8. TRANSITION AND INNER TRANSITION ELEMENTS

Do you know ?

In which block of the modern perodic table are the transition and inner transition elements placed ?

8.1 Introduction

The transition elements belong to d block of the periodic table. As per IUPAC convention the transition metal atom has an incomplete d-subshell or it give cations with incomplete d subshell. They exhibit properties between those of s and p block elements. The transition elements of the modern periodic table appear as groups 3 to 12 or as four long periods. The (n-1) d-orbital is comprised of successively filled in each element, where 'n' is the ultimate or valence shell. The 3d series is comprised of elements from scandium (Z=21) to zinc (Z=30), 4d series has elements from yttrium (Z=39) to cadmium (Z=48), 5d series from lanthanum (Z=57) to mercury (Z=80) without those from cerium to lutecium, and 6d series has actinium to curium without those fromthorium to lawrentium. The general electronic configuration of transition elements is $(n\text{-}1)d^{1\text{-}10}\ ns^{1\text{-}2}$.

8.2 Position in the periodic table

The transition elements are placed in the periods 4 to 7 and groups 3 to 12 those constitute 3d, 4d, 5d and 6d series (Fig.8.1).

They are placed at the centre with s block on one side and p on the other. The electropositivity, reactivity and other properties show a gradual change from s block to p block through those of the d block elements.

8.3 Electronic configuration

The 3d series begins with Sc (Z = 21) and ends with Zn (Z=30). Argon, Ar is the noble gas preceding to 3d series and its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. Calcium (Z = 20) belonging to 's' block of 4th period has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. Hence 21st electron in scandium (Z = 21) enters in the available 3d orbital. Electronic configuration of Sc is written as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$ or also can be represented as $[Ar]\ 3d^1\ 4s^2$.

Table 8.1 Shows the four transition series elements

Group d series	3	4	5	6	7	8	9	10	11	12
3d	Sc(21)	Ti(22)	V(23)	Cr(24)	Mn(25)	Fe(26)	Co(27)	Ni(28)	Cu(29)	Zn(30)
4d	Y(39)	Zr(40)	Nb(41)	Mo(42)	Tc(43)	Ru(44)	Rh(45)	Pd(46)	Ag(47)	Cd(48)
5d	La(57)	Hf(72)	Ta(73)	W(74)	Re(75)	Os(76)	Ir(77)	Pt(78)	Au(79)	Hg(80)
6d	Ac(89)	Rf(104)	Db(105)	Sg(106)	Bh(107)	Hs(108)	Mt(109)	Ds(110)	Rg(111)	Cn(112)

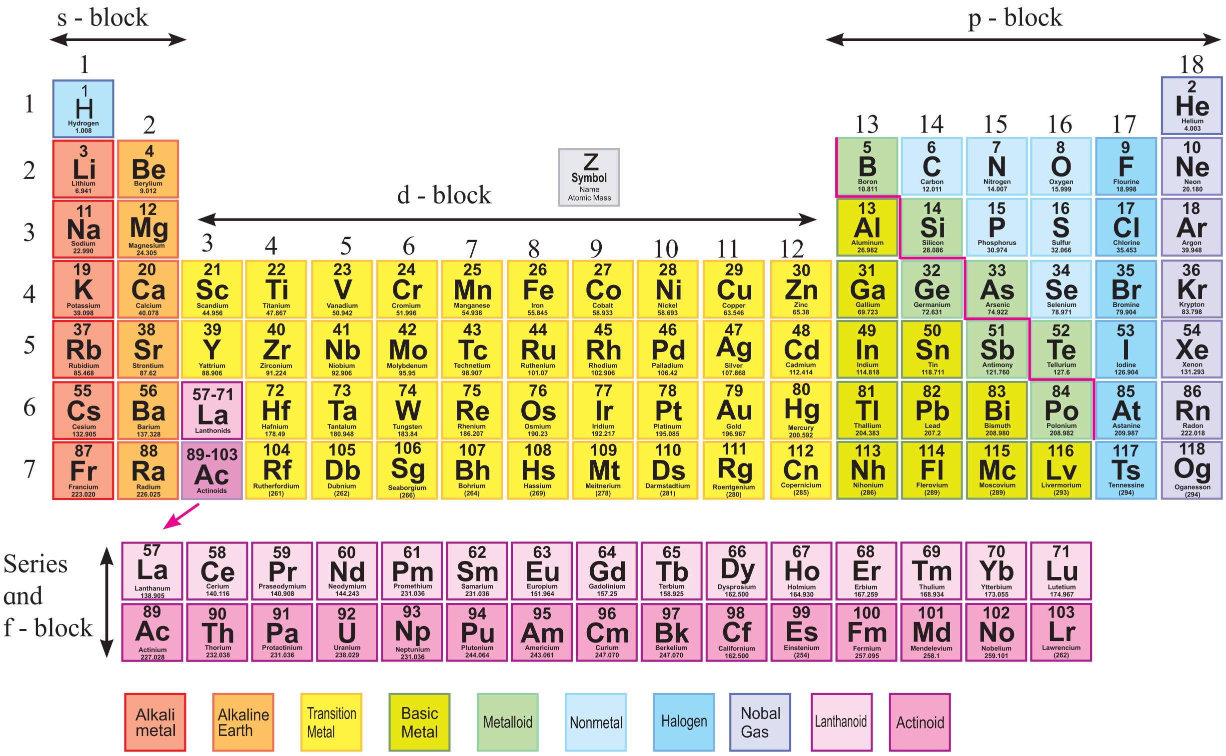


Fig. 8.1 Position of d-block elements in the modern periodic table

The electronic configuration of the elements of 3d series is given in Table 8.2.

Since zinc has completely filled (n - 1)d orbital in the ground state ($3d^{10}, 4s^2$) and ($3d^{10}$) in its common oxidation state +2, it is not regarded as transition element. On the same ground, cadmium and mercury from 4d and 5d series are not considered as transition elements. Copper in the elementary state ($3d^{10}$ $4s^1$) contains filled 3d orbitals but in the +2 oxidation state it has partly filled 3d orbital ($3d^9$), hence copper is a transition element.

General electronic configuration of four series of d-block elements of periodic table can be represented as given below:

i. 3d series : [Ar] $3d^{1-10}$ $4s^2$

ii. 4d series : [Kr] $4d^{1-10}$ $5s^{0-2}$

iii. 5d series : [Xe] $5d^{1-10}$ $6s^2$

iv. 6d series : [Rn] $6d^{1-10}$ $7s^2$

8.3.1 Electronic configuration of chromium and copper

Table 8.2 indicates that the expected electronic configuration of chromium (Z = 24) differs from the observed configuration.

This can be explained on the basis of the concept of additional stability associated with the completely filled and half filled subshells.

Remember...

Any subshell having a half filled or completely filled electronic configuration has extra stability.

The general electronic configuration of the elements of the 3d series is $3d^{1-10}$ $4s^2$ with the exceptions of Cr and Cu. The 3d and 4s orbitals are close in energy and in order to gain extra stability the last electron instead of occupying 4s orbital occupies the 3d orbital that assigns Cr the $3d^5$, $4s^1$ and Cu $3d^{10}$, $4s^1$ configuration.

Table 8.2 Electronic configuration of 3d series of d-block elements

Elements	Symbol	At. No.	Expected electronic configuration	Observed electronic configuration
Scandium	Sc	21	[Ar] $3d^1 4s^2$	[Ar] $3d^1 4s^2$
Titanium	Ti	22	[Ar] $3d^2 4s^2$	[Ar] $3d^2 4s^2$
Vanadium	V	23	[Ar] $3d^3 4s^2$	[Ar] $3d^3 4s^2$
Chromiun	Cr	24	[Ar] $3d^4 4s^2$	[Ar] $3d^5 4s^1$
Manganese	Mn	25	[Ar] $3d^5 4s^2$	[Ar] $3d^5 4s^2$
Iron	Fe	26	[Ar] $3d^6 4s^2$	[Ar] $3d^6 4s^2$
Cobalt	Co	27	[Ar] $3d^7 4s^2$	[Ar] $3d^7 4s^2$
Nickel	Ni	28	[Ar] $3d^8 4s^2$	[Ar] $3d^8 4s^2$
Copper	Cu	29	[Ar] $3d^9 4s^2$	[Ar] $3d^{10} 4s^1$
Zinc	Zn	30	[Ar] $3d^{10} 4s^2$	[Ar] $3d^{10} 4s^2$

Use your brain power

Fill in the blanks with correct outer electronic configurations.

2^{nd} series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
valence shell electronic configuration	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$		$4d^6 5s^1$		$4d^8 5s^1$	$4d^{10} 5s^0$		$4d^{10} 5s^2$

3rd series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
valence shell electronic configuration	$5d^1 6s^2$		$5d^3 6s^2$	$5d^4 6s^2$		$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$		$5d^{10} 6s^2$

4^{th} series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uvb
Z	89	104	105	106	107	108	109	110	111	112
valence shell electronic configuration	$6d^1 7s^2$	$6d^2 7s^2$		$6d^4 7s^2$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$		$6d^{10} 7s^2$

Table 8.3: Oxidation states of first transition series elements

Elements	Outer elecronic configuration	Oxidation states	Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3	Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Ti	$3d^2 4s^2$	+2, +3, +4	Co	$3d^7 4s^2$	+2, +3, +4, +5
V	$3d^3 4s^2$	+2, +3, +4, +5	Ni	$3d^{10} 4s^2$	+2, +3, +4
Cr	$3d^5 4s^1$	+2, +3, +4, +5, +6	Cu	$3d^{10} 4s^1$	+1, +2
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7	Zn	$3d^{10} 4s^2$	+2

Remember...

Electronic configuration of Cr is [Ar] $3d^5\ 4s^1$ and Cu is : [Ar]$3d^{10}$, $4s^1$.

8.4 Oxidation states of first transition series

One of the notable features of transition elements is the great variety of oxidation states they show in their compounds. Table 8.3 lists the common oxidation states of the first row transition elements.

Can you tell ?

Which of the first transition series elements shows the maximum number of oxidation states and why?

Which elements in the 4d and 5d series will show maximum number of oxidation states?

Loss of 4s and 3d electrons progressively leads to formation of ions. The transition elements display a variety of oxidation states in their compounds. Loss of one 4s electron leads to the formation of $M^{\oplus}$ ion, loss of two 4s electrons gives a $M^{2\oplus}$ ion while loss of unpaired 3d and 4s electrons gives $M^{3\oplus}$, $M^{4\oplus}$ ions and so on. Some examples are as shown in Table 8.4

Try this...

Write the electronic configuration of $Mn^{6\oplus}$, $Mn^{4\oplus}$, $Fe^{4\oplus}$, $Co^{5\oplus}$, $Ni^{2\oplus}$

From Table 8.3 it is clear that as the number of unpaired electrons in 3d orbitals increases, the number of oxidation states shown by the element also increases. Scandium has only one unpaird electron. It shows two oxidation states while manganese with 5 unpaired d electrons shows six different oxidation states.

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, shows oxidation states from +2 to +7.

8.5 Physical properties of first transition series : All transition elements are metals and show properties that are characteristic of metals. They are hard, lustrous, malleable, ductile and form alloys with other metals. They are good conductors of heat and electricity. Except Zn, Cd, Hg and Mn, all the other transition elements have one or more typical metallic structures at ambient temperature. These transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. They possess high melting and boiling points.

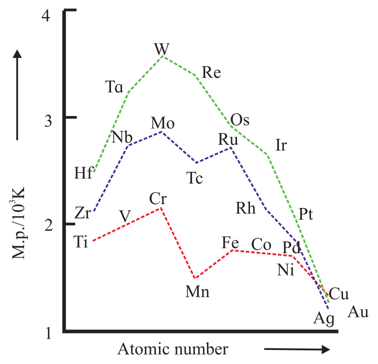


Fig. 8.2 : Trends in melting points of transition elements

Table 8.4: Electronic configuration of various ions of 3d elements

Elements Atomic no :	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30
Species	**Valence shell Electronic Configuration**									
M	$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^2$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^1\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$
$M^{\oplus}$	$3d^1\ 4s^1$	$3d^2\ 4s^1$	$3d^3\ 4s^1$	$3d^5$	$3d^5\ 4s^1$	$3d^6\ 4s^1$	$3d^7\ 4s^1$	$3d^8\ 4s^1$	$3d^{10}\ 4s^0$	$3d^{10}\ 4s^1$
$M^{2\oplus}$	$3d^2$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
$M^{3\oplus}$	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	-	-

8.6 Trends in atomic properties of the first transition series

8.6.1 Atomic and ionic radii

Atomic radii of the elements of the transition series decrease gradually from left to right (Fig. 8.3 and Table 8.5). As we move across a transition series from left to right the nuclear charge increases by one unit at a time. The last filled electron enters a penultimate (n-1)d subshell. However, d orbitals in an atom are less penetrating or more diffused and, therefore d electrons offer smaller screening effect. The result is that effective nuclear charge also increases as the atomi number increases along a transition series. Hence the atomic radii decrease gradually across a transition series from left to right.

The explanation for the minor variation in atomic radii within a particular transition series is out of the scope of this textbook.

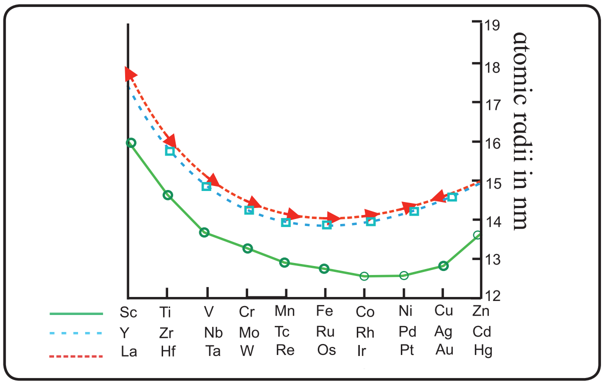


Fig. 8.3 : Trends in atomic radii of d block elements

Ionic radii of transition elements show the same trend as of the atomic radii (Table 8.5)

The elements of first transition series show variable oxidation states. The trends in ionic radii, thus, can be studied with (i) elements having same oxidation state or (ii) considering various oxidation states of the same element.

(i) For the same oxidation state, with an increase of nuclear charge a gradual decrease in ionic radii was observed. The trend is pronounced for the divalent ions of the first transition series ($Cr^{2\oplus}$ - 82 pm, $Cu^{2\oplus}$ - 72 pm).

Table 8.5 Atomic properties of first transition series elements

Element (M)	Atomic number (Z)	Density (g/cm^3)	Atomic/ionic radius (pm)			Ionisation enthalpy (kJ/mol)
			M	M$^{2\oplus}$	M$^{3\oplus}$	
Sc	21	3.43	164	-	73	631
Ti	22	4.1	147	-	67	656
V	23	6.07	135	79	64	650
Cr	24	7.19	129	82	62	653
Mn	25	7.21	127	82	65	717
Fe	26	7.8	126	77	65	762
Co	27	8.7	125	74	61	758
Ni	28	8.9	125	70	60	736
Cu	29	8.9	128	73	-	745
Zn	30	7.1	137	75	-	906

(ii) The oxidation states of the same element shows difference of one unit such as $M^{\oplus}$, $M^{2\oplus}$, $M^{3\oplus}$, $M^{4\oplus}$ and so on. With higher oxidation state the effective nuclear charge also increases and hence, decrease of ionic radii can be observed from $M^{2\oplus}$ to $M^{3\oplus}$ (Table 8.5). Ionic radii of transition elements are smaller than ionic radii of representative elements of the same period.

8.6.2 Ionisation Enthalpy : The ionisation enthalpies of transition elements are intermediate between those of s-block or p-block elements. This suggests that transition elements are less electropositive than elements of group 1 and 2. Depending on the conditions, they form ionic or covalent bonds. Generally in the lower oxidation states these elements form ionic compounds while in the higher oxidation states they form covalent compounds.

Ionisation enthalpies shown in Table 8.6 reveal that for a given element there is substantial increase from the first ionisation enthalpy IE_1 to the third ionisation enthalpy IE_3.

As we move across the transition series, slight variation is observed in the successive enthalpies IE_1, IE_2, IE_3 of these elements (Table 8.6).

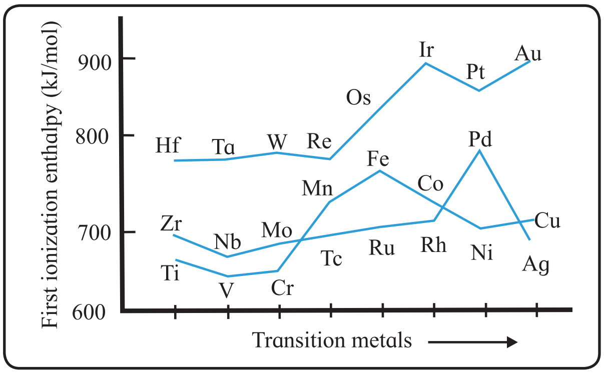


Fig. 8. 4: Trends in first ionisation enthalpies of d block elements

The atoms of elements of third transition series possess filled 4f- orbitals. 4f orbitals show poor shielding effect on account of their peculiar diffused shape. As a result, the valence electrons experience greater nuclear attraction. A greater amount of energy is required to ionize elements of the third transition series. The ionisation enthalpies of the elements of the third transition series are, therefore much higher than the first and second series (Fig.8.4).

8.6.3 Metallic character : Low ionization enthalpies and vacant d orbitals in the outermost shell are responsible for the metallic character of the transition elements. These favour the formation of metallic bonds and thus these elements show typical metallic properties. The hard nature of these elements suggests the formation of covalent bonds in them. This is possible due to the presence of unpaired (n-1)d electrons in these elements.

Nearly all transition metals have simple hexagonal closed packed (hcp), cubic closed packed (ccp) or body centered cubic (bcc) lattices which are characteristic of true metals (You have learnt more about this in Chapter 1).

Remember...

Hardness, high melting points and metallic properties of the transition elements indicate that the metal atoms are held strongly by metallic bonds with covalent character.

Table 8.6 Ionisation enthalpies of first transition series elements

Element IE	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE_1	632	659	650	652	717	762	756	736	744	906
IE_2	1245	1320	1376	1635	1513	1563	1647	1756	1961	1736
IE_3	2450	2721	2873	2994	3258	2963	3237	3400	3560	3838

(IE = Ionisation Enthalpy in kJ/mol)

In all the transition series the melting points steadily increase upto d^5 configuration. Cr, Mo and W show highest melting points in their respective series. Mn and Tc display anomalous values of melting points. After this with increasing atomic number the melting point decreases regularly.

8.6.4 Magnetic Properties :

Can you recall ?

1. What happens when magnetic field is applied to substances ?
2. What is meant by the terms paramagnetism and diamagnetism ?

The compounds of transition metals exhibit magnetic properties due to the unpaired electrons present in their atoms or ions. When a magnetic field is applied, substances which are attracted towards the applied magnetic field are called paramagnetic, while the ones which are repelled are called diamagnetic.

Some substances are attracted very strongly and these are called ferromagnetic substances.

Remember...

Paramagnetism and ferromagnetism arises due to presence of unpaired electrons in a species.

When all electron spins are paired, the compound becomes diamagnetic.

Among transition metals Fe, Co, Ni are ferromagnetic. When magnetic field is applied externally all the unpaired electrons in these metals and their compounds align in the direction of the applied magnetic field. Due to this the magnetic susceptibility is enhanced. These metals can be magnetized, that is, they aquire permanent magnetic moment.

Try this...

Pick up the paramagnetic species $Cu^{1\oplus}$, $Fe^{3\oplus}$, $Ni^{2\oplus}$, $Zn^{2\oplus}$, $Cd^{2\oplus}$, $Pd^{2\oplus}$.

Each unpaired electron gives rise to a small magnetic field (magnetic moment) due to its spin angular momentum and orbital angular momentum. In case of the first row transition elements, the contribution from the orbital angular momentum is quenched and hence, can be neglected. The spin-only formula for magnetic moment is :

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

where n is the number of unpaired electrons and μ is the magnetic moment expressed in Bohr Magneton (BM). A single unpaired electron has magnetic moment $\mu = 1.73$ BM.

From the magnetic moment (μ) measurements of the metal complexes of the first row transition elements, the number of unpaired electrons can be calculated, with the use of spin-only formula. As magnetic moment is directly related to number of unpaired electrons, value of μ will vary directly with the number of unpaired electrons.

Try this...

What will be the magnetic moment of transition metal having 3 unpaired electrons ?
a. equal to 1.73 BM,
b. less than 1.73 BM or
c. more than 1.73 BM ?

Magnetic moments are determined experimentally in solution or in solid state where the central metal is hydrated or bound to ligands. A slight difference in the calculated and observed values of magetic moments thus can be noticed.

Use your brain power

A metal ion from the first transition series has two unpaired electrons. Calculate the magnetic moment.

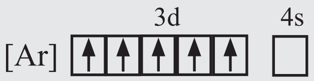
Table 8.7 gives the calculated and observed magnetic moments of cations of 3d series.

Table 8.7 Magnetic moments of ions of first transition series elements (values in BM)

Ion	Outer electronic configuration	Number of unpaired electrons	Calculated value of magnetic moment	Experimental value
$Sc^{3\oplus}$	$3d^0$	0	0	0
$Ti^{3\oplus}$	$3d^1$	1	1.73	1.75
$V^{3\oplus}$	$3d^2$	2	2.84	2.76
$Cr^{3\oplus}$	$3d^3$	3	3.87	3.86
$Cr^{2\oplus}$	$3d^4$	4	4.90	4.80
$Mn^{2\oplus}$	$3d^5$	5	5.92	5.96
$Fe^{2\oplus}$	$3d^6$	4	4.90	5.3-5.5
$Co^{2\oplus}$	$3d^7$	3	3.87	4.4-5.2
$Ni^{2\oplus}$	$3d^8$	2	2.84	2.9-3.0, 4.0
$Cu^{2\oplus}$	$3d^9$	1	1.73	1.8-2.2
$Zn^{2\oplus}$	$3d^{10}$	0	0	0

Problem : Calculate the spin only magnetic moment of divalent cation of a transition metal with atomic number 25.

Solution : For element with atomic number 25, electronic configuration for its divalent cation will be



There are 5 unpaired electrons, so n = 5.

$$\therefore\ \mu = \sqrt{5(5+2)} = 5.92\ \text{BM}$$

Try this...

Calculate the spin only magnetic moment of divalent cation of element having atomic number 27.

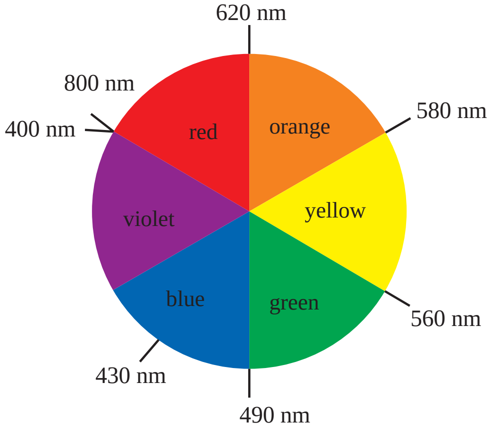
In second and third transition series, orbital angular moment is significant. Therefore, the simple spin only formula is not useful and more complicated equations have to be employed to determine magnetic moments. The magnetic moments further are found to be temperature dependent.

8.6.5 Colour : A substance appears coloured if it absorbs a portion of visible light. The colour depends upon the wavelength of absorption in the visible region of electromagnetic radiation.

Can you tell ?

Compounds of s and p block elements are almost white. What could be the absorbed radiation : uv or visible ?

The ionic and covalent compounds formed by the transition elements are coloured. Transition elements contain unpaired electrons in their d orbitals. When the atoms are free or isolated, the five d orbitals are degenerate; or have the same energy. In complexes, the metal ion is surrounded by solvent molecules or ligands. The surrounding molecules affect the energy of d orbitals and their energies are no longer the same [You will learn more about this in Chapter 9]. As the principal quantum number of ‘d’ orbitals is the same, the amount of energy required for transition of electron from one d orbital to another is quite small. The small energy required for this transition is available by absorption of radiation having certain wavelength from the visible region. Remaining light is transmitted and the observed colour of the compound corresponds to the complimentary colour of light absorbed. That means, if red light is absorbed then the transmitted light contains excess of other colours in the spectrum, in particular blue, so the compound appears blue. The ions having no unpaired electrons are colorless for example $Cu^{\oplus}(3d^{10})$; $Ti^{4\oplus}(3d^{0})$. Table 8.8 enlists colours of 3d transition metal ions.



Let us see how colour of the transition metal ion depends upon ligand and geometry of the complex formed by metal ion.

When cobalt chloride ($Co^{2\oplus}$) is dissolved in water, it forms a pink solution of the complex $[Co(H_2O)_6]^{2\oplus}$ which has octahedral geometry. But when this solution is treated with concentrated hydrochloric acid, it turns deep blue. This change is due to the formation of another complex $[CoCl_4]^{2\ominus}$ which has a tetrahedral structure.

$$[Co(H_2O)_6]^{2\oplus} + 4Cl^{\ominus} \longrightarrow [CoCl_4]^{2\ominus} + 6H_2O$$

Thus the colour of a transition metal ion relates to

1. presence of unpaired d electrons
2. d - d transitions
3. nature of ligands attached to the metal ion
4. geometry of the complex formed by the metal ion

Do you know ?

Colour of transition metal ions may arise due to a charge transfer. For example, $MnO_4^{\ominus}$ ion has an intense purple colour in solution. In $MnO_4^{\ominus}$, an electron is momentarily transferred from oxygen (O) to metal, thus momentarily changing $O^{2\ominus}$ to $O^{\ominus}$ and reducing the oxidation state of manganese from +7 to +6. For charge transfer transition to take place, the energy levels of the two different atoms involved should be fairly close. Colours of $Cr_2O_7^{2\ominus}$, $CrO_4^{\ominus}$, Cu_2O and Ni-DMG (where DMG = dimethyl glyoxime) complex thus can be explained through charge transfer transitions.

8.6.6 Catalytic Properties : Transition metals and their compounds exhibit good catalytic properties. They have proven to be good homogeneous and heterogeneous catalysts. Partly because of their ability to participate in different oxidation-reduction steps of catalytic reactions.

Table 8.8 Colour of 3d transition metal ions

Ion	Outer electronic configuration	Number of unpairedelectrons	Colour
$Sc^{3\oplus}$	$3d^{0}$	0	Colourless
$Ti^{3\oplus}$	$3d^{1}$	1	Purple
$Ti^{4\oplus}$	$3d^{0}$	0	Colourless
$V^{3\oplus}$	$3d^{2}$	2	Green
$Cr^{3\oplus}$	$3d^{3}$	3	violet
$Mn^{2\oplus}$	$3d^{5}$	5	Light pink
$Mn^{3\oplus}$	$3d^{4}$	4	Violet
$Fe^{2\oplus}$	$3d^{6}$	4	Pale green
$Fe^{3\oplus}$	$3d^{5}$	5	Yellow
$Co^{2\oplus}$	$3d^{7}$	3	Pink
$Ni^{2\oplus}$	$3d^{8}$	2	Green
$Cu^{2\oplus}$	$3d^{9}$	1	Blue
$Cu^{\oplus}$	$3d^{10}$	0	Colourless
$Zn^{2\oplus}$	$3d^{10}$	0	Colourless

These steps involve changes in the oxidation states of these metal ions. Compounds of Fe, Co, Ni, Pd, Pt, Cr, etc. are used as catalysts in a number of reactions. Their compounds enhance the rate of the chemical reactions.

In homogeneous catalysis reactions, the metal ions participate by forming unstable intermediates. In heterogeneous catalysis reactions on the other hand, the metal provides a surface for the reactants to react.

Examples :

1. MnO_2 acts as a catalyst for decomposition of $KClO_3$.
2. In manufacture of ammonia by Haber's process Mo/Fe is used as a catalyst.
3. Co-Th alloy is used in Fischer Tropsch process in the synthesis of gasoline.
4. Finely divided Ni, formed by reduction of the heated oxide in hydrogen is an extremely efficient catalyst in hydrogenation of ethene to ethane at 140 ^{0}C.

$$H_2C = CH_2 + H - H \xrightarrow[\text{Ni, 140 }^0\text{C}]{\Delta} H_3C - CH_3$$

Commercially, hydrogenation with nickel as catalyst is used to convert inedible oils into solid fat for the production of margarine.

5. In the contact process of industrial production of sulfuric acid; sulphur dioxide and oxygen from the air react reversibly over a solid catalyst of platinised asbestos.

$$2SO_2 + O_2 \underset{\text{asbestos}}{\overset{\text{platinised}}{\rightleftharpoons}} 2SO_3$$

6. Carbon dioxide and hydrogen are formed by reaction of the carbon monoxide and steam at about 500 ^{0}C with an Fe-Cr catalyst.

$$CO + \underset{\text{(steam)}}{H_2O} \underset{\text{catalyst}}{\overset{\text{Fe-Cr}}{\rightleftharpoons}} CO_2 + H_2$$

8.6.7 Formation of interstitial compounds

When small atoms like hydrogen, carbon or nitrogen are trapped in the interstitial spaces within the crystal lattice, the compounds formed are called interstitial compounds. Sometimes sulphides and oxides are also trapped in the crystal lattice of transition elements. Steel and cast iron are examples of interstitial compounds of carbon and iron. Due to presence of carbon, the malleability and ductility of iron is reduced while its tenacity increases.

Some properties of interstitial compounds

i. They are hard and good conductors of heat and electricity.

ii. Their chemical properties are similar to the parent metal.

iii. Their melting points are higher than the pure metals.

iv. Their densities are less than the parent metal.

v. The metallic carbides are chemically inert and extremely hard as diamond.

vi. Hydrides of transition metals are used as powerful reducing agents.

Remember...

- Tungsten carbide is used for cutting tools.
- Iron carbide is used in manufacture of steel.

8.6.8 Formation of Alloys

Can you recall ?

- What is an alloy ?
- Do atomic radii of 3d transition elements differ largely ?

Transition metals form alloys where atoms of one metal are distributed randomly in the lattice of another metal. The metals with similar radii and similar properties readily form alloys.

Alloys are classified into **ferrous and non-ferrous**.

Ferrous alloys have atoms of other elements distributed randomly in atoms of iron in the mixture. As percentage of iron is more, they are termed ferrous alloys eg. nickel steel, chromium steel, stainless steel etc. All steels have 2% carbon.

Non-ferrous alloys are formed by mixing atoms of transition metal other than iron with a non transition element. eg. brass, which is an alloy of copper and zinc. Ferrous and non-ferrous alloys are of industrial importance.

Uses of alloys

- Bronze, an alloy of copper and tin is tough, strong and corrosion resistant. It is used for making statues, medals and trophies.
- Cupra-nickel, an alloy of copper and nickel is used for making machinary parts of marine ships, boats. For example, marine condenser tubes.
- Stainless steels are used in the construction of the outer fuselage of ultra-high speed air craft.
- Nichrome an alloy of nickel and chromium in the ratio 80 : 20 has been developed specifically for gas turbine engines.
- Titanium alloys withstand stress up to high temperatures and are used for ultra-high speed flight, fire proof bulkheads and exhaust shrouds.

8.7 Compounds of Mn and Cr ($KMnO_4$ and $K_2Cr_2O_7$)

Remember...
Both $KMnO_4$ and $K_2Cr_2O_7$ are strong oxidising agents.

8.7.1 Preparation of potassium permaganate

i. Chemical oxidation

When a finely divided manganese dioxide (MnO_2) is heated strongly with fused mass of caustic potash (KOH) and an oxidising agent, potassium chlorate ($KClO_3$), dark green potassium manganate, K_2MnO_4 is formed.

$$3MnO_2 + 6KOH + KClO_3 \xrightarrow{\Delta} 3K_2MnO_4 + KCl + 3H_2O$$

In neutral or acidic medium the green potassium manganate disproportionates to $KMnO_4$ and MnO_2.

$$3K_2MnO_4 + 4CO_2 + 2H_2O \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

$$3MnO_4^{2\ominus} + 4H^{\oplus} \longrightarrow 2MnO_4^{\ominus} + MnO_2 + 2H_2O$$

The liquid is filtered through glass wool or sintered glass and evaporated until crystallisation occurs. Potassium permanganate forms small crystals which are almost black in appearance.

ii. Electrolytic oxidation

In electrolytic oxidation, alkaline solution of manganate ion is electrolysed between iron electrodes separated by a diaphragm. Overall reaction is as follows :

$$2K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

The oxygen evolved at the anode converts manganate to permanganate.

The solution is filtered and evaporated to get **deep purple black coloured** crystals of $KMnO_4$.

8.7.2 Chemical properties of $KMnO_4$:

a. In acidic medium :

The oxidizing reactions of $KMnO_4$ in acidic medium

i. Oxidation of iodide to iodine :

$$2MnO_4^{\ominus} + 10\ I^{\ominus} + 16H^{\oplus} \longrightarrow 2Mn^{2\oplus} + 8H_2O + I_2$$

ii. Oxidation of $Fe^{2\oplus}$ to $Fe^{3\oplus}$

$$MnO_4^{\ominus} + 5Fe^{2\oplus} + 8H^{\oplus} \longrightarrow 5Fe^{3\oplus} + Mn^{2\oplus} + 4H_2O$$

iii. Oxidation of H_2S

$$H_2S \longrightarrow 2H^{\oplus} + S^{2\ominus}$$

$$5S^{2\ominus} + 2MnO_4^{\ominus} + 16H^{\oplus} \longrightarrow 2Mn^{2\oplus} + 5S + 8H_2O$$

iv. Oxidation of oxalic acid :

$$2MnO_4^{\ominus} + 5H_2C_2O_4 + 6H^{\oplus} \longrightarrow 2Mn^{2\oplus} + 10CO_2 + 8H_2O$$

b. In neutral or weakly alkaline medium :

i. Oxidation of iodide $I^{\ominus}$ to iodate $IO_3^{\ominus}$.

$$2MnO_4^{\ominus} + H_2O + I^{\ominus} \longrightarrow 2MnO_2 + 2OH^{\ominus} + IO_3^{\ominus}$$

ii. Thiosulphate ($S_2O_3^{2\ominus}$) is oxidised to sulphate ($SO_4^{2\ominus}$)

$$8MnO_4^{\ominus} + 3S_2O_3^{2\ominus} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2\ominus} + 2OH^{\ominus}$$

iii. Manganous salt is oxidised to MnO_2.

$$2MnO_4^{\ominus} + 3Mn^{2\oplus} + 2H_2O \longrightarrow 5MnO_2 + 4H^{\oplus}$$

8.7.3 Uses of $KMnO_4$:

- An antiseptic.
- For unsaturation test in laboratory.
- In volumetric analysis of reducing agents.
- For detecting halides in qualitative analysis.
- Powerful oxidising agent in laboratory and industry.

8.7.4 $K_2Cr_2O_7$: Preparation of potassium dichromate

In the industrial production, finely powdered chromite ore ($FeOCr_2O_3$) is heated with anhydrous sodium carbonate (Na_2CO_3) and a flux of lime in air in a reverbatory furnace.

$$4(FeO.Cr_2O_3) + 8Na_2CO_3 + 7O_2 \xrightarrow{\Delta} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

Sodium chromate (Na_2CrO_4) formed in this reaction is then extracted with water and treated with concentrated sulphuric acid to get sodium dichromate and hydrated sodium sulphate :

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + 2NaCl + Na_2Cr_2O_7.H_2O$$

Addition of potassium chloride to concentrated solution of sodium dichromate precipitates less soluble orange-red coloured potassium dichromate, $K_2Cr_2O_7$.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

8.7.5 Chemical properties of $K_2Cr_2O_7$:

i. Oxidation of I^- from aq. solution of KI by acidified $K_2Cr_2O_7$ gives I_2. Potassium dichromate is reduced to chromic sulphate. Liberated I_2 turns the solution brown.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

ii. When H_2S gas is passed through acidified $K_2Cr_2O_7$ solution, H_2S is oxidised to pale yellow precipitate of sulphur. Simultaneously potassium dichromate is reduced to chromic sulphate, which is reflected as colour change of solution from orange to green.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

8.8 Common properties of d block elements

Physical properties

i. All d block elements are lustrous and shining.

ii. They are hard and have high density.

iii. Have high melting and boiling points.

iv. Are good electrical and thermal conductors.

v. Have high tensile strength and malleability.

vi. Can form alloys with transition and non transition elements.

vii. Many metals and their compounds are paramagnetic.

viii. Most of the metals are efficient catalysts.

Chemical properties

i. All d block elements are electropositive metals.

ii. They exhibit variable valencies and form colored salts and complexes.

iii. They are good reducing agents.

iv. They form insoluble oxides and hydroxides.

v. Iron, cobalt, copper, molybdenum and zinc are biologically important metals

vi. catalyse biological reactions.

Differences : Although most properties exhibited by d block elements are similar, the elements of first row differ from second and third rows in stabilization of higher oxidation states in their compounds.

For example, Mo(V) and W (VI) compounds are more stable than Cr(VI) and Mn (VIII).

Highest oxidation state for elements of first row is +7, and in the case of 3rd row +8 oxidation state as in (RuO_4) and (OsO_4).

Can you recall ?

- How are metals found in nature?
- Name two the salts of metals that are found in nature.

Internet my friend

1. Collect the information on different steps involved in the extraction of metals from their ores.
2. Collect information about place where deposits of iron ores are found.

8.9 Extraction of metals

Most metals are found in the earth's crust in the form of their salts, such as carbonates, sulphates, sulphides and oxides.

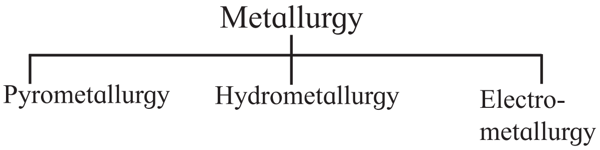
A few metals are nonreactive and occur in the free state in the earth's crust, for example, silver, gold, and platinum.

Mineral : A naturally occuring substance found in the earth's crust containing inorganic salts, solids, siliceous matter etc, is called a mineral.

The mineral which contains high percentage of the metal and from which the metal can be extracted economically is called an **ore**.

Table 8.9 : List of minerals and ores of some transition metals.

Metals	Mineral	Ore
Iron	Haematite Fe_2O_3 Magnetite Fe_3O_4 Limonite $2Fe_2O_3, 3H_2O$ Iron pyrites FeS_2 Siderite $FeCO_3$	Haematite
Copper	Chalcopyrite $CuFeS_2$ Chalcocite Cuprite Cu_2O	Chalcopyrite Chalcocite
Zinc	Zinc blende ZnS Zinccite ZnO Calamine $ZnCO_3$	Zinc blende



8.9.1 Metallurgy :

Commercial extraction of metals from their ores is called metallurgy. Different methods are used for their extraction depending on the nature of a metal and its ore.

a. Pyrometallurgy: A process in which the ore is reduced to metal at high temperature using reducing agents like carbon, hydrogen, aluminium, etc. is called pyrometallurgy.

b. Hydrometallurgy : The process of extracting metals from the aqueous solution of their salts using suitable reducing agent is called hydrometallurgy.

c. Electrometallurgy : A process in which metal is extracted by electrolytic reduction of molten (fused) metallic compound is called electrometallurgy.

Steps Involved in Process of Extraction

Do you know ?

1. Extraction of iron has been known to Indians since 700 BC. Indian blacksmiths also knew the thermo-mechnical process for forging. During Archaeological studies in Harappa, Madhya Pradesh different iron objects belonging to middle iron age were found.
2. Famous iron pillar in Delhi is 1300 years old and is free of rust till to date.

Concentration : After mining the ore from the earth's crust it is subjected to concentration. In this step, impurities termed as gangue are removed from the ore and the ore gets concentrated.

The sand, mud and other unwanted impurities which remain mixed with the ore deposit are called **gangue**.

During the process of concentration, the ore is separated from the gangue material using different methods such as washing, hydraulic classification, magnetic separation, froth floatation, etc.

The method chosen for concentration depends upon the nature of the ore.

8.9.2 Extraction of Iron from Haematite ore using Blast furnace

Do you know ?

Iron is the fourth most abundant element in the earth's crust

Composition of Haematite ore :

$$Fe_2O_3 + \underbrace{SiO_2 + Al_2O_3}_{\text{Gangue}} + \text{phosphates}$$

Internet my friend

Find percentage of oxygen, silicon, aluminium and iron in earth's crust.

Iron is extracted from haematite by its reduction using coke and limestone. Carbon in the limestone is reduced to carbon monoxide. Carbon and carbon monoxide together reduce Fe_2O_3 to metallic iron.

Limestone acts as flux, it combines with the gangue material to form molten slag. Extraction of iron from haematite ore involves the following steps.

i. Concentration : The powdered ore is washed in a powerful current of water introduced into the hydraulic classifier.

The lighter gangue particles are separated and the concentrated ore is collected at the bottom.

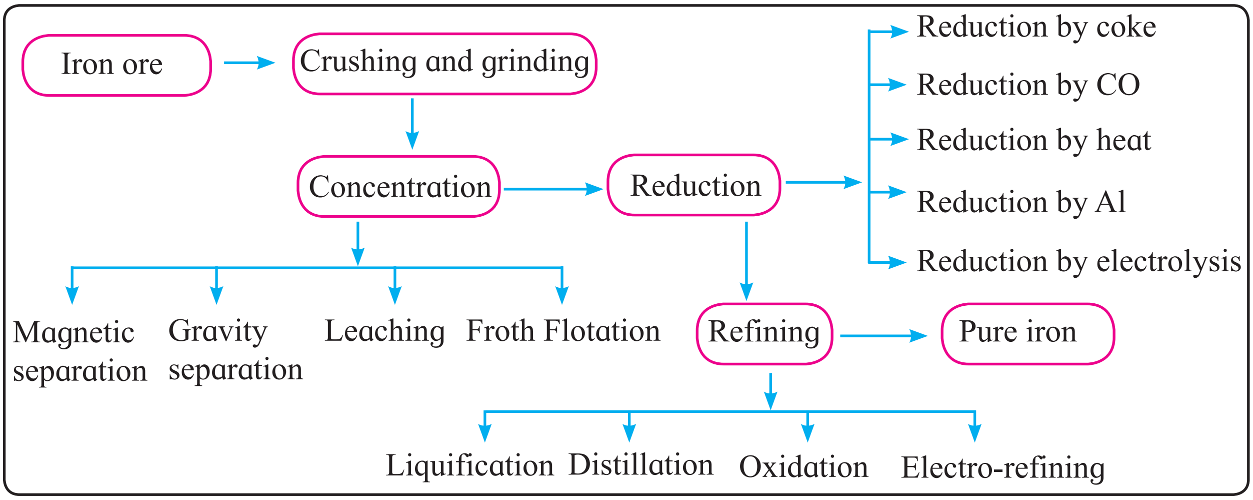
ii. Roasting : The concentrated ore is heated in a current of air. The sulfur and arsenic impurities present in the ore get converted into their oxides and escape as vapour. Ferrous oxide in the ore is converted to Fe_2O_3.

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

The roasted ore is converted into lumps by sintering.

iii. Reduction (Smelting) : This step is carried out in a blast furnace. Blast furnace is a tall cylindrical steel tower which is lined with refractory bricks.

The height of a typical blast furnace is 25 m and its diameter varies between 5 and 10 m. The furnace works on counter current principle where the charge comes down and



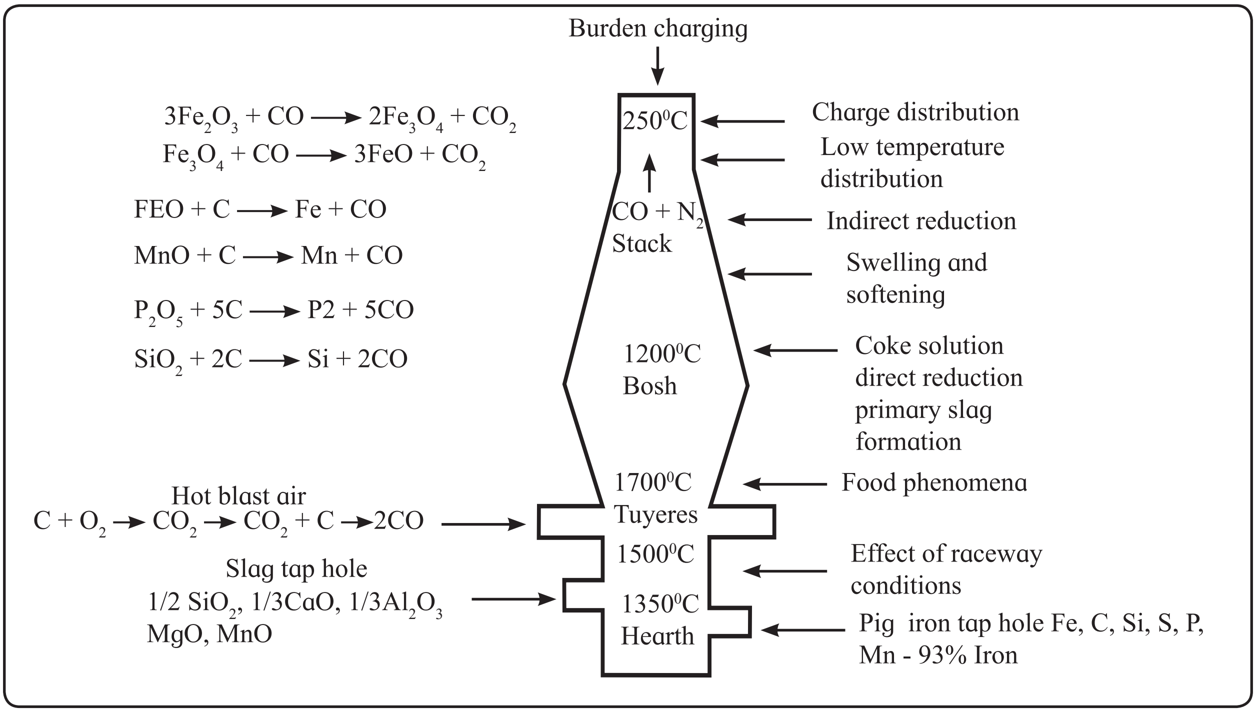


Fig. 8.5 : Blast furnace

hot gases move up the tower. The furnace is comprised of 3 parts - 1. Hearth, 2. Bosh and 3. Stack

The charge contaning ore and lime stone is introduced into the furnace through a cup and cone arrangement. In this arrangement the cone enables uniform distribution of charge and the cup prevents the loss of gases. A blast of preheated air is introduced into the furnance below the bosh. The charge and hot air come in contact with each other and various reactions take place.

Reactions in the blast furnace : There are different temperature zones in the blast furnace. The temperature goes on increasing from top to bottom in the furnace. At the top, the temperature is 500 K. Maximum temperature of the furnace is 2000 K above the tuyers.
There are 3 temperature zones in the furnace.

1. Zone of combustion - Combustion of coke with O_2 in the air.

2. Zone of reduction - Reduction of Fe_2O_3 to metallic iron

3. Zone of slag formation - Formation of slag by reaction of gangue with limestone

Chemical reactions taking place in different zones of the blast furnace

1. Zone of combustion : This is 5 - 10 m from the bottom. The hot air blown through the tuyers reacts with coke from the charge to form CO.

$$C + \frac{1}{2} O_2 \longrightarrow CO, \Delta H = -220 \text{ kJ}$$

The reaction is highly exothermic; thus the temperature of this zone is around 2000 K. Some of the CO formed dissociates to form finely divided carbon.

$$2\ CO \longrightarrow 2\ C + O_2$$

The hot gas rich in CO rises upwards in the blast furnace. The charge coming down gets heated and reacts with CO. Thus CO acts as a fuel and also a reducing agent.

2. Zone of Reduction (22-25 m near the top)

Here, the temperature is around 900 K. Fe_2O_3 is reduced to spongy iron by CO

$$Fe_2O_3 + 3\ CO \longrightarrow 2Fe + 3\ CO_2$$

some amount of Fe_2O_3 is reduced to iron by carbon

$$Fe_2O_3 + 3C \longrightarrow 2\ Fe + 3\ CO$$

Table 8.9 : Summary of reactions taking place in blast furnace at different temperature zones

Temp K	Changes taking place	Reaction
500	loss of moisture from ore	
900	Reduction of ore by CO	$Fe_2O_3 + 3CO \longrightarrow 2\,Fe + 3CO_2$
1200	Decomposition of lime	$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
1500	Reduction of ore by C	$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
2000	Fusion of iron	$CaO + SiO_2 \longrightarrow CaSiO_3$
	Slag formation	$12CaO + 2Al_2O_3 \longrightarrow 4Ca_3AlO_3 + 3\,O_2$

3. Zone of slag formation (20 m unit) : The gangue present in the ore is converted to slag. This slag can be used for making road foundation. Temperature of this zone is 1200 K. The gangue contains silica, alumina and phosphates. A removal of this gangue is effected by adding lime-stone in the charge, which acts as flux. Limestone decomposes to give CaO (quick lime)

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

CaO combines with gangue to form molten slag of calcium silicate and calcium aluminate.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$12\,CaO + 2Al_2O_3 \longrightarrow 4Ca_3\,AlO_3 + 3\,O_2$$

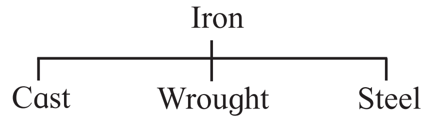
4. Zone of fusion (15 m ht) : MnO_2 and $Ca_3(PO_4)_2$ present in the iron ore are reduced to Mn and P. Some of the silica is also reduced to Si.

The spongy iron coming down in the furnace melt absorbs impurities like C, Si, Mn, P and S. This molten iron collects at the bottom in the furnace. The slag which is lighter floats on the surface of molten iron. Molten slag and iron are collected through separate outlets.

Molten iron is poured into moulds. These solid blocks are called pigs. This iron contains about 4% of carbon. When pig iron is remelted, run into moulds and cooled, it becomes cast iron. The waste gases containing N_2, CO and CO_2 escape through the outlet at the top. These hot gases are used for preheating the blast of air.

5. Refining : Pure iron can be obtained by electrolytic refining of impure iron or other methods given in the flow chart. The choice of extraction technique is governed by the following factors. 1. Nature of ore 2. Availability and cost of reducing agent, generally cheap coke is used. 3. Availability of hydraulic power. 4. Purity of product (metal) required. 5. Value of byproducts for example, SO_2 obtained during roasting of sulphide ores is vital for manufacture of H_2SO_4. Knowledge of electrochemical series provides solutions to many problems.

Commercial forms of Iron



Remember...

1. Iron melts at a very high temperature (1800 K). On addition of carbon its melting point decreases depending upon percentage of carbon.
2. Mechanical properties of steel can be modified by addition of small amounts of suitable elements such as manganese, chromium, sulfur, nickel etc. These elements are called alloying elements and steels are alloy steels.

Differences between cast iron, wrought iron and steel

Cast iron	Wrought iron	Steel
1. Hard and brittle	1. Very soft	1. Neither too hard nor too soft.
2. Contains 4% carbon.	2.Contains less than 0.2% carbon	2. Contains 0.2 to 2% carbon
3. Used for making pipes, manufacturing automotive parts, pots, pans, utensils	3. Used for making pipes, bars for stay bolts, engine bolts and rivetts.	3. Used in buildings infrastructure, tools, ships, automobiles, weapons etc.

Do you know ?

Iron possesses a high degree of magnetism below 1042 K. This is known as ferromagnetism.

8.10 Inner Transition (f-block) Elements: Lanthanoids and Actinoids :

Elements whose f orbitals get filled up by electrons, are called f block elements. These elements are placed separately at the bottom of the periodic table. They are a subset of 6th and 7th periods.

Can you tell ?

- Why f-block elements are called inner transition metals?
- Are there any similarities between transition and inner transition metals?

Since f orbital lies much inside the d orbital, in relation to the transition metals the f block elements are called inner transition elements. These elements have 1 to 14 electrons in their f orbital, 0 or 1 in the penultimate energy level and 2 electrons in the outermost orbital. The lanthanoids are characterized by gradual filling up of 4f and actinides by the 5 f orbitals. There are 14 elements filling the f orbital in each series. The relative energies of the nd and (n-1)f orbitals are very similar and are sensitive to electronic configurations.

Do you know ?

Glenn Seaborg first proposed a revised design of periodic table with a whole new series of elements. When he showed his design to two prominent inorganic chemists of the time, they warned him against publishing it. They told him that tampering with the established periodic table will affect his career. Seaborg went ahead and published it. He later remarked "I did not have any scientific reputation, so I published it anyway". Now we see that elements 89 -102 (filling of 5f orbitals) fit in Seaborg's proposed order.

8.11 Properties of f-block elements

i. Properties are similar to d block elements

ii. Electrons are added to f subshells of (n-2) level

iii. Placed between (n-1)d and ns block elements

Lanthanoids begin with atomic number 57 and end at 71. Although, historically, lanthanoids are termed as **rare earth elements**, they are fairly abundant in earth's crust. For example, thulium is found more in abundance than silver (4.5 x 10^{-5} vs 0.79 x 10^{-5} percent by mass). The name rare earth elements was coined because of difficulty in extracting them economically in pure form from other lanthanoids having similar chemical properties. Now, due to newer separation methods like ion exchange resins, the separation of these elements has become easier and more economical.

These metals are soft with moderate densities of about 7 g cm^{-3}. They have high melting (~1000 ^0C) and boiling points (~3000 ^0C). Similar to groups 1 and 2, lanthanoids in the metallic state are very reactive and resemble alkali and alkaline earth metals in their reactivities than transition metals. For example, they react with water to give the metal hydroxide and hydrogen gas

$$2M(s) + 6\,H_2O\,(l) \longrightarrow 2M(OH)_3(s) \;+\; 3H_2(g)$$

Although, the common oxidation state for lanthanoids is +3, the +2 oxidation state is also important. They all form stable oxides of the type M_2O_3 where M is metal ion. Eu^{2+} and Yb^{2+} are the most stable dipositive metal ions. Higher oxidation states are unusual for lanthanoids with the only exception of cerium which forms a stable +4 species. The energy required to break up the metal lattice is heat of atomization. Lanthanoids have lower heat of atomization than transition metals. This is because with d electrons, transition metals are much harder and require high heat of atomization. Europium and ytterbium have the lowest enthalpies of vaporization and largest atomic radii of lanthanoids, resemble barium. These two elements resemble alkaline earth elements; they dissolve in liquid ammonia to give blue conducting solutions.

Their ionic radii decrease from 117 pm of La to 100 pm for Lu. This is because 5f orbitals do not shield the outer 5s and 5p electrons effectively, leading to increase in effective nuclear charge and decrease in the ionic size. Such large ions have higher coordination number that varies from 6 (most common) to 9, 10 and upto12 in some cases. For example, hydrated lanthanum ion is a nonahydrate, $[La(H_2O)_9]^{3+}$.

All the lanthanoids form hydroxides of the general formula $Ln(OH)_3$(Ln represents any elements of lanthanoid series). These are ionic and basic. Since the ionic size decreases from La^{3+} to Lu^{3+}, the basicity of hydroxides decreases. $La(OH)_3$ is the strongest base while $Lu(OH)_3$ is the weakest base.

Lanthanoids react with nitrogen and halogens to give nitrides and halides of the formulae LnN and LnX_3 repectively. While doing so, lanthanoids lose their outermost 3 electrons to form stable compound in +3 oxidation state. When lanthanoids are heated at elevated temperatures (~ 2800 K) with carbon, the carbides with general formula LnC_2 are obtained.

In +3 oxidation state, many of the lanthanoids are coloured, mostly green, pink and yellow. This is attributed to the electronic transitions among the f orbitals. Like transition metals the electronic spectra of lanthanoids however, do not get affected with different ligands.

8.12 Properties of Lanthanoids

i. Soft metals with silvery white colour and moderate densities of ~ 7 g cm^{-3}. Colour and brightness reduces on exposure to air

ii. Good conductors of heat and electricity.

iii. Except promethium (Pm), all are non-radioactive in nature.

iv. The atomic and ionic radii decrease from lanthanum (La) to lutetium (Lu). This is known as **lanthanoid contraction**.

v. Binding to water is common (i.e.) such that H_2O is often found in products when isolated from aqueous solutions.

vi. Coordination numbers usually are greater than 6, typically 8, 9,... (up to 12 found).

vii. The lanthanoides are strongly paramagnetic. Gadolinium becomes ferromagnetic below 16 ^0C (Curie point). The other heavier lathanoids terbium, dysprosium, holmium, erbium, thulium, and ytterbium – become ferromagnetic at much lower temperatures.

viii. Magnetic and optical properties are largely independent of environment (similar spectra in gas/solution/solid).

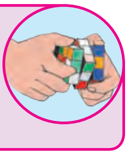
Table 8.11 : Electronic configuration and atomic ionic radii of lanthanoids

Element	Symbol	Atomic number	Electronic configuration				Atomic radii, pm	Ionic radii (Ln^{+3}, 6-coordinate), pm
			Expected (ground state)	Observed (ground state)	(+2 oxidation state)	(+3 oxidation state)		
Lanthanum	La	57	$[Xe]4f^{0}5d^{1}6s^{2}$	$[Xe]4f^{0}5d^{1}6s^{2}$	$4f^{0}$	$4f^{0}$	187	103
Cerium	Ce	58	$[Xe]4f^{2}6s^{2}$	$[Xe]4f^{1}5d^{1}6s^{2}$		$4f^{1}$	183	102
Praseodymium	Pr	59	$[Xe]4f^{3}6s^{2}$	$[Xe]4f^{3}6s^{2}$	$4f^{2}$	$4f^{2}$	182	99
Neodymium	Nd	60	$[Xe]4f^{4}6s^{2}$	$[Xe]4f^{4}6s^{2}$			181	98.3
Promethium	Pm	61	$[Xe]4f^{5}6s^{2}$	$[Xe]4f^{5}6s^{2}$	$4f^{4}$		181	97
Samarium	Sm	61	$[Xe]4f^{6}6s^{2}$	$[Xe]4f^{6}6s^{2}$	$4f^{5}$	$4f^{5}$	180	95.8
Europium	Eu	63	$[Xe]4f^{7}6s^{2}$	$[Xe]4f^{7}6s^{2}$		$4f^{6}$	199	94.7
Gadolinium	Gd	64	$[Xe]4f^{8}6s^{2}$	$[Xe]4f^{7}5d^{1}6s^{2}$	$4f^{7}$		178	93.8
Terbium	Tb	65	$[Xe]4f^{9}6s^{2}$	$[Xe]4f^{9}6s^{2}$		$4f^{8}$	177	92.3
Dysprosium	Dy	66	$[Xe]4f^{10}6s^{2}$	$[Xe]4f^{10}6s^{2}$		$4f^{9}$	176	91.2
Holmium	Ho	67	$[Xe]4f^{11}6s^{2}$	$[Xe]4f^{11}6s^{2}$	$4f^{10}$	$4f^{10}$	175	90.1
Erbium	Er	68	$[Xe]4f^{12}6s^{2}$	$[Xe]4f^{12}6s^{2}$			174	89
Thulium	Tm	69	$[Xe]4f^{13}6s^{2}$	$[Xe]4f^{13}6s^{2}$	$4f^{12}$	$4f^{12}$	173	88
Ytterbium	Yb	70	$[Xe]4f^{14}6s^{2}$	$[Xe]4f^{14}6s^{2}$	$4f^{13}$			86.8
Lutetium	Lu	71	$[Xe]4f^{14}5d^{1}6s^{2}$	$[Xe]4f^{14}5d^{1}6s^{2}$		$4f^{14}$		86.1

8.12.1 Electronic configuration : The electronic configuration of lanthanoids is [Xe] $4f^{0-14}$ 5d $^{0-2}$ $6s^2$. This is because $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$ is the electronic configuration of xenon and we can simplify the electronic configuration of lanthanoids by [Xe] $4f^{0-14}5d^{0-2}6s^2$. The lanthanoids involve gradual filling of f-orbitals. The energies of 5d and 4f orbitals are very close. For lanthanum 4f is slightly higher in energy than 5d. The lanthanum has electronic configuration $[Xe]6s^25d^1$ and not $[Xe]6s^24f^1$. Gadolinium (Gd) and lutetium (Lu) have $5d^1$ electron to make f-orbital half-filled and full-filled which render them extra stability. The electronic configuration of lanthanoids have variable occupancy in 4f (0 to 14) orbitals. This can be noticed from Table 8.10. Number of electrons in 6s orbitals remains constant in the ground state. The valence shell electronic configuration of these elements, thus can be represented as: $(n-2)f^{0,2-14}$ $(n-1)d^{0,1,2}$ ns^2

The electronic distribution in different orbitals of elements in their ground and excited states are shown in Table 8.11.

Try this...



Fill in the blanks in Table 8.11.

Ionization Enthalpies

Can you recall ?

- What is ionization enthalpy?
- Some elements have variable oxidation states and some have only two. Can this be justified based on their ionization enthalpies?

The ionization enthalpies of lanthanoids are given in Table 8.12

Table 8.12: First, second, third and fourth ionization enthalpies of lanthanoids in kJ/mol

Lanthanoid	IE_1	IE_2	IE_3
La	538.1	1067	1850.3
Ce	528.0	1047	1949
Pr	523.0	1018	2086
Nd	530.0	1034	2130
Pm	536.0	1052	2150
Sm	543.0	1068	2260
Eu	547.0	1085	2400
Gd	592.0	1170	1990
Tb	564.0	1112	2110
Dy	572.0	1126	2200
Ho	581.0	1139	2200
Er	589.0	1151	2190
Tm	596.7	1163	2284
Yb	603.4	1175	2415
Lu	523.5	1340	2022

Problem : Which of the following will have highest forth ionization enthalpy IE_4? $La^{4\oplus}$, $Gd^{4\oplus}$, $Lu^{4\oplus}$.

Solution : First write electronic configuration of that element/ion. Check for any unpaired electrons present. The energy required for removal of that electron will be less as compared to the energy required to remove an electron from an electron pair.Also compare the energies of the orbitals occupying those electrons. It will be easier to remove an electron from an orbital that is lower in energy than the one with higher in energy. First ionization enthalpy generally decrease across the period.

8.12.2 Oxidation state : +3 oxidation state is common to all elements in which 2 electrons of s- subshell and one from d or f- subshell are removed. The 4f electrons are strongly screened by inner electrons of 5s and 5p electrons. Thus, 4f electrons are not involved in the bonding. Besides these, some lanthanoids show oxidation states +2 and +4. They are formed in case of f^0, f^7 , f^{14} configurations or resulting ions.

For example : $Ce^{4\oplus}$ (f^0) ; $Eu^{2\oplus}$ and $Tb^{4\oplus}$ (f^7) ; $Yb^{2\oplus}$ (f^{14}) Refer Table 8.11.

8.12.3 Colour and Spectra :

Some trivalent ions ($M^{3\oplus}$) are coloured in solid state as well as in solution. The colour of lanthanoid ion is due to f-f transitions which correspond to energy in the visible region of the electromagnetic spectrum. The colour of ions having nf electrons is about the same as those having (14 – n)f electrons. (where n is an integer 1-13).

Ln ion	No. of f-electrons	Colour	
$Pr^{3\oplus}$	$4f^2$	green	(14 -n) f-electrons =14-2 =12
$Tm^{3\oplus}$	$4f^{12}$	green	n f-electrons =12
$Nd^{3\oplus}$	$4f^3$	pink	(14 -n) f-electrons =14-3 =11
$Er^{3\oplus}$	$4f^{11}$	pink	nf-electrons =11

8.12.4 Atomic and ionic radii (Lanthanoid Contraction) : As we move along the lanthanoid series, there is a decrease in atomic and ionic radii (Fig.8.6). This steady decrease in the atomic and ionic radii is called Lanthanoide contraction. As we move from one element to another the nuclear charge increases by one unit and one electron is added. The new electrons are added to the same inner 4f subshell. Thus the 4f electrons shield each other from the nuclear charge poorly owing to their diffused nature. With increasing atomic number and nuclear charge, the effective nuclear charge experienced by each 4f electrons increases. As a result, the whole of 4f electron shell contracts at each successive element.

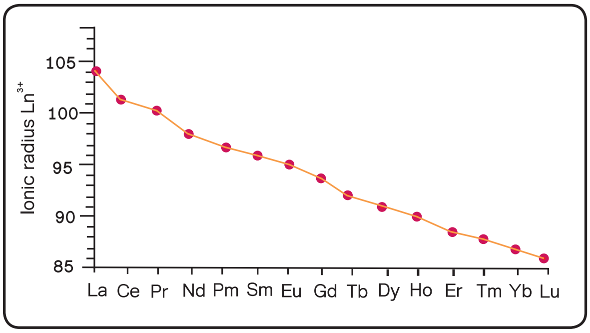


Fig. 8.6 : Ionic radii of lanthanoids in +3 oxidation state

In section 8.3.4 we have learnt about the magnetic behaviour of transition metal complexes.

Use your brain power

- Do you think that lanthanoid complexes would show magnetism?
- Can you calculate the spin only magnetic moment of lanthanoid complexes using the same formula that you used for transition metal complexes?
- Calculate the spin only magnetic moment of La^{3+}. Compare the value with that given in Table 8.13 Is it same or different?

Table 8.13: Effective magnetic moments of lanthanoids in +3 oxidation state

Ln	Ln^{3+} oxidation state	No. of unpaired electrons	Observed magnetic moment, $\mu_{eff\ B.M}$
La	$4f^0$	0	0
Ce	$4f^1$	1	2.3-2.5
Pr	$4f^2$	2	3.4-3.6
Nd	$4f^3$	3	3.5-3.6
Pm	$4f^4$	4	--
Sm	$4f^5$	5	1.4-1.7
Eu	$4f^6$	6	3.3-3.5
Gd	$4f^7$	7	7.9-8.0
Tb	$4f^8$	6	9.5-9.8
Dy	$4f^9$	5	10.4-10.6
Ho	$4f^{10}$	4	10.4-10.7
Er	$4f^{11}$	3	9.4-9.6
Tm	$4f^{12}$	2	7.1-7.6
Yb	$4f^{13}$	1	4.3-4.9
Lu	$4f^{14}$	0	0

8.13 Applications

The lanthanoid compounds are present in every household. It is inside the colour television tubes. When electrons are bombarded on certain mixed lanthanoid compounds, they emit visible light over a small wavelength range. Therefore, the inside surface of a television tube or computer monitor is coated with tiny patches of three different lanthanoid compositions to give three colours that make the colour image.


Promethium


Europium


Actinium


Brekelium

Nobelium


Mendelenium


Sebargium

For example, mixed oxide of europium and yttrium $(Eu,Y)_2O_3$ releases an intense red colour when bombarded with the high energy electrons. The optoelectronics applications use lanthanoid ions as active ions in luminescent materials. The most notable application is the Nd: YAG laser (Nd: YAG = neodymium doped yttrium aluminium garnet). Erbium-doped fibre amplifiers are significant devices in the optical-fibre communication systems. Lanthanoids are used in hybrid cars, superconductors and permanent magnets.

8.14 Actinoids : The last row of elements in the periodic table is the actinoid series. It begins at thorium (Z =72) and ends at lawrencium (Z=103). Most of these elements are not found in nature. They are all radioactive and man-made. The half-lives of the isotopes of thorium (Th-232=1.4 x 10^{10} years) and uranium (U-238=4.5 x 10^9 years) are so long that these elements exist in rocks on earth. The long lived isotopes such as thorium, protactinium, uranium, neptunium, plutonium and americium, are studied in more details. These elements have high densities (~ 15-20 g cm^{-3}), high melting points (~1000 °C) and high boiling points (~3000 °C). Actinoids are less reactive than lanthanoids. For example, they react with hot, but not cold water to give the hydroxide and hydrogen gas. Unlike lanthanoids, they exhibit a range of oxidation numbers in their compounds which varies from +2 to +8. The most common oxidation numbers of the actinoids are shown in Fig. 8.7.

As can be seen from Fig.8.7, the most common oxidation state of early actinoids reflects the loss of all outer electrons which is similar to transition metals than the lanthanoids. A ready loss of 5f electrons by early actinoids indicates that these electrons are much closer in energy to 7s and 6d electrons than the 4f electrons to 6s and 5d electrons as in lanthanoids. All three sets of orbitals that is 6d, 5f and 7s have similar energies. For Th, Pa and Np difference in energy levels is small

Internet my friend

With the help of internet find out the applications of the elements listed in table below. Share this information with your friends

Element	Applications
Lanthanum	
Ytterbium	
Erbium	
Praseodymium	
Samarium	
Promethium	

so electrons occupy either 6d or 5f oribitals. In actinoids series the 5f are orbitals appreciablly lower in energy, thus from Pu onwards 5f shell gets filled in a regular way.

The electronic configuration of actinoids is [Rn] $5f^{0-14}$ $6d^{0-2}$ $7s^2$, where Rn is the electronic configuration of radon. As seen from Fig. 8.7, the most stable oxidation state in actinoids is +3. The highest common oxidation states of early actinoids reflect the loss of all outer electrons which is similar to transition metals than lanthanoids. For example, uranium has electronic configuration of [Rn]$7s^2 5f^3 6d^1$. The formation of +6 oxidation state corresponds to an electronic configuration of [Rn]. Similar to lanthanoids, loss of s and d electrons occur before f electrons, in formation of 3+ ions. A ready loss of 5f electrons by early actinoids indicates that these electrons are much closer in energy to 7s and 6d electrons than the 4f electrons are to 6s and 5d electrons in the lanthanoids. In turn, 5f and 6s orbitals expand as they are partially shielded from the nuclear attraction by 7s electrons. As a result all three sets of orbitals i.e. 6d, 5f and 7s have very similar energies. The ionic radius decreases as we move across the series which is known as 'Actinoid contraction'. This is attributed to poor shielding offered by f electrons.

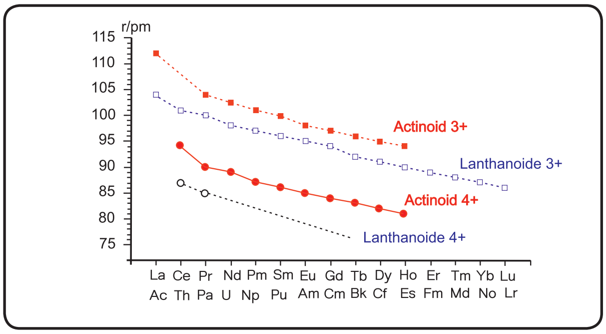


Fig. 8. 8 Figure depicting contraction of ionic radii of lanthanoides and actinoids

8.15 Properties of Actinoids

i. Similar to lanthanoids, they appear silvery white in colour.

ii. These are highly reactive radioactive elements

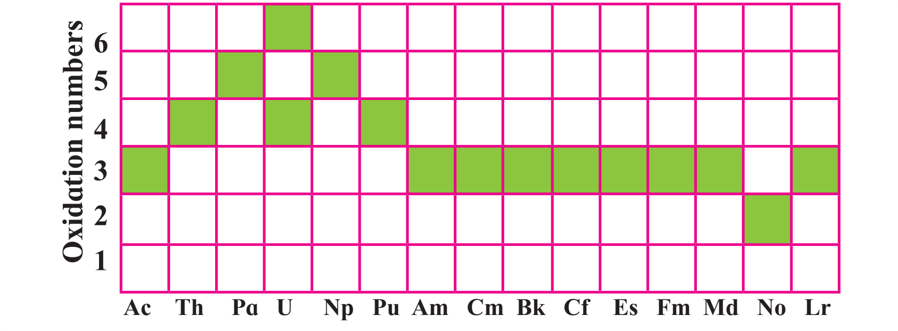


Fig. 8. 7 The most common oxidation numbers of actinoids

iii. Except promethium (Pm), all are non-radioactive in nature

iv. They experience decrease in the atomic and ionic radii from actinium (Ac) to lawrencium (Lw), known as **actinoid contraction**

v. They usually exhibit +3 oxidation state. Elements of first half of the series usually exhibit higher oxidation states.

8.16 Applications of actinoids : We have seen that the half-lives of natural thorium and uranium isotopes are so long that we get very negligible radiation from these elements. We find them in everyday use. For example, Th(IV) oxide, ThO_2 with 1% CeO_2 was used as a major source of indoor lighting before incandescent lamps came into existence only because these oxides convert heat energy from burning natural gas to an intense light. Even today, there is a great demand for these lights for outdoor camping.

Do you know ?

Uranium is another actinoid which is in great demand as it is used in the nuclear reactors. One of the extraction methods for uranium has a very interesting chemistry. The ore containing U(IV) oxide, UO_2, is first treated with Fe(III) ion to give U(VI) oxide, UO_3

$$UO_2\,(s) + H_2O(l) \rightarrow UO_3\,(s) + 2H^{\oplus}\,(aq) + 2e^{\ominus}$$

$$Fe^{3\oplus}\,(aq) + e^{\ominus} \rightarrow Fe^{2\oplus}\,(aq)$$

Addition of H_2SO_4 to this solution produces uranyl sulphate containing $UO_2^{2\oplus}$ cation:

$$UO_3\,(s) + H_2SO_4\,(aq) \rightarrow UO_2SO_4\,(aq) + H_2O\,(l)$$

After purification, ammonia is added to the solution giving bright yellow precipitate of ammonium diuranate, $(NH_4)_2U_7O_7$:

$$2\,UO_2SO_4\,(aq) + 6\,NH_3\,(aq) + 3\,H_2O\,(l) \rightarrow (NH_4)_2U_7O_7\,(s) + 2\,(NH_4)_2SO_4\,(aq)$$

This yellow cake is the marketable form of uranium!

Similarities and differences between lanthanides and actinoids

Similarities	Differences
Both the series show a +3 oxidation state	Lanthanoids show a maximum oxidation state of +4 while actinoids show oxidation states of +3, +4, +5, +6 and +7
In both the series, the f-orbitals are filled gradually	Lanthanoids do not form complexes easily. Actinoids have a greater tendency to form complexes with ligands such as thio-ethers
Ionic radius of the elements in both series decreases with an increase in atomic number	All lanthanoids are non-radioactive except promethium but actinides are radioactive in nature
The electronegativity of all the elements in both the series is low and are said to be highly reactive	Lanthanoids do not form oxocations, but actinides form oxocations such as UO^+, PuO^+, NpO_2^+
The nitrates, perchlorates and sulphates of all the elements are soluble while the hydroxides, fluorides and carbonates are insoluble	Most of the lanthanoids are colourless in nature whereas the actinoids are coloured ions

Table 8.14 Electronic configuration of actinoids and their ionic radii in +3 oxidation state

Element	Symbol	Atomic number	Electronic configuration		*Atomic radii, pm	*Ionic radii (Ac$^{3\oplus}$), pm
			ground state	+3 oxidation state		
Actinium	Ac	89	$[Rn]5f^{0}6d^{1}7s^{2}$	$5f^{0}$	203	126
Thorium	Th	90	$[Rn]5f^{0}6d^{2}7s^{2}$	$5f^{1}$	180	-
Protactinium	Pa	91	$[Rn]5f^{2}6d^{1}7s^{2}$	$5f^{2}$	162	118
Uranium	U	92	$[Rn]5f^{3}6d^{1}7s^{2}$	$5f^{3}$	153	118
Neptunium	Np	93	$[Rn]5f^{4}6d^{1}7s^{2}$	$5f^{4}$	150	116
Plutonium	Pu	94	$[Rn]5f^{6}6d^{0}7s^{2}$	$5f^{5}$	162	115
Americium	Am	95	$[Rn]5f^{7}6d^{0}7s^{2}$	$5f^{6}$	173	114
Curium	Cm	96	$[Rn]5f^{7}6d^{1}7s^{2}$	$5f^{7}$	174	112
Berkelium	Bk	97	$[Rn]5f^{9}6d^{0}7s^{2}$	$5f^{8}$	170	110
Californium	Cf	98	$[Rn]5f^{10}6d^{0}7s^{2}$	$5f^{9}$	186	109
Einsteinium	Es	99	$[Rn]5f^{11}6d^{0}7s^{2}$	$5f^{10}$	186	98
Fermium	Fm	100	$[Rn]5f^{12}6d^{0}7s^{2}$	$5f^{11}$	198	91
Mendelevium	Md	101	$[Rn]5f^{13}6d^{0}7s^{2}$	$5f^{12}$	194	90
Nobelium	No	102	$[Rn]5f^{14}6d^{0}7s^{2}$	$5f^{13}$	197	95
Lawrencium	Lr	103	$[Rn]5f^{14}6d^{1}7s^{2}$	$5f^{14}$	171	88

Table 8.15 : Some comparison between Pre-Transition, Lanthanoids and Transition Metals

Pre-Transition Metals	Lanthanoids	Transition Metals
Essentially monovalent - show group (n+) oxidation state	Essentially in (+3) oxidation state (+2/+4 for certain configurations)	Show variable oxidation states
Periodic trends dominated by effective nuclear charge at noble gas configuration	Lanthanoid contraction of Ln$^{3\oplus}$	Size changes of M$^{n\oplus}$, less marked
Similar properties for a given group	Similar properties	Substantial changes in properties
Always 'hard' (O, X, N donors, preferably negatively charged)	Always 'hard' (O, X, N donors, preferably negatively charged)	heavier metals (increasingly from Fe-Cu) may show a 'soft' character
No ligand field effects	Insignificant ligand field effects	Substantial ligand field effects
Poor coordination properties(C.N. determined by size)	High coordination numbers (C.N. determined by size)	Coordination number 6 is typical maximum (many exceptions)
Flexibility in geometry	Flexibility in geometry	Fixed geometries (ligand field effects)
No magnetism	Show magnetism	Show magnetism

8.17 Postactinoid elements : You have seen that elements with atomic number greater than 92 are called 'Transuranium'. Elements from atomic number 93 to 103 now are included in actinoid series and those from 104 to 118 are called as postactinoid elements. The postactinoid elements that are known so far are transition metals. They are included as postactinoids because similar to actinoid elements, they can be synthesized in the nuclear reactions. So far, nine postactinoid elements have been synthesized. It is difficult to study their chemistry owing their short half-lives. For example, element 112 has a half-life of only 2.8 x 10^{-4} seconds.

With half-lives of miliseconds only a little is known about the chemistry of these elements. Rutherfordium forms a chloride, $RfCl_4$, similar to zirconium and hafnium in the +4 oxidation state. Dubnium resembles to both, group 5 transition metal, niobium(V) and actinoid, protactinium(V).

Do you know ?

Traditionally, no element was named after a still-living scientist. This principle was put to an end with naming the element 106 as 'Seaborgium'.

Exercises

1. Choose the most correct option.

i. Which one of the following is dimagnetic

a. $Cr^{2\oplus}$ b. $Fe^{3\oplus}$

c. $Cu^{2\oplus}$ d. $Sc^{3\oplus}$

ii. Most stable oxidation state of Titanium is

a. +2 b. +3

c. +4 d. +5

iii. Components of Nichrome alloy are are

a. Ni, Cr, Fe b. Ni, Cr, Fe, C

c. Ni, Cr d. Cu, Fe

iv. Most stable oxidation state of Ruthenium is

a. +2 b. +4

c. +8 d. +6

v. Stable oxidation states for chromiom are

a. +2, +3 b. +3, +4

c. +4, +5 d. +3, +6

vi. Electronic configuration of Cu and Cu^{+1}

a. $3d^{10}, 4s^0; 3d^9, 4s^0$

b. $3d^9, 4s^1; 3d^9 4s^0$

c. $3d^{10}, 4s^1; 3d^{10}, 4s^0$

d. $3d^8, 4s^1; 3d^{10}, 4s^0$

vii. Which of the following have d^0s^0 configuration

a. $Sc^{3\oplus}$ b. $Ti^{4\oplus}$

c. $V^{5\oplus}$ d. all of the above

viii. Magnetic moment of a metal complex is 5.9 B.M. Number of unpaired electrons in the complex is

a. 2 b. 3

c. 4 d. 5

ix. In which of the following series all the elements are radioactive in nature

a. Lanthanides

b. Actinides

c. d-block elements

d. s-block elements

x. Which of the following sets of ions contain only paramagnetic ions

a. $Sm^{3\oplus}$, $Ho^{3\oplus}$, $Lu^{3\oplus}$

b. $La^{3\oplus}$, $Ce^{3\oplus}$, $Sm^{3\oplus}$

c. $La^{3\oplus}$, $Eu^{3\oplus}$, $Gd^{3\oplus}$

d. $Ce^{3\oplus}$, $Eu^{3\oplus}$, $Yb^{3\oplus}$

xi. Which actinoid, other than uranium, occur in significant amount naturally?

a. Thorium b. Actinium

c. Protactinium d. Plutonium

xii. The flux added during extraction of Iron from teamatite are its?

a. Silica

b. Calcium carbonate

c. Sodium carbonate

d. Alumina

2. Answer the following

i What is the oxidation state of Manganese in (i) MnO_4^{2-} (ii) MnO_4^{-} ?

ii. Give uses of $KMnO_4$

iii. Why salts of $Sc^{3\oplus}$, $Ti^{4\oplus}$, $V^{5\oplus}$ are colourless ?

iv. Which steps are involved in manufacture of potassium dichromate from chromite ore ?

v. Balance the following equation

(i) $KMnO_4 + H_2C_2O_4 \longrightarrow MnSO_4 + K_2SO_4 + H_2O + O_2$

(ii) $K_2Cr_2O_7 + KI + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

vi. What are the stable oxidation states of plutonium, cerium, manganese, Europium ?

vii. Write probable electronic configuration of chromium and copper.

viii. Why nobelium is the only actinoid with +2 oxidation state?

ix. Explain with the help of balanced chemical equation, why the solution of Ce(IV) is acidic.

x. What is meant by ‘shielding of electrons’ in an atom?

xi. The atomic number of an element is 90. Is this element diamagnetic or paramagnetic?

3. Answer the following

i. Explain the trends in atomic radii of d block elements

ii. Name different zones in the Blast furnace. Write the reactions taking place in them.

iii. What are the differences between cast iron, wrought iron and steel.

iv. Iron exhibits +2 and +3 oxidation states. Write their electronic configuration. Which will be more stable ? Why ?

v. Give the similarites and differences in elements of 3d, 4d and 5d series.

vi. Explain trends in ionisation enthalpies of d block elements.

vii. What is meant by diamagnetic and paramagnetic? Give one example of diamagnetic and paramagnetic transition metal and lanthanoid metal.

viii. Why the ground-state electronic configurations of gadolinium and lawrentium are different than expected?

ix. Write steps involved in metallugical process

x. Cerium and Terbium behaves as good oxidising agents in +4 oxidation state. Explain.

xi. Europium and xtterbium behave as good reducing agents in +2 oxidation state explain.

Activity :

Make groups and each group prepares a powerpoint presentation on properties and applications of one element. You can use your imagination to create some innovative ways of presenting data.

You can use pictures, images, flow charts, etc. to make the presentation easier to understand. Don’t forget to cite the reference(s) from where data for presentation is collected (including figures and charts). Have fun!