	**Blue**	**Colurless**
(III)	**Colurless**	**Purple**	**Green**	**Green**	**Violet**	**Yellow**	**Blue**			
(IV)		**Colurless**	**Blue**							

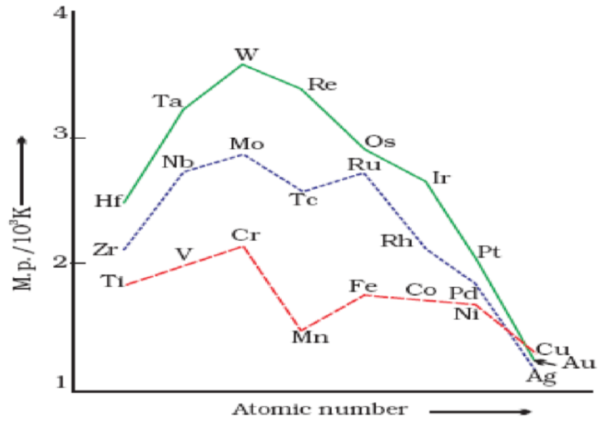
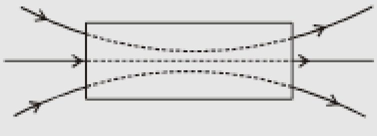
7 **Electrode potential**

$E^0_{M^{2+}/M}$

There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies (IE_1 + IE_2), hydration energies and the sublimation energies in the period.

<table>
<tr>
<td></td>
<td></td>
<td>Memory warning : Need not memorize the table but remember the comments.
<table>
<tr><th>Element (M)</th><th>$E^0_{M^{3+}/M^{2+}}$</th><th>$E^0_{M^{2+}/M}$</th><th>Comments</th></tr>
<tr><td>Ti</td><td>–0.37</td><td>–1.63</td><td>+3 Oxidation states is more stable</td></tr>
<tr><td>V</td><td>–0.26</td><td>–1.18</td><td>+3 Oxidation states is more stable</td></tr>
<tr><td>Cr</td><td>–0.41</td><td>–0.9</td><td>+3 Oxidation states is more stable</td></tr>
<tr><td>Mn</td><td>1.57</td><td>–1.18</td><td>+2 Oxidation states is more stable</td></tr>
<tr><td>Fe</td><td>0.77</td><td>–0.44</td><td>+2 Oxidation states is more stable</td></tr>
<tr><td>Co</td><td>1.97</td><td>–0.28</td><td>+2 Oxidation states is more stable</td></tr>
<tr><td>Ni</td><td>–</td><td>–0.25</td><td>+3 Oxidation states does not exist for Ni</td></tr>
<tr><td>Cu</td><td>–</td><td>0.34</td><td>+3 Oxidation states does not exist for Cu.
0 Oxidation states is more stable</td></tr>
<tr><td>Zn</td><td>–</td><td>0.76</td><td>+3 Oxidation states does not exist for Zn</td></tr>
</table>
</td>
</tr>
<tr>
<td></td>
<td>Comparative graph of $E^0_{M^{2+}/M}$ and $E^0_{M^{3+}/M^{2+}}$</td>
<td>

The stability of the half-filled <i>d</i> sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their $E^{\ominus}$ values, whereas $E^{\ominus}$ for Ni is related to the highest negative hydration energy.
It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., Ca = –2.87 V, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomisation). Compared to group 2 elements. These reduce their electrode potentials though their hydration enthalpies are large.</td>
</tr>
<tr>
<td>8</td>
<td>Density</td>
<td>Elements with highest densities are
Osmium (Os) = 22.51 g/cm^3 , Iridium (Ir) = 22.61 g/cm^3</td>
</tr>
<tr>
<td>9</td>
<td>Melting and Boiling point</td>
<td>High melting points are attributed to involvement of greater number of electrons from (n–1)d in addition to the ns electrons in inter atomic metallic bonding thus highest for d^5, except for anamolous value for Mn and Tc fall regularly.
m.p. and b.p. are generally very high exceptions
→ Zn (420ºC)
→ Cd (321ºC)
→ Hg liquid at room temperature.
Last of each d-series element behave a typically because the d-shell is complete and d-electrons do not participate in metallic bonding.</td>
</tr>
</table>

<table>
<tr><td></td><td></td><td>They have high enthalpies of atomization, which are maximum at middle of each series , indicates that one unpaired e⁻ per d-orbital is particularly favorable for strong interatomic interaction.
Metals of 2nd and 3rd transition series has higher melting pt. bonding pt. as well as enthalpy of atomization, than corresponding elements of the 1st series this is due to metal-metal bonding of heavy transition metals.
 </td></tr>
<tr><td colspan="3">Section (C) : Magnetic properties, formation of coloured ions.</td></tr>
<tr><td>10</td><td>Magnetic character</td><td>Metals, which have unpaired electrons show paramagnetism.
Spin only magnetic moment μ = $\sqrt{n(n+2)}$ here n = no. of unpaired electron.
Diamagnetic substance is one which is slightly repelled by a magnetic field.
A paramagnetic substance is one which is attracted into a magnetic field.
In paramagnetic substance the magnetic field lines of force travel easier than they travel in vacuum. Thus it can be seen that a paramagnetic material attracts lines of force, if it is free to move, a paramagnetic material will move from a weaker to a stronger part of the field.
Paramagnetic material</td></tr>
<tr><td></td><td>Ferromagnetism</td><td>Ferromagnetic materials may be regarded as special case of paramagnetism in which the moments of individual domains becomes aligned and all points in the same direction. Ferromagnetic materials ⇒ Fe, Co, Ni.</td></tr>
<tr><td colspan="3">Section (D) : Catalytic properties, formation of interstitial compounds, alloy formation.</td></tr>
<tr><td>11</td><td>Catalytic Properties</td><td>The transition metals and their compounds are known for their catalytic activity. This is due to ability to adopt multiple oxidation states and to form complexes.
<table>
<tr><th>Catalyst</th><th>Used</th></tr>
<tr><td>Fe</td><td>Haber's process for manufacture of NH_3.</td></tr>
<tr><td>V_2O_5</td><td>Contact process for H_2SO_4 manufacture.</td></tr>
<tr><td>Pt</td><td>Ostwald's process of nitric acid.</td></tr>
<tr><td>Ni</td><td>Hydrogenation of oils.</td></tr>
<tr><td>$FeSO_4$& H_2O_2</td><td>Fenton's reagent for oxidising alcohol to aldehyde.</td></tr>
<tr><td>Cu</td><td>Dehydrogenation of alcohols</td></tr>
<tr><td>$Al_2(C_2H_5)_6$ + $TiCl_4$</td><td>Ziegler-Natta catalyst in the production of Polyethene.</td></tr>
<tr><td>$FeCl_3$</td><td>For making CCl_4 from CS_2 and Cl_2.</td></tr>
<tr><td>Pt/PtO</td><td>Adams catalyst, used for reduction.</td></tr>
</table></td></tr>
<tr><td>12</td><td>FORMATION</td><td>Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non</td></tr>
</table>

	OF INTERSTITIAL COMPOUNDS	stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal physical and chemical characteristics of these compounds are as follows: (i)They have high melting points, higher than those of pure metals. (ii)They are very hard, some borides approach diamond in hardness. (iii)They retain metallic conductivity. (iv)They are chemically inert.
13	**FORMATION OF ALLOYS**	(i) Transition elements have maximum tendency to form alloys. (ii) The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys. (iii) In the alloys, ratio of component metals is fixed. (iv) These are extremely hard and have high melting point.
	SOME IMPORTANT ALLOY	***Note- Memorize the * marked alloys***

*(a)	Bronze	Cu (75 - 90 %) +Sn (10 - 25 %)
*(b)	Brass	Cu (60 - 80 %) +Zn (20 - 40 %)
(c)	Gun metal	(Cu + Zn + Sn) (87 : 3 : 10)
(d)	German Silver	Cu + Zn + Ni (2 : 1 : 1)
(e)	Bell metal	Cu (80 %) + Sn(20 %)
(f)	Nichrome	(Ni + Cr + Fe)
(g)	Alnico	(Al, Ni,Co)
(h)	Type Metal	Pb + Sn + Sb
(i)	Alloys of steel	
	• Vanadium steel	V (0.2 - 1 %)
	• Chromium steel	Cr (2 - 4 %)
	• Nickel steel	Ni (3 -5 %)
	• Manganese steel	Mn (10 -18 %)
	• Stainless steel	Cr (12 - 14 %)& Ni (2 - 4 %)
	• Tunguston steel	W (10 - 20 %)
(j)	14 Carat Gold	54 % Au + Ag (14 to 30 %) + Cu (12 - 28 %)
(k)	24 Carat Gold	100 %Au
*(l)	Solder	Pb + Sn
(m)	Magnellium	Mg (10%) + Al (90%)
(n)	Duralumin	(Al + Mn + Cu)
*(o)	Artificial Gold	Cu (90 %) + Al (10%)
(p)	Constantan	Cu(60%) + Ni (40%)

% of Carbon in different type of Iron

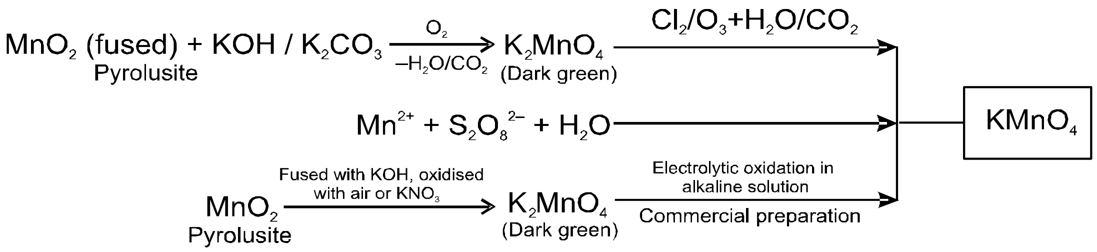
	Name	% of C
(a)	Wrought Iron	0.1 to 0.25
(b)	Steel	0.25 to 2.0
(c)	Cast Iron/Pig Iron	2.6 to 4.3

Section (E) : Important d-block metal compounds

Preparations and properties of important d-Block metal compounds

1. Potassium Permanganatic ($KMnO_4$)

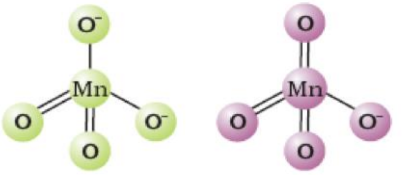
PREPARATION



***Physical Properties**:*

Purple coloured crystalline compound.

Moderately soluble in water at room temperature.



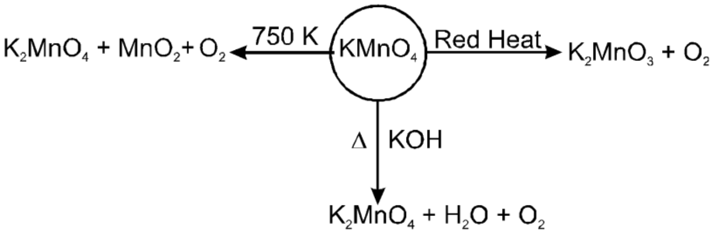
Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

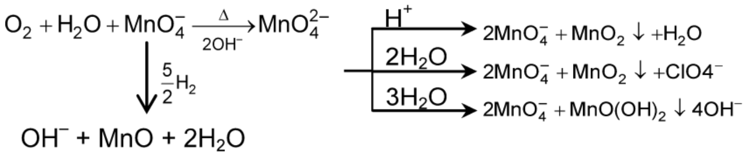
Structure of manganate and permanganate ion.

Chemical Properties

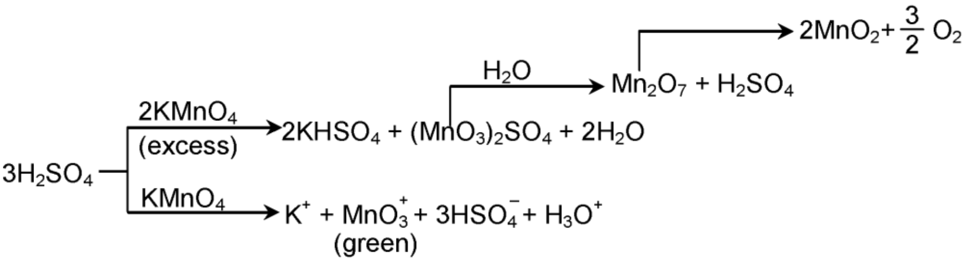
(i) Heating effect



(ii) Reactions with MnO_4^{2-} in dil. alkaline, water and acidic solutions



(iii) with conc. H_2SO_4,



(iv) $KMnO_4$ is a powerful O.A.

Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.
A mixture of sulphur, charcoal and $KMnO_4$ forms an explosive powder. A mixture of oxalic acid and $KMnO_4$ catches fire spontaneous after a few seconds. The same thing happens when glycerine is poured over powdered $KMnO_4$

In alkaline & neutral medium :

In strongly alkaline medium $KMnO_4$ is reduced to manganate.

$$2KMnO_4 + 2KOH\ (conc.) \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

or $e^- + MnO_4^- \longrightarrow MnO_4^{2-}$

However if solution is dilute then K_2MnO_4 is converted in to MnO_2 which appears as a brownish precipitate.

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2[O]$$

or $2e^- + 2H_2O + MnO_4^{2-} \longrightarrow MnO_2 + 4OH^-$

This type of behaviour is shown by $KMnO_4$ itself in neutral medium.

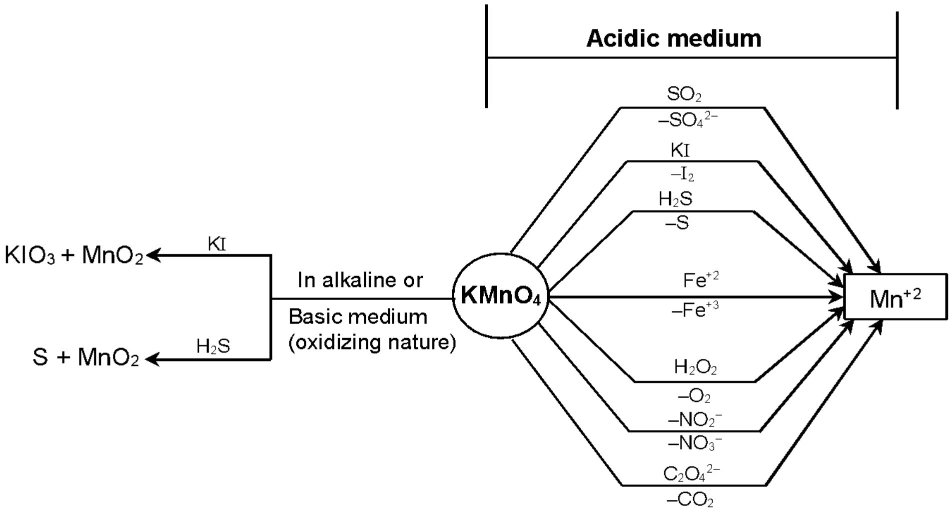
$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$$

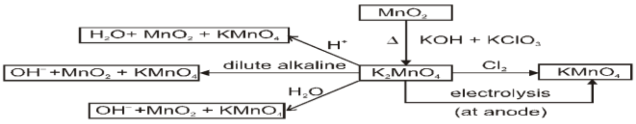
$$\boxed{3e^- + 2H_2O + MnO_4^- \xrightarrow[\text{dilute}]{} \underset{\text{brown ppt}}{MnO_2} \downarrow + H_2O \xleftarrow{-2[O]} 2MnO_4^{2-} + 2H_2O}$$

Note- $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

This medium is used in quantitative (Volumetric) Estimations. The eq. mass of $KMnO_4$ in acidic medium is $= \dfrac{\text{Molecular Mass}}{5}$

Reactions of $KMnO_4$:





Uses : It is used

(i) $KMnO_4$ is used as an oxidising agent in laboratory and industry.

(ii) Alkaline potassium permanganate is called Bayer's reagent. This reagent is used in organic chemistry for the test of unsaturation. $KMnO_4$ is used in the manufacture of saccharin, benzoic acid, acetaldehyde etc.

(iii) $KMnO_4$ is used in qualitative analysis for detecting halides, sulphites, oxalates, etc.

14. POTASSIUM DICHROMATE ($K_2Cr_2O_7$) :

Preparation :

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace.

$$4FeO.Cr_2O_3 + 8Na_2CO_3 \xrightarrow[+7O_2]{\text{Roasting in air}} \underset{\text{(yellow)}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$\big\downarrow 4H_2SO_4$$

$$\underset{\text{(orange)}}{4Na_2CrO_7} + \underset{\text{(Crystalise)}}{4Na_2SO_4} + 4H_2O$$

$$\big\downarrow 8\text{ KCl}$$

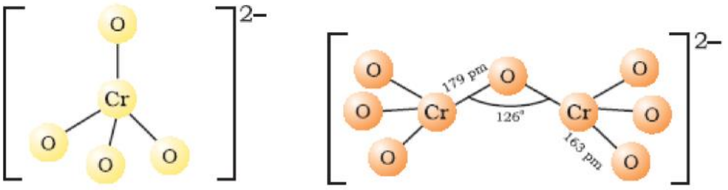
$$\boxed{K_2Cr_2O_7} + 8NaCl$$

Properties

(a) Physical :

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.

Structure of Chromate and Dichromate ion

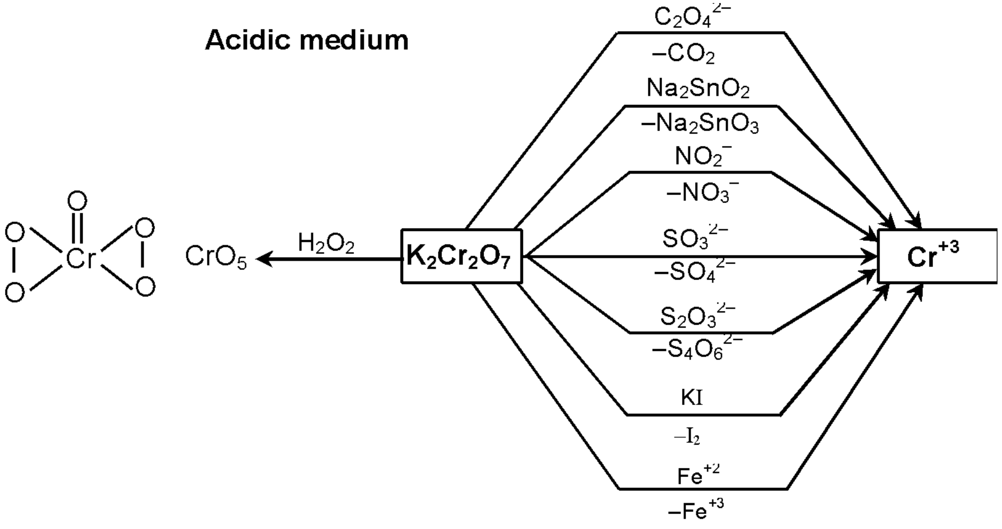


Chromate ion Dichromate ion

(b) Chemical :

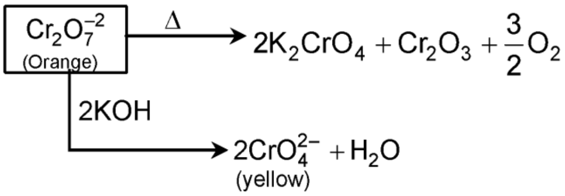
Chemical Properties →

Reactions of $K_2Cr_2O_7$:



Note-$K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.

(i) Effect of heating : On heating strongly, it decomposes liberating oxygen.

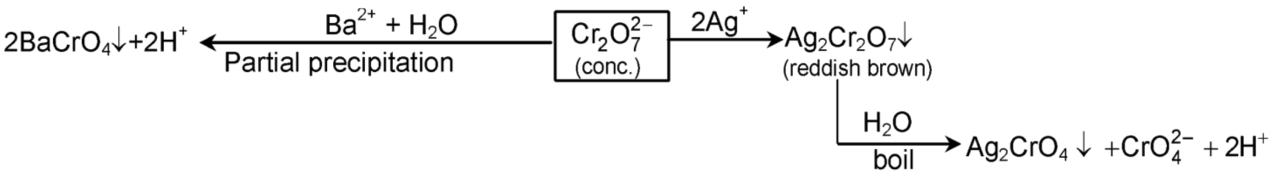


$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium and are interconvertable by altering the pH of solution.

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.

Reaction of potassium dichromate with Ag^+ :



$$Cr_2O_7^{2-} + Ba^{2+} + H_2O \rightleftharpoons 2BaCrO_4\downarrow + 2H^+$$

As strong acid is produced, the precipitation is only partial. But if NaOH or CH_3COONa is added, precipitate becomes quantitative.

Uses : It is used :

(i) as a volumetric reagent in the estimation of reducing agents such as oxalic acid, ferrous ions, iodide ions, etc. It is used as a primary standard.

(ii) for the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.

(iii) in dyeing, chrome tanning, calico printing, photography etc.

(iv) as a cleansing agent for glass ware in the form of chromic acid.

(iv) in leather industry and as an oxidant for preparation of azo compounds

Photography :

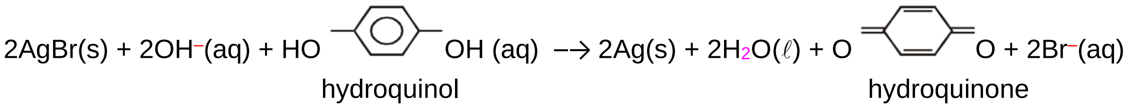
(i) A photographic film consists of a light sensitive emulsion of fine particles (grains) of silver salts in gelatine spread on a clear celluloid strip or a glass plate. AgBr is mainly used as the light sensitive material.

(ii) The film is placed in a camera. When the photograph is exposed, light from the subject enters the camera and is focussed by the lens to give a sharp image on the film. The light starts a photochemical reaction by exciting a halide ion, which loses an electron. The electron moves in a conduction band to the surface of the grain, where it reduces a Ag^+ ion to metallic silver.

$$2AgBr(s) \xrightarrow{\text{light}} 2Ag + Br_2$$

(iii) In modern photography only a short exposure of perhaps 1/100th of a second is used. In this short time, only a few atoms of silver (perhaps 10–50) are produced in each grain exposed to light. Parts of the film which have been exposed to the bright parts of the subject contain a lot of grains with some silver.

(iv) Next the film is placed a developer solution. This is a mild reducing agent, usually containing quinol. Its purpose is to reduce more silver halide to Ag metal. Ag is deposited mainly where there are already some Ag atoms. Thus the developing process intensifies the latent image on the film so it becomes visible.



(v) If the film was brought out into daylight at this stage, the unexposed parts of the emulsion would turn black and thus destroy the picture. To prevent this happening any unchanged silver halides are removed by placing the film in a fixer solution. A solution of sodium thiosulphate is used as fixer. It forms a soluble complex with silver halides.

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

After fixing, the film can safely be brought out into daylight. This is called "negative".
Light is passed through the negative onto a piece of paper coated with AgBr emulsion. This is then developed and fixed in the same way as before.

Section (F) : Lanthanoids and actinoids

<table>
<tr><th colspan="3">f-block elements (JEE-Mains only)</th></tr>
<tr><td colspan="3">Differentiating electrons enters in (n – 2)f subshell.
f-block elements lie on the Bottom portion of periodic table.</td></tr>
<tr><td>S.No.</td><td>Properties</td><td>DISCRIPTION</td></tr>
<tr><td>1.</td><td>General character's</td><td>All the f-block elements are heavy metals.
It shows high melting and boiling point.
The most common oxidation state of these elements is +3.</td></tr>
<tr><td>2.</td><td>No. of elements</td><td>Total number of f-block elements – (28)</td></tr>
<tr><td>3.</td><td>Groups</td><td>IIIB/3rd group is called longest group having 32 elements including 14 Lanthanides and 14 Actinides.
<table>
<tr><td>III B/ 3rd</td><td></td></tr>
<tr><td>Sc</td><td></td></tr>
<tr><td>Y</td><td></td></tr>
<tr><td>La</td><td>Lanthanides (14) Ce_{58} – Lu_{71}</td></tr>
<tr><td>Ac</td><td>Actinides (14) Th_{90} – Lr_{103}</td></tr>
</table></td></tr>
<tr><td>4.</td><td>E.C.</td><td>Lanthanide series $4f^{1-14}\ 5d^{0 \text{ or } 1}\ 6s^{2}$
Actinide series $5f^{1-14}\ 6d^{0 \text{ or } 1}\ 7s^{2}$</td></tr>
<tr><td>5.</td><td>Period</td><td>
<table>
<tr><th>Period</th><th>III B/ 3rd</th><th></th></tr>
<tr><td></td><td>Sc</td><td></td></tr>
<tr><td></td><td>Y</td><td></td></tr>
<tr><td>6th period</td><td>La</td><td>Lanthanides (14) Ce_{58} – Lu_{71}</td></tr>
<tr><td>7th period</td><td>Ac</td><td>Actinides (14) Th_{90} – Lr_{103}</td></tr>
</table></td></tr>
<tr><td>6.</td><td>Inner transition elements</td><td>The elements in which all the three shells that is ultimate (n) penultimate (n– 1) and pre or antipenultimate (n – 2) shell are incomplete are called inner transition elements.Ce_{58} = [Xe] $6s^2$, $5d^1$, $4f^1$
Inner transition elements are divided into two series.</td></tr>
<tr><td></td><td>(i) Lanthanide series or Rare earth elements or Lanthenones</td><td>Ce_{58} – Lu_{71} 14 elements
Lanthanides are found rarely on earth so these are called rare earth metals.
The first element of this series is Cerium and not Lanthanum.
In these elements, last electron enters into 4f subshell.
They are present in IIIB group and 6th period of the periodic table.
Promethium ($_{61}Pm$) is the only lanthanide which is synthetic and radioactive in nature.</td></tr>
<tr><td></td><td>(ii) Actinide series or</td><td>Th_{90} – Lr_{103}14 elements.
All the actinides are radioactive elements.
The first element of this series is Thorium and not Actinium.
In these elements, last electron enters into 5f subshell.</td></tr>
</table>

	Man made elements or Actinones	They are present in IIIB group and 7th period of the periodic table. All the actinides are radioactive in nature. First three elements (Th, Pa, U) are found in nature while others are synthetic in nature. Transuranic actinides are man-made elements (Np_{93} – Lw_{103}) After U_{92} i.e. from Np_{93} onwards elements are called transuranic elements because (i) They are heavier than uranium. (ii) They are derived from uranium by nuclear reactions.

The Lanthanides : The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanide (for which the general symbol Ln is used) are given in Table.

Electronic Configurations : It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level (Table). However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanides) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

Atomic and Ionic Sizes : The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanide contraction). The shielding of one 4 f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number. The cumulative effect of the contraction of the lanthanide series, known as lanthanide contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanide contraction.

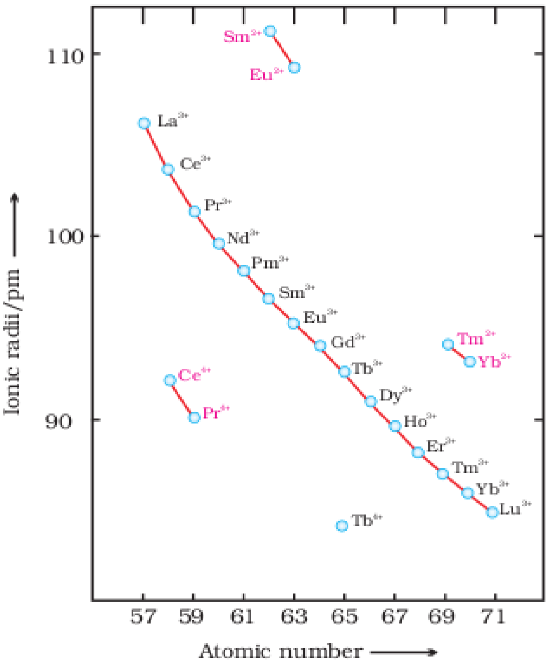


Fig. 8.6: Trends in ionic radii of lanthanoids

Oxidation States : In the lanthanides, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained.
This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^{\ominus}$ value for Ce^{4+}/Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.
Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion.
However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f 14 configuration is a reductant.
Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

Table :- Electronic Configurations and Radii of Lanthanum and Lanthanides

Atomic Number	Name	symbol	Electronic configurations*				Radii/pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^16s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^15d^16s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^36s^2$	$4f^3$	$4f^2$	$4f^1$	182	101

60	Neodymium	Nd	$4f^46s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^56s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^66s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^76f^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^75d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^96s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12}6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^1$	$4f^{14}$	-	-	-

General Characteristics :

All the lanthanides are silvery white soft metals and tarnish rapidly in air.

The hardness increases with increasing atomic number, samarium being steel hard.

Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.

They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Many trivalent lanthanide ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f level.

The lanthanide ions other than the f° 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.

The first ionisation enthalpies of the lanthanides are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium.

A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy consideration (as in 3d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionization enthalpy of lanthanum, gadolinium and lutetium.

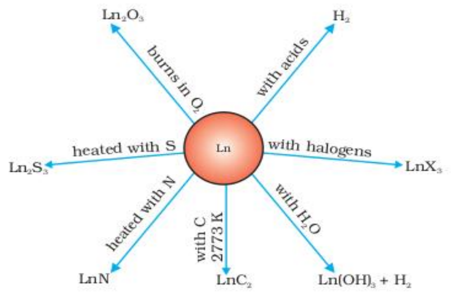


Fig 8.7: Chemical reactions of the lanthanoids.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium.

Values for E^- for the half-reaction:

Ln^{3+} (aq) + $3e^-$ → Ln(s) are in the range of –2.2 to –2.4 V except for Eu for which the value is – 2.0 V. This is, of course, a small variation.

The metals combine with hydrogen when gently heated in the gas.

The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.

They liberate hydrogen from dilute acids and burn in halogens to form halides.

They form oxides M_2O_3 and hydroxides M $(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides.

They are basic like alkaline earth metal oxides and hydroxides.

The best single use of the lanthanides is for the production of alloy steels for plates and pipes. A well known alloy is mischmetall which consists of a lanthanide 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. Mixed oxides of lanthanides are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

The Actinides :

The actinides include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table.

Table : Electronic Configurations and Radii of Actinium and Actinoids

Atomic Number	Name	symbol	Electronic configurations*			Radii/pm	
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^17s^2$	$5f^0$		111	
90	Thorium	Th	$6d^27s^2$	$5f^1$	$5f^0$		99
91	Proctactiniium	Pa	$5f^26d^17s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^67s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^77s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^76d^17s^2$	$5f^7$	$5f^7$	99	88
97	Berkelium	Bk	$5f^97s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10}7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11}7s^2$	$5f^{10}$	$5f^9$	-	-
100	Fermium	Fm	$5f^{12}7s^2$	$5f^{11}$	$5f^{10}$	-	-
101	Mendelevium	Md	$5f^{13}7s^2$	$5f^{12}$	$5f^{11}$	-	-
102	Nobelium	No	$5f^{14}7s^2$	$5f^{13}$	$5f^{12}$	-	-
103	Lawrencium	Lr	$5f^{14}6s^17s^2$	$5f^{14}$	$5f^{13}$	-	-

The actinides are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

Electronic Configurations :

All the actinides are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells.

The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103.

The irregularities in the electronic configurations of the actinides, like those in the lanthanides are related to the stabilities of the f° , f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^77s^2$ and [Rn] $5f^7$ $6d^1$ $7s^2$.

Ionic Sizes :

The general trend in lanthanides is observable in the actinides as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinide contraction (like lanthanide contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

Oxidation States :

There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The known oxidation states of actinides are listed in Table.

Table : Oxidation States of Actinium and Actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

The actinides show in general +3 oxidation state.

The elements, in the first half of the series frequently exhibit higher oxidation states. For example, 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 actinides resemble the lanthanides in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse.

Because the distribution of oxidation states among the actinides is so uneven and so different for the earlier and latter elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

General Characteristics and Comparison with Lanthanides :

The actinide metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanides.

The actinides are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non-metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinides are more complex than those of the lanthanides. Although the variation in the magnetic susceptibility of the actinides with the number of unpaired 5 f electrons is roughly parallel to the corresponding results for the lanthanides, the latter have higher values.

It is evident from the behaviour of the actinides that the ionisation enthalpies of the early actinides, though not accurately known, but are lower than for the early lanthanides. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanides. Because the outer electrons are less firmly held, they are available for bonding in the actinides.

A comparison of the actinides with the lanthanides, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanides is not evident until the second half of the actinide series. However, even the early actinides resemble the lanthanides in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanide and actinide contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanide contraction is more important because the chemistry of elements succeeding the actinides are much less known at the present time.

Some Applications of d- and f-Block Elements :

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni.

TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd.

The ‘silver’ UK coins are a Cu/Ni alloy.