

4. The d and f Block Elements

Elements from 3rd group to 12th group in the Modern Periodic table are called d-block elements. In these elements their last electron enters in the penultimate d- sub shell. They are placed in between s-block and p-block elements. They show a regular transition from the highly electropositive metals of s-block elements to the less electropositive p-block elements. So they are called transition elements.

Transition elements can be defined as elements which contain partially filled d orbitals in their atomic state or in any of their oxidation state. The elements Zn, Cd and Hg contain only completely filled d-orbitals. So they are not regarded as transition elements. Or, they are called pseudo transition elements.

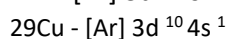
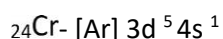
There are four series of transition elements.

- 1) 3d series [from Scandium (sc, z = 21) to zinc (Zn, z = 30)]
- 2) 4d series [from Yttrium(Y, z = 39) to cadmium, (Cd, z = 48)]
- 3) 5d series [from Lanthanum, (La, z =57), Hafnium, (Hf, z = 72) to Mercury, (Hg, z=80)]
- 4) 6d series [from Actinium, (Ac, z=89), Rutherfordium, (Rf, z=104) to copernicium, (Cn, z=112)]

Electronic Configuration

General outer electronic configuration of d-block elements is $(n-1) d^{1-10} ns^{1-2}$. There is only a small difference in energy between $(n-1)d$ orbital and ns orbital. So in some cases ns electrons are also transferred to $(n-1)d$ level.

The electronic configurations of Cr and Cu in the 3d series show some exceptions.



This is due to the extra stability of half-filled (d^5) and completely-filled electronic configurations (d^{10}).

The electronic configurations of Zn, Cd and Hg are represented by the general formula $(n-1)d^{10} ns^2$.

The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. So they are not regarded as transition elements.

Electronic configuration of first row transition series elements:

Atomic number	Element	Symbol	Electronic configuration
21	Scandium	sc	$[\text{Ar}] 3d^1$
22	Titanium		$[\text{Ar}] 3d^2 4s^2$
23	Vanadium		$[\text{Ar}] 3d^3 4s^2$
24	Chromium	Cr	$[\text{Ar}] 3d^5 4s^1$
25	Manganese		$[\text{Ar}] 3d^5 4s^2$

26	Iron		[Ar] 3d ⁶ 4s ²
27	Cobalt	co	[Ar] 3d ⁷ 4s ²
28	Nickel		[Ar] 3d ⁸
29	Copper	cu	[Ar] 3d ¹⁰ 4s ¹
30	Zinc		[Ar] 3d ¹⁰ 4s ²

General characteristics of transition elements

1. Atomic and ionic radii

In a transition series, the atomic and ionic radii first decrease, then become constant and increases towards the end of the series. This is because in transition elements, the new electron enters in a penultimate d-orbital. Initially since there is a few numbers of d electrons, the shielding effect is very poor. As the atomic number increases, the nuclear charge also increases, so the atomic radius decreases. Towards the middle of the series, the increase in nuclear charge is balanced by the shielding effect and so the atomic radius becomes constant. Towards the end of the series, as the e⁻ - e⁻ repulsion increases the atomic radius also increases

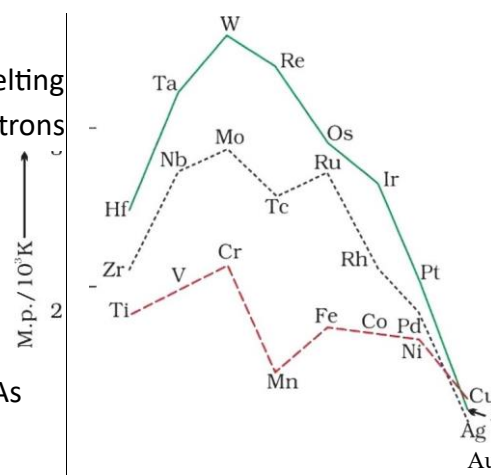
The atomic and ionic radii of 2nd and 3rd row transition metals are quite similar. This is due to the Lanthanide contraction. In between the 2nd and 3rd row transition elements, 4f electrons are present. The 4f electrons have very poor shielding effect and as a result the atomic and ionic radii of Lanthanides decrease from left to right (Lanthanide contraction).

2. Melting and boiling points

Transition elements are generally very hard and have high melting and boiling points. This is due to the participation of (n-1)d electrons (penultimate d electrons) in addition to the 3 ns electrons (valence s electrons) in metallic bonding.

In a transition series, the melting and boiling points 1st increases up to the middle and then decreases. This can be explained in terms of metallic bond strength and heat of atomization which depend on the number of unpaired electrons. As the number of unpaired electrons increases, the metallic bond strength increases and hence the heat of 1 atomization. In a transition series, the number of unpaired Atomic number → electrons increases up to the middle and then decreases.

Hence the melting point also increases first and then decreases.



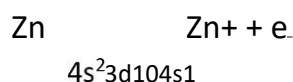
Manganese (Mn) and Technetium (Tc) have low melting point even though they have d^5 configuration. This is because of their low heat of atomization. The m.p.s of second and third row transition series are higher than that of the first row due to their higher enthalpies of atomization.

3. Ionisation enthalpy

The ionisation enthalpy of transition elements generally increases from left to right. This is due to increase in the nuclear charge from left to right. But the increase is not regular. This can be explained as follows.

After the removal of one electron, the relative energies of 4s and 3d orbitals get changed. Hence the remaining electron in the 4s level is transferred to 3d level. So the unipositive ions have d^n configuration with no 4s electrons. During this re-organisation of electrons, some energy is released and it is known as exchange energy. So the net energy required to remove the 1st electrons is equal to the sum of ionisation enthalpy and exchange energy.

The first ionisation enthalpies of Cr and Cu are low. This is because the removal of one electron does not change their d configuration. Similarly first ionisation enthalpy of Zn is high because after the removal of one electron there is no change in the d configuration.



The 2nd I.E of Cr and Cu are very high. This is because the removal of one more e^- from these metals disrupted their stable configuration (d^5 or d^{10})

The 2nd ionisation enthalpies of Mn and Zn are low, this is because after the removal of one more electron, they attain the stable half filled or completely filled electronic configuration.

4. Oxidation State

Transition metals show variable oxidation states. This is because in these elements d and s electrons have comparable energies. So in chemical reaction along with s-electrons, d-electrons also participate.

In a given transition series, the maximum oxidation state increases up to the middle and then decreases. This is due to the half-filled or fully filled electronic configuration (noble gas configuration). The common oxidation state of 1st row transition elements is +2. The maximum oxidation state increases from top to bottom in a group. In lower oxidation state, the transition element mainly forms ionic compounds.

Scandium generally shows +3 oxidation state because after the removal of 3 electrons, it gets a stable noble gas configuration (d^0). The oxidation state of Zinc is +2, because of the completely filled configuration of Zn^{2+} .

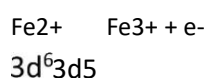
5. Electrode Potential

The electrode potential values of first row transition series elements generally increases from left to right with some exceptions. The value of Cu is positive (+0.34V), while the values of all the other first row transition elements are —ve. This is because the electrode potential depends on heat of atomization, ionization

enthalpies and hydration enthalpy. For copper, the high energy to transform solid Cu to aqueous Cu^{2+} is not balanced by its hydration enthalpy. So, copper does not easily react with acid and liberate H_2 . Only oxidizing acids [e.g. HNO_3 and hot conc. H_2SO_4] react with Cu and the acid get reduced.

Along the series the E° values become less —ve due to the increase in the sum of 1st and 2nd ionisation enthalpies. The E° values of Mn^{2+} and Zn^{2+} are more —ve, this is because of the half-filled configuration of Mn^{2+} (d^5) and completely filled configuration of Zn^{2+} (d^{10}). $E^\circ(\text{M}^{\text{II}}/\text{M}^{\text{I}})$ value of scandium (sc) is very low and that for zinc (Zn) is very high. This is because of their stable electronic configuration.

$E^\circ(\text{Mn}^{3+}/\text{Mn}^{2+})$ is high because of the stable half-filled configuration of Mn^{2+} . Similarly $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$ is low, this is because after the removal of one electron from Fe^{2+} , it gets a stable electronic configuration.



Q. Cu^{2+} is more stable than Cu^+ in aqueous solution. Why?

This is due to the greater —ve hydration enthalpy of Cu^{2+} than Cu^+ . In the case of Cu^{2+} the (aq)

hydration enthalpy is compensated by second ionisation enthalpy.

6. Magnetic Properties

Transition metals show mainly two types of magnetic properties - paramagnetism and diamagnetism. Some transition metals also show ferromagnetism which is an extreme case of paramagnetism.

Paramagnetism arises from the presence of unpaired electrons. Each unpaired e⁻ is associated with a spin magnetic moment and an orbital magnetic moment. For the compounds of 1st row transition elements, the contribution of orbital magnetic moment is effectively cancelled and so only spin magnetic moment is considered. It is determined by the no. of unpaired e⁻s and is calculated by the spin only formula:

$\mu_s : \sqrt{n(n+2)}$ where n is the no. of unpaired electrons and μ_s is the spin only magnetic moment in the unit of Bohr Magnetron (B.M).

The magnetic moment increases with increase in no. of unpaired e⁻s. Thus the observed magnetic moment gives an idea about the no. of unpaired e⁻s present in the atom or ion.

7. Formation of coloured ions or compounds

Most of the Transition metals ions or compounds are coloured. This is because of the presence of partially filled d orbitals. When an electron from a lower energy d orbital is excited to higher d level, it absorbs energy and this is equal to the energy of certain colours in visible region. So the colour observed is the complementary colour of the light absorbed.

In aqueous solution most of the transition metal ions are coloured since water molecules act as the ligands.

Among Ti^{2+} and Ti^{4+} Ti^{2+} is coloured while Ti^{4+} is colourless. This is because Ti^{4+} has no partially filled d orbitals.



Similarly among Cu^+ and Cu^{2+} Cu^{2+} is coloured while Cu^+ is colourless. This is due to the lack (absence) of partially filled d orbitals in Cu^+ .

8. Formation of Complexes

Transition metals form a large no. of complexes. This is due to:

1. Comparatively smaller size
2. High ionic charge
3. Presence of partially filled d orbitals
4. Ability to show variable oxidation state Eg: $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Ni(CO)_4]$ etc.

9. Catalytic Property

Transition metals act as catalysts in a large no. of chemical reactions. This is due to their large surface area and their ability to show variable oxidation state.

10. Interstitial Compound Formation

These are formed when smaller atoms like H, N, C, B etc. are trapped inside the crystal lattice of the metal. They are usually non-stoichiometric and neither typically ionic nor covalent. E.g.: Fe_3H , Mn_4N , TiC , $VH_{0.56}$, $TiH_{1.7}$ etc.

Some the properties of these compounds are:

- 1) They have high melting point.
- 2) They are very hard.
- 3) They retain metallic conductivity.
- 4) They are chemically inert.

11. Alloy Formation

Alloys are homogeneous solid solutions of elements in which at least one element is a metal. They are formed by atoms with metallic radii within about 15% of each other. Because of similar radii and other characteristics of transition metals, they readily form alloys. The alloys formed are hard and have high melting point. E.g.: Bronze (Cu and Sn), Brass (Cu and Zn), Stainless steel (Fe, C, Ni, Mn and Cr) etc.

Some Important Compounds of Transition Elements

1. Potassium dichromate ($K_2Cr_2O_7$)

Potassium dichromate is generally prepared from chromite ore ($FeCr_2O_4$). The preparation involves three steps.

1. Conversion of chromite ore to sodium chromate

Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate.



2. Acidification of sodium chromate to sodium dichromate

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.

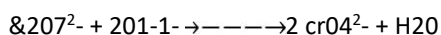


3. Conversion of sodium dichromate to potassium dichromate

The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out.



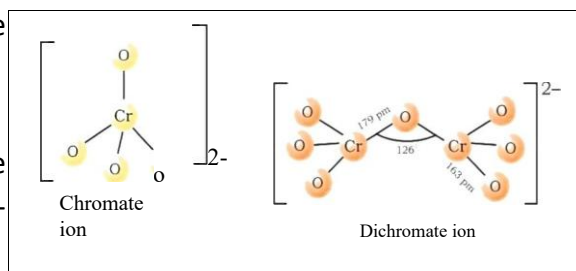
Properties: The chromate and dichromate are inter convertible in aqueous solution depending upon pH of the solution. Chromate on acidification gives dichromate and the dichromate on treating with alkali gives chromate.



The oxidation state of chromium in chromate and dichromate is +6.

Structure

The chromate ion is tetrahedral while, the dichromate ion consists of two tetrahedra sharing one corner with $\text{Cr}-\text{O}-\text{Cr}$ bond angle of 126° .

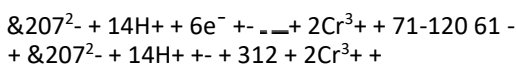


Sodium and potassium dichromates are strong oxidising agents. Sodium dichromate is most commonly used as oxidizing agent, due to its greater solubility in water. Potassium dichromate is used as a primary standard in volumetric analysis.

Oxidising Property

$\text{Cr}_2\text{O}_7^{2-}$ is a good oxidising agent in acidic medium. Its oxidising action can be represented as follows: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ Thus, acidified potassium dichromate will oxidise:

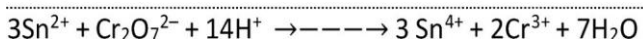
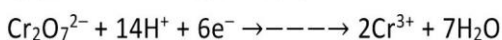
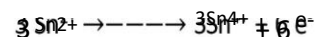
1) Iodide to iodine



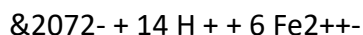
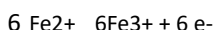
2) Sulphide to sulphur $3\text{S}^{2-} \rightarrow 3\text{S} + 6\text{e}^-$



3) Tin(II) to tin(IV)



4) Iron(II) to iron(III) OR, Ferrous ion to ferric ion



USES: It is used as a primary standard in volumetric analysis, as an oxidising agent in many reactions, in leather industry etc.

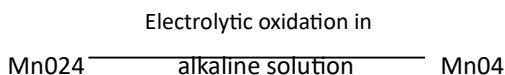
2. Potassium permanganate (KMnO_4)

Potassium permanganate is commercially prepared from MnO_2 (Pyrolusite). The preparation involves two steps:

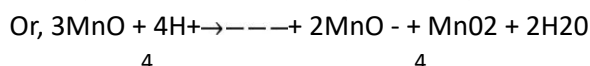
i) Conversion of MnO_2 to potassium manganate (K_2MnO_4) by fusing with KOH in presence of air (or an oxidizing agent like KNO_3).



ii) Potassium manganate is oxidised to potassium permanganate either by electrolysis or by acidification.



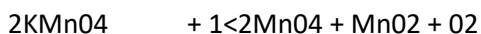
manganate permanganate ion



Properties:

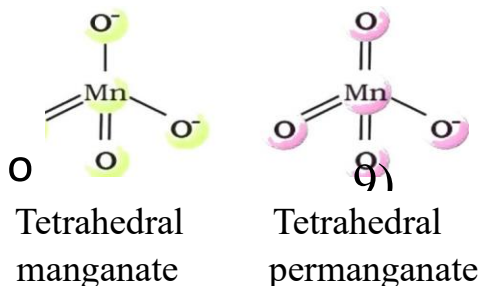
Potassium permanganate forms dark purple crystals which are iso-structural with those of potassium perchlorate (KClO_4).

When heated it decomposes and liberate O_2 .



Note: In permanganate ion, Mn is in +7 oxidation state with no d-electrons. So the colour of permanganate is due to ligand to metal charge transfer. i.e. an electron is transferred from oxygen atom to the vacant d-orbital of Mn.

Structure: The manganate and permanganate ions are tetrahedral. The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

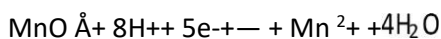


(green) ion

(purple) ion

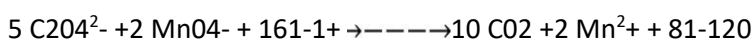
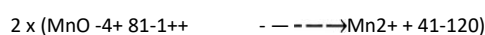
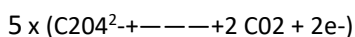
Oxidising Property of KMnO₄

KMnO₄ is a good oxidizing agent in acidic, basic and neutral media. The oxidizing action in acidic medium is due to the reaction:

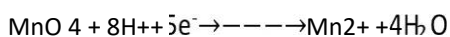


Acidified permanganate solution oxidises:

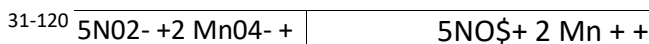
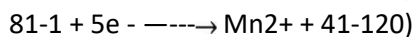
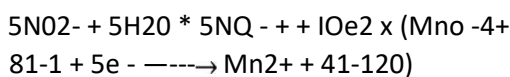
1) Oxalate to carbon dioxide



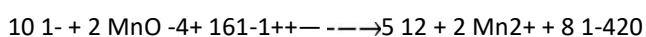
2) Iron(II) to iron(III)



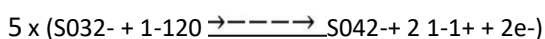
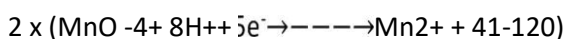
3) Nitrite to nitrate



4) Iodide to free iodine.



5) Sulphite to sulphate

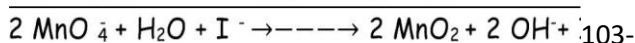
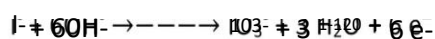
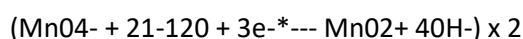


In alkaline or neutral medium, permanganate ion is reduced to MnO₂

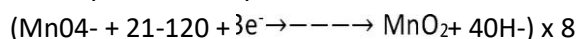


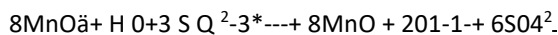
In alkaline medium it oxidises 1)

Iodide to iodate



2) Thiosulphate to sulphate





Note: For acidification of permanganate, hydrochloric acid (HCl) is not used, since it is oxidised to chlorine. Uses: It is used as an oxidising agent in acidic, basic and neutral medium. It is used as a primary standard in volumetric analysis. It is used for the bleaching of wool, cotton, silk and other textile fibres and also for the decolourisation of oils.

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last electron enters in the anti-penultimate f-subshell are called f-block elements. They include lanthanides of the 6th period and actinides of the 7th period. They are also called inner transition elements. Since lanthanum (57La) closely resembles lanthanides, it is also included along with them. Similarly, actinium (89Ac) is included along with actinoids because of its close resemblance with them.

The Lanthanoids or lanthanides

The 14 elements after lanthanum of the 6th period are called lanthanides or lanthanoids or lanthanones or rare earths. They include elements from 58Ce to 71Lu. They are generally represented as Ln.

Atomic and ionic radii - Lanthanide Contraction

In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanide series (though very slightly) is called lanthanide contraction.

Reason: In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and as a result the radii decreases.

Consequences of Lanthanide contraction:

- 1) Due to Lanthanide Contraction the 2nd and 3rd row transition series elements have similar radii. E.g. Zr - 160pm and Hf -159pm
- 2) Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.
- 3) The basic character of their hydroxides decreases from lanthanum to lutetium. i.e, La(OH)₃ is more basic than Lu(OH)₃.

Oxidation number

In lanthanoids, the most common oxidation state is +3. However, +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filled or filled f subshells. Cerium shows the oxidation state +4 due to its noble gas configuration.

Praseodymium (Pr), neodymium (Nd), terbium (Tb) and dysprosium (Dy) also exhibit +4 state but only in

oxides, MO₂. Europium (Eu) and ytterbium (Yb) shows +2 oxidation state because of the stable f⁷ or f¹⁴ configuration. Samarium (Sm) shows +2 oxidation state also.

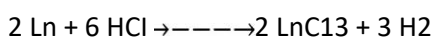
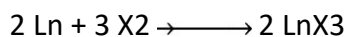
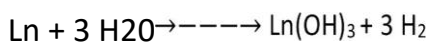
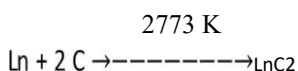
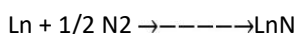
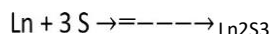
General properties of Lanthanoids

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. Their hardness increases with increasing atomic number. They have typical metallic structure and are good conductors of heat and electricity.

Most of the lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions is due to the presence of f electrons. But La³⁺ or Lu³⁺ ion are colourless. The lanthanoid ions other than the f⁰ type (La³⁺ and Ce⁴⁺) and the f¹⁴ type (Yb²⁺ and Lu³⁺) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

Chemical properties

Some of the chemical reactions of lanthanides are:



Uses of Lanthanides

The main use of the lanthanoids is for the production of alloy steels. An important alloy is mischmetall which consists of a lanthanoid metal (95%) and iron (5%) and traces of S, C, Ca and Al. It is mainly used in Magnesium based alloy to produce bullets, shell and lighter flint.

Mixed oxides of lanthanoids are used as catalysts in petroleum cracking. Some lanthanide oxides are used as phosphors in television screens and similar fluorescing surfaces.

The Actinoids or Actinones

The 14 elements after actinium in the 7th period of modern periodic table are called actinides or actinoids or actinones. They include elements from 90Th to 103Lr. Most of them are artificially prepared and are short lived. They are radioactive. The elements after Uranium are artificially prepared and so they are called trans-uranium elements or trans-uranic elements.

Atomic and ionic radii

In actinoid series the atomic and ionic radii decrease regularly from left to right. This is known as Actinoid contraction.

Oxidation state

Common oxidation state of actinoids is +3. The elements in the first half of the series show higher oxidation states. The maximum oxidation state increases from +4 in thorium (Th) to +5, +6 and +7 respectively in protactinium (Pa), uranium (U) and neptunium (Np) but decreases in succeeding elements.

The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.

Comparison between lanthanoids and actinoids

1. Most of the actinoids are artificially prepared and are radioactive.
2. The first ionisation enthalpy of early actinoids is lower than those of lanthanoids.
3. Actinoid contraction is greater from elements to elements than lanthanoid contraction. This is due to greater shielding effect of 5f electrons.

USES OF d AND f BLOCK ELEMENTS I. d and f block elements and their compounds are used as catalysts in many chemical reactions.

II. In the Wacker process, the oxidation of ethyne to ethanal is catalysed by PdCl₂.

Iron and steels are the most important construction materials.

IV. Alloys of d and f block elements are used in various fields.

V. Copper (Cu), Silver (Ag), Gold (Au) and some alloys are used for making coins.

VI. TiO₂ is used in pigment industry.

VII. Zn, Ni, cadmium (Cd), MnO₂ etc are used in making batteries.

VIII. Compounds of Ag are used in photography.

IX. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene.

X. An alloy of lanthanoids known as mischmetal is used in Magnesium based alloy to produce bullets, shell and lighter flint.

XI. Uranium is used as fuel in nuclear reactors.

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