

Unit - II D-block elements

d-block elements :- The elements in which the differentiating electron entering into the penultimate d orbital are called as d-block elements.

Transition elements :- The elements which have partially filled d orbitals are called as 'Transition elements'.

* All the transition elements are d-block elements but all d-block elements are not transition elements. namely, there are 3 types of d-block elements.

→ 3d block elements (3d-series)

Ex: Sc, Ti, V, etc.

→ 4d block elements (4d-series)

Ex: Y, Zr, Nb, etc.

→ 5d block elements (5d-series)

Ex: La, Hf, Ta, etc.

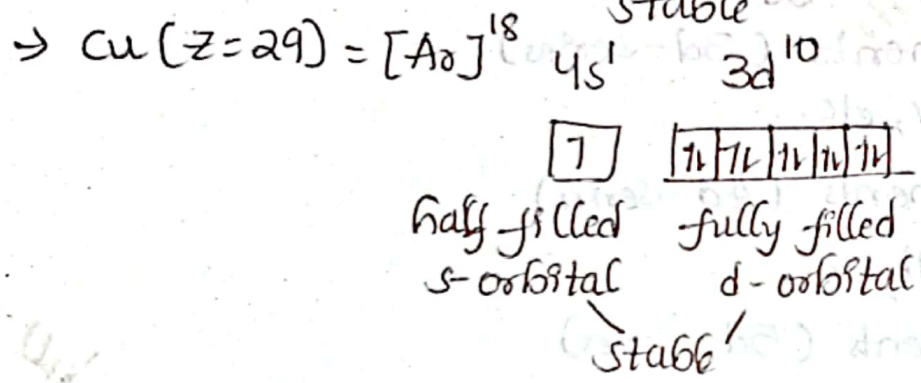
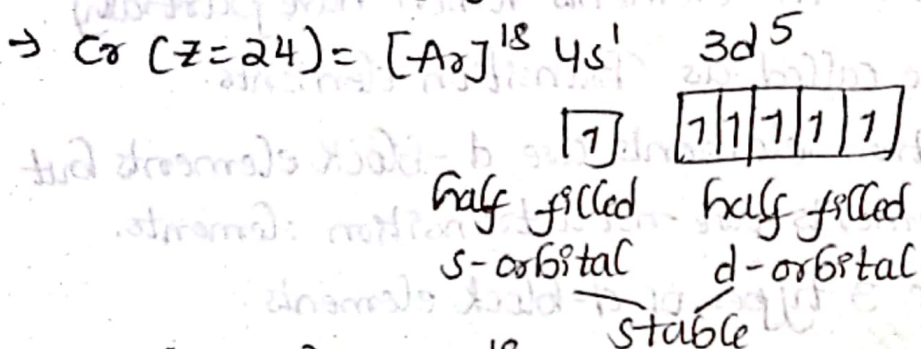
Characteristic properties of d-block elements

1) Electronic configuration of 3d-block elements :-

<u>Element</u>	<u>Name</u>	<u>Atomic No</u>	<u>Electronic configuration</u>
Sc	Scandium	21	$[Ar]^{18} 4s^2 3d^1$
Ti	Titanium	22	$[Ar]^{18} 4s^2 3d^2$
V	Vanadium	23	$[Ar]^{18} 4s^2 3d^3$
Cr	Chromium	24	$[Ar]^{18} 4s^1 3d^5$
Mn	Manganese	25	$[Ar]^{18} 4s^2 3d^5$
Fe	Iron	26	$[Ar]^{18} 4s^2 3d^6$
Co	Cobalt	27	$[Ar]^{18} 4s^2 3d^7$
Ni	Nickel	28	$[Ar]^{18} 4s^2 3d^8$
Cu	Copper	29	$[Ar]^{18} 4s^1 3d^{10}$
Zn	Zinc	30	$[Ar]^{18} 4s^2 3d^{10}$

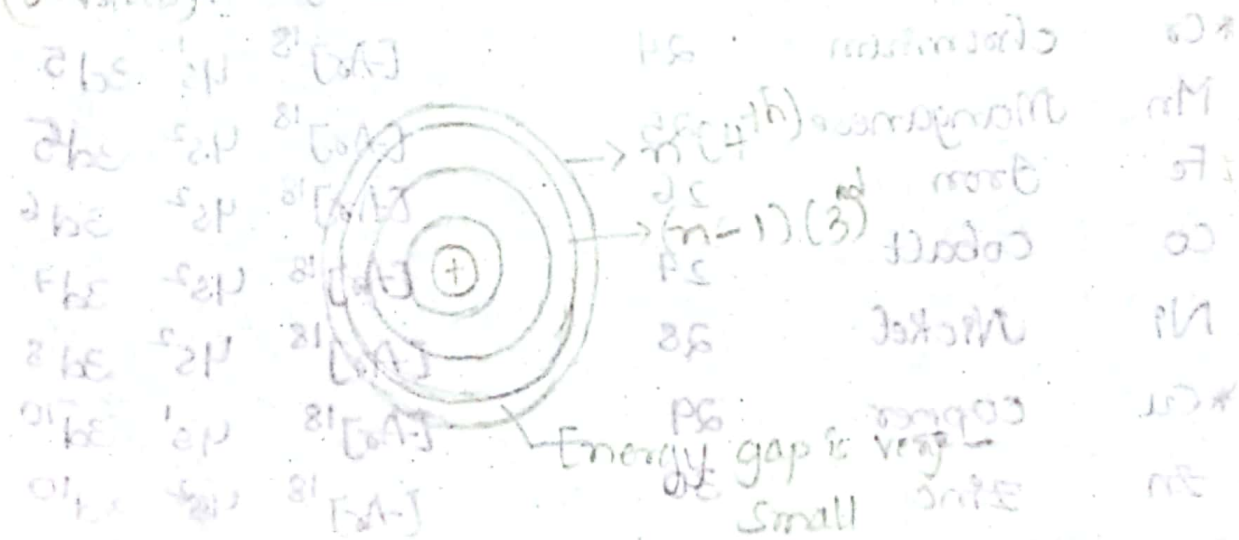
The general electronic configuration of d-block elements is $(n-1)d^{1-10} ns^{1-2}$

→ In 3d series Cr (24) and Cu (29) exhibit abnormal electronic configuration because fully filled orbitals and exactly half filled orbitals have more stability



② Variable oxidation states of d-block elements:-

d-block elements exhibit variable oxidation states because in d-block elements, the energy gap between ultimate shell (n) and penultimate shell (n-1) is very small (The energy gap between ns and (n-1)d is very small)



variable oxidation states of 3d-block elements

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

No. of types of oxidation states increase (↑)
 No. of types of oxidation states decrease (↓)

→ In 3d-series no. of types of oxidation states increase from Sc to Mn, from Mn to Zn no. of types of oxidation state decreases.

→ In 3d-series Mn exhibits more types of oxidation states (6 types) +2, +3, +4, +5, +6 & +7

→ In 3d-series, Mn exhibit 5 highest oxidation state (+7)

→ In 3d-series, Cr and Cu exhibit 5 lowest oxidation state i.e. (1)

In 4d series Ru exhibits more types of oxidation state (7 types). The highest oxidation state exhibited by Ru is +8. In 5d series Os exhibits 5 more types of oxidation states (6 types). The highest oxidation state exhibited by Os is +8.

stability of oxidation state

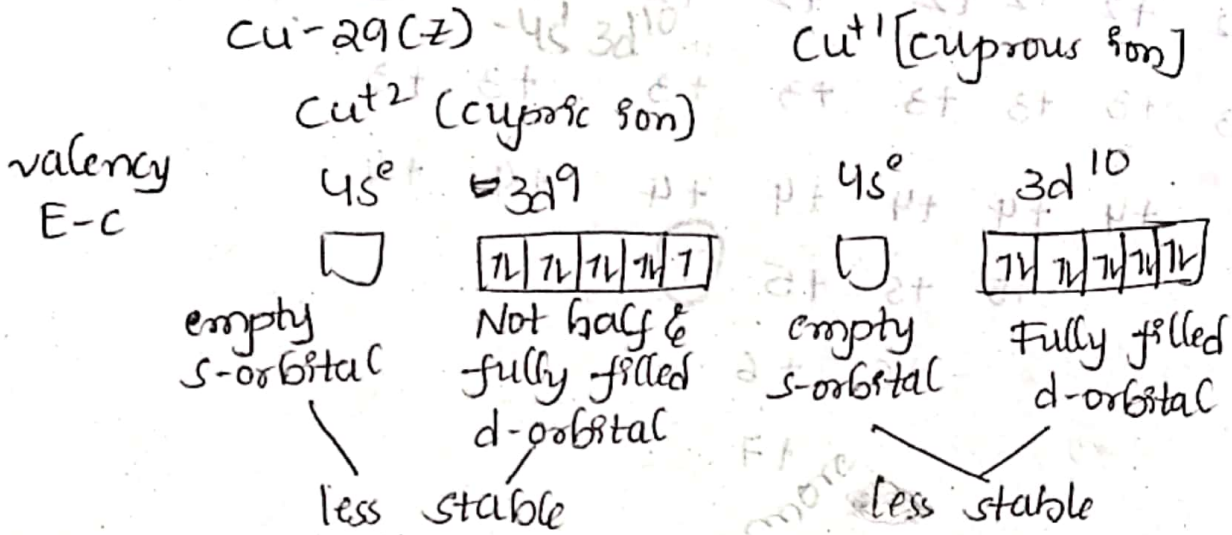
→ stability order of Fe^{+3} and Fe^{+2} :-

	Fe^{+3} (Ferric Iron)	Fe^{+2} (Ferrous Ion)										
valency	4s ⁰	4s ⁰										
E-c	3d ⁵	3d ⁶										
	empty <input type="checkbox"/>	empty <input type="checkbox"/>										
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1	1	1	1	1								
1	1	1	1	1								
	half-filled d orbital	not fully filled d orbital										
	more stable	less stable										

stability order :- Fe > Fe

Fe⁺³ is more stable than Fe⁺²

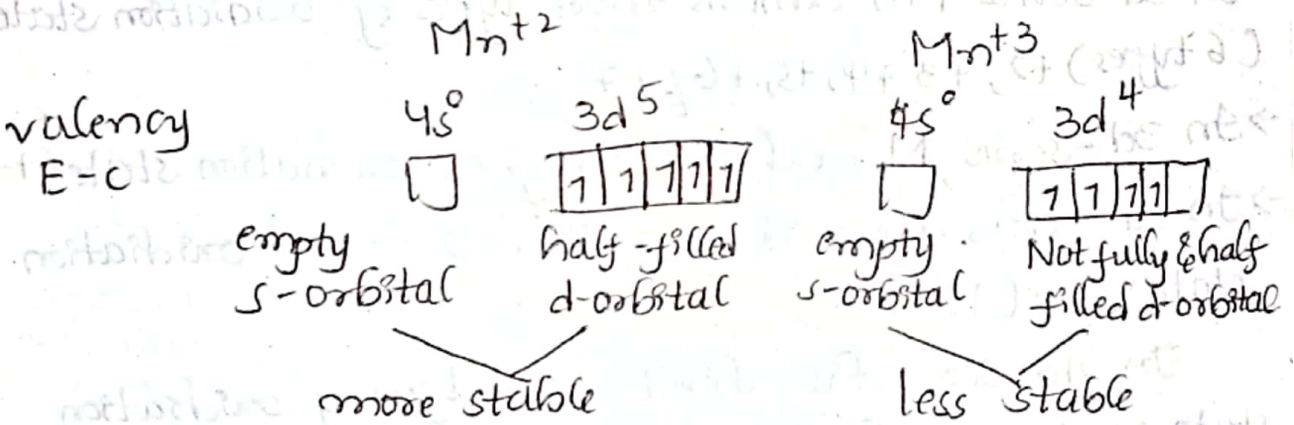
→ stability order of Cu⁺² & Cu⁺¹ :-



stability order :- Cu⁺² < Cu⁺¹

Cu⁺¹ is more stable than Cu⁺²

⇒ stability order of Mn⁺² & Mn⁺³ :- Mn-25(Z) = [Ar] 4s² 3d⁵



stability order :- Cu⁺² < Cu⁺¹

Cu⁺¹ is more stable than Cu⁺²

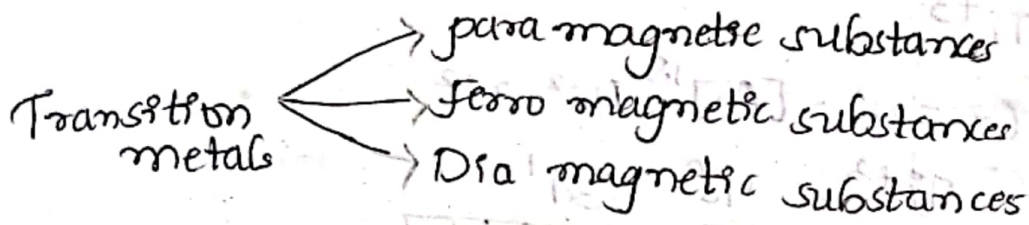
⇒ stability order :- Mn⁺² > Mn⁺³

Mn⁺² is more stable than Mn⁺³

③ Magnetic properties

d-block elements (or) Transition metals exhibits

3 types of magnetic properties.



para magnetic substances

The substances which are weakly attracted by external magnetic field are called as paramagnetic substances.

Generally transition metals or ions which have less no. of ^{un}paired electrons exhibit para magnetism. (para magnetic character)

Ex:- Fe^{+3} , Co^{+2} , Mn^{+2} , etc... Ti^{+3} , V^{+3} , Cu^{+2} , etc

Ferro magnetic substances

The substances which are strongly attracted by external magnetic field are called as Ferro magnetic substances. Generally transition metal or ions which have more no. of unpaired electrons exhibit ferro magnetic character.

Ex:- Fe^{+3} , Co^{+2} , Mn^{+2}

Dia magnetic substances

The substances which are repelled by the external magnetic field are called as Dia magnetic substances. Generally the transition metals (or) ions which do not have unpaired electrons exhibit dia magnetic character.

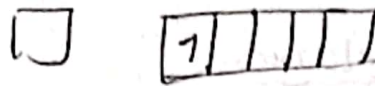
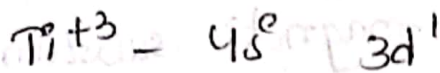
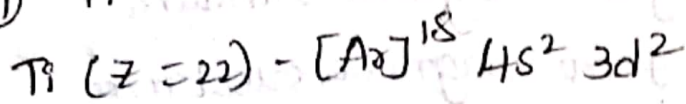
Ex:- Zn^{+2} , Cu^{+1} , Ti^{+4} , etc...

The magnetic moment of 3d elements can be calculated by using the following formula.

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

Here n = no. of unpaired electrons.

Ex: ① Ti^{+3}



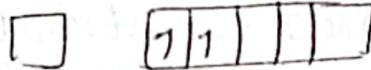
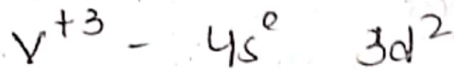
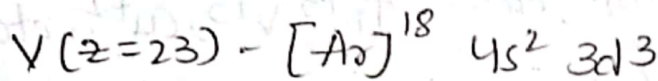
Here $n=1$

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

$$= \sqrt{1(1+2)} \text{ BM}$$

$$\mu = \sqrt{3} \text{ BM} = 1.73 \text{ BM}$$

Ex: ② V^{+3}



Here $n=2$

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

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

$$= \sqrt{8} \text{ BM}$$

$$\mu = 2\sqrt{2} \text{ BM} = 2.825 \text{ BM}$$

For diamagnetic substances, μ value is always 0 (since $n=0$ for diamagnetic compound)

The magnetic moment of 4d and 5d elements can be calculated by the following formula

$$\mu = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

Here,

S = spin quantum number

L = Azimuthal quantum number.

④ catalytic properties

catalyst :- The chemical substances used to speed up the chemical reactions are called as catalysts.

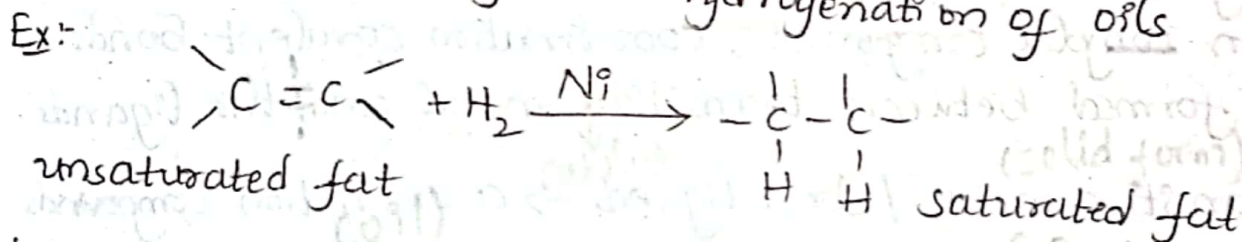
Generally transition metals and transition metal compounds are widely used as catalysts.

→ The catalytic properties of transition metals are due to the following reasons:

- i, presence of vacant d orbitals
- ii, ability to exhibit variable oxidation states
- iii, ability to form complexes with ligands.
- iv, Having large surface areas in finely powdered state

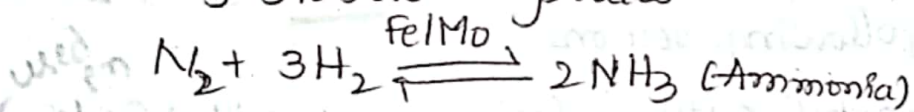
Ex:-

→ Ni is used as catalyst in hydrogenation of oils



⇒ V₂O₅ is used as catalyst in the manufacture of H₂SO₄ by contact's process.

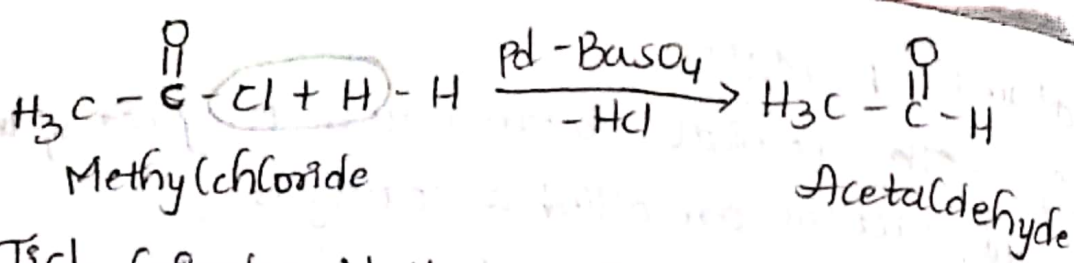
→ Fe/Mo is used as catalyst in the manufacture of ammonia by Haber's process.



→ Pt is used as catalyst in the manufacture of HNO₃ by Ostwald's process.

→ CuCl₂ is used as catalyst in the manufacture of Cl₂ gas by Deacon's process.

→ Pd - Baso₄ (kind Lind catalyst) is used as catalyst in manufacture of Acetaldehyde by Rosemund's reduction.



→ TiCl_4 (Ziegler Natta catalyst) is used as catalyst in polymerization reaction

→ Zn-Hg (ZMC Amalgam) is used as catalyst in polymerisation reactions & elementson's reduction.

⑤ Ability to form complex compounds (or) co-ordination compounds

→ Transition metals have general tendency to form complexes with several molecules (or) ions called as ligands.

→ In complex compounds, coordination covalent bonds are formed between transition metal and the ligands

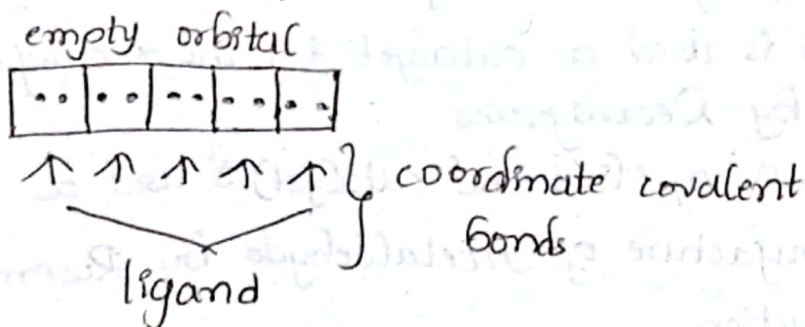
Transition metal / Ion + ligands → coordination compounds

Ex: $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$, etc...

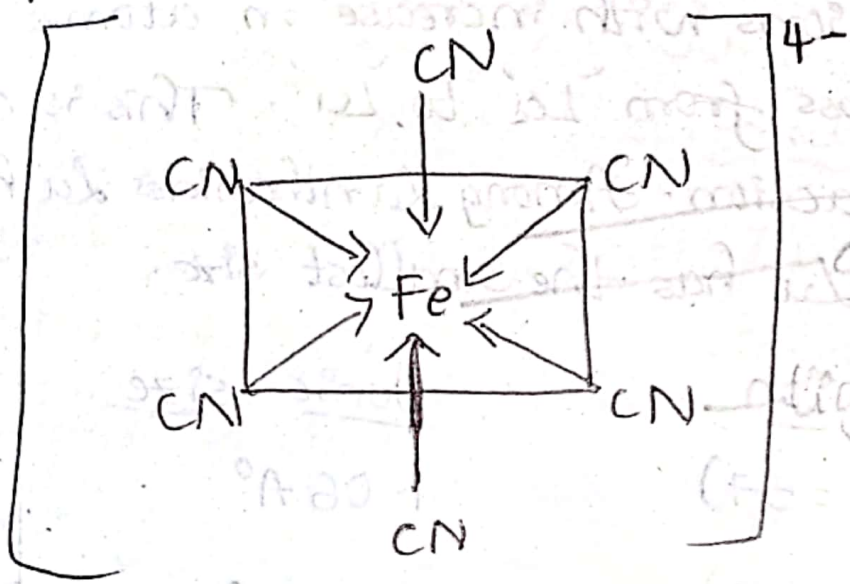
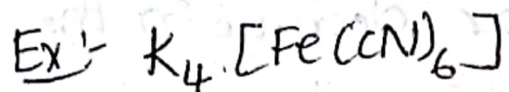
Reasons for formation of complex compounds

→ Transition metals easily form complex compounds due to the following reasons

1. Transition metal cations have empty d orbitals to receive electron pairs from the ligands to form coordinate covalent bonds



99, Transition metal cations have small size and high positive charge, which favours the formation of coordinate covalent bonds.



Octahedral shape

central metal ion \rightarrow takes e from ligands
(d-block)

Ligands \rightarrow have extra e pairs give to central metal

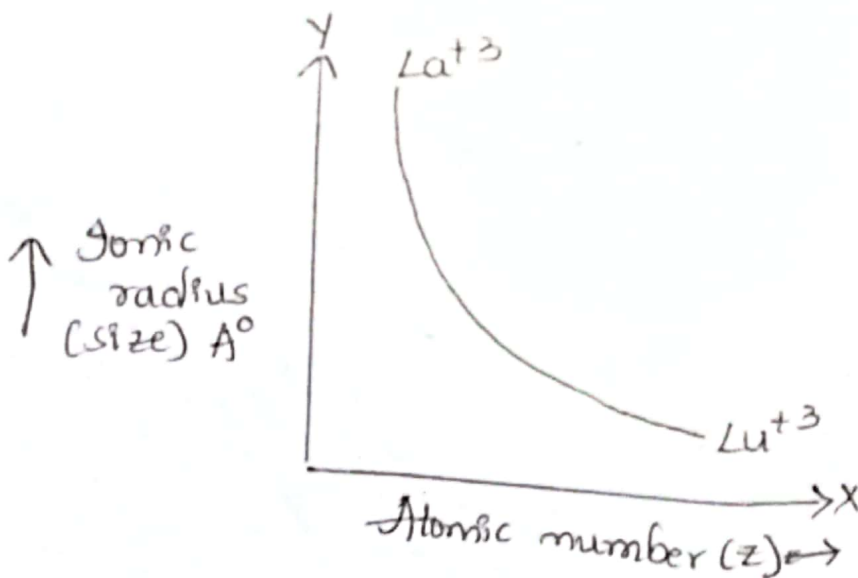
f-block elements

Lanthanide contraction

Lanthanides show a regular decrease in the size of atoms or ions with increase in atomic number as we move across from 'La' to 'Lu'. This is called Lanthanide contraction. Among lanthanides La has the largest size and Lu has the smallest size.

<u>Lanthanide Ion</u>	<u>Ionic size</u>
La^{+3} (z = 57)	1.06 Å
Ce^{+3} (z = 58)	1.03 Å
Pr^{+3} (z = 59)	1.01 Å
⋮	⋮
Tm^{+3} (z = 69)	0.87 Å
Yb^{+3} (z = 70)	0.86 Å
Lu^{+3} (z = 71)	0.85 Å

↓
Lanthanide contraction



Lanthanide contraction

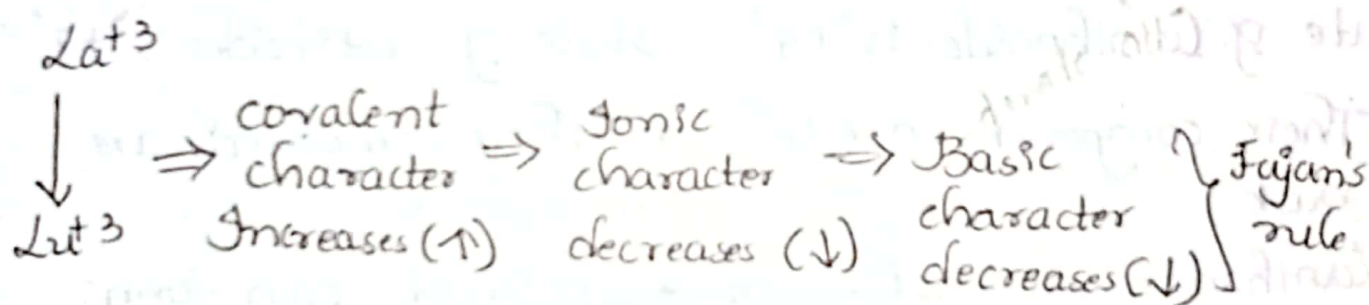
causes of Lanthanide contraction

Lanthanide contraction is due to the poor shielding effect of orbitals, the poor shielding of 4f orbitals is due to their diffused shape.

consequences of Lanthanide contraction

* Anomalous behaviour of post-lanthanide elements can be explained by using Lanthanide contraction.

* The decrease in basic character of hydroxides of Lanthanides from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$ can be explained by Lanthanide contraction.



* Lanthanide contraction provides a basis for separation of Lanthanides & by fractional crystallisation.

* The occurrence of Yttrium (Y) with heavy Lanthanides can be explained by using Lanthanide contraction.

Differences between Lanthanides and Actinoids

Lanthanides

- * In lanthanides, the differentiating electron enters in to '4f' orbital.
- * Binding energies of 4f orbitals are higher.
- * 4f electrons have greater shielding effect.
- * The maximum oxidation state of lanthanides is '+4'.
- * Their compounds are less basic.
- * Lanthanides do not form oxo-cations.
- * Except 'Pr_{III}' all are non radio active elements.
- * Most of the lanthanide ions are colourless.
- * Lanthanide contraction is low.
- * Lanthanides cannot form complexes easily.
- * They are paramagnetic and their magnetic properties can be explained easily.

Actinoids

- * In actinoids, the differentiating electron enters into '5f' orbital.
- * Binding energies of 5f orbitals are lower.
- * 5f electrons have poor shielding effect.
- * The maximum oxidation state of actinoids is '+7'.
- * Their compounds are more basic.
- * Actinoids can form oxo-cations.
Ex: UO_2^{2+} , NpO_2^{2+} , etc.
- * All actinoids are radio active elements.
- * Most of the actinoides ions are coloured.
- * Actinoid contraction is high.
- * Actinoids can form complexes easily.
- * They are also paramagnetic but their magnetic properties are very difficult to explain.

Unit - II

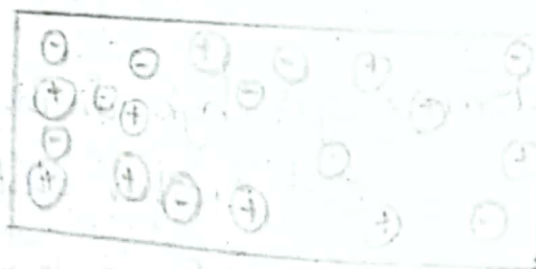
Theories of Bonding in Metals

Characteristics of Metals

- * Metals possess peculiar shine on their surface called the metallic lusture.
- * They have high density. So they are hard substances.
- * They have high M.P and B.P
- * They are good conductors of heat.
- * They have high electric conductivity which decrease with temperature.
- * They have malleable and ductile. i.e; they can be hammered into sheets can be drawn into thin wires.
- * They have high elasticity i.e; they can with stand high stress.
- * Metals are opaque light
- * They have high coordination numbers (8 or 12)
- * They form solid solutions (alloys)
- * They are generally electropositive elements.

Free Electron theory

This theory was proposed by Lorentz and drude.



Main points

- * They postulated that on account of low ionisation energies of metals. some of the atoms lose one or more
- * of their valence electrons and charged into cations.
- * The loss of electrons are not localised. They move freely and randomly throughout the volume of the metal.
- * Thus according to this view a metal may be

regarded as an assembly of +ve immersed in a sea of mobile electrons or a sea of -ve charge cloud.

* The strong electrostatic attraction between the electron cloud and +ve ions holds the crystal together.

* According to free electron model, the metallic bond is delocalised and non-directional.

* Alkali metals are soft and have low M.P, while the transition metals are hard and have high M.P because alkali metals have only one valency electron.

* The presence of mobile valence electrons explains the high electrical and thermal conductivities of metals.

* The ductility and malleability of the metals can also be explain due to non-directional nature of metallic bond.

Draw backs :- It doesn't offer a satisfactory explanation of semi conductance and the specific heat of metals.

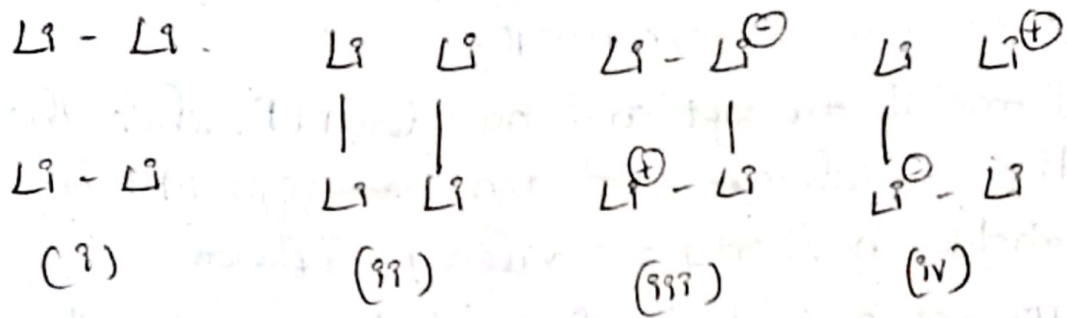
Valence Bond theory

This theory was proposed by Pauling. According to this theory, the structure of metals may be described in terms of covalent bonds that resonate among the alternate interatomic position in metals.

consider the case of metals which crystallizes in a body centered cubic lattice. In this arrangement each Lithium atom is in direct contact with eight other Li atoms.

This each Lithium atom must form covalent bonds with 8 other Lithium atoms which require 16 electrons for the formation of localized electron-pair bonds. However, each Lithium atom has only one as valence electron and hence only 9 electrons are available for bond can only be explained on the basis that the covalent bonds between two Lithium atoms are not localised but they are highly delocalised.

Let us illustrate the phenomenon of resonance in metallic bonding by considering four lithium atoms. Since every lithium atom has only one valence electron, no lithium atom can form 2 bonds simultaneously.



As in other cases of resonance, resonating structures leading to ionic forms and also be written. Ionic forms are obtained when a bond between two atoms shifts to the new place without simultaneous shifting of the other bond.

This results a +1 charge motion. The resonance is called as unsynchronized resonance.

Limitations

- * This theory provides only a qualitative explanation of various metallic properties like electrical conductance, thermal conductance, high degree of malleability and ductility, high elasticity and high density.
- * The theory also does not ~~contain~~ explain metallic character in the liquid state or in solution.

Electrical properties of solids

conductors:- These allow the maximum portion of the applied electric field to flow through them. The electrical conductivity of good conductors is of the order of $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$. Metals are good conductors of electricity.

Insulators:- They do not practically allow the electric current to flow through them, the electrical conductivity is of the order of $10^{-22} \text{ ohm}^{-1} \text{ cm}^{-1}$!

Most of the organic and inorganic solids are poor conductors of electricity.

Semi-conductors :- At room temperature, semi-conductors allow a portion of electric current to flow through them. The electrical conductivity of a semi conductor at normal temperature lies between that of a 10^{-9} to $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$.

Semi conductors are insulator at absolute zero temperature and they are conductors at room temperature. ^{-use.}
Ex :- Si, Ge

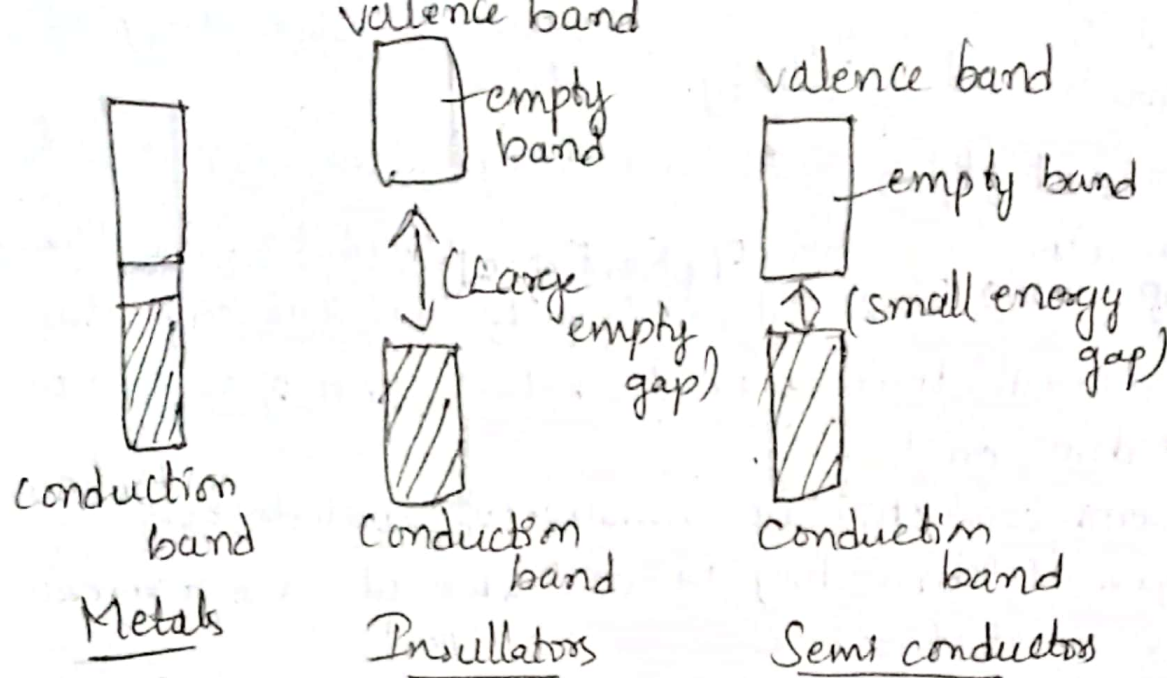
Band theory of Semi conductors

Crystals which conduct electricity to very moderate extent are called semi conductors. In semi conductors, the energy gap between adjacent bands is sufficiently small for thermal energy, a small number of electrons are promoted from the full valence band to empty conduction band. Both the promoted electrons in the conduction band and the unpaired electrons left in the valence band can conduct electricity. Since the probability of promoting electrons rises with temperature, the conductivity of semi conductors increases with temperature. Semi conductors are also produced if a suitable impurity is added to an insulator, the impurity acts as a bridge for the energy gap between valence band and conduction band. ^(Doping)

Semi conductors are classified into two types.

- > Intrinsic semi conductor
- > Extrinsic semi conductor

Examples for semi conductors are silicon & Germanium.



Intrinsic semiconductors

Germanium and silicon have four valency electrons in their outer shell. They form four covalent bonds with the four neighbouring atoms. Hence there are no free electrons in the crystal. But on heating sufficiently one of the covalent bond in the crystal breaks to produce free electrons. Under the influence of electric field the free electrons move around the crystal and conduct electricity. This type of conductivity is called intrinsic conductivity and the crystals are known as intrinsic semiconductors.

Extrinsic semiconductor

Germanium or silicon crystal can also be made as conductors by a process known as doping.

Extrinsic semiconductor are classified into two types.

n-type semiconductor

When silicon or Germanium crystal is doped with V-group element, one Germanium or silicon atom is substituted by the V-group element having five

electrons. The 5th electron of V-group element remains free. And this extra electron is responsible for the electrical conductivity in the crystal. This conductivity is called extrinsic conduction. And the crystals are known as extrinsic semiconductors. In this current is carried by excess of electrons in the normal way and hence it is called n-type semiconductors.

p-type semiconductors

When silicon or germanium crystals is doped with III-group elements. One germanium or silicon atom is substituted by the III-group element having 3 electrons. As the III-group elements has 3 electrons, the tetra valency of silicon or germanium will not be completed. Hence some of the sites normally occupied by electrons become vacant. These electron vacant sites are called positive holes. Under the influence of electric field the adjacent electrons move into nearby positive holes. i.e., the positive hole migrates in opposite direction to that of electron. Thus the current is carried by positive holes. Since the current is carried by hole it is called p-type semiconductors.