

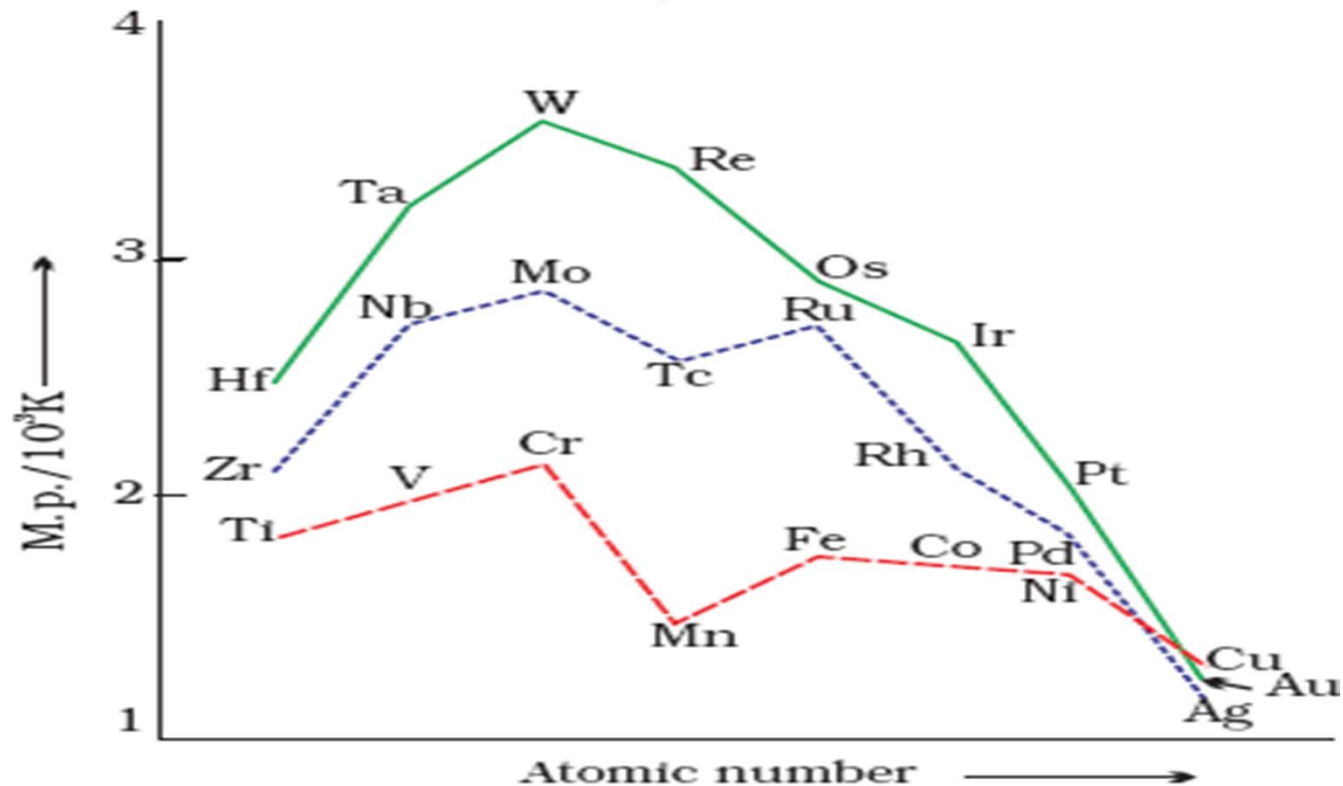


d – AND f – BLOCK ELEMENTS

MELTING POINT AND BOILING POINT

- High M.P and B.P - Due to strong metallic bond and the presence of half filled d-orbitals
- Involvement of greater number of electrons from $(n-1)d$ in addition to the ns electrons in the inter atomic metallic bonding.
- Because of stronger interatomic bonding, transition elements have high M.P and B.P

- In moving along the period from left to right, the M.P of these metals first **INCREASES** to MAXIMUM and the **DECREASES** regularly towards the end of the period.



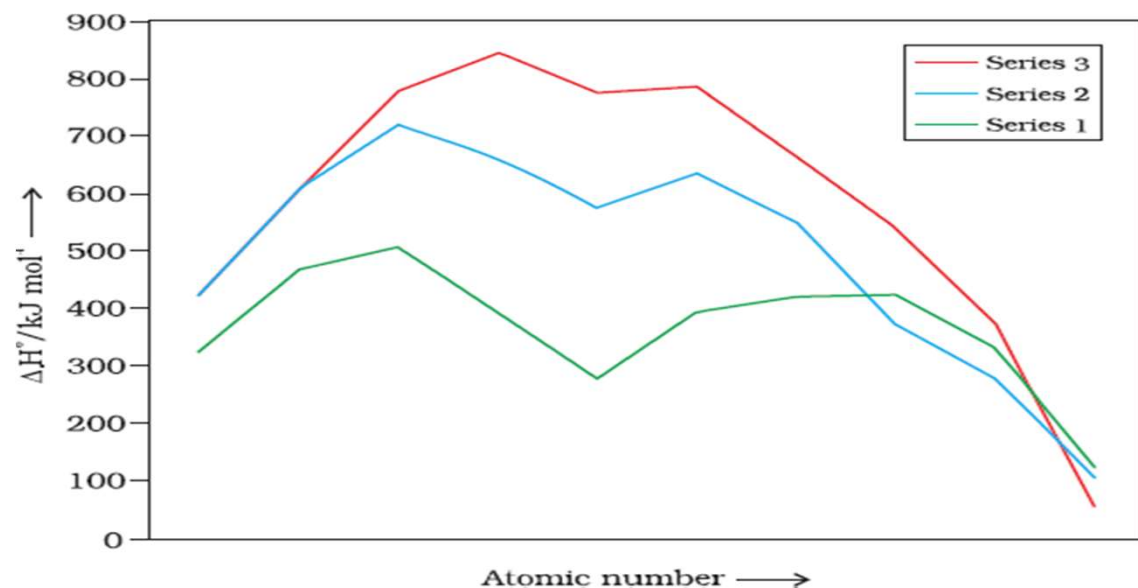
Trends in melting points of transition elements

- melting points of these metals rise to a maximum at d^5 except for anomalous values of **Mn and Tc** and fall regularly as the atomic number increases.

TRENDS OF M.P OF 3- d , 4-d AND 5-d TRANSITION METALS

- The strength of interatomic bonds in transition elements is roughly related to the number of half filled d- orbitals
- In the beginning the no. of half filled d- orbitals increases till the middle of the period causing increase in strength of interparticle bonds But thereafter the pairing of electrons in d – orbitals occurs and the no. of half filled orbitals decreases , which also cause decrease in M.P

Trends in enthalpies of atomization of transition elements



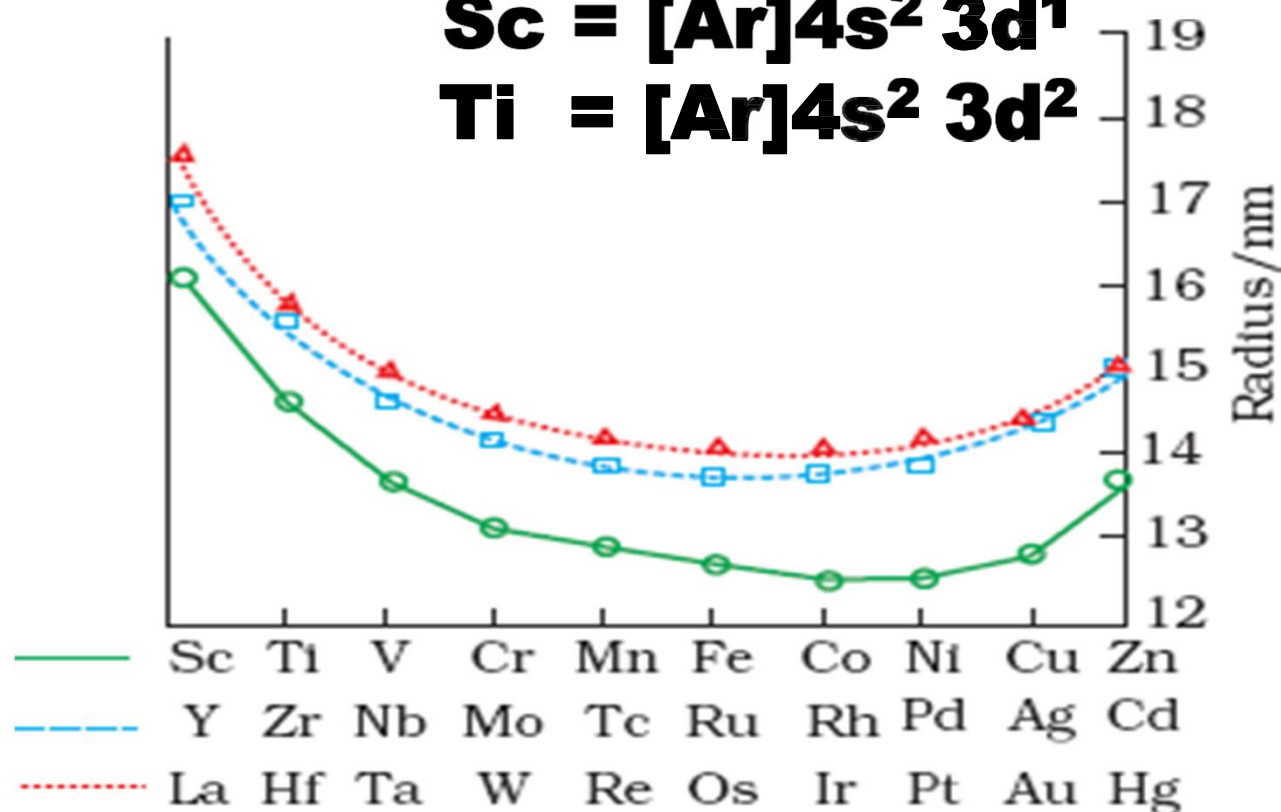
$3d < 4d < 5d$

1. greater the number of valence electrons, stronger the inter atomic attraction, hence stronger bonding between atoms resulting in higher enthalpies of atomization.
2. metals of the second and third series have greater enthalpies of atomization than the corresponding elements of the first series

Atomic and ionic radii

- The Atomic/ionic radii first **DECREASES** till the middle, becomes **almost constant** and then **INCREASES** towards the end of the period.
- New electron enters a *d* orbital each time the nuclear charge increases by unity, But the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases

- However the increased nuclear charge is partly cancelled by the **increased screening effect of electrons in the d – orbitals** of penultimate shell.
- When the increased nuclear charge and increased Screening effect balance each other, the atomic radii becomes almost constant.
- Increase in atomic radii towards the end may be attributed to the electron – electron repulsion.
- In fact the pairing of electrons in d – orbitals occurs after **d⁵ configuration**.
- **The repulsive interaction between the paired electron causes Increase in Atomic/ ionic radii**



Trends in atomic radii of transition elements

3d < 4d = 5d

- There is increase from the first ($3d$) to the second ($4d$) series of the elements.
- But the radii of the third ($5d$) series are virtually the same as $4d$
- This is due to the **intervention of the $4f$ orbital which must be filled before the $5d$ series of elements begin.**
- There is a steady decrease in atomic radii from La due to the poor shielding of inner core electrons ($4f$) is known **lanthanoid contraction.**

IONISATION ENTHALPIES

- Due to an increase in nuclear charge there is an increase in ionisation enthalpy along each series of the transition elements from left to right.
- Ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states.
- Although the first ionisation enthalpy, in general, increases, the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.
- Mostly $IE_1 < IE_2 < IE_3$ in each group

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Atomic number	21	22	23	24	25	26	27	28	29	30	
M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$	
Ionisation enthalpy/ $\Delta_i H^\circ/\text{kJ mol}^{-1}$											
$\Delta_i H^\circ$	I	631	656	650	<u>653</u>	717	762	758	736	745	906
$\Delta_i H^\circ$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	<u>1734</u>
$\Delta_i H^\circ$	III	2393	2657	2833	2990	<u>3260</u>	<u>2962</u>	3243	3402	3556	3829

- The increase in IE is primarily due to **increase in nuclear charge**. As the transition elements involve the gradual filling of (n-1)d orbitals, the effect of increase in nuclear charge is partly cancelled by the increase in screening effect.
- Consequently, the increase in I.E along the periods of d – block elements is very small.

$3d < 4d < 5d$ (in 5d series - ineffective shielding by 4f electrons)

Relation between I.E and Stability of a metal in a given oxdn state

- With the help of I.E, we can predict which of the two metals in a given oxdn state is thermodynamically more stable.

Eg

- When a metal M (0) is converted into M(II), the energy required is equal to $I_1 + I_2$

Similarly **M (IV)** = $I_1 + I_2 + I_3 + I_4$

- $\text{Ni (0)} \longrightarrow \text{Ni (II)} \quad I_1 + I_2 = 2.49 \times 10^3 \text{ kJ mol}^{-1}$
- $\text{Pt (0)} \longrightarrow \text{Pt (II)} \quad I_1 + I_2 = 2.66 \times 10^3 \text{ kJ mol}^{-1}$
- $\text{Ni (0)} \longrightarrow \text{Ni (IV)}$

$$I_1 + I_2 + I_3 + I_4 = 11.299 \times 10^3 \text{ kJ mol}^{-1}$$

- $\text{Pt (0)} \longrightarrow \text{Pt (IV)}$

$$I_1 + I_2 + I_3 + I_4 = 9.36 \times 10^3 \text{ kJ mol}^{-1}$$

$I_1 + I_2$ for Ni (II) is less than $I_1 + I_2$ for Pt (II). So Ni (II) is more stable

Similarly Pt (IV) is more stable

OXIDATION STATES

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	to	to	to	+3	+3	+3	+2	
	+4	+5	+6	+7	+4	+4	+4		
					+6				

- One of the notable features of a transition element is the great variety of oxidation states it may show in its compounds
- Stability of a particular oxdn state depends up on nature of the element with which the transition metals form the compound

- The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.
- Elements in the beginning of the series exhibit **fewer oxidation state** (have small no. of electrons in which they lose or contribute for sharing).
- Elements at the end of the series shows fewer oxdn states because they have **too many electrons in d – orbitals. So they have few vacant d – orbitals** which can be invoved in bonding.

- Lower oxdn state – Covalent character
- Higher oxdn state – ionic
- Higher oxdn states are more stable for heavier members.

Eg : in group VI, Mo (VI) and W (VI) are more stable than Cr (VI). So Cr (VI) act as strong oxidizing agent.

- The highest oxdn state - **+8 (Ruthenium and Osmium)**.
- Low oxidation states are found when a complex compound has ligands capable of π -acceptor character in addition to the σ -bonding. For example, in Ni(CO)_4 and Fe(CO)_5 , the oxidation state of nickel and iron is zero.

Trends in Stability of Higher Oxidation States

- Stability – compounds with F and Oxygen
- The ability of Fluorine to stabilize the highest oxidation state is due to either high lattice energy as in case of CoF_3 or high bond enthalpy as in case of VF_5 and CrF_6 .
- The ability of Oxygen to stabilize the highest oxidation state is due to its ability to form multiple bonds with metals.

Stable halides of first transition elements

Oxdn no.	4	5	6	7	8	9	10	11	12
+6			Cr F ₆						
+5		VF ₅	Cr F ₅						
+4	TiX ₄	VX ₄ ^I	Cr X ₄	MnF ₄					
+3	TiX ₃	VX ₃	Cr X ₃	MnF ₃	Fe X ₃	Co F ₃			
+2	TiX ₂ ^{III}	VX ₂ ^I	Cr X ₂	MnX ₂	Fe X ₂	Co X ₂	Ni X ₂	Cu X ₂ ^{II}	ZnX ₂
+1								Cu X ^{III}	

X = F to I,

X^I = F to Br ,

X^{II} = F,

X^{III} = Cl to I

- The highest oxidation numbers are achieved in **TiX₄ (tetrahalides), VF₅ and CrF₆**. The +7 state for Mn is not represented in simple halides but MnO₃F is known, and beyond Mn, no metal has a trihalide except FeX₃ and CoF₃.
- Although V(V) is represented only by VF₅, the other halides, however, undergo hydrolysis to give oxohalides, VOX₃. Another feature of fluorides is their instability in the low oxidation states e.g., VX₂ (X = Cl, Br or I)

- All Cu(II) halides are known except the iodide. In this case, Cu^{2+} oxidises I^- to I_2 :



- However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



- The stability of $\text{Cu}^{2+}(\text{aq})$ rather than $\text{Cu}^+(\text{aq})$ is due to the much more negative $\Delta_{\text{hyd}}H^0$ of $\text{Cu}^{2+}(\text{aq})$ than Cu^+ , which more than compensates for the second ionisation enthalpy of Cu.

- Transition metals also exhibit the highest Oxidation state in their Oxides.
- The ability of Oxygen to stabilize higher oxidation states is much higher than Fluorine..
- The highest Oxidation state with Fluorine by **Mn** is **+4 in MnF_4** while **it is + 7 in Mn_2O_7** .
- Oxygen has the ability to form Multiple bonds with Metal atom.

The oxides of 3 – d transition elements are given below :

- The highest oxidation number in the oxides coincides with the group number and is attained in **Sc₂O₃** to **Mn₂O₇**.
- Beyond Group 7, no higher oxides of Fe above Fe₂O₃, are known, although ferrates (VI) (FeO₄)²⁻, are formed in alkaline media but they readily decompose to Fe₂O₃ and O₂.
- Besides the oxides, oxocations stabilise V(v) as VO₂⁺, V(IV) as VO²⁺ and Ti(IV) as TiO²⁺.

STANDARD ELECTRODE POTENTIAL

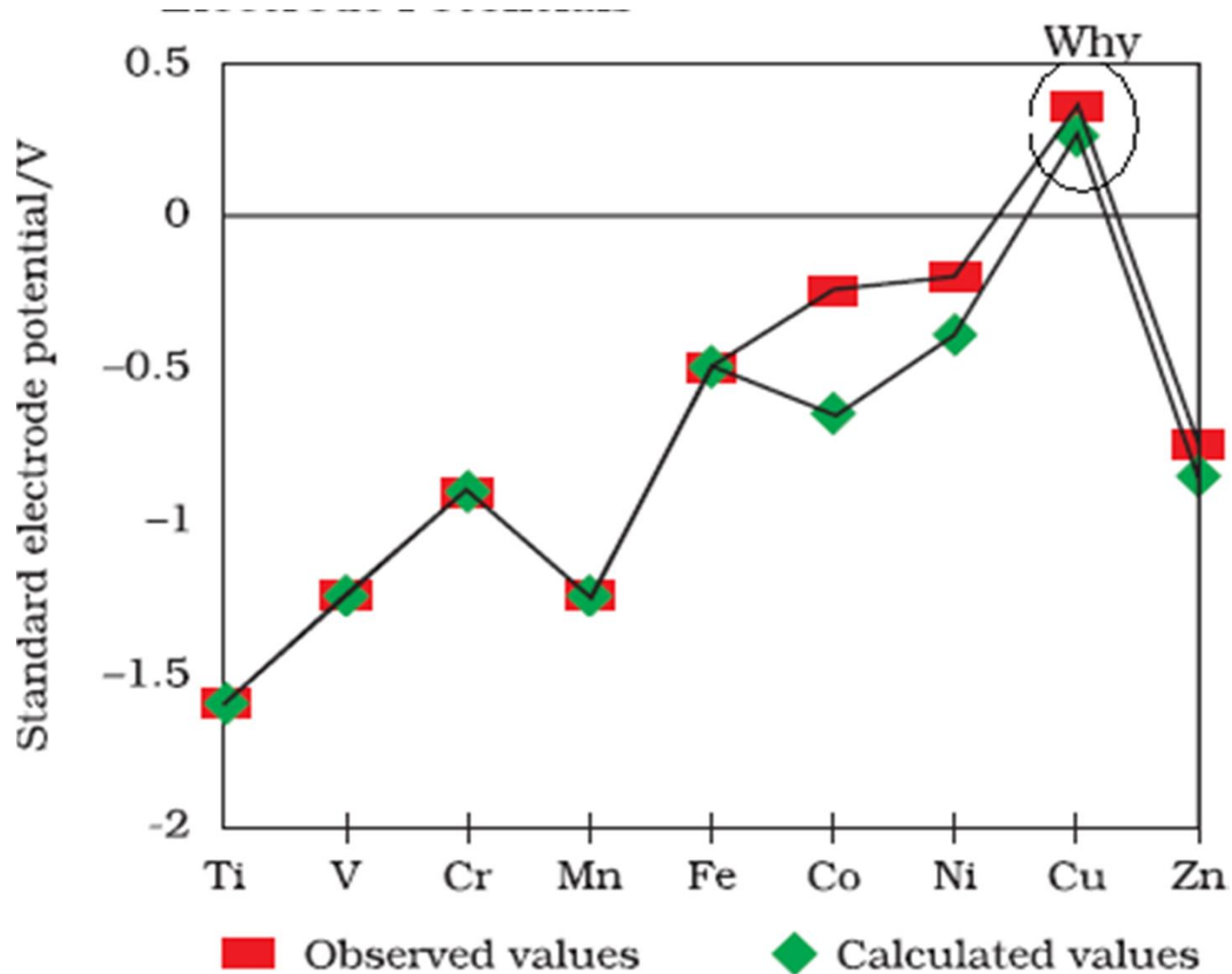
- ELECTRODE POTENTIALS ARE THE MEASURE OF THE VALUE OF TOTAL ENTHALPY CHANGE.
- **Electrode Potentials value depends enthalpy of atomization ΔH_a & hydration ΔH_{hyd}**
- Lower the std E. P (E°_{red}), the more stable is the oxdn state of the metal in aqueous state.

For the first row transition metals the E^\ominus values are:

E^\ominus	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

The $E^\ominus (M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionisation enthalpies ($\Delta_1 H_1 + \Delta_1 H_2$) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.



The $E_0(M_{2+}/M)$ value for copper is positive (+0.34V) : high ΔH_a and low ΔH_{hyd} . --- GREATER AMNT OF ENERGY REQUIRED TO TRANSFORM **Cu** INTO **Cu²⁺**

- Due to +ve E° , Cu does not liberate hydrogen from acids.
- The general trend towards less negative E° *values across the* series is related to the general **increase in the sum of the first and second ionisation enthalpies.**
- It is interesting to note that the value of E° for Mn, Ni and Zn are more negative than expected from the trend.

- The stability of the half-filled d sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their E° values, whereas E° for Ni is related to the highest negative $\Delta_{hyd}H^\circ$.
- The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+} . The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas comparatively low value for Fe shows the extra stability of $Fe^{3+}(d^5)$.

CHEMICAL REACTIVITY

- Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by simple acids.
- The metals of the first series with the exception of **copper** are relatively more reactive and are oxidised by 1M H⁺, though the actual rate at which these metals react with oxidising agents like hydrogen ion (H⁺) is sometimes slow.

- The E^0 values for M^{2+}/M indicate a decreasing tendency to form divalent cations across the series.
- This general trend towards less negative E^0 values is related to the increase in the sum of the first and second ionisation enthalpies.
- It is interesting to note that the E^0 values for Mn , Ni and Zn are more negative than expected from the general trend.

- *E⁰ values for the redox couple M³⁺/M²⁺ shows that Mn³⁺ and Co³⁺ ions are the strongest oxidising agents in aqueous solutions. The ions Ti²⁺, V²⁺ and Cr²⁺ are strong reducing agents and will liberate hydrogen from a dilute acid,*

e.g.,

- $2 \text{Cr}^{2+}(\text{aq}) + 2 \text{H}^{+}(\text{aq}) \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + \text{H}_2(\text{g})$

MAGNETIC PROPERTIES

- Substances which contain species (Atoms/ions/molecules) with unpaired electrons in their orbitals – PARAMAGNETIC.
- PARAMAGNETIC SUBSTANCES are weakly attracted by the magnetic field.
- Strongly attracted called FERROMAGNETIC.
- Substances which do not contain any unpaired electrons and are repelled by magnetic field – DIAMAGNETIC.

- Transition metals usually contains unpaired electrons – so it is paramagnetic.
- Paramagnetic behavior increases with increase in unpaired electron.
- Paramagnetism expressed in terms of Magnetic moment., it is related to no. of unpaired electrons.
- The magnetic moments calculated from the ‘spin-only’ formula and those derived experimentally.

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

n- no. of unpaired electrons

BM – Bohr magnetone (unit of M.M)

$BM = 9.27 \times 10^{-21} \text{ erg/gauss}$

- Single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).
- magnetic moment of an electron is due to its spin angular momentum and orbital angular momentum

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc ³⁺	3d ⁰	0	0	0
Ti ³⁺	3d ¹	1	1.73	1.75
Ti ²⁺	3d ²	2	2.84	2.76
V ²⁺	3d ³	3	3.87	3.86
Cr ²⁺	3d ⁴	4	4.90	4.80
Mn ²⁺	3d ⁵	5	5.92	5.96

Formation of Coloured Ions

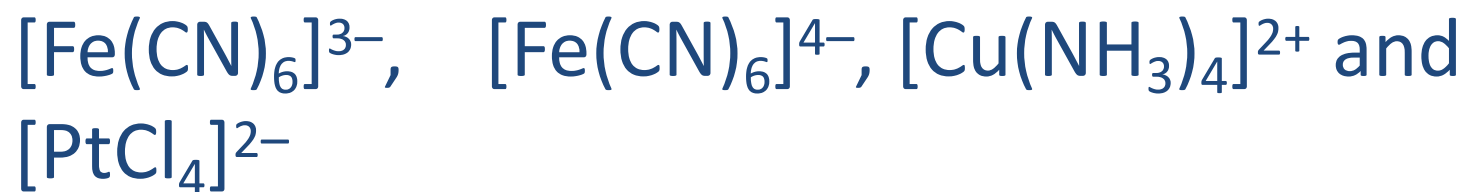
- When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed.
- This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.
- The frequency of the light absorbed is determined by the nature of the ligand.

- $\text{Zn}^{2+} / \text{Cd}^{2+}$ - all d orbitals are fully filled
- Ti^{4+} - all d orbitals are vacant

so, no d – d transition occurs. Therefore they do not absorb radiations. So they are colourless.

Formation of Complex Compounds

- Metal ions bind a number of anions or neutral molecules giving complex



.

This is due to the

- Comparatively smaller sizes of the metal ions,
- Their high ionic charges and
- The availability of *d* orbitals for bond formation.

Formation of Interstitial Compounds

- When small atoms like H, C or N are trapped inside the crystal lattices of metals
 - They are usually non stoichiometric
 - example, TiC , Mn_4N , Fe_3H , $\text{VH}_{0.56}$ and $\text{TiH}_{1.7}$
- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

Alloy Formation

- Because of similar radii and other characteristics of transition metals,
- The alloys so formed are hard and have often high melting points.
- ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel.
- Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin),

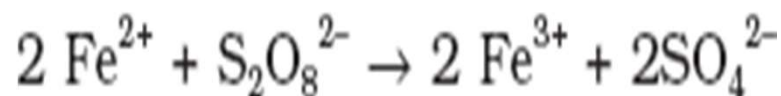
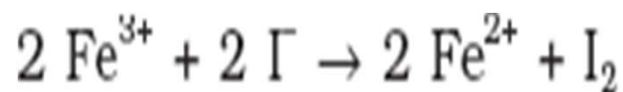
CATALYTIC ACTIVITY

- The transition metals and their compounds are known for their catalytic activity.
- This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes.

iron(III) catalyses

$$2 \text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2 \text{SO}_4^{2-}$$

the reaction between
iodide and persulphate ions.



DISPROPORTIONATION

- When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.



Oxides and Oxoanions of Metals

- The elements of first transition series form variety of oxides of different oxidation states having general formula MO , M_2O_3 , M_3O_6 , MO_2 , MO_3 .
- These oxides are generally formed by heating the metal with oxygen at high temperature.

Sc – **Sc₂O₃** Basic

Ti – **TiO** Basic, **Ti₂O₂** Basic, **TiO₂** Amphoteric

V – **VO** Basic, **V₂O₃** Basic, **VO₂** Ampho, **V₂O₅** Acidic

Cr – **CrO** Basic, **Cr₂O₃** Ampho, **CrO₂** Ampho,
CrO₃ Acidic

Mn – **MnO** basic, **Mn₂O₃** Basic, **Mn₃O₄** Ampho,
MnO₂ Ampho, **Mn₂O₇** Acidic

Fe – **FeO** Basic, **Fe₂O₃** Amph, **Fe₃O₄** Basic

Co – **CoO** Basic

Ni – **NiO** Basic

Cu – **Cu₂O** Basic, **CuO** Ampho

Zn – **ZnO** Ampho

- In general
lower oxidation state metal – BASIC
Higher oxidation state metal – ACIDIC
Intermediate oxidation state - AMPHOTERIC

- Example

MnO (+2)basic, **Mn₂O₃** (+3)Basic, **Mn₃O₄** (+
8/3)Ampho,

MnO₂ (+4) Ampho, **Mn₂O₇** (+7)Acidic

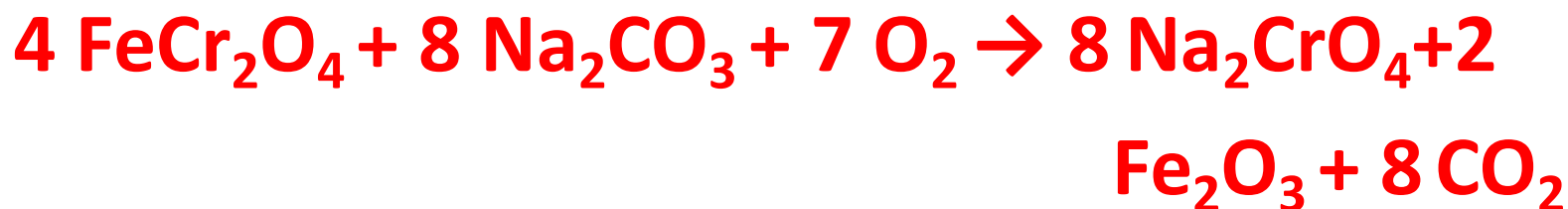
- The highest oxidation number in the oxides coincides with the group number and is attained in **Sc_2O_3 to Mn_2O_7** .
- Beyond Group 7, no higher oxides of Fe above Fe_2O_3 , are known, although ferrates (VI) $(\text{FeO}_4)^{2-}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2 .
- Besides the oxides, oxocations stabilise V(v) as VO_2^+ , V(IV) as VO^{2+} and Ti(IV) as TiO^{2+} .

- As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant.

Potassium dichromate $K_2Cr_2O_7$

STEP 1

- Dichromates are generally prepared from chromate which in turn are obtained by the fusion of **chromite ore ($FeCr_2O_4$)** with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:



STEP 2

- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallised.

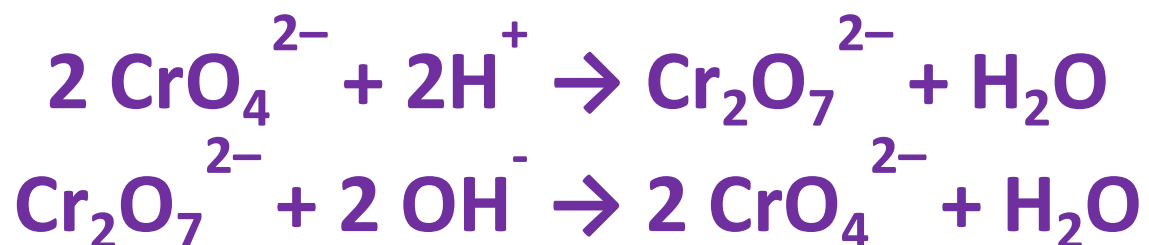


STEP 3

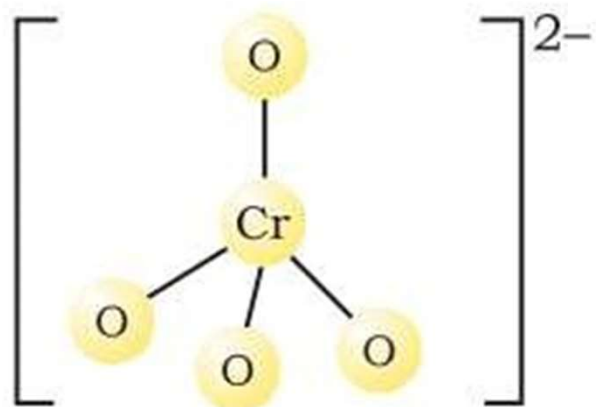
Conversion of Sodium dichromate in to Potassium dichromate



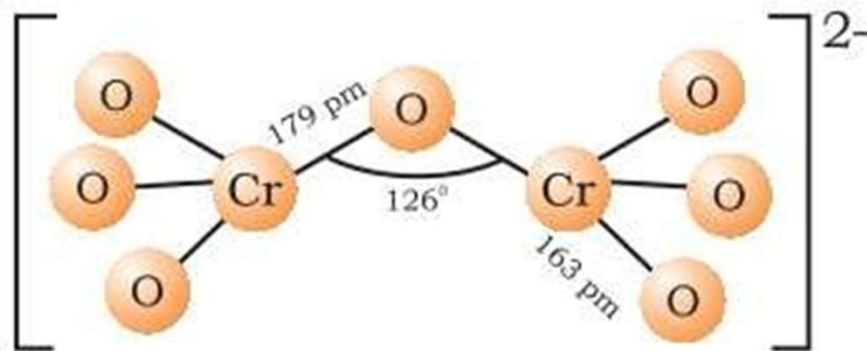
- The oxidation state of chromium in chromate and dichromate is the same.



- The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126° .



Chromate ion



Dichromate ion

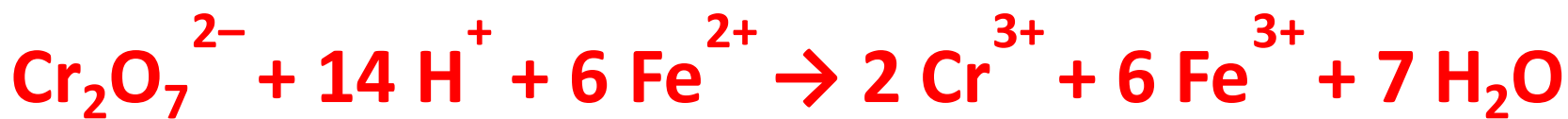
- Sodium and potassium dichromates are strong oxidising agents

Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:



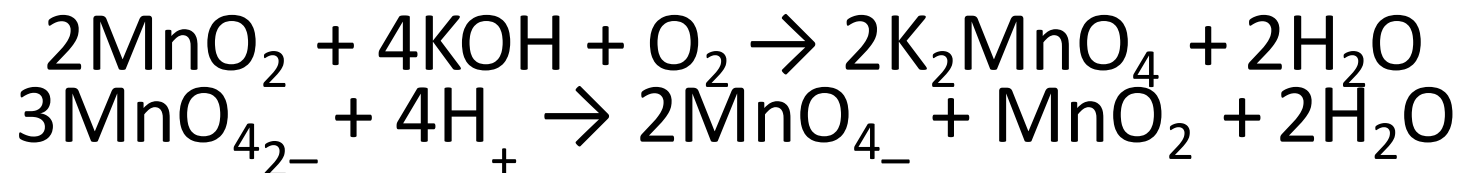
- acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

- $6 \text{I}^- \rightarrow 3\text{I}_2 + 6 \text{e}^-$;
- $3 \text{H}_2\text{S} \rightarrow 6\text{H}^+ + 3\text{S} + 6\text{e}^-$
- $3 \text{Sn}^{2+} \rightarrow 3\text{Sn}^{4+} + 6 \text{e}^-$
- $6 \text{Fe}^{2+} \rightarrow 6\text{Fe}^{3+} + 6 \text{e}^-$



Potassium permanganate $KMnO_4$

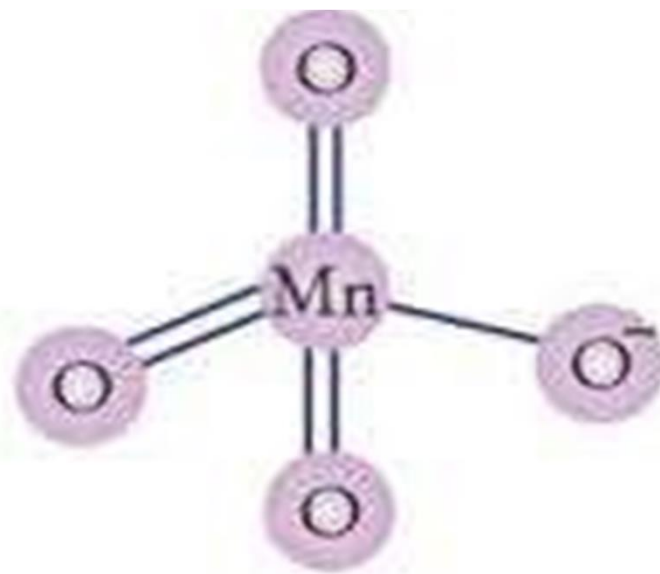
- Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3 . This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.



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



Tetrahedral manganate
(green) ion



Tetrahedral permanganate
(purple) ion

THE INNER TRANSITION ELEMENTS (*f-BLOCK*)

- The elements in which the additional electrons enter $(n-2)f$ orbitals are called **inner transition elements**. The valence shell electronic configuration of these elements can be represented as **$(n-2)f^{0-14}(n-1)d^{0-1}ns^2$** .
- 4f inner transition metals are known as lanthanides because they come immediately after lanthanum and 5f inner transition metals are known as actinoids because they come immediately after actinium.

Electronic Configuration

Element name	Symbol	Z	Ln	Ln ³⁺	Radius	Ln ³⁺ / pm
Lanthanum	La	57		[Xe]6s ² 5d ¹	[Xe]4f ⁰	116
Cerium	Ce	58		[Xe]4f ¹ 6s ² 5d ¹	[Xe]4f ¹	114
Praesodymium	Pr	59		[Xe]4f ³ 6s ²	[Xe]4f ²	113
Neodymium	Nd	60		[Xe]4f ⁴ 6s ²	[Xe]4f ³	111
Promethium	Pm	61		[Xe]4f ⁵ 6s ²	[Xe]4f ⁴	109
Samarium	Sm	62		[Xe]4f ⁶ 6s ²	[Xe]4f ⁵	108
Europium	Eu	63		[Xe]4f ⁷ 6s ²	[Xe]4f ⁶	107
Gadolinium	Gd	64		[Xe]4f ⁷ 6s ² 5d ¹	[Xe]4f ⁷	105
Terbium	Tb	65		[Xe] 4f ⁹ 6s ²	[Xe]4f ⁸	104
Dysprosium	Dy	66		[Xe] 4f ¹⁰ 6s ²	[Xe]4f ⁹	103
Holmium	Ho	67		[Xe] 4f ¹¹ 6s ²	[Xe]4f ¹⁰	102
Erbium	Er	68		[Xe] 4f ¹² 6s ²	[Xe]4f ¹¹	100
Thulium	Tm	69		[Xe] 4f ¹³ 6s ²	[Xe]4f ¹²	99
Ytterbium	Yb	70		[Xe] 4f ¹⁴ 6s ²	[Xe]4f ¹³	99
Lutetium	Lu	71		[Xe] 4f ¹⁴ 6s ² 5d ¹	[Xe]4f ¹⁴	98

Atomic and ionic sizes: The Lanthanide Contraction

- **As the atomic number increases, each succeeding element contains one more electron in the 4f orbital and one proton in the nucleus. The 4f electrons are ineffective in screening the outer electrons from the nucleus causing imperfect shielding. As a result, there is a gradual increase in the nucleus attraction for the outer electrons. Consequently gradual decrease in size occur. This is called lanthanide contraction.**

Consequences of L. C

- There is close resemblance between 4d and 5d transition series.
- Ionization energy of 5d transition series is higher than 3d and 4d transition series.
- Difficulty in separation of lanthanides