

d and f Block Elements

d-Block Elements: Introduction.

A transition element may be defined as an element whose atom in the ground state or ion in common oxidation state has **incomplete sub-shell, has electron 1 to 9**. It is called transition element due to fact that it is lying between most electropositive (s-block) and most electronegative (p-block) elements and represent a transition from them. The **general electronic configuration** of these element is $(n-1)^{1\text{to}10} ns^{0\text{to}2}$.

The definition of transition metal excludes *Zn, Cd* and *Hg* because they have complete d- orbital. Their common oxidation state is $Zn^{++}, Cd^{++}, Hg^{++}$. They also do not show the characteristics of transition element. *Zn, Cd, Hg* are called non typical transition element. Some **exceptional electronic configuration of transition element are**: $Cr = 3d^5 4s^1$, $Nb = 4d^4 5s^1$, $Pb = 4d^{10} 5s^0$, $Ag = 4d^{10} 5s^1$, $Cu = 3d^{10} 4s^1$, $Mo = 4d^5 5s^1$, $Ru = 4d^7 5s^1$, $Pt = 5d^0 6s^1$, $Au = 5d^{10} 6s^1$. These irregularities can be explain on the basis of half filled and full filled stability of d-orbital.

Classification : Transition element are classified in following series :

- (1) First transition series (3d) = 21 to 30 i.e. Sc to Zn .
- (2) Second transition series (4d) = 39 to 48 i.e. Y to Cd .
- (3) Third transition series (5d) = 57 La and 72 – 80 Hf to Hg .
- (4) Fourth transition series or 6d series = 89 Ac and 104 – 112 Rf .

So there are 39 transition element at present in the periodic table.

	1	2											13	14	15	16	17	18	
	H		Transition Elements (d-block elements)																He
			3	4	5	6	7	8	9	10	11	12							
s-block elements	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	p-block elements								
	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd									
	* 57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg									
	* 69	104	105	106	107	108	109	110											
	58-71 Lanthanide series (Lanthanides)																		
	90-103 Actinide series (actinides)																		

Physico- Chemical Properties of d-Block Elements .

(1) **Atomic radii** : The atomic, radii of 3d-series of elements are compared with those of the neighbouring s-and p-block elements.

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
227	197	144	132	122	117	117	117	116	115	117	125	135	122*

* in pm units

The atomic radii of transition elements show the following characteristics,

d and f Block Elements

(i) The atomic radii and atomic volumes of d-block elements in any series decrease with increase in the atomic number. The decrease however, is not regular. The atomic radii tend to reach minimum near at the middle of the series, and increase slightly towards the end of the series.

Explanation : When we go in any transition series from left, to right, the nuclear charge increases gradually by one unit at each elements. The added electrons enter the same penultimate shell, (inner d- shell). These added electrons shield the outermost electrons from the attraction of the nuclear charge. The increased nuclear charge tends to reduce the atomic radii, while the added electrons tend to increase the atomic radii. At the beginning of the series, due to smaller number of electrons in the *d*-orbitals, the effect of increased nuclear charge predominates, and the atomic radii decrease. Later in the series, when the number of *d*-electrons increases, the increased shielding effect and the increased repulsion between the electrons tend to increase the atomic radii. Somewhere in the middle of the series, therefore the atomic radii tend to have a minimum value as observed.

(ii) The atomic radii increase while going down in each group. However, in the third transition series from hafnium (Hf) and onwards, the elements have atomic radii nearly equal to those of the second transition elements.

Explanation : The atomic radii increase while going down the group. This is due to the introduction of an additional shell at each new element down the group. Nearly equal radii of second and third transition series elements is due to a special effect called *lanthanide contraction*.

(2) **Ionic radii :** For ions having identical charges, the ionic radii decrease slowly with the increase in the atomic number across a given series of the transition elements.

Elements (m):	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ionic radius, (M ²⁺)/pm:	--	90	88	84	80	76	74	72	69	74
Pm: (M ³⁺)/pm:	81	76	74	69	66	64	63	-	-	-

Explanation : The gradual decrease in the values of ionic radius across the series of transition elements is due to the increase in the effective nuclear charge.

(3) **Ionisation energies :** The ionisation energies of the elements of first transition series are given below:

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ionisation E.										
I_1	632	659	650	652	716	762	758	736	744	906
I_2	1245	1320	1376	1635	1513	1563	1647	1756	1961	1736
I_3	2450	2721	2873	2994	3258	2963	3237	3400	3560	3838

* in kJ mol^{-1}

The following generalizations can be obtained from the ionisation energy values given above.

(i) The ionisation energies of these elements are high, and in the most cases lie between those of s- and d-block elements. This indicates that the transition elements are less electropositive than s-block elements.

Explanation : Transition metals have smaller atomic radii and higher nuclear charge as compared to the alkali metals. Both these factors tend to increase the ionisation energy, as observed.

(ii) The ionisation energy in any transition series increases in the nuclear with atomic number; the increase however is not smooth and as sharp as seen in the case of s- and p-block elements.

d and f Block Elements

Explanation : The ionisation energy increases due to the increase in the nuclear charge with atomic number at the beginning of the series. Gradually, the shielding effect of the added electrons also increases. This shielding effect tends to decrease the attraction due to the nuclear charge. These two opposing factors lead to a rather gradual increase in the ionisation energies in any transition series.

(iii) The first ionisation energies of 5d-series of elements are much higher than those of the 3d and 4d series elements.

Explanation : In the 5d-series of transition elements, after lanthanum (La), the added electrons go to the next inner 4f orbitals. The 4f electrons have poor shielding effect. As a result, the outermost electrons experience greater nuclear attraction. This leads to higher ionisation energies for the 5d-series of transition elements.

(4) **Metallic character :** All the transition elements are metals. These are hard, and good conductor of heat and electricity. All these metals are malleable, ductile and form alloys with other metals. These elements occur in three types e.g., face-centered cubic (fcc), hexagonal close-packed (hcp) and body-centered cubic (bcc), structures.

Explanation : The ionisation energies of the transition elements are not very high. The outermost shell in their atoms have many vacant/ partially filled orbitals. These characteristics make these elements metallic in character. The hardness of these metals, suggests the presence of covalent bonding in these metals. The presence of unfilled d-orbitals favour covalent bonding. Metallic bonding in these metals is indicated by the conducting nature of these metals. Therefore, it appears that there exists covalent and metallic bonding in transition elements.

(5) **Melting and boiling points :** The melting and boiling points of transition elements except Cd and Hg, are very high as compared to the s-block and p-block elements. The melting and boiling points first increase, pass through maxima and then steadily decrease across any transition series. The maximum occurs around middle of the series.

Explanation : Atoms of the transition elements are closely packed and held together by strong metallic bonds which have appreciable covalent character. This leads to high melting and boiling points of the transition elements. The strength of the metallic bonds depends upon the number of unpaired electrons in the outermost shell of the atom. Thus, greater is the number of unpaired electrons stronger is the metallic bonding. In any transition element series, the number of unpaired electrons first increases from 1 to 5 and then decreases back to the zero. The maximum five unpaired electrons occur at Cr (3d series). As a result, the melting and boiling points first increase and then decrease showing maxima around the middle of the series.

The low melting points of Zn, Cd, and Hg may be due to the absence of unpaired d-electrons in their atoms.

(6) **Enthalpies of atomization :** Transition metals exhibit high enthalpies of atomization.

Explanation : This is because the atoms in these elements are closely packed and held together by strong metallic bonds. The metallic bond is formed as a result of the interaction of electrons in the outermost shell. Greater the number of valence electrons, stronger is the metallic bond.

(7) **Oxidation states :** Most of the transition elements exhibit several oxidation states i.e., they show variable valency in their compounds. Some common oxidation states of the first transition series elements are given below in table,

Outer electronic configurations and oxidation states for 3d- elements

Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+ 2, + 3
Ti	$3d^2 4s^2$	+ 2, + 3, + 4

d and f Block Elements

V	$3d^3 4s^2$	+ 2, + 3, + 4, + 5
Cr	$3d^5 4s^1$	+ 1, + 2, + 3, + 4, + 5, + 6
Mn	$3d^5 4s^2$	+ 2, + 3, + 4, + 5, + 6, + 7
Fe	$3d^6 4s^2$	+ 2, + 3, + 4, + 5, + 6
Co	$3d^7 4s^2$	+ 2, + 3, + 4
Ni	$3d^8 4s^2$	+ 2, + 3, + 4
Cu	$3d^{10} 4s^1$	+ 1, + 2
Zn	$3d^{10} 4s^2$	+ 2

Explanation : The outermost electronic configuration of the transition elements is $(n - 1)d^{1-10}ns^2$. Since, the energy levels of $(n-1)d$ and ns -orbitals are quite close to each other, hence both the ns - and $(n-1) d$ -electrons are available for bonding purposes. Therefore, the number of oxidation states shown by these elements depends upon the number of d -electrons it has. For example, Sc having a configuration $3d^1 4s^2$ may show an oxidation state of + 2 (only s -electrons are lost) and + 3 (when d -electron is also lost). The highest oxidation state which an element of this group might show is given by the total number of ns - and $(n - 1) d$ -electrons.

The relative stability of the different oxidation states depends upon the factors such as, electronic configuration, nature of bonding, stoichiometry, lattice energies and solvation energies. The highest oxidation states are found in fluorides and oxides because fluorine and oxygen are the most electronegative elements. The highest oxidation state shown by any transition metal is eight. The oxidation state of eight is shown by *Ru* and *Os*.

An examination of the common oxidation states reveals the following conclusions.

(i) The variable oxidation states shown by the transition elements are due to the participation of outer ns and inner $(n - 1) d$ -electrons in bonding.

(ii) Except scandium, the most common oxidation state shown by the elements of first transition series is +2. This oxidation state arises from the loss of two $4s$ elements. This means that after scandium, d -orbitals become more stable than the s -orbital.

(iii) The highest oxidation states are observed in fluorides and oxides. The highest oxidation state shown by any transition element (by *Ru* and *Os*) is 8.

(iv) The transition elements in the + 2 and + 3 oxidation states mostly form ionic bonds. In compounds of the higher oxidation states (compound formed with fluorine or oxygen), the bonds are essentially covalent. For example, in permanganate ion MnO_4^- , all bonds formed between manganese and oxygen are covalent.

(v) Within a group, the maximum oxidation state increases with atomic number. For example, iron shows the common oxidation state of + 2 and + 3, but ruthenium and osmium in the same group form compounds in the + 4, + 6, and + 8 oxidation states.

(vi) Transition metals also form compounds in low oxidation states such as +1 and 0. For example, nickel in nickel tetracarbonyl, $Ni(CO)_4$ has zero oxidation state.

The bonding in the compounds of transition metals in low oxidation states is not always very simple.

(vii) **Ionisation energies and the stability of oxidation states :** The values of the ionisation energies can be used in estimating the relative stability of various transition metal compounds (or ions). For example, Ni^{2+} compounds are found to be thermodynamically more stable than Pt^{2+} , whereas Pt^{4+} compounds are more stable

d and f Block Elements

than Ni^{4+} compounds. The relative stabilities of Ni^{2+} relative to Pt^{2+} , and that of Pt^{4+} relative to Ni^{4+} can be explained as follows,

The first four ionisation energies of Ni and Pt

Metal	$(IE_1+IE_2) \text{ kJ mol}^{-1}, (IE_3+IE_4) \text{ kJ mol}^{-1},$		$E_{total}, \text{ kJ mol}^{-1}$ <small>$(= IE_1 + IE_2 + IE_3 + IE_4)$</small>
Ni	2490	8800	11290
Pt	2660	6700	9360

Thus, the ionisation of Ni to Ni^{2+} requires lesser energy (2490 kJ mol^{-1}) as compared to the energy required for the production of Pt^{2+} (2660 kJ mol^{-1}). Therefore, Ni^{2+} compounds are thermodynamically more stable than Pt^{2+} compounds.

On the other hand, formation of Pt^{4+} requires lesser energy (9360 kJ mol^{-1}) as compared to that required for the formation of Ni^{4+} ($11290 \text{ kJ mol}^{-1}$). Therefore, Pt^{4+} compounds are more stable than Ni^{4+} compounds.

This is supported by the fact that $[\text{PtCl}_6]^{2-}$ complex ion is known, while the corresponding ion for nickel is not known. However, other factors which affect the stability of a compound are,

- (a) Enthalpy of sublimation of the metal.
- (b) Lattice and the solvation energies of the compound or ion.

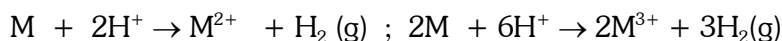
(8) **Electrode potentials (E°)** : Standard electrode potentials of some half-cells involving 3d-series of transition elements and their ions in aqueous solution are given in table,

Standard electrode potentials for 3d-elements

Elements	Ion	Electrode reaction	$E^\circ / \text{ volt}$
Sc	Sc^{3+}	$\text{Sc}^{3+} + 3e^- \rightarrow \text{Sc}$	- 2.10
Ti	Ti^{2+}	$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	- 1.60
V	V^{2+}	$\text{V}^{2+} + 2e^- \rightarrow \text{V}$	- 1.20
Cr	Cr^{3+}	$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	- 0.71
Mn	Mn^{2+}	$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	- 1.18
Fe	Fe^{2+}	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	- 0.44
Co	Co^{2+}	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	- 0.28
Ni	Ni^{2+}	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	- 0.24
Cu	Cu^{2+}	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+ 0.34
Zn	Zn^{2+}	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	- 0.76

The negative values of E° for the first series of transition elements (except for Cu^{2+}/Cu) indicate that,

(i) These metals should liberate hydrogen from dilute acids i.e., the reactions,

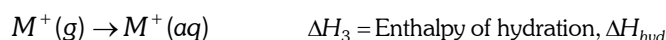
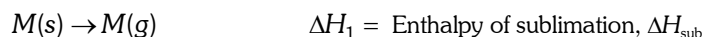


are favourable in the forward direction. In actual practice however, most of these metals react with dilute acids very slowly. Some of these metals get coated with a thin protective layer of oxide. Such an oxide layer prevents the metal to react further.

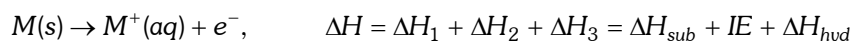
(ii) These metals should act as good reducing agents. There is no regular trend in the E° values. This is due to irregular variation in the ionisation and sublimation energies across the series.

d and f Block Elements

Relative stabilities of transition metal ions in different oxidation states in aqueous medium can be predicted from the electrode potential data. To illustrate this, let us consider the following,



Adding these equations one gets,



The ΔH represents the enthalpy change required to bring the solid metal M to the monovalent ion in aqueous medium, $M^+(aq)$.

The reaction, $M(s) \rightarrow M^+(aq) + e^-$, will be favourable only if ΔH is negative. More negative is the value of ΔH , more favourable will be the formation of that cation from the metal. Thus, the oxidation state for which ΔH value is more negative will be stable in the solution.

Electrode potential for a M^{n+}/M half-cell is a measure of the tendency for the reaction, $M^{n+}(aq) + ne^- \rightarrow M(s)$

Thus, this reduction reaction will take place if the electrode potential for M^{n+}/M half-cell is positive. The reverse reaction, $M(s) \rightarrow M^{n+}(aq) + ne^-$

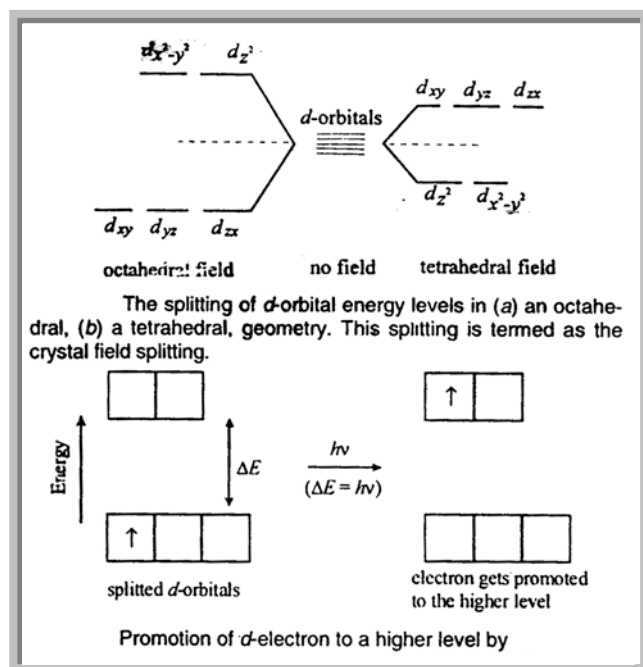
Involving the formation of $M^{n+}(aq)$ will occur if the electrode potential is negative, i.e., the tendency for the formation of $M^{n+}(aq)$ from the metal M will be more if the corresponding E° value is more negative. In other words, **the oxidation state for which E° value is more negative (or less positive) will be more stable in the solution.**

When an element exists in more than one oxidation states, the standard electrode potential (E°) values can be used in the predicting the relative stabilities of different oxidation states in aqueous solutions. The following rule is found useful.

The oxidation state of a cation for which $\Delta H = (\Delta H_{\text{sub}} + IE + \Delta H_{\text{hyd}})$ or E° is more negative (for less positive) will be more stable.

(9) Formation of coloured ions : Most of the compounds of the transition elements are coloured in the solid state and /or in the solution phase. The compounds of transition metals are coloured due to the presence of unpaired electrons in their d-orbitals.

Explanation : In an isolated atom or ion of a transition element, all the five d-orbitals are of the same energy (they



d and f Block Elements

are said to be regenerate). Under the influence of the combining anion(s), or electron- rich molecules, the five *d*-orbitals split into two (or sometimes more than two) levels of different energies. The difference between the two energy levels depends upon the nature of the combining ions, but corresponds to the energy associated with the radiations in the visible region, ($\lambda = 380 - 760\text{nm}$). Typical splitting for octahedral and tetrahedral geometries are shown in fig.

The transition metals in elements form or in the ionic form have one or more unpaired electrons. When visible light falls on the sample, the electrons from the lower energy level get promoted to a higher energy level due to the absorption of light of a characteristic wavelength (or colour). This wavelength (or colour) of the absorbed light depends upon the energy difference of the two levels. Rest of the light gets transmitted. The transmitted light has a colour complementary to the absorbed colour. Therefore, the compound or the solution appears to be of the complementary colour. For example, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ions absorb red radiation, and appear blue-green (blue-green is complementary colour to red). Hydrated Co^{2+} ions absorb radiation in the blue-green region, and therefore, appear red in sunlight. Relationship between the colour of the absorbed radiation and that of the transmitted light is given in table

Relationship between the colours of the absorbed and transmitted light: the complementary colours.

Colour of the		Colour of the	
Absorbed light	Transmitted light	Absorbed light	Transmitted light
IR	White	Blue-green	Red
Red	Blue-green	Blue	Orange
Orange	Blue	Indigo	Yellow
Yellow	Indigo	Violet	Yellow-green
Yellow-green	Violet	UV	White
Green	Purple		

However, if radiations of all the wavelengths (or colours) except one are absorbed, then the colour of the substance will be the colour of the transmitted radiation. For example, if a substance absorbs all colours except green, then it would appear green to the eyes.

The transition metal ions which have completely filled *d*-orbitals are colourless, as there are no vacant *d*-orbitals to permit promotion of the electrons. Therefore, Zn^{2+} ($3d^{10}$), Cd^{2+} ($4d^{10}$) and Hg^{2+} ($5d^{10}$) ions are colourless. The transition metal ions which have completely empty *d*-orbitals are also colourless, Thus, Sc^{3+} and Ti^{4+} ions are colourless, unless a coloured anion is present in the compound.

Colours and the outer- electronic configurations of the some important ions of the first transition series elements are given bellow,

Ion	Outer configuration	Number of unpaired electrons	Colour of the ion
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{2+}	$3d^5$	5	Light pink

d and f Block Elements

Mn³⁺	3d⁴	4	Violet
Fe²⁺	3d⁶	4	Green
Fe³⁺	3d⁵	5	Yellow
Co³⁺	3d⁷	3	Pink
Ni²⁺	3d⁸	2	Green
Cu²⁺	3d⁹	1	Blue
Cu⁺	3d¹⁰	0	Colourless
Zn²⁺	3d¹⁰	0	Colourless

(10) Magnetic properties : Most of the transition elements and their compounds show paramagnetism. The paramagnetism first increases in any transition element series, and then decreases. The maximum paramagnetism is seen around the middle of the series. The paramagnetism is described in Bohr Magneton (BM) units. The paramagnetic moments of some common ions of first transition series are given below in Table

Explanation : A substance which is attracted by magnetic field is called paramagnetic substance. The substances which are repelled by magnetic field are called diamagnetic substances. Paramagnetism is due to the presence of unpaired electrons in atoms, ions or molecules.

The magnetic moment of any transition element or its compound/ion is given by (assuming no contribution from the orbital magnetic moment).

$$\mu_s = \sqrt{4S(S+1)} \quad BM = \sqrt{n(n+2)} \quad BM$$

where, S is the total spin ($n \times s$): n is the number of unpaired electrons and s is equal to $\frac{1}{2}$ (representing the spin of an unpaired electron).

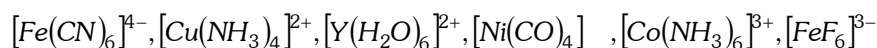
From the equation given above, the magnetic moment (μ_s) increases with an increase in the number of unpaired electrons.

Magnetic moments of some ions of the 3d-series elements

Ion	Outer configuration	No. of unpaired electrons	Magnetic moment (BM)	
			Calculated	observed
Sc³⁺	3d⁰	0	0	0
Ti³⁺	3d¹	1	1.73	1.75
Ti²⁺	3d²	2	2.84	2.86
V²⁺	3d³	3	3.87	3.86
Cr²⁺	3d⁴	4	4.90	4.80
Mn²⁺	3d⁵	5	5.92	5.95
Fe²⁺	3d⁶	4	4.90	5.0-5.5
Co²⁺	3d⁷	3	3.87	4.4-5.2
Ni²⁺	3d⁸	2	2.84	2.9-3.4
Cu²⁺	3d⁹	1	1.73	1.4-2.2
Zn²⁺	3d¹⁰	0	0	0

In d-orbitals belonging to a particular energy level, there can be at the maximum five unpaired electrons in d⁵ cases. Therefore, paramagnetism in any transition series first increases, reaches a maximum value for d⁵ cases and then decreases thereafter.

(11) Formation of complex ions : Transition metals and their ions show strong tendency for complex formation. The cations of transition elements (d-block elements) form complex ions with certain molecules containing one or more lone-pairs of electrons, viz., CO, NO, NH₃ etc., or with anions such as, F⁻, Cl⁻, CN⁻ etc. A few typical complex ions are,



d and f Block Elements

Explanation : This complex formation tendency is due to,

- (i) Small size and high nuclear charge of the transition metal cations.
- (ii) The availability to vacant inner d-orbitals of suitable energy.

(12) Formation of interstitial compounds : Transition elements form a few interstitial compounds with elements having small atomic radii, such as hydrogen, boron, carbon and nitrogen. The small atoms of these elements get entrapped in between the void spaces (called interstices) of the metal lattice. Some characteristics of the interstitial compound are,

(i) These are non-stoichiometric compounds and cannot be given definite formulae.

(ii) These compounds show essentially the same chemical properties as the parent metals, but differ in physical properties such as density and hardness. Steel and cast iron are hard due to the formation of interstitial compound with carbon. Some non-stoichiometric compounds are, $VSe_{0.98}$ (Vanadium selenide), $Fe_{0.94}O$, and titanium nitride.

Explanation : Interstitial compounds are hard and dense. This is because, the smaller atoms of lighter elements occupy the interstices in the lattice, leading to a more closely packed structure. Due to greater electronic interactions, the strength of the metallic bonds also increases.

(13) Catalytic properties : Most of the transition metals and their compounds particularly oxides have good catalytic properties. Platinum, iron, vanadium pentoxide, nickel, etc., are important catalysts. Platinum is a general catalyst. Nickel powder is a good catalyst for hydrogenation of unsaturated organic compound such as, hydrogenation of oils some typical industrial catalysts are,

- (i) Vanadium pentoxide (V_2O_5) is used in the Contact process for the manufacture of sulphuric acid,
- (ii) Finely divided iron is used in the Haber's process for the synthesis of ammonia.

Explanation : Most transition elements act as good catalyst because of,

- (i) The presence of vacant d-orbitals.
- (ii) The tendency to exhibit variable oxidation states.
- (iii) The tendency to form reaction intermediates with reactants.
- (iv) The presence of defects in their crystal lattices.

(14) Alloy formation : Transition metals form alloys among themselves. The alloys of transition metals are hard and high melting as compared to the host metal. Various steels are alloys of iron with metals such as chromium, vanadium, molybdenum, tungsten, manganese etc.

Explanation : The atomic radii of the transition elements in any series are not much different from each other. As a result, they can very easily replace each other in the lattice and form solid solutions over an appreciable composition range. Such solid solutions are called alloys.

(15) Chemical reactivity : The d-block elements (transition elements) have lesser tendency to react, i.e., these are less reactive as compared to s-block elements.

Explanation : Low reactivity of transition elements is due to,

- (i) Their high ionisation energies.
- (ii) Low heats of hydration of their ions.
- (iii) Their high heats of sublimation.

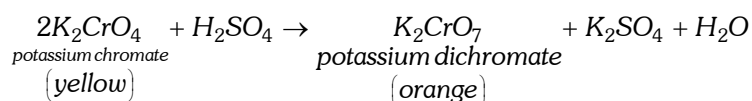
Some Compounds of d-Block Elements.

Potassium dichromate, (K₂Cr₂O₇)

Potassium dichromate is one of the most important compound of chromium, and also among dichromates. In this compound Cr is in the hexavalent (+6) state.

Preparation : It can be prepared by any of the following methods,

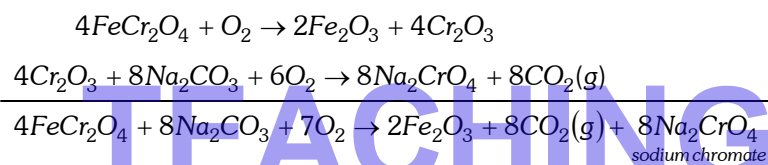
(i) **From potassium chromate :** Potassium dichromate can be obtained by adding a calculated amount of sulphuric acid to a saturated solution of potassium chromate.



K₂Cr₂O₇ Crystals can be obtained by concentrating the solution and crystallisation.

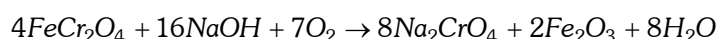
(ii) **Manufacture from chromite ore :** K₂Cr₂O₇ is generally manufactured from chromite ore (FeCr₂O₄). The process involves the following steps.

(a) Preparation of sodium chromate. Finely powdered chromite ore is mixed with soda ash and quicklime. The mixture is then roasted in a reverberatory furnace in the presence of air. Yellow mass due to the formation of sodium chromate is obtained.

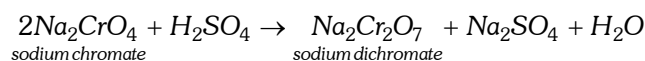


The yellow mass is extracted with water, and filtered. The filtrate contains sodium chromate.

The reaction may also be carried out by using NaOH instead of Na₂CO₃.The reaction in that case is,

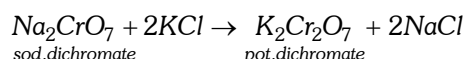


(b) Conversion of chromate into dichromate. Sodium chromate solution obtained in step(a) is treated with concentrated sulphuric acid when it is converted into sodium dichromate.



On concentration, the less soluble sodium sulphate, Na₂SO₄.10H₂O crystallizes out. This is filtered hot and allowed to cool when sodium dichromate, Na₂Cr₂O₇.2H₂O, separates out on standing.

(c) Concentration of sodium dichromate to potassium dichromate. Hot concentrated solution of sodium dichromate is treated with a calculated amount of potassium chloride. When potassium dichromate being less soluble crystallizes out on cooling.



Physical properties

(i) Potassium dichromate forms orange-red coloured crystals.

(ii) It melts at 699 K.

(iii) It is very stable in air (near room temperature) and is generally, used as a primary standard in the volumetric analysis.

(iv)It is soluble in water though the solubility is limited.

d and f Block Elements

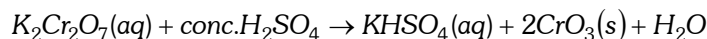
Chemical properties

(i) **Action of heat** : Potassium dichromate when heated strongly, decomposes to give oxygen.



(ii) **Action of acids**

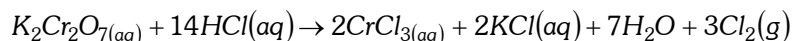
(a) In cold, with concentrated H_2SO_4 , red crystals of chromium trioxide separate out.



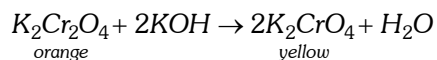
On heating a dichromate-sulphuric acid mixture, oxygen gas is given out.



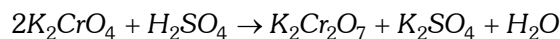
(b) With HCl , on heating chromic chloride is formed and Cl_2 is liberated.



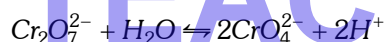
(iii) **Action of alkalis** : With alkalis, it gives chromates. For example, with KOH ,



On acidifying, the colour again changes to orange-red owing to the formation of dichromate.



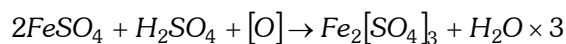
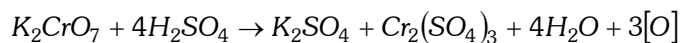
Actually, in dichromate solution, the $Cr_2O_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions.



(iv) **Oxidising nature** : In neutral or in acidic solution, potassium dichromate acts as an excellent oxidising agent, and $Cr_2O_7^{2-}$ gets reduced to Cr^{3+} . The standard electrode potential for the reaction,

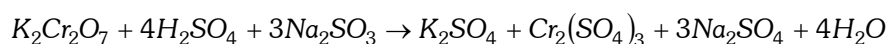
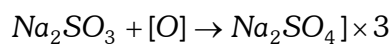
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ is +1.31 V. This indicates that dichromate ion is a fairly strong oxidising agent, especially in strongly acidic solutions. That is why potassium dichromate is widely used as an oxidising agent, for quantitative estimation of the reducing agents such as, Fe^{2+} . It oxidises,

(a) Ferrous salts to ferric salts



Ionic equation: $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

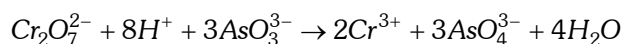
(b) Sulphites to sulphates and arsenites to arsenates.



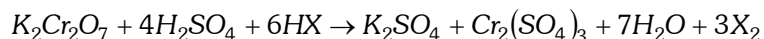
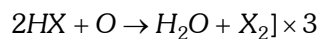
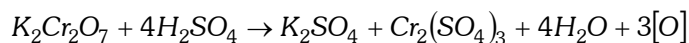
Ionic equation: $Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

d and f Block Elements

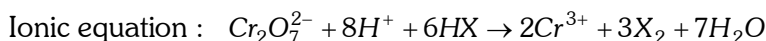
Similarly, arsenites are oxidised to arsenates.



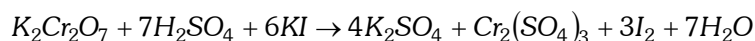
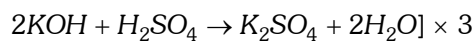
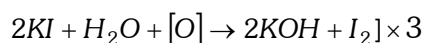
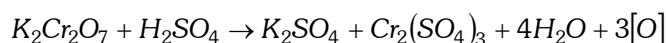
(c) Hydrogen halides to halogens.



where, X may be Cl, Br, I.

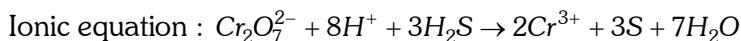
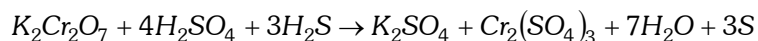
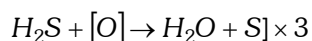
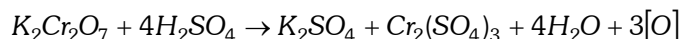


(d) Iodides to iodine

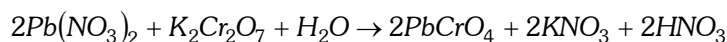


Thus, when KI is added to an acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ iodine gets liberated.

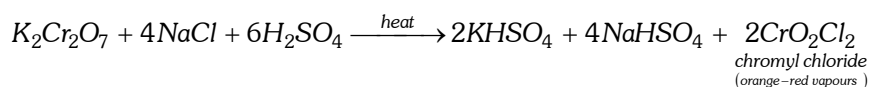
(e) It oxidises H_2S to S.



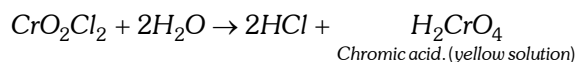
(v) **Formation of insoluble chromates** : With soluble salts of lead, barium etc., potassium dichromate gives insoluble chromates. Lead chromate is an important yellow pigment.



(vi) **Chromyl chloride test** : When potassium dichromate is heated with conc. H_2SO_4 in the presence of a soluble chloride salt, the orange-red vapours of chromyl chloride (CrO_2Cl_2) are formed.



Chromyl chloride vapours when passed through water give yellow-coloured solution containing chromic acid.



Chromyl chloride test can be used for the detection of chloride ion in any mixture.

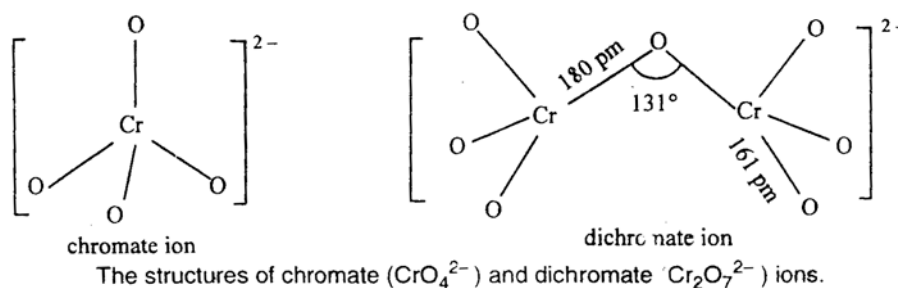
Uses : Potassium dichromate is used as,

d and f Block Elements

- (i) An oxidising agent
- (ii) In chrome tanning
- (iii) The raw material for preparing large number of chromium compounds
- (iv) Primary standard in the volumetric analysis.

Structures of Chromate and Dichromate Ions

Chromates and dichromates are the salts of chromic acid (H_2CrO_4). In solution, these ions exist in equilibrium with each other. Chromate ion has four oxygen atoms arranged tetrahedrally around Cr atom. (see Fig). Dichromate ion involves a Cr–O–Cr bond as shown in Fig.

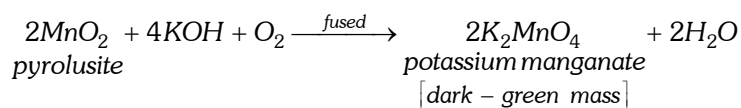
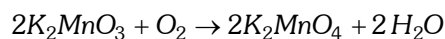
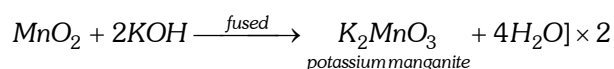


Potassium Permanganate, ($KMnO_4$)

Potassium permanganate is a salt of an unstable acid $HMnO_4$ (permanganic acid). The Mn is an +7 state in this compound.

Preparation : Potassium permanganate is obtained from pyrolusite as follows.

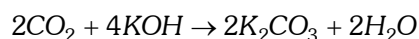
Conversion of pyrolusite to potassium manganate : When manganese dioxide is fused with potassium hydroxide in the presence of air or an oxidising agent such as potassium nitrate or chlorate, potassium manganate is formed, possibly via potassium manganite.



Oxidation of potassium manganate to potassium permanganate : The potassium manganate so obtained is oxidised to potassium permanganate by either of the following methods.

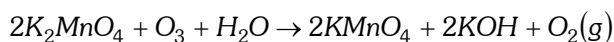
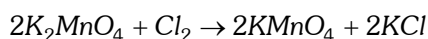
By chemical method : The fused dark-green mass is extracted with a small quantity of water. The filtrate is warmed and treated with a current of ozone, chlorine or carbon dioxide. Potassium manganate gets oxidised to potassium permanganate and the hydrated manganese dioxide precipitates out. The reactions taking place are,

When CO_2 is passed



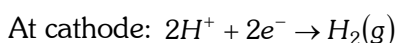
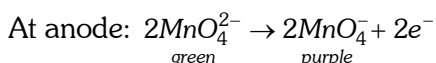
d and f Block Elements

When chlorine or ozone is passed



The purple solution so obtained is concentrated and dark purple, needle-like crystals having metallic lustre are obtained.

Electrolytic method : Presently, potassium manganate (K_2MnO_4) is oxidised electrolytically. The electrode reactions are,



The purple solution containing $KMnO_4$ is evaporated under controlled condition to get crystalline sample of potassium permanganate.

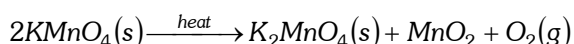
Physical properties

$KMnO_4$ crystallizes as dark purple crystals with greenish luster (m.p. 523 K).

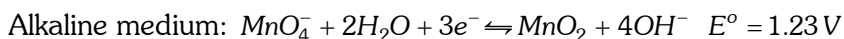
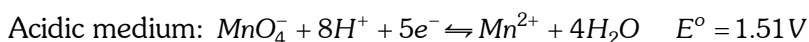
It is soluble in water to an extent of 6.5g per 100g at room temperature. The aqueous solution of $KMnO_4$ has a purple colour.

Chemical properties : Some important chemical reactions of $KMnO_4$ are given below,

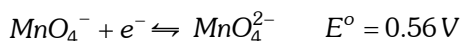
Action of heat : $KMnO_4$ is stable at room temperature, but decomposes to give oxygen at higher temperatures.



Oxidising actions : $KMnO_4$ is a powerful agent in neutral, acidic and alkaline media. The nature of reaction is different in each medium. The oxidising character of $KMnO_4$ (to be more specific, of MnO_4^-) is indicated by high positive reduction potentials for the following reactions.



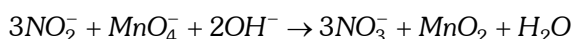
In strongly alkaline solutions and with excess of MnO_4^- , the reaction is



There are a large number of oxidation-reduction reactions involved in the chemistry of manganese compounds. Some typical reactions are,

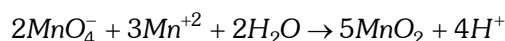
In the presence of excess of reducing agent in acidic solutions permanganate ion gets reduced to manganous ion, e.g., $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

An excess of reducing agent in alkaline solution reduces permanganate ion only to manganese dioxide e.g.,



d and f Block Elements

In faintly acidic and neutral solutions, manganous ion is oxidised to manganese dioxide by permanganate.

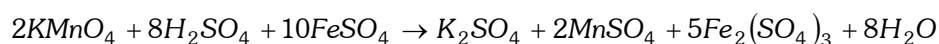
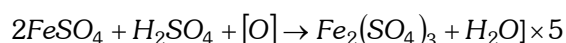


In strongly basic solutions, permanganate oxidises manganese dioxide to manganate ion.



In acidic medium, KMnO_4 oxidises,

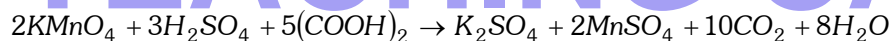
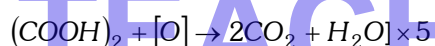
Ferrous salts to ferric salts



Ionic equation: $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Fe}^{2+} \rightarrow 2\text{Mn}^{2+} + 10\text{Fe}^{3+} + 8\text{H}_2\text{O}$

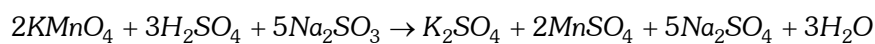
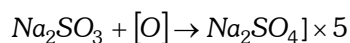
The reaction forms the basis of volumetric estimation of Fe^{2+} in any solution by KMnO_4 .

Oxalic acid to carbon dioxide



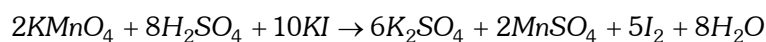
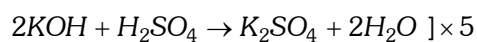
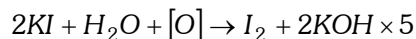
Ionic equation : $2\text{MnO}_4^- + 6\text{H}^+ + 5(\text{COOH})_2 \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$

Sulphites to sulphates



Ionic equation : $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{SO}_3^{2-} \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}$

Iodides to iodine in acidic medium

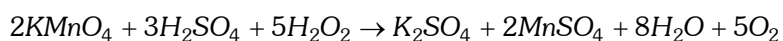
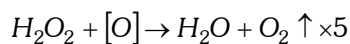


Ionic equation : $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{I}^- \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$

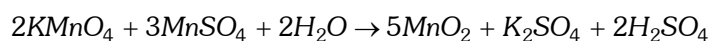
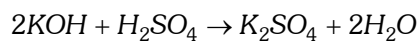
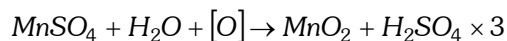
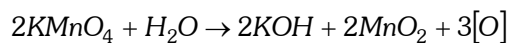
Hydrogen peroxide to oxygen



d and f Block Elements

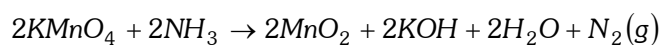
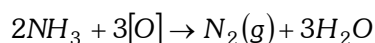


Manganous sulphate (MnSO₄) to manganese dioxide (MnO₂)



Ionic equation : $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

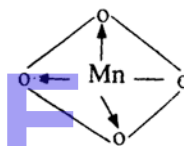
Ammonia to nitrogen



Uses : KMnO₄ is used,

(i) As an oxidising agent. (ii) As a disinfectant against disease-causing germs. (iii) For sterilizing wells of drinking water. (iv) In volumetric estimation of ferrous salts, oxalic acid etc.

Structure of Permanganate Ion (MnO₄⁻) : Mn in MnO₄⁻ is in +7 oxidation state. Mn⁷⁺ exhibits sp³ hybridisation in this ion. The structure of MnO₄⁻ is, shown in fig.



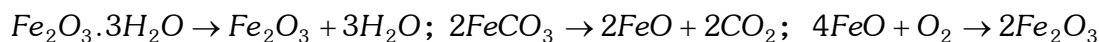
Structure of MnO₄⁻ ion.

Iron and its Compounds.

(1) **Ores of iron :** Haematite (Fe₂O₃), Magnetite (Fe₃O₄), Limonite (Fe₂O₃·3H₂O), Iron pyrites (FeS₂), Copper pyrites (CuFeS₂) etc.

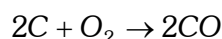
(2) **Extraction :** Cast iron is extracted from its oxides by reduction with carbon and carbon monoxide in a blast furnace to give pig iron.

Roasting : Ferrous oxide convert into ferric oxide.



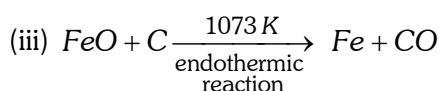
Smelting : Reduction of roasted ore of ferric oxide carried out in a blast furnace.

(i) The reduction of ferric oxide is done by carbon and carbon monoxide (between 1473k to 1873k)



Note : * The CO is the essential reducing agent.

(ii) $Fe_2O_3 + 3CO \xrightarrow{673K} 2Fe + 3CO_2$. It is a reversible and exothermic reaction. Hence according to Le - chatelier principle more iron will be produced in the furnace at lower temp. $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$ (it is not reversible)



d and f Block Elements

Note : *The gases leaving at the top of the furnace contain up to 28% CO, and are burnt in cowper's stove to pre-heat the air for blast

Varieties of iron : The three commercial varieties of iron differ in their carbon contents. These are;

(1) **Cast iron or Pig-iron** : It is most impure form of iron and contains highest proportion of carbon (2.5–4%).

(2) **Wrought iron or Malleable iron** : It is the purest form of iron and contains minimum amount of carbon (0.12–0.25%).

(3) **Steel** : It is the most important form of iron and finds extensive applications. Its carbon content (Impurity) is mid-way between cast iron and wrought iron. It contains 0.2–1.5% carbon. Steels containing 0.2–0.5% of carbon are known as mild steels, while those containing 0.5–1.5% carbon are known as hard steels.

Steel is generally manufactured from cast iron by three processes, viz, (i) Bessemer Process which involves the use of a large pear-shaped furnace (vessel) called Bessemer converter, (ii) L.D. process and (iii) open hearth process, Spiegeleisen (an alloy of Fe, Mn and C) is added during manufacture of steel.

Heat treatment of steels : Heat treatment of steel may be defined as the process of carefully heating the steel to high temperature followed by cooling to the room temperature under controlled conditions. Heat treatment of steel is done for the following two purposes,

(i) To develop certain special properties like hardness, strength, ductility etc. without changing the chemical composition.

(ii) To remove some undesirable properties or gases like entrapped gases, internal stresses and strains. The various methods of heat treatment are,

(a) **Annealing** : It is a process of heating steel to redness followed by slow cooling.

(b) **Quenching or hardening** : It is a process of heating steel to redness followed by sudden cooling by plunging the red hot steel into water or oil.

(c) **Tempering** : It is a process of heating the hardened or quenched steel to a temperature much below redness (473–623K) followed by slow cooling.

(d) **Case-hardening** : It is a process of giving a thin coating of hardened steel to wrought iron or to a strong and flexible mild steel by heating it in contact with charcoal followed by quenching in oil.

(e) **Nitriding** : It is a process of heating steels at about 700 °C in an atmosphere of ammonia. This process imparts a hard coating of iron nitride on the surface of steel.

Properties of steel : The properties of steel depend upon its carbon contents. With the increase in carbon content, the hardness of steel increases while its ductility decreases.

(i) Low carbon or soft steels contain carbon upto 0.25%.

(ii) Medium carbon steels or mild steels contain 0.25–0.5% carbon.

(iii) High carbon or hard steels contains 0.1 – 1.5 percent carbon.

(iv) Alloy steels or special steels are alloys of steel with Ni, Cr, Co, W, Mn, V etc., For example – stainless steel is an alloy of Fe, Cr and Ni and it is used for making automobile parts and utensils. Tool steel is an alloy of Fe, W, V etc.

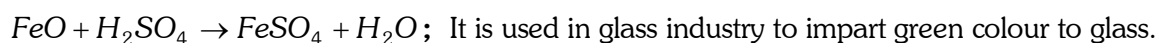
Uses of steel: In general, steels are used for making machinery parts, girders, tools, knives, razors, household utensils, etc. The specific use of steel depend upon the nature of metal added to iron.

Compounds of iron

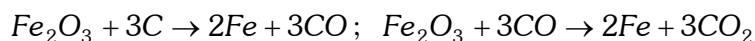
d and f Block Elements

(1) **Oxides of Iron** : Iron forms three oxides FeO, Fe_2O_3 (Haematite), Fe_3O_4 (magnetite also called magnetic oxide or load stone).

(i) **Ferrous oxide**, FeO : It is a black powder, basic in nature and reacts with dilute acids to give ferrous salts.



(ii) **Ferric oxide** Fe_2O_3 : It is a reddish brown powder, not affected by air or water; amphoteric in nature and reacts both with acids and alkalis giving salts. It can be reduced to iron by heating with C or CO .

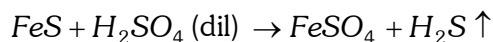


It is used as red pigment to impart red colour to external walls and as a polishing powder by jewellers.

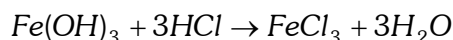
(iii) **Ferrosferric oxide** $Fe_3O_4 (FeO.Fe_2O_3)$: It is more stable than FeO and Fe_2O_3 , magnetic in nature and dissolves in acids giving a mixture of iron (II) and iron (III) salts.



(2) **Ferrous sulphide** FeS : It is prepared by heating iron filing with sulphur. With dilute H_2SO_4 , it gives H_2S .



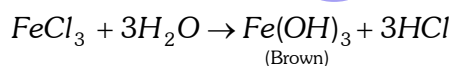
(3) **Ferric chloride** $FeCl_3$: It is prepared by treating $Fe(OH)_3$ with HCl



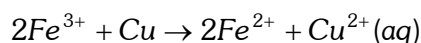
The solution on evaporation give yellow crystals of $FeCl_3 \cdot 6H_2O$

Properties : (i) Anhydrous $FeCl_3$ forms reddish-black deliquescent crystals.

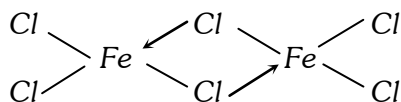
(ii) $FeCl_3$ is hygroscopic and dissolves in H_2O giving brown acidic solution due to formation of HCl



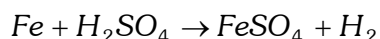
(iii) Due to oxidising nature Fe^{3+} ions $FeCl_3$ is used in etching metals such as copper



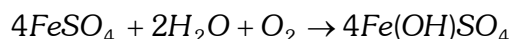
(iv) In vapour state $FeCl_3$ exists as a dimer, Fe_2Cl_6



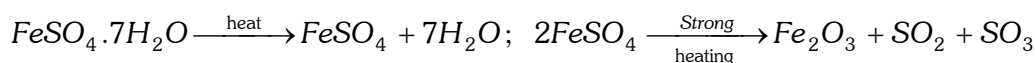
(4) **Ferrous sulphate**, $FeSO_4 \cdot 7H_2O$ (Green vitriol) : It is prepared as follow ,



(i) On exposure to moist air crystals become brownish due to oxidation by air.



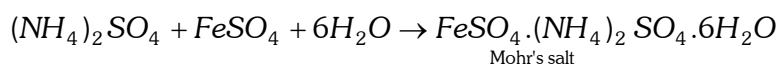
(ii) On heating, crystals become anhydrous and on strong heating it decomposes to Fe_2O_3, SO_2 and SO_3 .



(iii) It can reduce acidic solution of $KMnO_4$ and $K_2Cr_2O_7$

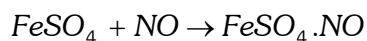
(iv) It is generally used in double salt with ammonium sulphate.

d and f Block Elements



Mohr's salt is resistant to atmospheric oxidation.

(v) It is used in the ring test for nitrate ions where it gives brown coloured ring of compound $FeSO_4 \cdot NO$.



(5) **Mohr's salt** $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$: It is also known as ferrous ammonium sulphate and is a light green coloured double salt.

Copper and its Compounds.

Ores : Copper pyrites (chalcopyrite) $CuFeS_2$, Cuprite (ruby copper) Cu_2O , Copper glance (Cu_2S), Malachite [$Cu(OH)_2 \cdot CuCO_3$], Azurite [$Cu(OH)_2 \cdot 2CuCO_3$]

Extraction : Most of copper (about 75%) is extracted from its sulphide ore, copper pyrites.

Concentration of ore : Froth floatation process.

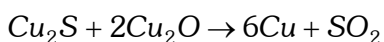
Roasting : Main reaction : $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$.

Side reaction : $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$; $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$.

Smelting : $FeO + SiO_2 \rightarrow FeSiO_3$ (slag); $Cu_2O + FeS \rightarrow FeO + Cu_2S$

Note : * The mixture of copper and iron sulphides melt together to form 'matte' and the slag floats on its surface.

Conversion of matte into Blister copper (Bessemerisation) : Silica is added to matte and a hot blast of air is passed $FeO + SiO_2 \rightarrow FeSiO_3$ (slag). Slag is removed. By this time most of iron sulphide is removed.



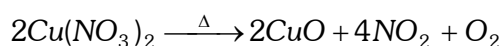
Note : * Blister copper : Which contain about 98% pure copper and 2% impurities (Ag, Au, Ni, Zn etc.)

Properties of copper : It has reddish brown colour. It is highly malleable and ductile. It has high electrical conductivity and high thermal conductivity. In presence of CO_2 and moisture Cu is covered with a green layer of $CuCO_3 \cdot Cu(OH)_2$. $2Cu + H_2O + CO_2 + O_2 \rightarrow CuCO_3 \cdot Cu(OH)_2$. It undergoes displacement reactions with lesser reactive metals e.g. with Ag . It can displace Ag from $AgNO_3$. The finally divided Ag so obtained is black in colour.

Compounds of copper

Cuprous oxide Cu_2O : It is a reddish brown powder insoluble in water but soluble in ammonia solution, where it forms diammine copper (I) ion. $Cu^+ + 2NH_3 \rightarrow [Cu(NH_3)_2]^+$. It is used to impart red colour to glass in glass industry.

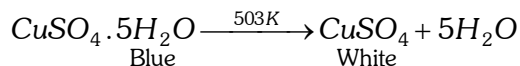
Cupric oxide CuO : It is dark black, hygroscopic powder which is reduced to Cu by hydrogen, CO etc. It is used to impart light blue colour to glass. It is prepared by heating copper nitrate.



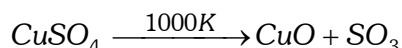
d and f Block Elements

Copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Blue vitriol) : It is prepared by action of dil H_2SO_4 on copper scrap in presence of air. $2\text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2 \xrightarrow{\text{(air)}} \text{CuSO}_4 + 2\text{H}_2\text{O}$

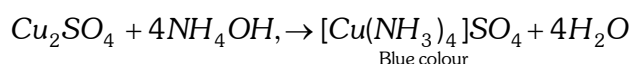
(i) On heating this blue salt becomes white due to loss of water of crystallization.



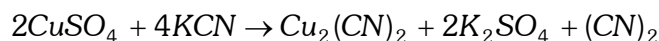
At about 1000 K, CuSO_4 decomposes to give CuO and SO_3 .



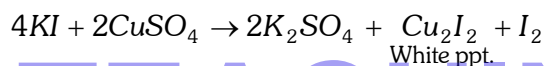
(ii) It gives a deep blue solution of tetrammine copper (II) sulphate with NH_4OH .



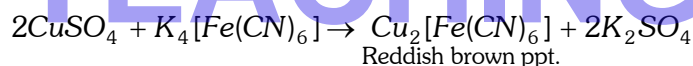
(iii) With KCN it first gives yellow precipitate of CuCN which decomposes to give $\text{Cu}_2(\text{CN})_2$. $\text{Cu}_2(\text{CN})_2$ dissolves in excess of KCN to give $\text{K}_3[\text{Cu}(\text{CN})_4]$



(iv) With KI it gives white ppt. of Cu_2I_2



(v) With $\text{K}_4[\text{Fe}(\text{CN})_6]$, CuSO_4 gives a reddish brown ppt. of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$



Uses : For electroplating and electrorefining of copper. As a mordant in dyeing. For making Bordeaux mixture (11 parts lime as milk of lime + 16 parts copper sulphate in 1,000 parts of water). It is an excellent fungicide. For making green pigments containing copper carbonate and other compounds of copper. As a fungicide in starch paste for book binding work.

Cupric sulphide CuS : It is prepared as follows : $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{S} \rightarrow \text{CuS} + 2\text{HNO}_3$.
Black ppt.

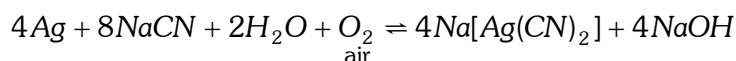
Cupric chloride CuCl_2 : It is a dark brown solid soluble in water and its aqueous solution first changes to green and then to blue on dilution.

Cuprous chloride Cu_2Cl_2 : It is a white solid insoluble in water and dissolves in conc. HCl due to formation of $\text{H}[\text{CuCl}_2]$ complex.

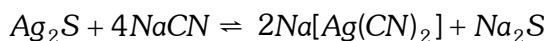
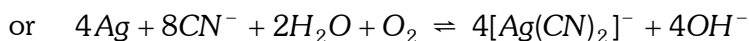
Silver and its Compounds.

Ores : Argentite (silver glance) Ag_2S , Horn silver (AgCl), Ruby silver (Pyrargyrite) $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$.

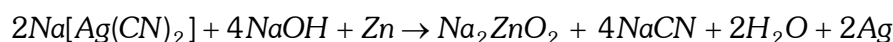
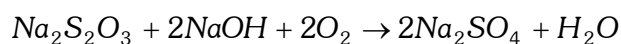
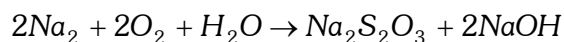
Extraction : Cyanide process or Mac Arthus-Forrest cyanide process : This method depends on the fact that silver, its sulphide or chloride, forms soluble complex with alkali cyanides in the silver. This implies that silver compounds will dissolve in solution of alkali cyanides in the presence of blast of air.



d and f Block Elements



The reaction with the sulphide is reversible and accumulation of Na_2S must be prevented. A free excess of air is continuously passed through the solution which oxidizes Na_2S into sulphate and thiosulphate.

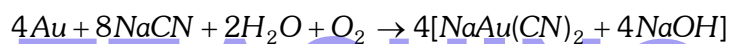


Compounds of silver : AgNO_3 , Ag_2S , AgCl , AgBr , AgI , and AgO .

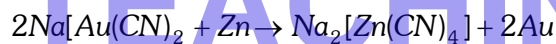
Gold and its Compounds.

Ores : Bismuthaurite (BiAu_2), Syvanite (AgAuTe_2), Calverite (AuTe_2).

Extraction : By cyanide or Mac-Arther forest cyanide process,



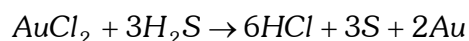
Sodium aurocyanide



Refining : Anode : Crude gold; Cathode : Pure gold.

Electrolytic Solution : Gold chloride in hydrochloric acid.

Plattner chlorine extraction process,



Quartation process : Refining of gold carried out by this method. It involves separation of gold and Ag by H_2SO_4 .

Gold is soft and hence for making ornaments it is generally hardened by adding Ag or Cu. The weight of gold is expressed in terms of **Carats. Pure gold is taken as 24 carats.**

20 carats means, it contain 20 parts by wt. of gold in 24 parts by wt. of given alloy.

$$\therefore \text{percentage of gold in 20 carat gold sample} = \frac{20}{24} \times 100 = \frac{250}{3} = 83.33\%$$

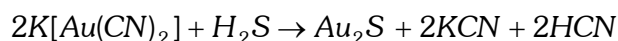
Properties : Gold is not affected by conc. H_2SO_4 , conc. HNO_3 or by strong alkalis. However it dissolves in aqua regia to form $\text{H}[\text{AuCl}_4]$; $2\text{Au} + 3\text{HNO}_3 + 11\text{HCl} \rightarrow 2\text{H}[\text{AuCl}_4] + 6\text{H}_2\text{O} + 3\text{NOCl}$.

Compounds of gold

AuCl_3 : It is a reddish solid soluble in water. It reacts with HCl to give $\text{H}[\text{Au}(\text{Cl})_4]$ which is used in toning process in photography. $\text{HCl} + \text{AuCl}_3 \rightarrow \text{H}[\text{Au}(\text{Cl})_4]$

d and f Block Elements

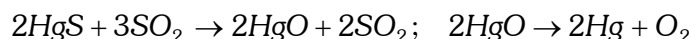
Au₂S : It is a dark brown solid insoluble in water prepared as follows :



Mercury and its Compounds.

Ores : Cinnabar (HgS)

Extraction : *Roasting* : The concentrated ore roasted at 770 K to 780 K in the pressure of air.

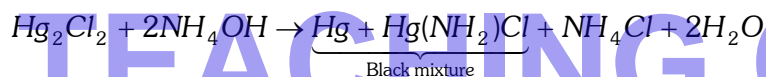


Refining : By filtering impure Hg through thick canvass or chamois leather. It is then dropped into 5% HNO_3 .

Compounds of Mercury

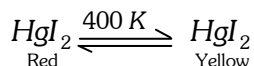
Mercuric chloride $HgCl_2$ (Corrosive sublimate) : It is a colourless solid, sparingly soluble in water. It forms red ppt. of HgI_2 with KI : $HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$. With NH_4OH it gives white ppt. of $Hg(NH_2)Cl$.
 $HgCl_2 + 2NH_4OH \rightarrow Hg(NH_2)Cl + NH_4Cl + 2H_2O$.
white ppt.

Mercurous chloride Hg_2Cl_2 (Calomel) : It is a white solid insoluble in water. With NH_4OH it forms a black mixture composed of black metallic mercury and white mercuric amino chloride, $Hg(NH_2)Cl$.



It is used as purgative in medicine and it sublimes on heating.

Mercuric iodide HgI_2 : It is a yellow solid below 400K but changes to red solid above 400K.



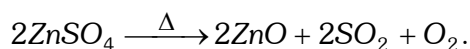
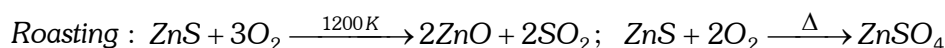
It dissolves in excess of KI forming K_2HgI_4 ; $HgI_2 + 2KI \rightarrow K_2HgI_4$

Alkaline solution of K_2HgI_4 is called Nessler's reagent.

Zinc and its Compounds.

Ores : Zincite (red zinc ore) ZnO , Franklinite ($ZnOFe_2O_3$), Zinc blende (ZnS), Calamine (Zinc spar) $ZnCO_3$.

Extraction : *Concentration* : Froth floatation



Reduction of ZnO : The oxide ore is mixed with crushed coke and heated to about 1670K in fire clay retorts (Belgian process). The crude metal obtained called Zinc spelter.

Refining : By distillation and by electrolytic method

Anode : Spelter; Cathode : Pure zinc wire; Electrolyte : Zinc sulphate.

d and f Block Elements

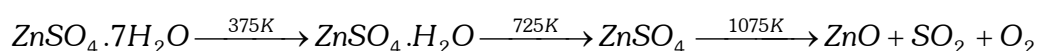
Note : * Zinc is a volatile metal (easily vaporisable)

*At ordinary temperature zinc metal is brittle but on heating at 120 – 150° C it is malleable and ductile.

Compounds of zinc

Zinc oxide ZnO : Zincite (ZnO) is also called Philosopher's wool. It is white powder, become yellow on heating and again white on cooling. It is amphoteric in nature. It is used as a white pigment under the name Zinc white or Chinese white.

Zinc Sulphate (white vitriol), $ZnSO_4 \cdot 7H_2O$: It is a colourless transparent crystal highly soluble in water. It is used as an eye-lotion and for preparing double salts. On heating it loses its molecules of water as,



Tin and Lead .

Tin

Ores of Tin : Cassiterite or tin stone (SnO_2)

- The concentrated and roasted ore is reduced with carbon to get impure tin which is purified by *liquation process*.
- Tin forms two series of salts, i.e., Sn (II) and Sn (IV). Whereas Sn (II) salts are ionic Sn (IV) salts are covalent.
- Tin dissolves in hot conc. NaOH forming Na_2SnO_3 and evolving H_2 gas.
- Tin reacts with conc. HNO_3 forming metastannic acid (H_2SnO_3).
- Tin is not attacked by organic acids and hence is used for *tinning of utensils* to resist corrosion. Tin foils are used for wrapping cigarettes, confectionary items and for making tooth-paste tubes.
- SnO_2 is an amphoteric oxide.
- Stannous chloride ($SnCl_2$) acts as a good reducing agent. It reduces $HgCl_2$ to first Hg_2Cl_2 and then to Hg . It also reduces $FeCl_3$ to $FeCl_2$.
- Stannic chloride ($SnCl_4$) is a liquid and fumes in air due to hydrolysis. It acts as a *Lewis acid* and dissolves in concentration HCl forming H_2SnCl_6 .
- $SnCl_4 \cdot 5H_2O$ is called *butter of tin*.
- SnS dissolves in yellow ammonium sulphide.

Lead

d and f Block Elements

Ores of lead : Galena (PbS), Anglesite ($PbSO_4$) and Cerussite ($PbCO_3$).

• Lead is extracted from galena. The ore is concentrated by *froth-floatation process* and roasted when a part of the ore is converted into PbO and $PbSO_4$. The unchanged galena then brings about the reduction of PbO or $PbSO_4$ to Pb .

• Lead dissolves in hot conc. NaOH forming sodium plumbite (Na_2PbO_2) and evolving H_2 gas.

• Lead forms two series of salts, i.e., Pb (II) and Pb (IV) but Pb (II) compounds are more stable than Pb (IV) compounds. Lead (II) compounds are essentially **ionic while lead** (IV) compounds are covalent.

• Lead is used in making bullet shots, lead accumulators, tetraethyl lead (*antiknocking agent*) and a number of pigments such as red lead (Pb_3O_4), white lead or basic lead carbonate [$2PbCO_3.Pb(OH)_2$] and lead chromate ($PbCrO_4$).

• Litharge is PbO . It is obtained by heating $Pb(NO_3)_2$ or $PbCO_3$. It is an amphoteric oxide and is reduced back to Pb by H_2 , C and CO.

• Red lead (Pb_3O_4) or Sindhur is a mixed oxide ($2PbO.PbO_2$). It acts as an oxidising agent and as such oxidises HCl to Cl_2 .

• Lead dioxide (PbO_2) is obtained either by treating Pb_3O_4 with conc. HNO_3 or by treating lead acetate with bleaching powder. It acts as an oxidising agent and oxidises HCl to Cl_2 .

• The ionic character of lead dihalides decreases in the order: $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$.

• PbF_4 and $PbCl_4$ are stable while $PbBr_4$ and PbI_4 are however, unknown. The non-existence of $PbBr_4$ and PbI_4 is due to strong oxidising character of Pb^{4+} ions and reducing character of Br^- and I^- ions.

• PbF_4 is ionic while $PbCl_4$ is a volatile liquid.

• Lead is readily corroded by water containing dissolved air forming $Pb(OH)_2$ which has appreciable solubility in water. This action of water on lead called is *Plumbosolvency*. $2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2$

Whereas organic acids, NH_4^+ salts and nitrates increase while salts like carbonates, phosphate and sulphates decrease Plumbosolvency. Hard water, however, has no solvent action on lead.

Lanthanides and Actinides.

Lanthanides and actinides are collectively called *f*-block elements because last electron in them enters into *f*-orbitals of the antepenultimate (i.e., inner to penultimate) shell partly but incompletely filled in their elementary or ionic states. The name inner transition, elements is also given to them because they constitute transition series with in transition series (*d*-block elements) and the last electron enters into antepenultimate shell ($n-2$) *f*. In addition to incomplete *d*-subshell, their *f*-subshell is also incomplete. Thus, these elements have three incomplete outer shells i.e., ($n-2$), ($n-1$) and n shells and the general electronic configuration of *f*-block elements is $(n-2) f^{1-14} (n-1) d^{0-10} ns^2$.

d and f Block Elements

(1) **Lanthanides** : The elements with atomic numbers 58 to 71 i.e. cerium to lutetium (which come immediately after lanthanum $Z = 57$) are called lanthanides or **lanthanones or rare earths**. These elements involve the filling of 4 *f*-orbitals. Their general electronic configuration is, $[Xe]4f^{1-14}5d^{0-10}6s^2$. Promethium (*Pm*), atomic number 61 is the only synthetic (man made) radioactive lanthanide.

Properties of lanthanides

(i) These are highly dense metals and possess high melting points.

(ii) They form alloys easily with other metals especially iron. e.g. **misch metal** consists of a rare earth element (94–95%), iron (upto 5%) and traces of S, C, Ca and Al, pyrophoric alloys contain Ce (40–5%), La + neodymium (44%), Fe (4–5%), Al (0–5%) and the rest is Ca, Si and C. It is used in the preparation of ignition devices e.g., trace bullets and shells and flints for lighters.

(iii) **Oxidation state** : Most stable oxidation state of lanthanides is + 3. Oxidation states + 2 and + 4 also exist but they revert to + 3 e.g. $Sm^{2+}, Eu^{2+}, Yb^{2+}$ lose electron to become + 3 and hence are good reducing agents, where as $Ce^{4+}, Pr^{4+}, Tb^{4+}$ in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4 *f* and 5 *d* subshells and thus the number of oxidation states is limited.

(iv) **Colour** : Most of the trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. This is due to the partly filled *f*-orbitals which permit *f*–*f* transition. The elements with *xf* electrons have a similar colour to those of (14 – *x*) electrons.

(v) **Magnetic properties** : All lanthanide ions with the exception of Lu^{3+}, Yb^{3+} and Ce^{4+} are paramagnetic because they contain unpaired electrons in the 4 *f* orbitals. These elements differ from the transition elements in that their magnetic moments do not obey the simple “spin only” formula $\mu_{eff} = \sqrt{n(n+2)}$ B.M. where *n* is equal to the number of unpaired electrons. In transition elements, the orbital contribution of the electron towards magnetic moment is usually quenched by interaction with electric fields of the environment but in case of lanthanides the 4 *f*-orbitals lie too deep in the atom for such quenching to occur. Therefore, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions and a more complex formula

$$\mu_{eff} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

which involves the orbital quantum number *L* and spin quantum number *S*.

(vi) **Complex formation** : Although the lanthanide ions have a high charge (+3) yet the size of their ions is very large yielding small charge to size ratio i.e., low charge density. As a consequence, they have poor tendency to form complexes. They form complexes mainly with strong chelating agents such as EDTA, β -diketones, oxine etc. No complexes with π -bonding ligands are known.

(vii) **Lanthanide contraction** : The regular decrease in the size of lanthanide ions from La^{3+} to Lu^{3+} is known as lanthanide contraction. It is due to greater effect of the increased nuclear charge than that of the screening effect.

Consequences of lanthanide contraction

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange

(b) Each element beyond lanthanum has same atomic radius as that of the element lying above it in the group (e.g. Zr 145 pm, Hf 144 pm); Nb 134 pm, Ta 134 pm ; Mo 129 pm, W 130 pm).

d and f Block Elements

(c) The covalent character of hydroxides of lanthanides increases as the size decreases from La^{3+} to Lu^{3+} . However basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic. Similarly, the basicity of oxides also decreases in the order from La^{3+} to Lu^{3+} .

(d) Tendency to form stable complexes from La^{3+} to Lu^{3+} increases as the size decreases in that order.

(e) There is a slight increase in electronegativity of the trivalent ions from La to Lu .

(f) Since the radius of Yb^{3+} ion (86 pm) is comparable to the heavier lanthanides Tb , Dy , Ho and Er , therefore they occur together in natural minerals.

(2) **Actinides** : The elements with atomic numbers 90 to 103 i.e. thorium to lawrencium (which come immediately after actinium, $Z = 89$) are called actinides or actinones. These elements involve the filling of 5 f -orbitals. Their general electronic configuration is, $[Rn]5f^{1-14}6d^{0-1}7s^2$.

They include three naturally occurring elements thorium, protactinium and uranium and eleven transuranium elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or man made elements. All actinides are radioactive.

Properties of actinides

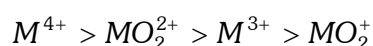
(i) **Oxidation state** : The dominant oxidation state of actinides is +3 which shows increasing stability for the heavier elements. Np shows +7 oxidation state but this is oxidising and is reduced to the most stable state +5. Pu also shows states upto +7 and Am upto +6 but the most stable state drops to Pu (+4) and Am (+3). Bk in +4 state is strongly oxidising but is more stable than Cm and Am in +4 state due to f^7 configuration. Similarly, No is markedly stable in +2 state due to its f^4 configuration. When the oxidation number increases to +6, the actinide ions are no longer simple. The high charge density causes the formation of oxygenated ions e.g., UO_2^{2+} , NpO_2^{2+} etc. The exhibition of large number of oxidation states of actinides is due to the fact that there is a very small energy gap between 5 f , 6 d and 7 s subshells and thus all their electrons can take part in bond formation.

(ii) **Actinide contraction** : There is a regular decrease in ionic radii with increase in atomic number from Th to Lr . This is called actinide contraction analogous to the lanthanide contraction. It is caused due to imperfect shielding of one 5 f electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

(iii) **Colour of the ions** : Ions of actinides are generally coloured which is due to $f-f$ transitions. It depends upon the number of electrons in 5 f orbitals.

(iv) **Magnetic properties** : Like lanthanides, actinide elements are strongly paramagnetic. The magnetic moments are lesser than the theoretically predicted values. This is due to the fact that 5 f electrons of actinides are less effectively shielded which results in quenching of orbital contribution.

(v) **Complex formation** : Actinides have a greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms. They form complexes even with π -bonding ligands such as alkyl phosphines, thioethers etc, besides EDTA, β -diketones, oxine etc. The degree of complex formation decreases in the order.



d and f Block Elements

where M is element of actinide series. There is a high concentration of charge on the metal atom in MO_2^{2+} which imparts to it relatively high tendency towards complex formation.

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