The First Transition Series

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❖ Introduction

❖ General features and Electronic Configuration of atoms

❖ General Features of the *d*-Block Elements from Sc to Zn

❖ Characteristic Properties of the *d*-Block Elements and their Compounds

Introduction

_d_-Block elements (transition elements):

- Lie **between _s_-block and _p_-block** elements

- Include elements of **Groups 3 to 12**

- Start/Occur in the **fourth and subsequent periods**

- All contains **1or 2 electrons in their s-orbital** and the **last electron** enters the **last but one d-subshell i.e. (n-1)d**

- In at least one of their oxidation state **incomplete _d_ sub-shell** (i.e. 1 – 9 electrons) is present.

- Represent a **gradual transition/change** from **most electropositive s- block element to least electropositive p-block elements**

Metals

Pre-transition metals	Rare earths	Transition metals	Poor metals	Metalloids
	Actinides			

Nonmetals

Core nonmetals	Noble gases

Unknown chemical properties

Group

*Group names***

1	Hydrogen & the alkali metals	14	Carbon Group
2	Alkaline earth metals	15	Pnictogens
11	Coinage metals (Cu, Ag & Au)	16	Chalcogens
12	Volatile metals	17	Halogens
13	Boron Group	18	Noble gases

Periodic table elements:

1 H, 2 He, 3 Li, 4 Be, 5 B, 6 C, 7 N, 8 O, 9 F, 10 Ne,
11 Na, 12 Mg, 13 Al, 14 Si, 15 P, 16 S, 17 Cl, 18 Ar,
19 K, 20 Ca, 21 Sc, 22 Ti, 23 V, 24 Cr, 25 Mn, 26 Fe, 27 Co, 28 Ni, 29 Cu, 30 Zn, 31 Ga, 32 Ge, 33 As, 34 Se, 35 Br, 36 Kr,
37 Rb, 38 Sr, 39 Y, 40 Zr, 41 Nb, 42 Mo, 43 Tc, 44 Ru, 45 Rh, 46 Pd, 47 Ag, 48 Cd, 49 In, 50 Sn, 51 Sb, 52 Te, 53 I, 54 Xe,
55 Cs, 56† Ba, 71 Lu, 72 Hf, 73 Ta, 74 W, 75 Re, 76 Os, 77 Ir, 78 Pt, 79 Au, 80 Hg, 81 Tl, 82 Pb, 83 Bi, 84 Po, 85 At, 86 Rn,
87 Fr, 88‡ Ra, 103 Lr, 104 Rf, 105 Db, 106 Sg, 107 Bh, 108 Hs, 109 Mt, 110 Ds, 111 Rg, 112 Cn, 113 Uut, 114 Fl, 115 Uup, 116 Lv, 117 Uus, 118 Uuo

Group columns: 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18

Lanthanides: †57 La, 58 Ce, 59 Pr, 60 Nd, 61 Pm, 62 Sm, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho, 68 Er, 69 Tm, 70 Yb

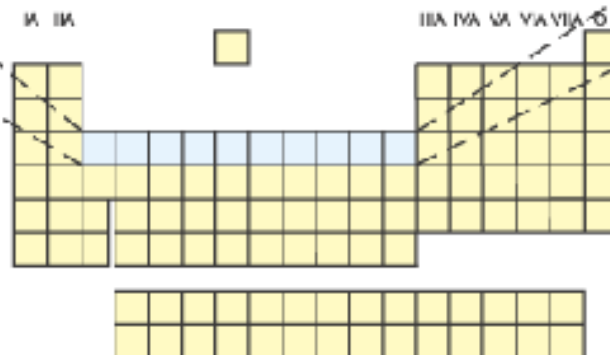Actinides: ‡89 Ac, 90 Th, 91 Pa, 92 U, 93 Np, 94 Pu, 95 Am, 96 Cm, 97 Bk, 98 Cf, 99 Es, 100 Fm, 101 Md, 102 No

*Groups 3–10 are named after their first members i.e. Group 3 is the Scandium Group

The first transition series

First Transition series : Scandium (Z = 21) to Zinc (Z = 30)

4th Period; 3d orbitals are filled

Electronic Configuration of Atoms : A Recollection

➢ In Hydrogen atom, only one electron is present, so all the s, p, d, f orbitals of the same shell have the same energy.

➢ In case of multielectron atoms, the s, p, d, f orbitals in the same shell have different energies.

➢ This difference arises due to shielding effect of the inner electrons of the atom.

➢ This shielding varies depending on the principal shell and the subshell in which the electron is entering.

➢ Due to shielding, the actual nuclear charge felt by the electron decreases.

➢ So each electron is **imperfectly shielded** by inner electrons from the nuclear charge.

➢ The energy of an electron in an atom **due to shielding** is given as

$$E = -\frac{2\pi^2\, me^4\, (Z^*)^2}{n^2\, h^2}$$

where **Z*** is the effective nuclear charge

➢ The energy of electron **decreases with increase** in the value of **Z*** with increase in atomic number.

➢ The various subshells (s, p, d, f) in the same principal shell are **shielded to different extent** due to their different shapes.

➤ The order of shielding effect of electrons in different orbitals is

s > p > d > f

➤ From Hydrogen (Atomic No= 1) to Argon (Atomic No= 18) , the electronic configuration is filled accordingly i.e. 1s, 2s, 2p, 3s and 3p.

➤ The next electron having (Atomic No= 19) should enter the **3d subshell** , but the electron enters the **4s subshell instead of 3d.**

➤ This **anomalous behaviour** is explained in the electronic configuration of transition elements and is seen in all the transition series.

➢ Due to **different penetration power** of the subshells in a given principal shell (s> p> d> f), orbital which penetrates more to the nucleus

- will be less shielded from other electrons

- Will feel more nuclear charge

- Will be strongly attracted by the nucleus

- Will have lower energy

Radial Probability Distribution Curve for 3d and 4s orbitals
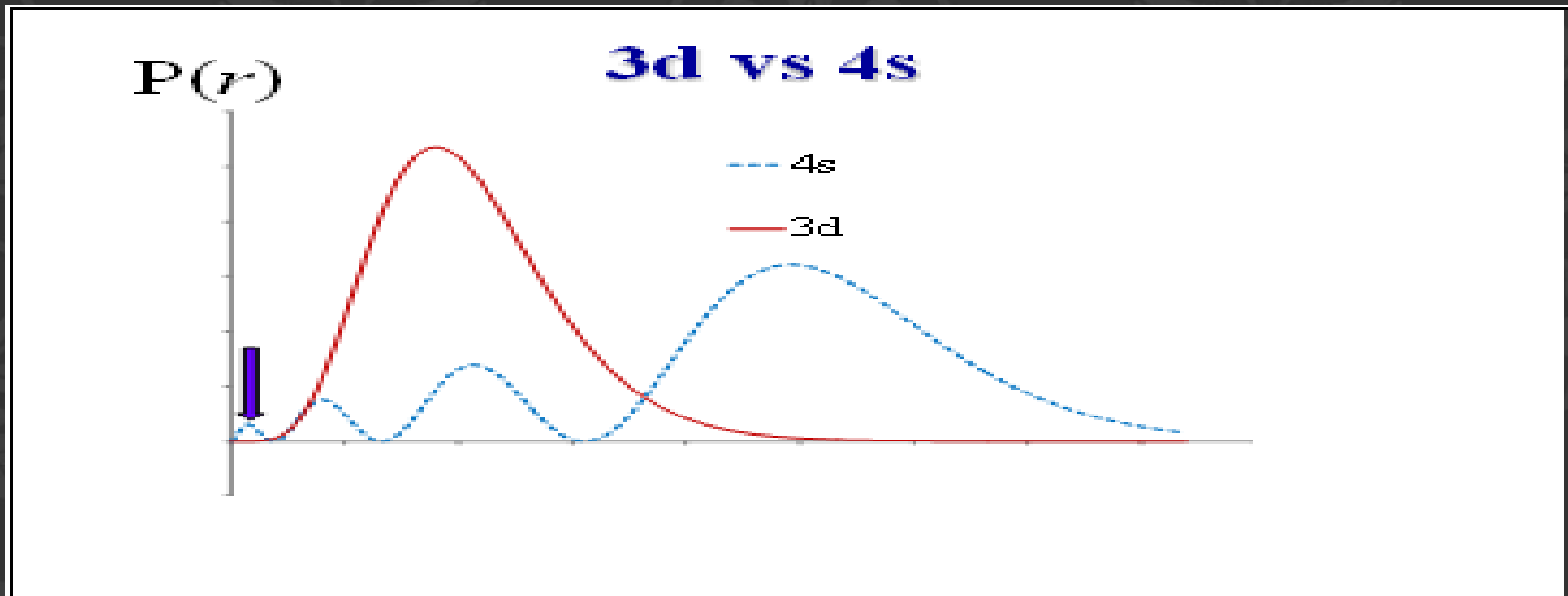
For 3d

- Consist of a single peak
- Radius of maximum probability is closer to the nucleus
- Less penetration of the Inner core (Argon Core)

For 4s

- Consist of four peaks
- Radius of maximum probability is much farther from the nucleus
- More penetration of the Inner core (Argon Core)

➢ The penetration power of 4s orbitals **is quite great** as compared to 3d orbital .

➢ So, 4s orbitals are **more attracted by the nucleus** and are more strongly held than 3d orbitals .

➢ Thus , 4s electron has **lesser energy** than 3d electron and are **filled first**.

➢ As soon as 4s orbital is filled , the 3d electrons **penetrate** the electron density of 4s orbital.

➢ Effective nuclear charge on 3d electrons **increases** and their **energy drops even lower** than the energy of 4p electron.

Electronic Configurations

Relative energy levels of orbitals before and after filling with electrons

➢ Before filling electrons, the energy of 4s sub-shell is **lower** than that of 3d sub-shell

⇒ 4s sub-shell is **filled** **before** 3d sub-shell

➢ Once the 4s sub-shell is filled, its energy will increase

⇒ The lowest energy sub-shell becomes **3d sub-shell**, so the next electron is put into 3d sub-shell

➢ Thus, the elements from Scandium (Z=21) to Zinc (Z=30) involves the filling of the 3d subshell and is called the First Transition Series.

ELECTRONIC CONFIGURATION OF ATOMS OF FIRST TRANSITION SERIES

General Electronic Configuration for all d- block elements is
$$(n-1)d^{1-10}\ ns^{1-2}$$

Element		3d					4s	Configuration
Sc	[Ar]	↑					↑↓	[Ar] $3d^1 4s^2$
Ti	[Ar]	↑	↑				↑↓	[Ar] $3d^2 4s^2$
V	[Ar]	↑	↑	↑			↑↓	[Ar] $3d^3 4s^2$
Cr*	[Ar]	↑	↑	↑	↑	↑	↑	[Ar] $3d^5 4s^1$
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓	[Ar] $3d^5 4s^2$
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓	[Ar] $3d^6 4s^2$
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	[Ar] $3d^7 4s^2$
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	[Ar] $3d^8 4s^2$
Cu*	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	[Ar] $3d^{10} 4s^1$
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	[Ar] $3d^{10} 4s^2$

ANAMOLOUS CONFIGURATION OF CHROMIUM & COPPER

Why do Chromium and Copper have anomalous Configuration?

❖ Half filled and fully filled d orbitals are more stable

❖ Energy difference between 4s & 3d orbitals is less

❖ Electron from filled s orbital shifts to the d orbital, resulting in half and fully filled d orbital
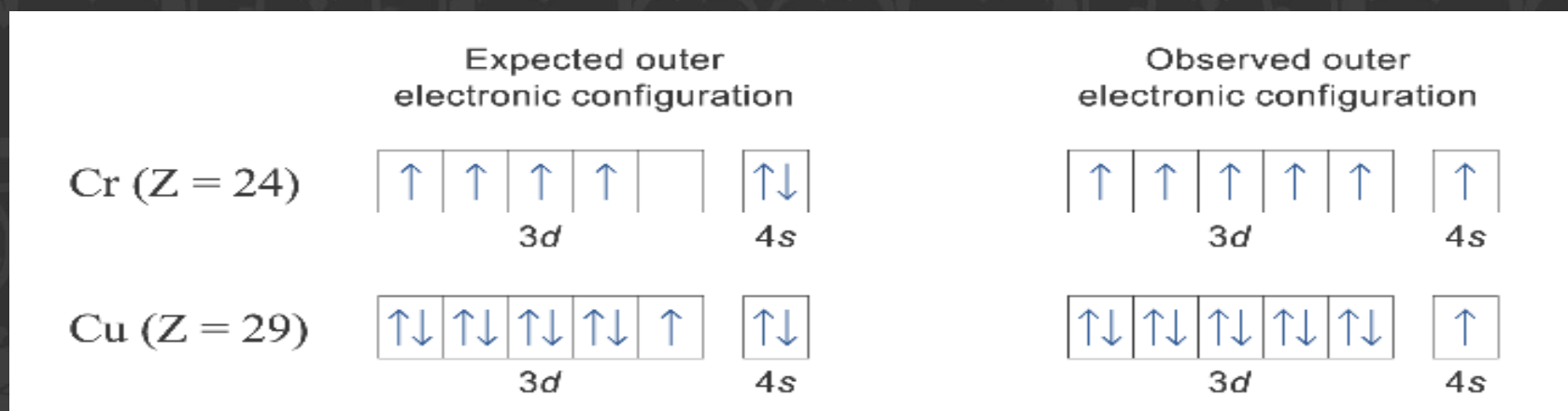
❖ Electronic Configuration of Cr is $4s^1, 3d^5$ instead of $4s^2, 3d^4$

❖ Electronic Configuration of Cu is $4s^1, 3d^{10}$ instead of $4s^2 , 3d^9$

ELECTRONIC CONFIGURATION OF IONS

❖ Ions are formed by of electrons from the outermost orbital of atoms. loss

❖ Transition Metals form ions by loss of electrons first from the 4s subshell and then from 3d subshell.

❖ Once electron start entering 3d subshell, its energy becomes less than that of 4s subshell.

❖ 3d orbitals become inner orbitals and more stable as compared to 4d.

- Strictly speaking, **Scandium (Sc) and Zinc (Zn) are not transitions elements**

    ∵ Sc forms **Sc^{3+} ion which has an empty** *d* **sub-shell ($3d^0$)** Zn forms **Zn^{2+} ion which has a completely filled** *d* **sub-shell ($3d^{10}$)**
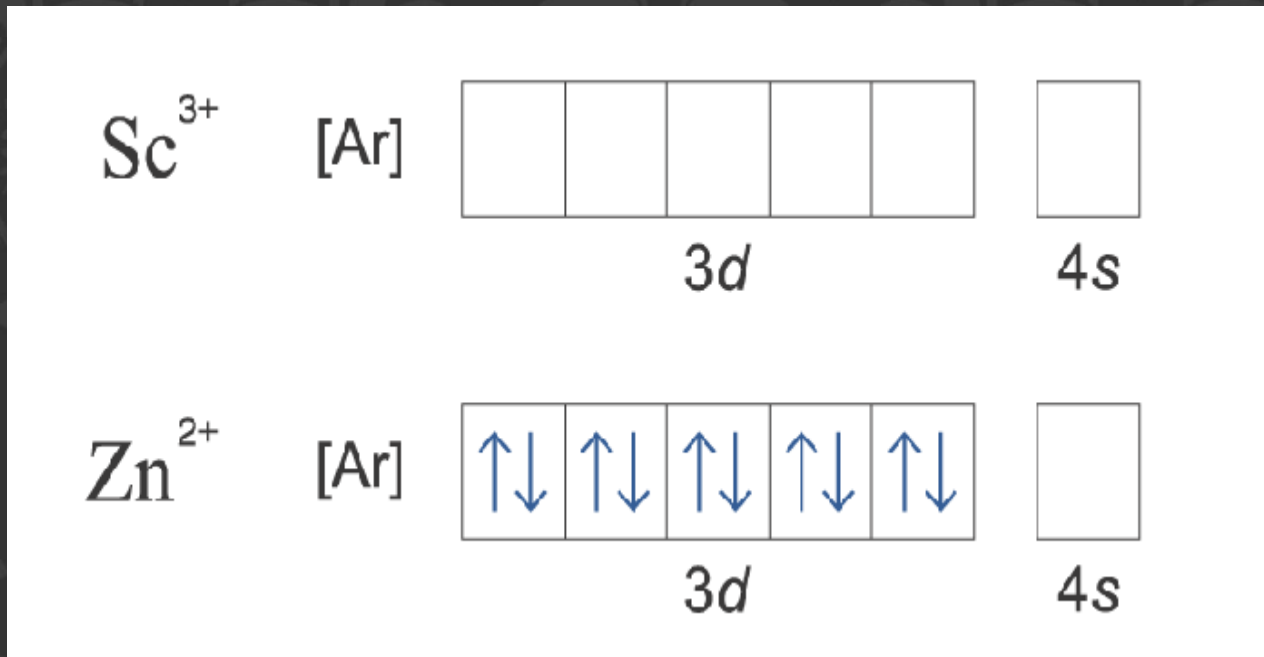
- Cu shows some **intermediate behaviour** between transition and non-transition elements because of two oxidation states, **Cu(I) & Cu(II)**

- **Cu$^+$ is not a transition metal ion** as it has a **completely filled** *d* **sub-shell**

- **Cu^{2+} is a transition metal ion** as it has an **incompletely filled** *d* **sub-shell**
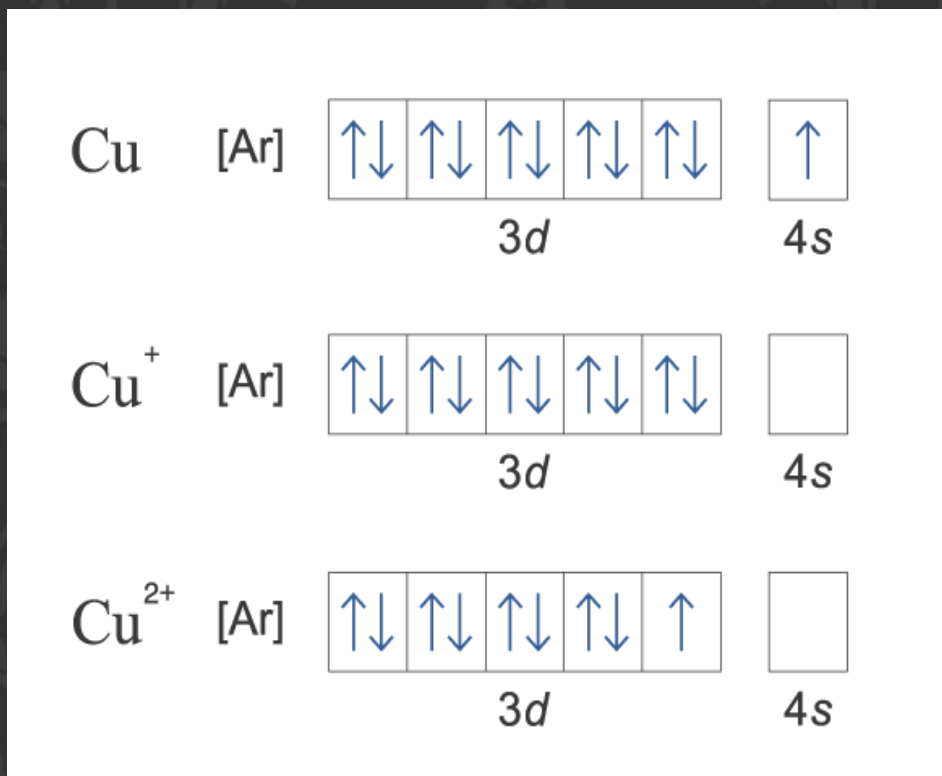
d-Block Elements as Metals

❑ *d*-block elements are typical metals

- Are hard (except Group 11 elements)

- Electropositive in nature, High heats of vapourisation

- good conductors of heat and electricity, strong, malleable, ductile and lustrous

- high melting and boiling points except Hg is a liquid at room temperature

- Form coloured compounds

- Tend to form large number of complexes

- Show many oxidation states

- Paramagnetic in nature generally

- Form alloy with other metals (Transition elements have similar atomic radii which make them possible for the atom of one element to replace those of another element in the formation of alloy)

  e.g. Mn is used for **giving hardness** and **wearing resistance** to its alloy (duralumin)

  Cr is used for **giving inertness to stainless steel**

- Show good catalytic behaviour

# Atomic Radii and Ionic Radii
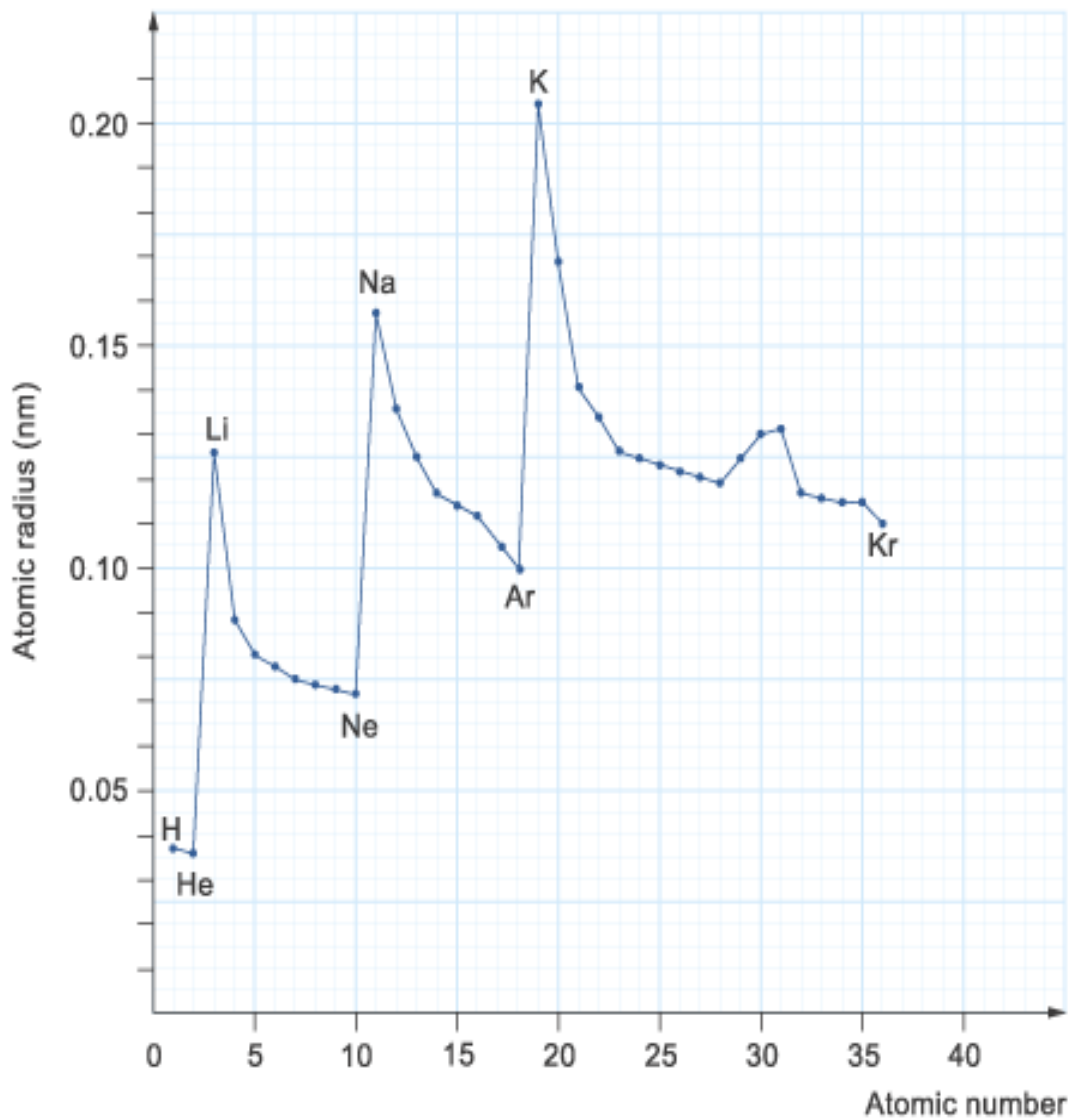
Observations:

- *d*-block metals have **smaller** atomic radii than *s*-block metals

- The atomic radii of the *d*-block metals **do not show much variation** across the series

- The atomic radii **decrease initially**, **remain almost constant in the middle** and then **increase at the end of series**

Group :										
Element :	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electron Configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
First Ionisation energy	631	658	650	653	717	759	758	737	745	906
Atomic radius (A°)	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.24
Density (g/cm^3)	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420
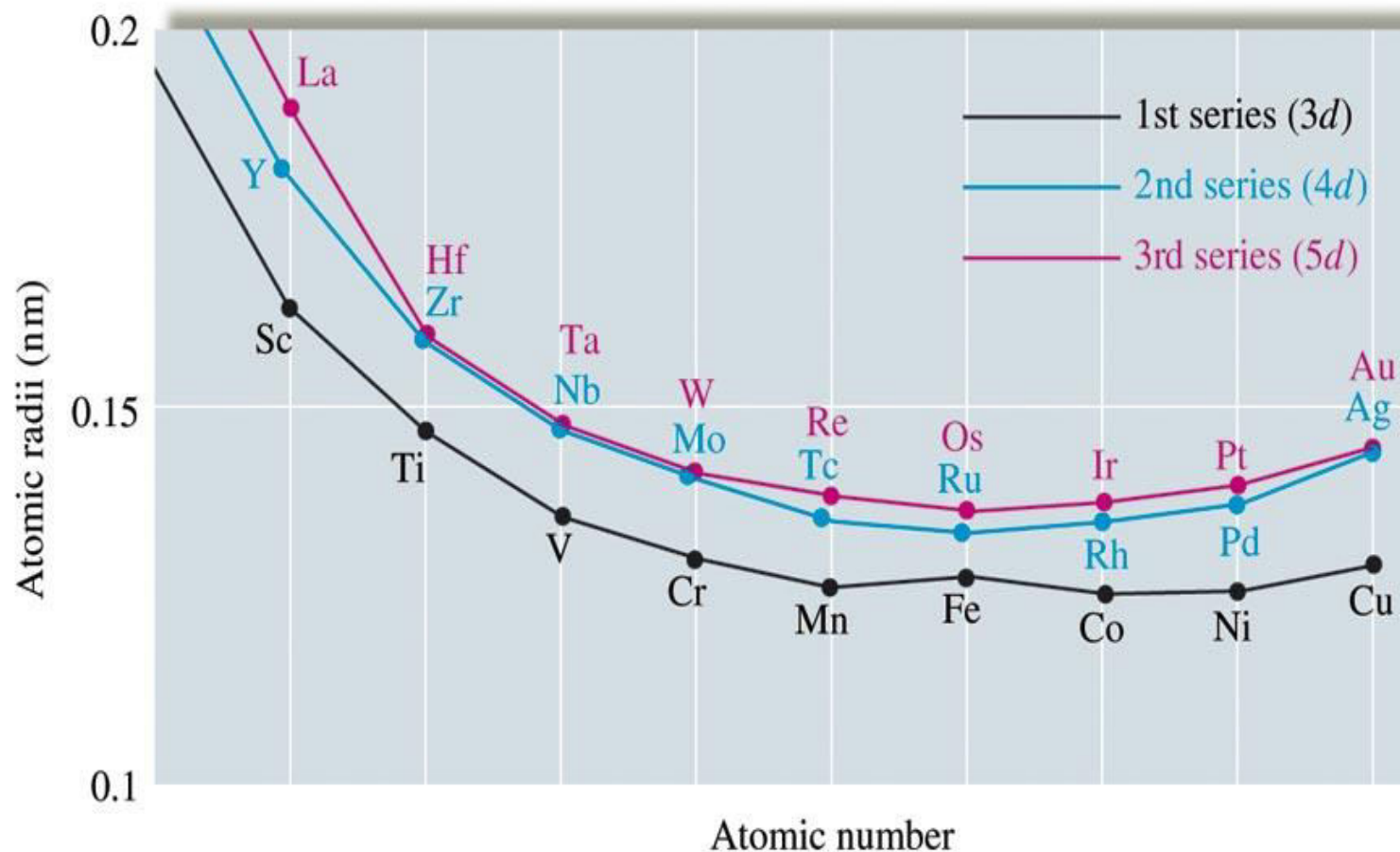
- The atomic size **reduces** at the **beginning of the series**

  ∵ increase in effective nuclear charge with atomic numbers as electrons are being added in (n-1) d subshell

  ⇒ the electron clouds are pulled closer to the nucleus

  ⇒ causing a reduction in atomic size

- The atomic size **decreases** slowly in the **middle of the series**

  ∵ when more and more electrons enter the inner $3d$ sub-shell

  ⇒ the screening and repulsive effects of the electrons in the $3d$ sub-shell increase

  ⇒ the effective nuclear charge increases slowly

- The atomic size **increases at the end of the series**

  ∵ the screening and repulsive effects of the $3d$ electrons reach a maximum

Ionic Radii

- The reasons for the trend of the ionic radii of the d-block elements are similar to those for the atomic radii

Ion	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
r $(M^{2+})(A^0)$	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.72

- Ionic radii generally decreases with increase in nuclear charge

Density

Densities (in g cm^{-3}) of the s-block metals and the first series of d-block metals

❖ *d*-block metals are generally **denser** than the *s*-block metals because the filling of the inner 3d orbital causes an increase in nuclear charge.

❖ Atomic volume of transition metals decrease .

❖ Density = Mass / Volume

❖ So, **density increases, as volume decreases**

❖ This is in agreement with the general **decrease in atomic radius** across the series

❖ Therefore, transition metals have very high densities

❖ Density reaches a **maximum value** till Ni of Group10 after that it decreases.

❖ Cu and Zn have fully filled 3d orbitals, which result in **increased forces of repulsion** between the added electrons.

❖ These forces of repulsion **are more than** the attractive force due to increased nuclear charge.

❖ Atomic volume of Cu and Zn **increases**, resulting in **decrease** in their density

Melting Point and Boiling Point
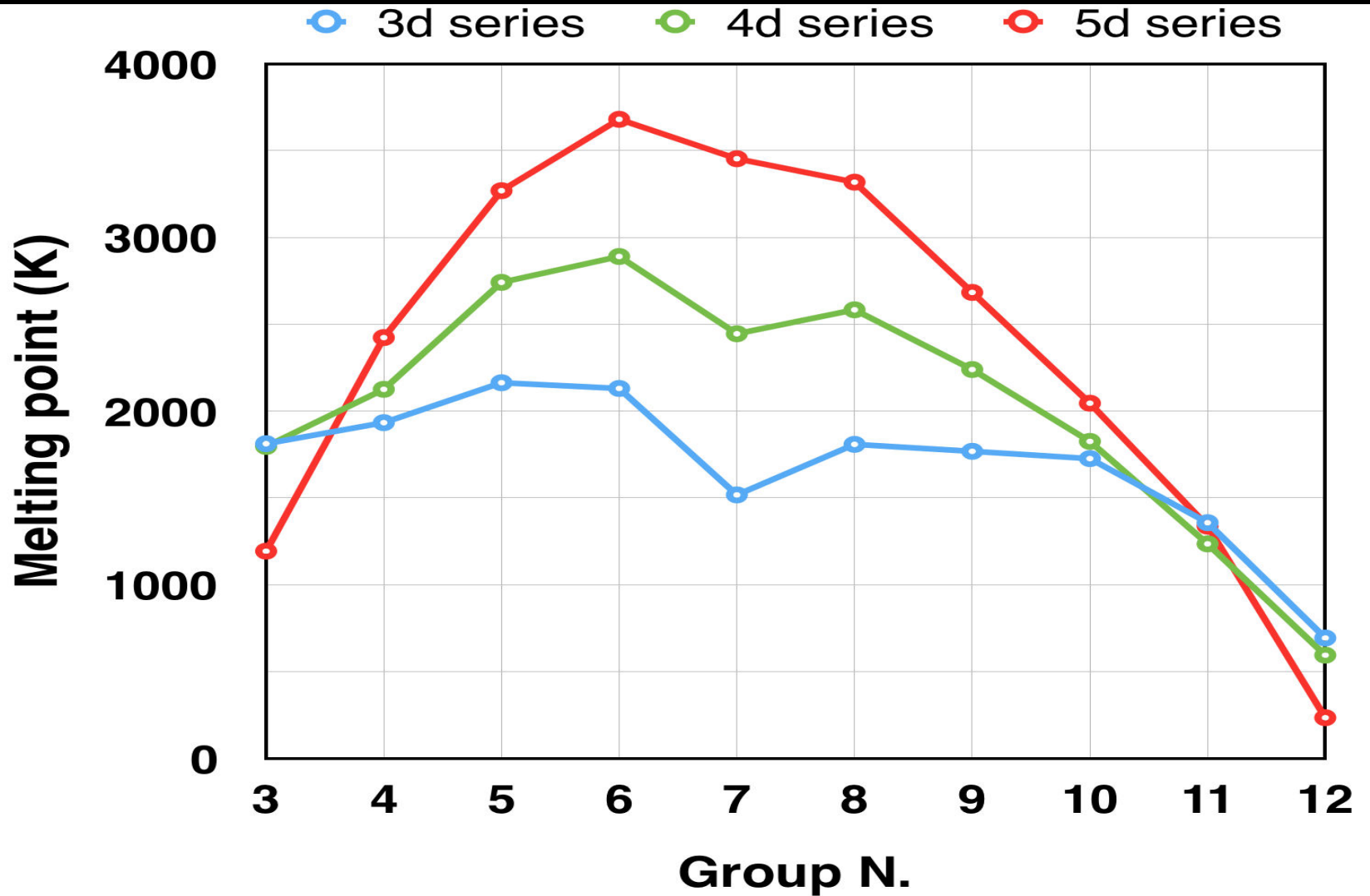
❑ **d- block elements have very high melting and boiling points.**

▪ The melting and boiling points increase, reach a maximum and then decrease.

• *Reasons:*

1. *d*-block metal atoms are **small in size** and **closely packed** in the metallic lattice.

2. The atoms in transition elements have **strong metallic bonding**.

3. Strength of metallic bonding depends on the **interaction of the unpaired electrons** in the outermost orbital.

- From Sc to Cr the number of **unpaired electrons increase**, resulting in **increase** in metallic strength.

- From Mn to Zn there is a **continuous decrease** in the number of unpaired electrons, resulting in **decrease** in metallic strength.

- Melting point increase till Cr and then it decreases.

- **EXCEPTIONAL CASES OF Mn & Zn**

- Mn has **quite low value** of melting point as compared to others.

- Mn has stable electronic configuration (**$3d^5$: half filled and $4s^2$: fully filled).**

- The 3d electrons are **tightly held**, resulting in their **less delocalization**.

- Metallic bond is **weaker** in Mn, resulting in lower melting point than Cr.

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- Similarly , Group12 elements (Zn, Cd, Hg) have fully filled electronic configuration.

- Due to **absence of unpaired electrons**, no metallic bonding occurs.

- So, the have low melting points.

IONIZATION ENERGY

- 1st I.E. of *d*-block metals are **greater** than those of *s*-block elements but **lesser** than those of *p*- block elements in the same row of the Periodic Table.

  - ∵ the *d*-block metals are **smaller in size** than the *s*-block metals, thus they have **greater effective nuclear charge**,

  - ∵ the *d*-block metals are **greater in size** than the *p*-block metals, thus they have **lesser effective nuclear charge.**

- The increase in ionization energy from Sc to Zn is not regular.

Ionization Enthalpy

Element	Ionization enthalpy (kJ mol^{-1})			
	1st	2nd	3rd	4th
K	418	3 070	4 600	5 860
Ca	590	1 150	4 940	6 480
Sc	632	1 240	2 390	7 110
Ti	661	1 310	2 720	4 170
V	648	1 370	2 870	4 600
Cr	653	1 590	2 990	4 770
Mn	716	1 510	3 250	5 190
Fe	762	1 560	2 960	5 400
Co	757	1 640	3 230	5 100
Ni	736	1 750	3 390	5 400
Cu	745	1 960	3 550	5 690
Zn	908	1 730	3 828	5 980

❖ The 1st I.E. of the *d*-block metals **increase slightly** and **irregularly across the series**

∵ Going across the first transition series, the **nuclear charge** of the elements **increases**

∵ Additional electrons are being added in the inner 3*d* sub-shell i.e. (n-1)d sub shell , the **screening effect increases**

∵ The 4s electrons are **shielded more and more.**

∵ The **screening effect** of the additional $3d$ electrons opposes the increase in nuclear charge

∴ The **effective nuclear charge** of the elements **increases** very **slowly** across the period, as does the **Ionization energy**

• Successive ionization enthalpies exhibit a **similar gradual increase** across the first transition series

• The increase in the 3rd and 4th ionization enthalpies across the series are progressively **more rapid**
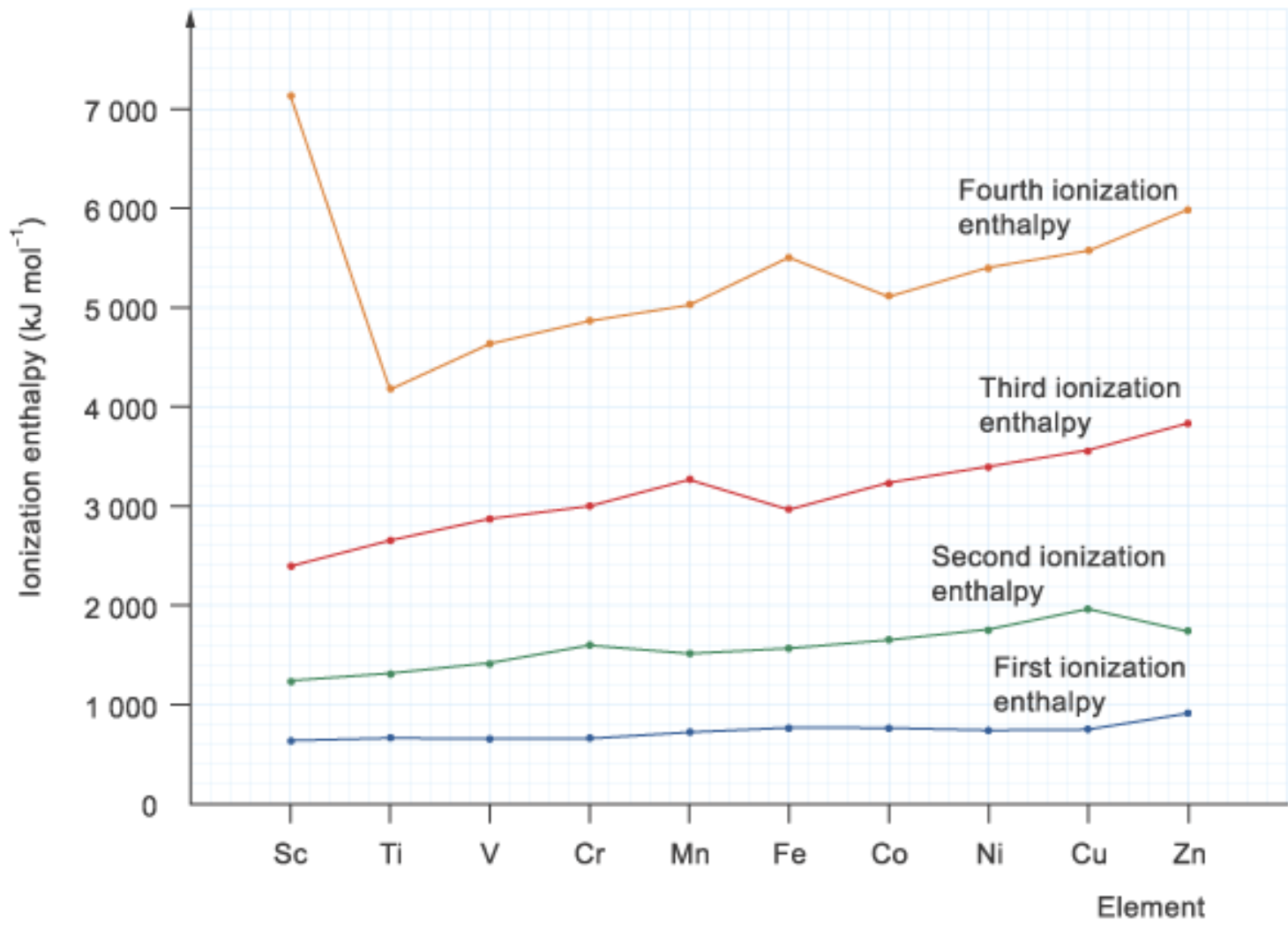
Variation of successive ionization enthalpies of the first series of the *d*-block elements

Explain the following variation in terms of electronic configurations.

The second ionization enthalpies of both Cr and Cu are higher than those of their next elements respectively.

The second ionization enthalpies of both Cr and Cu are higher than those of their next elements respectively. In the case of Cr, the second ionization enthalpy involves the removal of an electron from a half-filled $3d$ sub-shell, which has extra stability. Therefore, this second ionization enthalpy is relatively high. The case is similar for copper where its second ionization enthalpy involves the removal of an electron from a fully-filled $3d$ sub-shell which also has extra stability. Thus, its second ionization enthalpy is also relatively high.

METALLIC CHARACTER

- All transition elements are metals .

- Except for Zn, Cd and Hg , the transition elements are hard, brittle and less volatile.

- Metallic character of TM is due to their low ionization energies and number of vacant orbitals in their outermost shell.

- The **hardness of a metal** depends on the strength of the metallic bonds which arises due to overlap of unpaired electrons between different metal atoms.

REDUCING CHARACTER

➢ Reducing character of a metal depends on its tendency to be oxidized

$$M \rightarrow M^{n+} + ne^-$$

➢ The reducing potential is measured in terms of reduction potential (E^o)of an element.

➢ More negative the value of E^o , stronger is the reducing nature.

➢ D- block elements act as strong reducing agents.

ELECTRODE POTENTIAL VALUES

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

❖ s-block elements are **stronger reducing agents** than d – block elements

❖ d – block elements have large ionization energies and very high enthalpies of atomisation , as compared to s-block elements .

❖ These result in reduction of electrode potential values of d – block elements.

❖ Zn has low electrode potential value despite having low enthalpy of atomisation due to very high value of Ionization energy.

What are the differences between the structures and bonding of the *d*-block and *s*-block metals? How do these differences affect their melting points?

The *d*-block metals are comparatively small, and the metallic atoms are closely packed in the metallic lattice. Besides, both the $3d$ and $4s$ electrons of the *d*-block metals participate in metallic bonding by delocalizing into the electron sea. The strength of metallic bond in these metals is thus very strong. In the case of *s*-block metals, the metallic radius is larger and most of them do not have close-packed structures. Also , as they have only one or two valence electrons per atom delocalizing into the electron sea, the metallic bond formed is weaker. Therefore, the *d*-block metals have a much higher melting point than the *s*-block metals.

REACTIVITY

- Transition metals are very less reactive :

- Small atomic size,

- High ionization energies

- Due to covalent bonding they have high heat of sublimation

- Low heat of hydration

OXIDATION STATES

Variable Oxidation States

- *d*-block elements have the ability to show **variable oxidation states** because

  ∵ **3*d* & 4*s* electrons** have almost **same energy**

  ∵ Both **3*d* & 4*s* electrons** are available for bond formation

- Stability of a particular oxidation state depends on the nature of element with which the transition metal enters into compound formation

Variable Oxidation states of the elements of the first transition series

Element	Outer Electronic Configuration	Oxidation States
Sc	$3d^1\ 4s^2$	(+2) ,+3
Ti	$3d^2\ 4s^2$	+2 ,+3 , +4
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

GENERALIZATIONS

❖ Variable oxidation states shown by TM is due to the participation of the inner (n-1) d and the outer ns orbitals.

❖ Except **Sc**, all elements have +2 oxidation state.

❖ Except **Cu & Zn**, all elements have +3 oxidation state.

❖ The first five elements of the 1st transition series,

▪ Minimum oxidation state is equal to the electrons in the outer ns orbital.

▪ Maximum oxidation state is equal to the electrons in the inner (n-1) d and outer ns orbital.

❖ The highest oxidation state observed is that of **Mn (+7).** This corresponds to removal of **all 3d & 4s electrons**.

❖ There is **reduction** in the number of oxidation states after Mn. ∵ decrease in the number of unpaired electrons and increase in nuclear charge which holds the 3d electrons more firmly.

❖ The relative stability of various oxidation states can be correlated with the stability of empty, half-filled and fully-filled configuration

e.g.   Ti^{4+} is more stable than Ti^{3+} (∵ [Ar]3d^0 configuration)

Mn^{2+} is more stable than Mn^{3+} (∵ [Ar]3d^5 configuration)

Zn^{2+} is more stable than Zn$^+$ (∵ [Ar]3d^{10} configuration)

❖ Compounds of transition metals having +2 and +3 oxidation states, generally form ionic bonds with ligands.

❖ Compounds of transition metals showing higher oxidation states, bonds formed are covalent in nature.

❖ This is because + 2 or +3 O.S. are formed due to loss of electrons.

❖ Whereas in higher O.S. loss of so many electrons is not possible and the bonds are formed due to sharing of d-electrons.

❑Transition metals also form compounds in low oxidation states like +1, 0 and negative.

- When the metal is in zero or low oxidation state, there are no forces of attraction between the metal and the ligands forming the bonds.

- As metal forms a number of bonds with the ligands, it should result in increase in –ve charge on the metal .

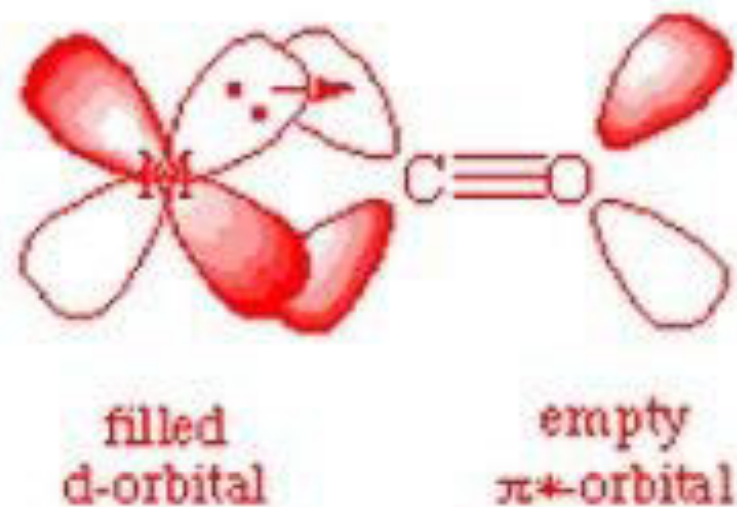- So, compounds of TM in the lower or zero oxidation state should be unstable, but they are not.

- In such cases TM having zero or low oxidation state , tend to form compounds with ligands like CO, NO, CN^-. For e.g. $Ni(CO)_4$ & $Fe(CO)_5$

- In both these compounds the metal have zero oxidation state.

- The vacant orbitals of the metal accepts lone pair of electrons from the ligands, forming a normal σ – covalent bond.

- Simultaneously, electrons from the filled metal orbitals are back donated to the vacant orbitals of the ligand forming a π bond (d π - p π bond)

- This π bond reinforces the σ bond.

- Due to back donation of electrons from metal to ligands, no accumulation of –ve charge occurs on the metal.

σ bond: π backbond:

M → C≡O

empty
d or p-orbital   filled
σ-orbital

M   C≡O

filled
d-orbital   empty
π*-orbital

RELATIVE STABILITY OF OXIDATION STATES OF TM

Factors which determine the stability of different oxidation states of transition metals are :

✓ Ionisation energy

✓ Electrode potential

✓ Nature of solvent

IONISATION ENERGY

✓ Gives information about the thermodynamic stability of TM compounds in different oxidation states.

✓ Lesser the ionisation energy , more is the stability of the compound in that particular O.S.

✓ Consider the first four ionisation energies of Ni & Pt

	$(IE_1 + IE_2)$	$(IE_3 + IE_4)$	Total (KJ/mol^{-1})
• Ni	2.49×10^3	8.80×10^3	11.29×10^3
Pt	2.66×10^3	6.70×10^3	9.36×10^3

- ✓ The sum of the first two ionisation energies of Ni is less than that of Pt.

- ✓ So, Ni^{2+} complexes are more stable thermodynamically than Pt^{2+} complexes.

  However, if the sum of first four ionisation energies is considered then

- ✓ Pt^{4+} complexes are more stable thermodynamically than Ni^{4+} complexes , as Pt^{4+} complexes have lower value of ionisation energies.

ELECTRODE POTENTIAL

✓ It also helps to predict the stability of different oxidation states.

✓ Lower the value of E^o_{red} , greater is the stability of that oxidation state.

✓ Comparison of E^o_{red} values of Cu^+ and Cu^{2+}

$$Cu^+ (aq) + e^- \longrightarrow Cu\ (s)\ ;\ E^o_{red} = 0.52V$$

$$Cu^{2+} (aq) + 2e^- \longrightarrow Cu\ (s)\ ;\ E^o_{red} = 0.34V$$

✓ Thus, Cu^{2+} O.S. is more stable than Cu^+ O.S. in aqueous solution

Electrode potential depends on many factors :

- ✓ Sublimation energy
- ✓ Ionisation energy
- ✓ Hydration energy

- ✓ In order to explain how , lets consider the oxidation potential of a metal.

- ✓ $$M\,(s) \longrightarrow M^+\,(aq)\ +\ e^-$$

- ✓ The Oxidation potential involves the following steps:

❖ First Step : Involves the isolation of atom and changing it from solid state to gaseous state.

This process is called sublimation and the energy required for this conversion is called Enthalpy of Sublimation.

❖ Second Step : Involves the ionisation (removal of the outermost electron)of the gaseous atom.

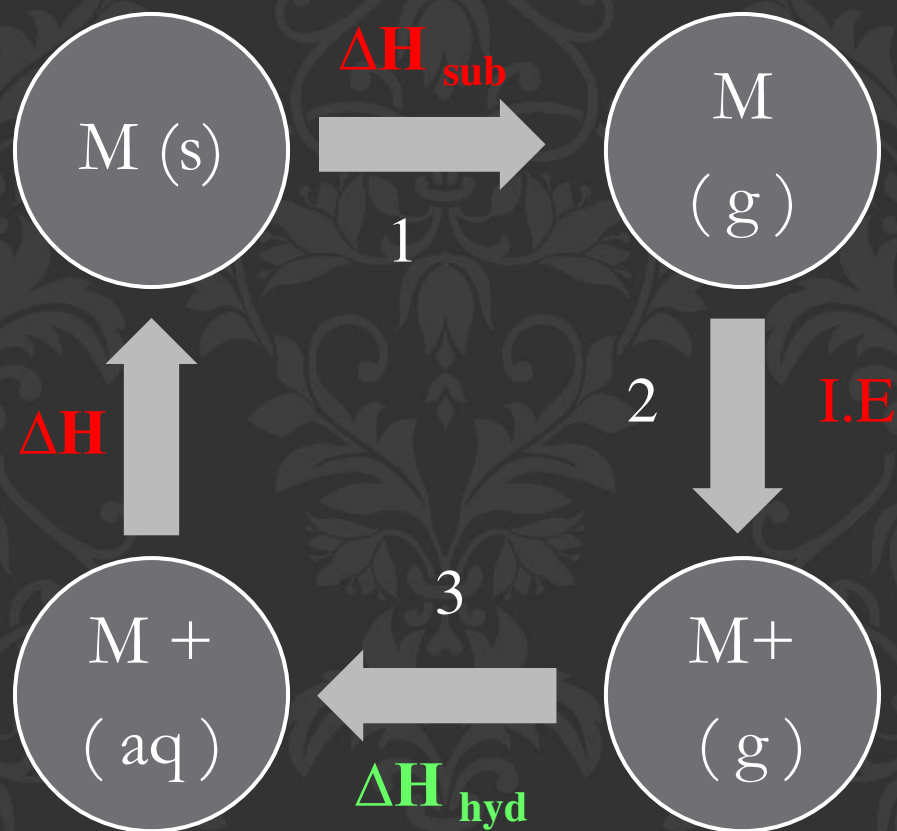The energy required for the removal of the outermost electron of the gaseous atom is called Ionisation energy.

❖ Third Step : Involves the hydration of gaseous metal ion.

During hydration, energy is liberated & is called Hydration energy.

❖ The oxidation potential depends on the sum of the above three steps

$$\Delta H = \Delta H_{sub} + I.E + \Delta H_{hyd}$$

Stability of an O.S. ∞ $\dfrac{1}{\Delta H}$

M (s) → ΔH_{sub} → M (g)
1

M (g) → 2 I.E → M+ (g)

M+ (g) → 3 ΔH_{hyd} → M + (aq)

M + (aq) → ΔH → M (s)

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The electrode potential values of the first transition series for the M^{2+} (aq) / M(s) are as

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E° $(M^{2+}(aq)/ M(s))$ (in V)	-1.63	-1.20	-0.91	-1.18	-0.44	-0.28	-0.25	0.34	-0.76

OBSERVATIONS :

• The electrode potential values show no regular trend, due to variation in the (I.E$_1$ + I.E$_2$) and heat of sublimation.

- E^o value of TM is **low** as compared to Group 2 elements (ns^2).

- TM have **high value of ionisation energies and very large energy of atomisation** as compared to Group 2 elements. These result in the decrease of E^o value of TM.

- Copper has **+ve value** of E^o . This is because the conversion of $Cu(s)$ to Cu^{2+} (aq) requires very high value ionisation potential which is not compensated even on hydration of Cu^{2+} ion.

- E^o values of TM **decrease** as we move from left to right in a series, due to increase in ($I.E_1 + I.E_2$) .

- The values of E^o of Mn, Ni, Zn are more –ve than expected.

- This is due to stability of half filled d - subshell in Mn^{2+} ($3d^5$) and the completely filled d - subshell in Zn^{2+} ($3d^{10}$).

- High E^o of Ni^{2+} is due to highest –ve energy of hydration of Ni^{2+} ion.

NATURE OF SOLVENT

- The stability of oxidation states in a particular solvent depends on the nature of solvent .

- In that solvent, the TM may undergo oxidation or reduction depending on the conditions under which the reaction is occurring.

- For e.g. Cr^{3+} is stable in water but Cr^{2+} is unstable.

TRENDS IN M^{3+} / M^{2+} STANDARD POTENTIAL

- Except **Cu and Zn**, all elements of the first transition series show +3 O.S.

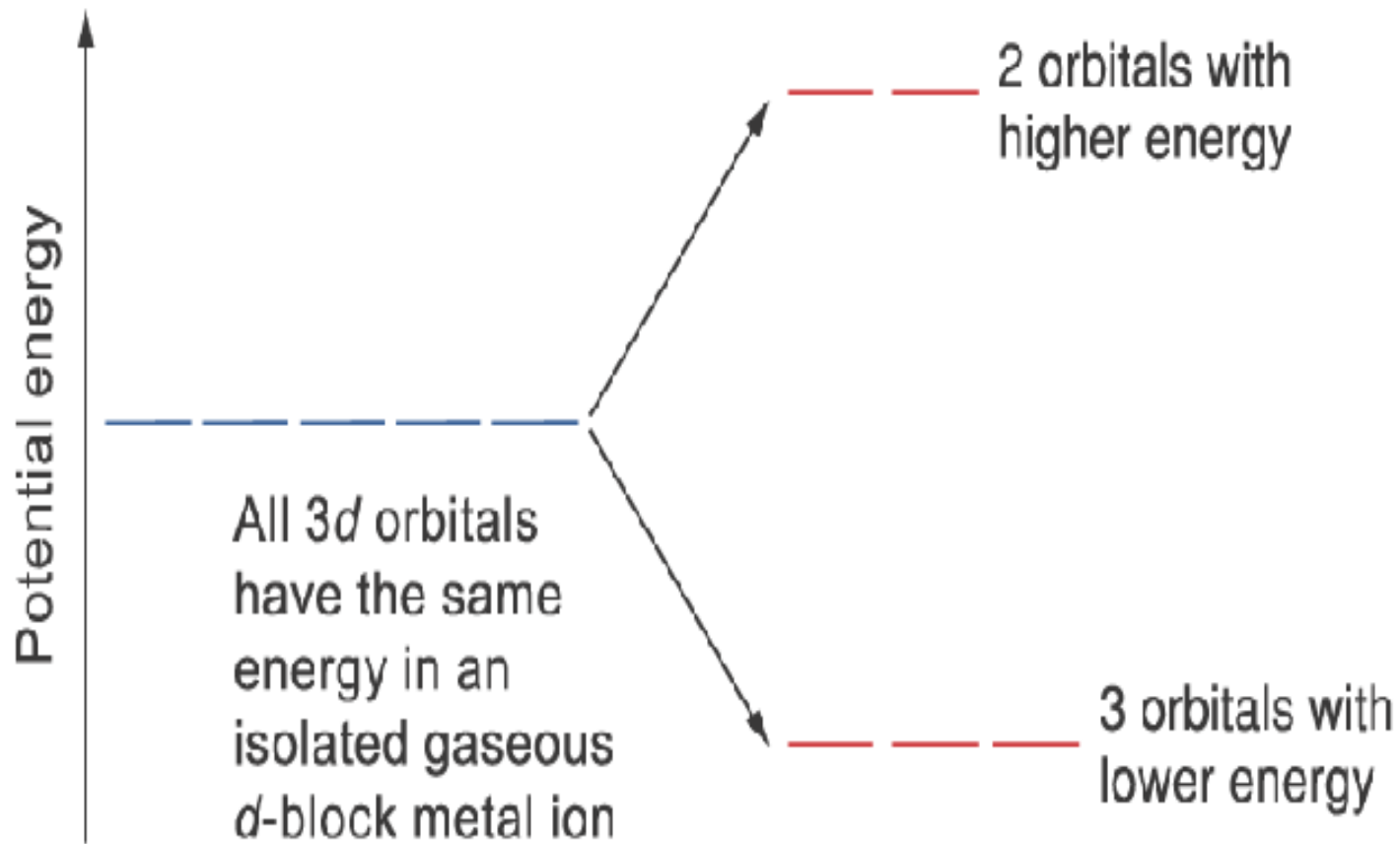|	Ti	V	Cr	Mn	Fe	Co
$E°$ (M^{3+}(aq)/ M^{2+}(aq)) (in V)	- 0.37	- 0.26	- 0.41	+1.57	+ 0.77	+ 1.97

OBSERVATIONS

- Sc^{3+} has low value of E^o as in **+3 O.S.** , it has noble gas configuration.

- High value of Mn^{3+} indicates that **Mn in +2 O.S.** is highly stable due to half filled d – subshell.

- Low value of Fe^{3+} indicates that **Fe in +3 O.S.** is highly stable due to half filled d – subshell.

- Low value of V is due to the stability of V^{2+}

Formation of Coloured Ions

- The natural colours of precious gemstones are due to the **existence of small quantities of *d*-block metal ions**

- Most of the *d*-block metals form **coloured** compounds and most of their complexes are **coloured** too
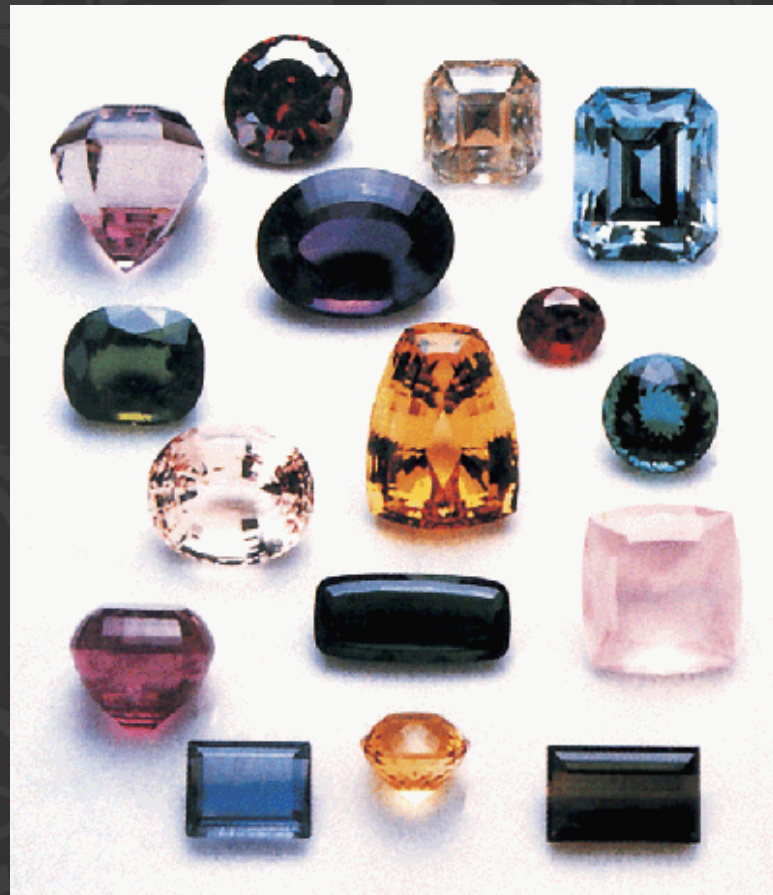
❖ The colour of the compounds of TM is due to the presence of **incompletely filled (n – 1)d orbitals.**

❖ The unpaired electrons can be easily **promoted** from lower energy level to higher energy level in the **same d – subshell**.

❖ For the d-block elements, the five $3d$ orbitals are **degenerate** **(have the same energy)** in **gaseous ions**.

❖ However, when compound formation occurs, the $3d$ orbitals **split into 2 sets of orbitals** having **different energies.**

❖ This is called **crystal field splitting**

Potential energy

All 3*d* orbitals have the same energy in an isolated gaseous *d*-block metal ion

2 orbitals with higher energy

3 orbitals with lower energy

❖ The amount of energy required to excite the electrons from lower to higher energy level within the same d – subshell **is equal to / corresponds** to energies of certain colour invisible light.

❖ When light falls on a TM compound, it **absorbs visible light** (corresponding to some colour) **of a certain wavelength** causing **excitation of d – electrons**.

❖ Light of wavelengths of **other regions** of the visible light spectrum will be **reflected** or **transmitted**.

❖ The colour seen is always **complementary of** the colour of the absorbed wavelength of visible light.

COLOUR OF DIFFERENT TRANSITION METAL IONS

Ion	Outer Configuration	No. of unpaired electrons	Colour of the ion
Sc (III), Ti (IV)	$3d^0$	0	White
Ti (III)	$3d^1$	1	Purple
V (III)	$3d^2$	2	Green
V (II), Cr (III)	$3d^3$	3	Violet
Mn (III)	$3d^4$	4	Violet
Mn (II)	$3d^5$	5	Pink
Fe (III)	$3d^5$	5	Yellow
Fe (II)	$3d^6$	4	Green
Co (II)	$3d^7$	3	Pink
Ni (II)	$3d^8$	2	Green
Cu (II)	$3d^9$	1	Blue
Cu (I)	$3d^{10}$	0	White
Zn (II)	$3d^{10}$	0	White

❖ *d*-block metal ions have specific **colours.**

❖ For *d-d* electronic transition and absorption of visible light to occur, there must be **unpaired *d* electrons** in the transition metal atoms or ions.

❖ **Sc^{3+} and Zn^{2+} are colourless** due to the **empty** and **fully-filled 3*d* sub-shell** respectively.

❖ The **colours** of hydrated metal ions are determined by the **oxidation states** of the particular *d*-block elements

  e.g. Fe^{2+}(*aq*) is green while Fe^{3+}(*aq*) is yellow

❖ TM ions having completely filled d-orbitals are colourless

MAGNETIC PROPERTIES

TRANSITION METALS

Paramagnetic

a) Attracted by magnetic field

b) arises due to unpaired electrons

Diamagnetic

a) Repelled by magnetic field

b) Arises due to paired electrons

- Most of the Transition metals are **paramagnetic** in nature due to the presence of unpaired electrons in d – orbitals.

- Magnetic character is expressed in terms of **magnetic moment.**

- **Greater** the number of unpaired electrons , **greater** is the paramagnetic character and **greater** is the magnetic moment.

- The magnetic moment is expressed in **Bohr Magneton (B.M.)**

- The magnetic moment is **only due to the spin of the electrons.**

- This is confirmed due to **close agreement** of theoretical and calculated values of magnetic moment of TM ions.

Magnetic moment of ions of first transition series

Elements	Outer Electronic Configuration	Number of Unpaired Electrons	Observed Magnetic Moment (in BM)	Theoretical Magnetic Moment (in BM)
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.75	1.73
V^{3+}	$3d^2$	2	2.76	2.83
Cr^{3+}	$3d^3$	3	3.86	3.87
Cr^{2+}	$3d^4$	4	4.80	4.90
Mn^{2+}	$3d^5$	5	5.96	5.92
Fe^{2+}	$3d^6$	4	5.10	4.90
Co^{2+}	$3d^7$	3	4.4 – 5.2	3.87
Ni^{2+}	$3d^8$	2	2.9 – 3.4	2.84
Cu^{2+}	$3d^9$	1	1.8 -2.2	1.73
Zn^{2+}	$3d^{10}$	0	0	0

- The magnetic moment due to spin contribution only can be calculated by

$$\mu = \sqrt{n(n+2)} \quad \text{B.M.}$$

Where **n** stands for the number of unpaired electrons.

- For e.g. , Cr (3d) has three unpaired electrons.

i.e. its **n** value will equal to **3.**

Substituting this value in the above relation, the magnetic moment is

$$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87$$

MAGNETISM IN IRON METAL

❖ In addition to **Paramagnetism** and **Diamagnetism**, the compounds of Iron and some other metals show another kind of magnetic behaviour known as **Ferro magnetism**.

❖ In some materials, the **permanent atomic magnetic moments** have a strong tendency to **align themselves** even without any external field.

❖ These materials are said to be **Ferromagnetic materials.**

❖ Some of the examples of ferromagnetic materials are **cobalt, iron, nickel, gadolinium, dysprosium.**

❖ The **ferromagnetic materials** are those substances which exhibit strong magnetism in the same direction of the field, when a magnetic field is applied to it.

❖ In solid state , the metal ions of ferromagnetic substances are **grouped together** into small regions called **Domains.**

❖ They get their **strong magnetic properties** due to the presence of magnetic domains.

❖ In these domains, large numbers of atom's moments (10^{12} to 10^{15}) are **aligned parallel** so that the magnetic force within the domain is strong.

❖ When a ferromagnetic material is in the **unmagnitized state**, the domains are nearly randomly organized and the net magnetic moment s get cancelled.

❖ When a magnetizing field is applied, the domains become aligned in the direction of the magnetic field.

❖ Ferromagnetic substances can be classified into **three types** depending upon on the **alignment of magnetic domains**.

❖ **They are:**
a) Ferromagnetic substances
b) Anti ferromagnetic substances
c) Ferrimagnetic Substances

A. FERROMAGNETIC SUBSTANCES

- They have **large, positive susceptibility** to an external magnetic field.

- The magnetic moment of the domains get **spontaneously aligned** in the direction of the applied magnetic field.

- They are able to **retain their magnetic properties** after the external field has been removed.

- It means it becomes **permanently magnetized** even after the removal of the external magnetic field.

- Example : **Ni, Co, Fe_2O_3 , CrO_2 etc.**
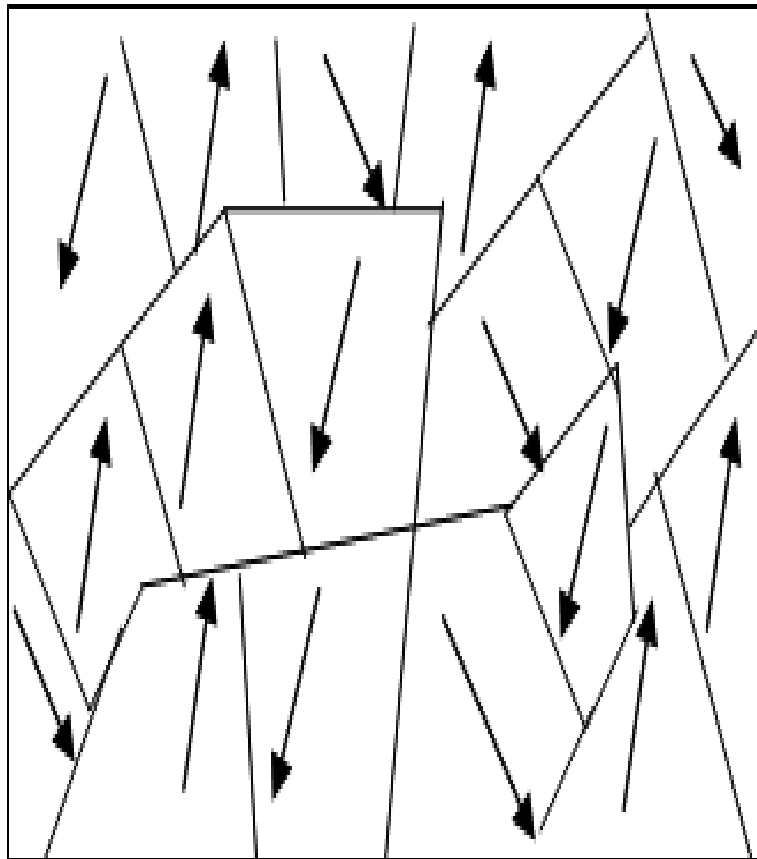
A. Random domain orientation
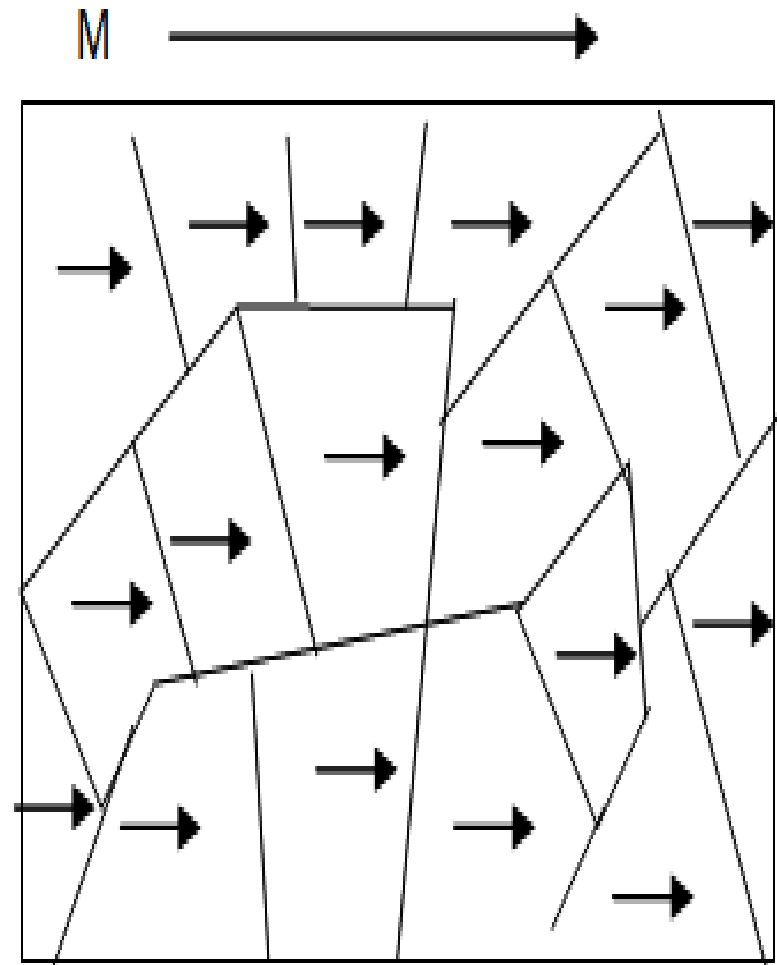
B. After magnetization

B. ANTI FERROMAGNETIC SUBSTANCES

- In this the adjacent ions/ domains that behave as tiny magnets spontaneously align themselves into opposite or antiparallel arrangement throughout the material

- The magnetism from magnetic atoms or ions oriented in one direction is canceled out by the set of magnetic atoms or ions that are aligned in the reverse direction.

- So that the compound exhibits almost no gross external magnetism.

- This type of behaviour is observed at low temperatures.

Examples of anti ferromagnetic substances are MnO, FeO, NiO, MnO_2, $V_2 O_3$.
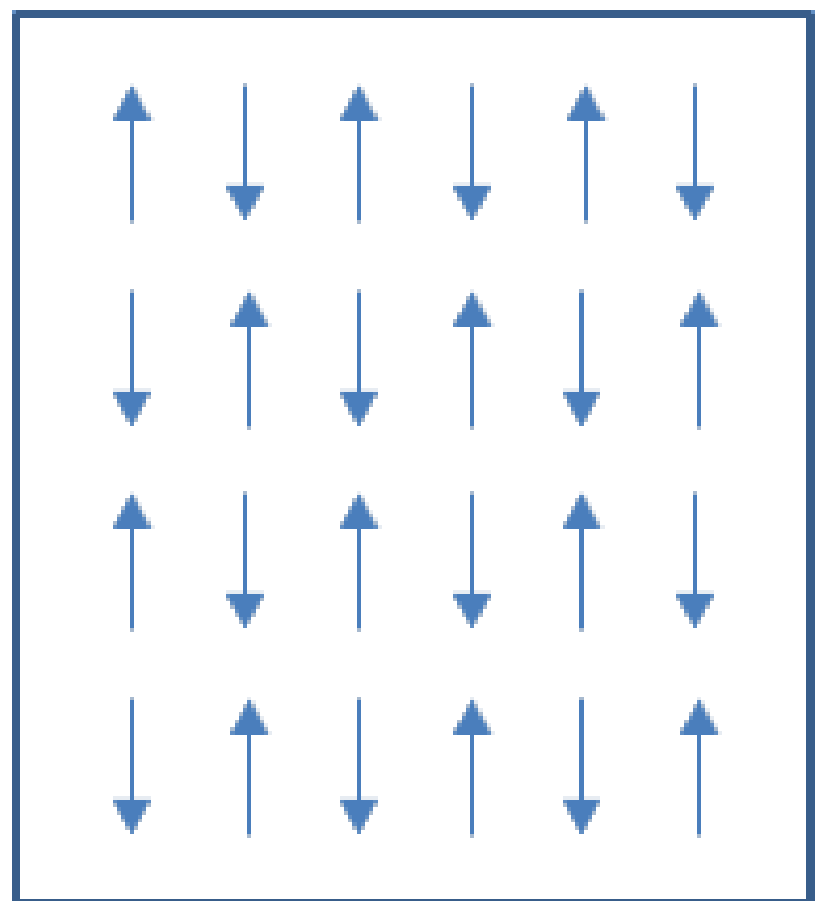
Antiferromagnetic ordering

C. FERRIMAGNETIC SUBSTANCES

- It has population of atoms with **opposing magnetic moments**, as in anti ferromagnetic substances.

- However, in ferrimagnetic materials, the opposing magnetic moments are **unequal** .

- This results in a **spontaneous magnetization** i.e. a net magnetic moment is observed.

- Such compounds are **weakly attracted** by the magnetic field.

- This happens when the populations consist of different materials or ions (such as Fe^{2+} and Fe^{3+}).

- Example of **ferrimagnetic** substances are $\mathbf{Fe_3O_4}$ (made up of FeO & Fe_2O_3) , and ferrites having the formula $\mathbf{M^{2+}Fe_2O_4}$; where M can be either Mg, Cu, Zn etc.
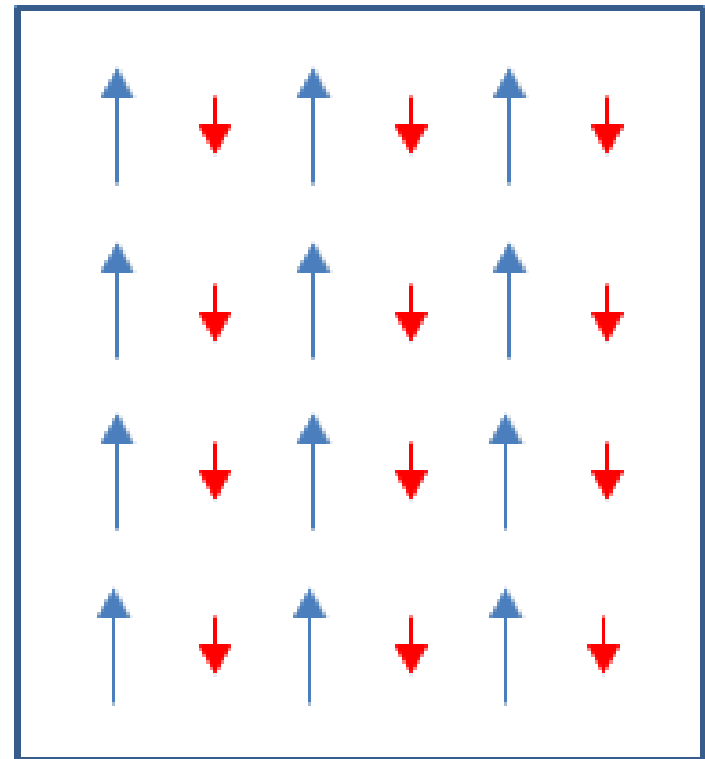
Ferrimagnetic ordering

ALIGNMENT OF MAGNETIC MOMENTS

Ferromagnetic ↑ ↑ ↑ ↑ ↑ ↑ ↑	Below T_C, spins are aligned parallel in magnetic domains
Antiferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_N, spins are aligned antiparallel in magnetic domains
Ferrimagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_C, spins are aligned antiparallel but do not cancel
Paramagnetic ↑ ↓ ↑ ↑ ↓ ↑ ↓	Spins are randomly oriented (any of the others above T_C or T_N)

- However, all **magnetically ordered solids** i.e. ferromagnetic, anti ferromagnetic and ferrimagnetic **change to paramagnetic state at high temperature.**

- This happens due to **randomisation of their spins** at high temperature

- **Curie Temperature** T_c is the temperature at which certain materials **lose their permanent magnetic properties**, to be replaced by induced magnetism.

- In other words, it is the temperature above which a **ferromagnetic material becomes paramagnetic.**

- The **Néel temperature** or **magnetic ordering temperature**, T_N, is the temperature above which an **antiferromagnetic material becomes paramagnetic**.

- It means the thermal energy **becomes large enough to destroy** the microscopic magnetic ordering within the material.

- **Fe$_3$O$_4$** at 580^0C **loses** its ferrimagnetic character and becomes paramagnetic in character.

COMPLEX FORMATION

➢ Transition metals have a **high tendency** to form complexes.

➢ The **high tendency** of transition metal atom/ ions **to form complexes is due to:**

a) **Small size of transition metal atom/ ions**

b) **High nuclear charge**

c) **Availability of vacant d- orbitals of suitable energies in transition metal atom/ ions to form bonds with ligands**

➤ The bonds between the central metal atom/ ion is formed due to **sharing of an electron pair** of the ligand with the metal.

➤ The bonds formed are **Coordinate covalent bond** and so, the complexes are called **Coordinate complexes**.

➤ Coordinate complexes have **different geometries** (linear, tetrahedral, square planar, octahedral etc.) depending on the **number of ligands forming bonds** with the central metal atom/ ion.

GENERALIZATIONS

✓ The stability of TM complexes **increases with increase in atomic number** of the element.

✓ **Greater the oxidation state** of an element, **smaller** is its **atomic size**, **more** will be its **stability**.

✓ For example:

Co^{2+} does **not form stable** complex with ammonia (NH_3) whereas Co^{3+} does and form complex of the type $[Co(NH_3)_6]^{3+}$.

FORMATION OF INTERSTITIAL COMPOUNDS

- Transition metals form **interstitial compounds** with non metallic elements like H, B,C and N.

- Transition metals have **vacant spaces in their lattices** and small atoms of H, B,C and N **get trapped** in these vacant spaces.

- The interstitial spaces **get filled up** leading to transition metals becoming **hard and rigid**.

- **Chemical properties** of the interstitial compounds **resemble** that of the parent compound but their **physical properties are different.**

CATALYTIC PROPERTY

- Many transition metal (V, Cr, Mn, Fe, Co, Ni, etc.) and their compounds **act as good catalysts** for various reactions.

- **Iron – molybdenum (Fe – Mo)** is used as catalyst in the synthesis of ammonia by Haber's process.

- **Nickel** is used as catalyst in hydrogenation reactions in organic chemistry.

- **Vanadium pentoxide** is used for oxidation of SO_2 to SO_3 in contact process.

- The transition metals form **suitable reaction intermediates** with the substrate .

- Formation of reaction intermediates involves the **use of empty d- orbitals** of the TM.

- The reaction intermediates give **reaction paths of lower activation energies**, resulting in increase in rate of reaction

- Consider the **conversion of SO_2 to SO_3 in which V_2O_5 is used as a catalyst.**

- A molecule of SO_2 is **adsorbed on the surface** of solid catalyst V_2O_5

- V_2O_5 changes to V_2O_4 **giving out O atom** which is taken up by SO_2 to form SO_3 .

- V_2O_4 gets **converted back** into V_2O_5 by reaction with oxygen.

$$V_2O_5 + SO_2 \longrightarrow SO_3 + V_2O_4$$

Catalyst   **Vanadium tetraoxide**

$$V_2O_4 + O_2 \longrightarrow V_2O_5$$

ALLOY FORMATION

❖ Transition metals form **large number** of alloys.

❖ Transition metals have approximately **same size** due to which atoms of one metal **can substitute** atoms of other metal in its crystal lattice.

❖ **Solid alloys** are formed by cooling a **mixture solution** of two or more transition metals.

❖ For e.g. a solution of manganese and iron gives an alloy called **manganese steel**.