

CHAPTER 2 CHEMISTRY OF OUTER TRANSITION ELEMENTS

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	IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIIIA
2																		
3																		
4			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						
5			Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
6			La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
7			Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

*Lanthanides

**Actinides

Transition Elements:

The elements in periodic table from group I-B to VIII-B are called transition elements. They are also known as transition metals.

Transition elements can be further classified into two blocks.

- (i) d-block elements (Outer Transition Elements)
- (ii) f-block elements (Inner Transition Elements)

Outer Transition Elements:

d-block elements are also known as outer transition elements. Their valence electron enters in d-orbital that's why they are known as d-block elements.

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

The general valence shell electronic configuration of all the groups are given below:

GVSEC of group III-B $\rightarrow ns^2, (n-1) d^1$

GVSEC of group IV-B $\rightarrow ns^2, (n-1) d^2$

GVSEC of group V-B $\rightarrow ns^2, (n-1) d^3$

GVSEC of group VI-B	→	$ns^1, (n-1) d^5$	(Stable Configuration)
GVSEC of group VII-B	→	$ns^2, (n-1) d^5$	
GVSEC of group VIII-B	→	$ns^2, (n-1) d^6$	$ns^2, (n-1) d^7$ $ns^2, (n-1) d^8$
GVSEC of group I-B	→	$ns^1, (n-1) d^{10}$	(Stable Configuration)
GVSEC of group II-B	→	$ns^2, (n-1) d^{10}$	

There are total four series of d-block elements found in the 4th, 5th, 6th and 7th periods.

3d – series:

This ten element series is located in the 4th period. It includes elements from scandium (Sc) to zinc (Zn).

4d – series:

This series is placed in 5th period and consists of elements from yttrium (Y) to cadmium (Cd).

5d – series:

This series is situated in the sixth period and consists of elements from lanthanum (La) to mercury (Hg).

6d – series:

This series consists of elements from actinium (Ac) to copernicium (Cn).

GENERAL FEATURES OF OUTER TRANSITION ELEMENTS



Variable Oxidation States

The number of electrons lost or gained by an atom to acquire stability is called oxidation number. Transition elements exhibit variable oxidation states or variable valency because they can make bond with ns orbital as well as (n-1)d orbital.

Elements of group I-B such as Zn/Cd/Hg/Cn only have +2 oxidation state. Due to this reason, they are also known as pseudo transition elements.

Elements	Outer Electronic Configuration	Oxidation States
Scandium (Sc)	$[\text{Ar}]3d^1 4s^2$	+2, +3
Titanium (Ti)	$[\text{Ar}]3d^3 4s^2$	+2, +3, +4
Vanadium (V)	$[\text{Ar}]3d^3 4s^2$	+2, +3, +4, +5
Chromium (Cr)	$[\text{Ar}]3d^5 4s^1$	+1, +2, +3, +4, +5, +6
Manganese (Mn)	$[\text{Ar}]3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Iron (Fe)	$[\text{Ar}]3d^6 4s^2$	+2, +3, +4, +5, +6
Cobalt (Co)	$[\text{Ar}]3d^7 4s^2$	+2, +3, +4
Nickel (Ni)	$[\text{Ar}]3d^8 4s^2$	+2, +3, +4
Copper (Cu)	$[\text{Ar}]3d^{10} 4s^1$	+1, +2
Zinc (Zn)	$[\text{Ar}]3d^{10} 4s^2$	+2

Catalytic Activity

Transition elements and their compounds can be used as catalyst to increase the rate of reaction.

For example:

In contact process, V_2O_5 is used as catalyst.

In Haber's process Fe is used as catalyst.

In Ostwald's process Pt is used as catalyst.

In hydrogenation reactions Ni is used as catalyst etc.

Magnetic Behavior

Those elements which are attracted towards magnetic are called para magnetic elements and those elements which are not attracted towards magnet are called diamagnetic elements.

Most of the transition elements are paramagnetic in nature due to the presence of unpaired electron. Unpaired electrons give rise to magnetic behavior in an element.

The elements of group II-B do not have unpaired electron, that's why they are diamagnetic.

Alloy Formation

The combination of two or more than two metals is called alloy. Transition elements have the ability to form alloy.

Alloys	Compositions	Important Uses
Stainless steel	Iron, Chromium and Nickel	In making cutlery, and surgical instruments.
Duralumin	Aluminum, Copper Magnesium and Manganese	In making utensils, aeroplane etc.
Brass	Copper and Zinc	In plumbing and automotive parts etc
Bronze	Copper and Aluminum	In making medals, statues, coins etc

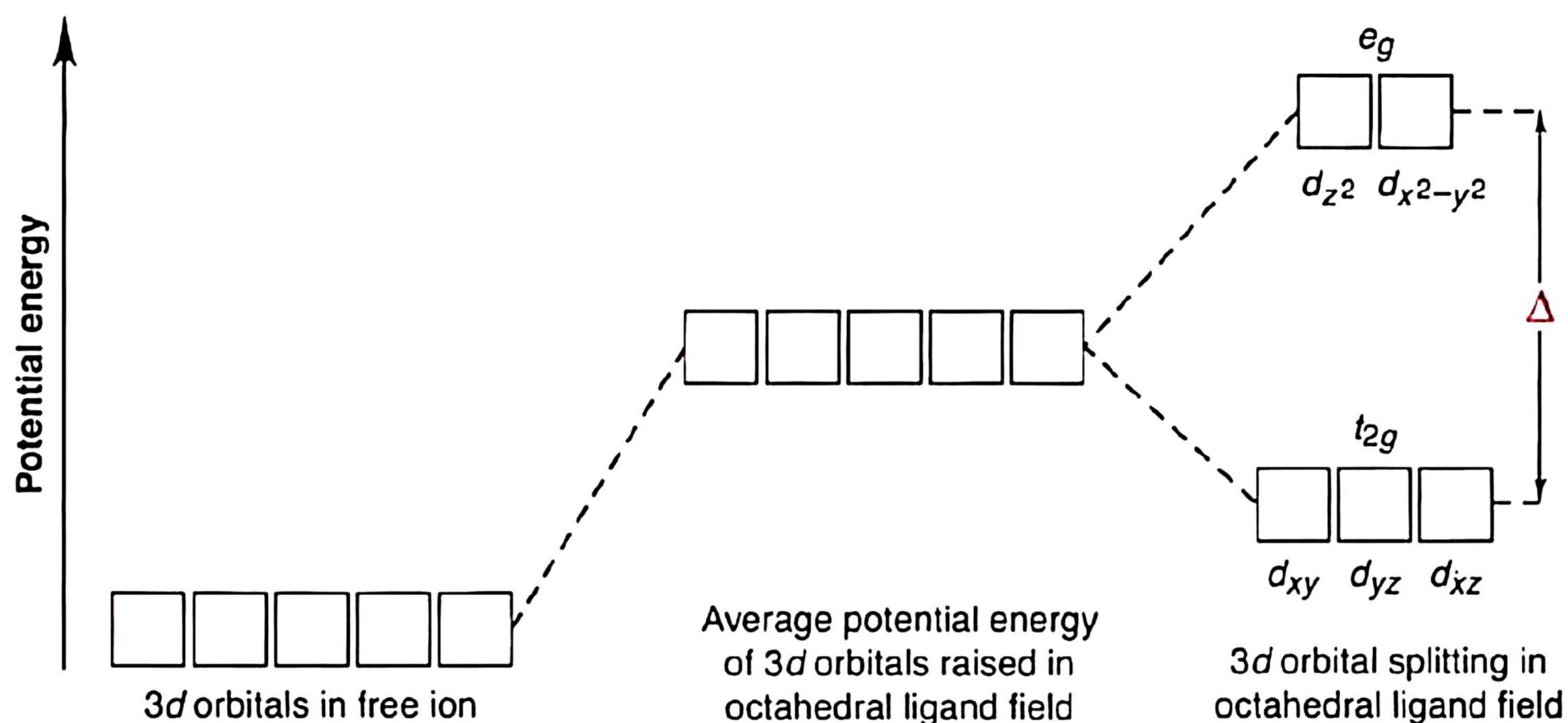
Colour of Complexes



Transition elements can form colored compounds which can be explained by Crystal Field Theory (CFT). According to this theory, d-orbitals split into two parts i.e; t_{2g} and e_g orbitals. t_{2g} has lower energy than e_g orbitals. The difference in energies between t_{2g} and e_g orbital is Δ_o . When light rays fall on any transition metal compound then t_{2g} orbitals absorb light of a specific wavelength and jumps to e_g orbital. When electrons from e_g orbitals return back to t_{2g} orbital, they emit light rays of reciprocal wavelength.

For example, Copper Sulphate (CuSO_4) contains Cu^{+2} ions. Cupric ions absorb red and green light. They radiate blue light afterwards so that copper sulphate appears blue in color.

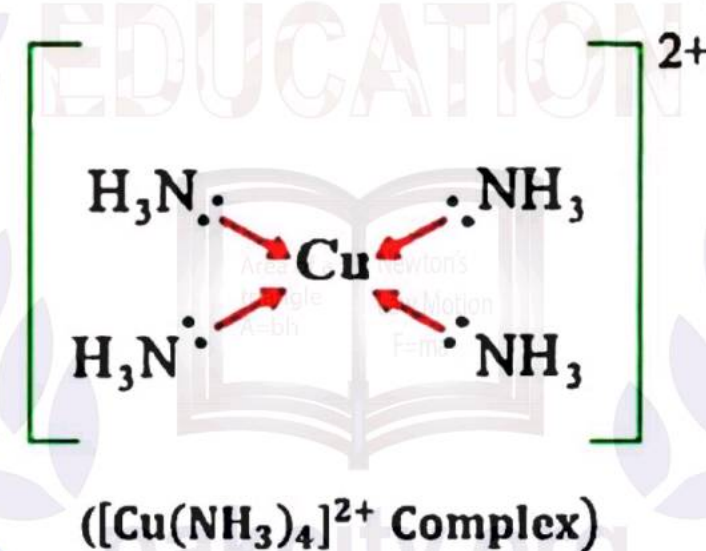
Elements of group II-B have full filled valence orbital so that d-d transition is not possible. Due to this reason, they form white compounds instead of colored compounds. Hence, they are called pseudo transition elements.



COORDINATION COMPOUNDS

Those compounds in which a transition element is bonded to a ligand by means of co-ordinate covalent bond is called co-ordination compound. It's also called complex compound because it contains a complex ion. The complex ion may be cationic or anionic. complex ion is written inside a large bracket which is called co-ordination sphere.

Let's take the following example of a complex ion,



Here, Cu is a transition metal which is also called central metal atom. NH_3 is the ligand which is donating lone pair of electrons to central metal atom. Since, there are four molecules of NH_3 which is bonded to copper hence the co-ordination number is 4.

The general formula of a complex ion is given by: $[\text{M}(\text{:L})_n]^{-/+}$

Here, M is the central metal atom.

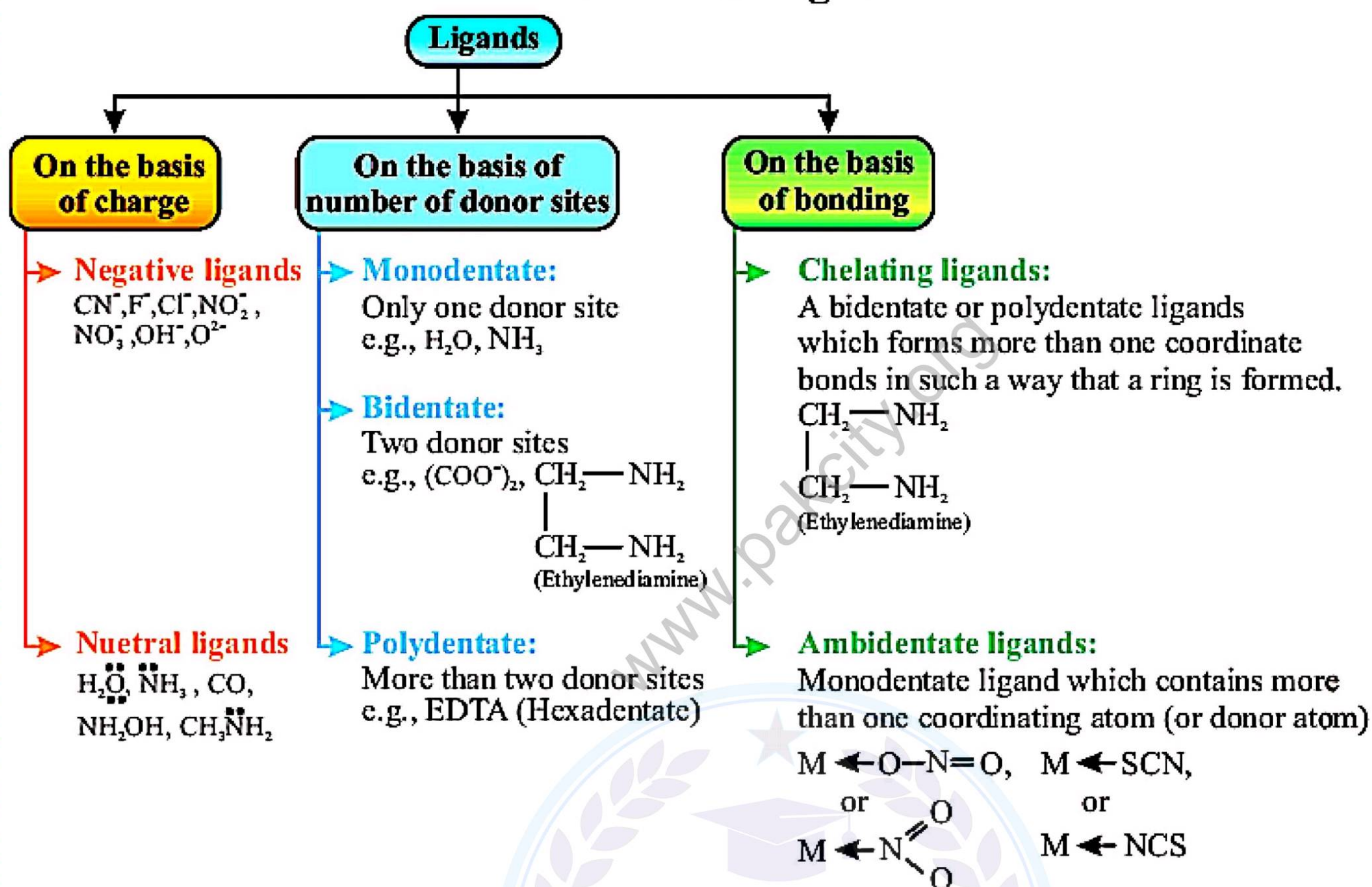
L is ligand

n is co-ordination number

LIGANDS:

Ligands are the species that can donate lone pair of electrons to central metal atom. They are Lewis bases.

Classification of ligands



Co-Ordination Number:

The total number of lone pair of electrons donated by ligands is called co-ordination number.

Denticity:

The number of electron pairs donated by a ligand to central metal atom is called denticity.

If a ligand donates 1 pair of electrons, then it is called mono-dentate ligand.

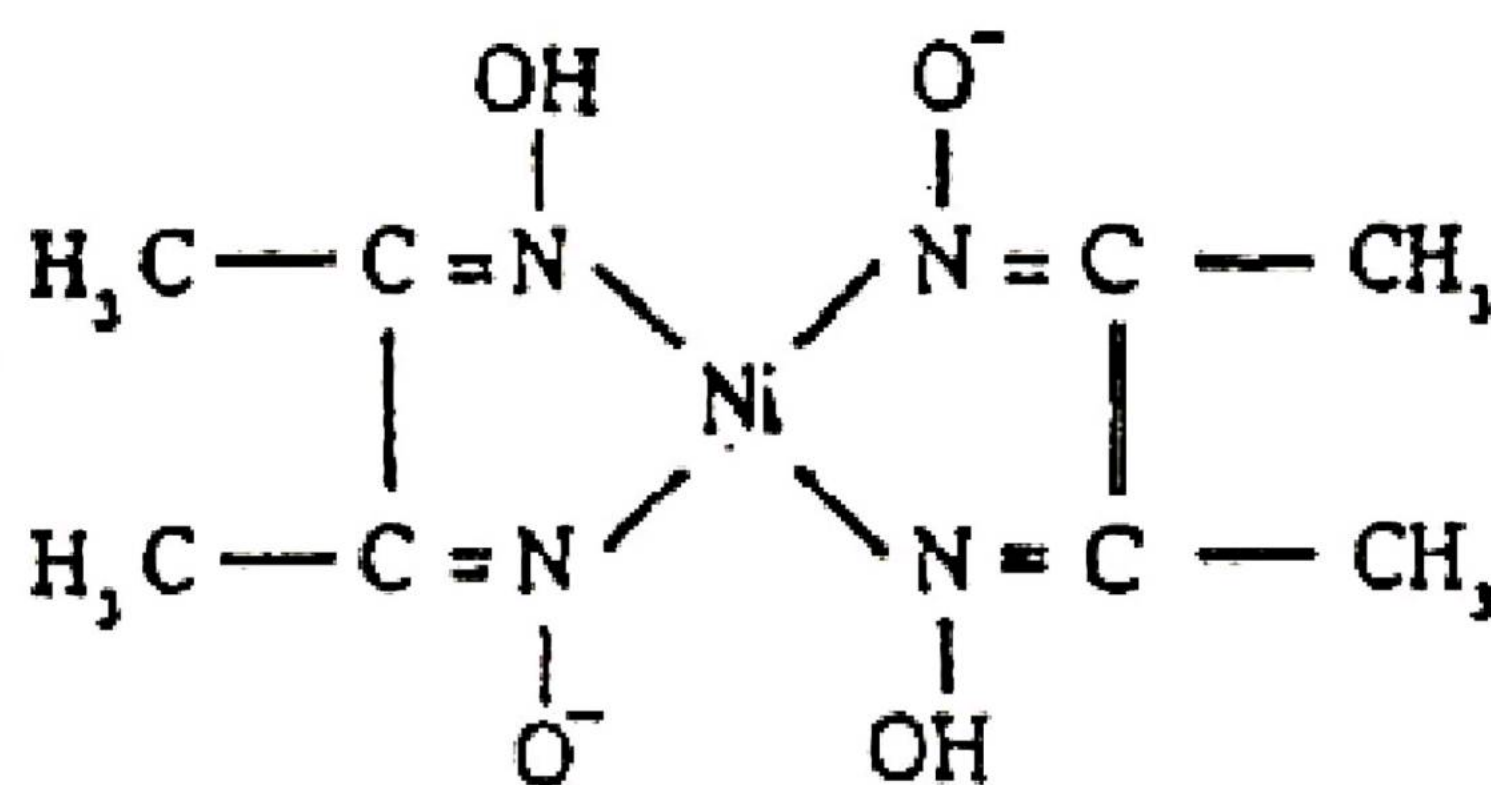
If a ligand donates 2 pair of electrons, then it is called bi-dentate ligand.

If a ligand donates 3 pair of electrons, then it is called tri-dentate ligand and so on.

Chelating Ligands:



Polydentate or multidentate ligands are also known as chelating ligands because when they are bonded to a central metal atom, they form a chelate. Chelate is a Greek word which means Crab's claw.



(Nickel dimethyl glyoximate)
(Chelate)

General rules of IUPAC naming of coordination compounds

Co-ordination Compound General Formula: $C[M(:L)_n]A$

Naming Pattern: $C + L + M + A$

- Use only small letters
- Don't leave any space between words

1. Write the name of cation first if cation is present in the compound.
2. Write the name of ligand. If more than one type of ligand is present then follow alphabetical order. For inorganic ligands write **di/tri/tetra/penta** etc. for multiple ligand of same type and for inorganic ligands write **bis/tris/tetrakis/pentakis** etc. for multiple ligand of same type.
3. Write the name of metal. If complex contains a +ve charge then write the english name of metal. If complex contains a -ve charge then write the Latin name of metal. While writing Latin names replace -um with -ate.

Symbol	English Name	Latin Name	Um → ate
Fe	Iron	Ferrum	Ferrate
W	Tungsten	Wolfram	Wolfrate
Pb	Lead	Plumbum	Plumbate
Sn	Tin	Stannum	Stannate

Ag	Silver	Argentum	Argentate
Au	Gold	Aurum	Aurate
Hg	Mercury	Hydrargyrum	Hydragryate
Cu	Copper	Cuprum	Cuprate
Al	Aluminum	-	Aluminate
Ni	Nickel	-	Nickelate
Co	Cobalt	-	Cobaltate
Cr	Chromium	-	Chromate
Mn	Manganese	-	Manganate
Pt	Platinum	-	Platinate
Zn	Zinc	-	Zincate

4. Write the oxidation number of metal in parenthesis in roman numerals. Remember that 0 oxidation state is also possible.



5. Name the anion, if anion is present in the compound.

6. Write 'ion' at the end if the compound contains a positive or negative charge.

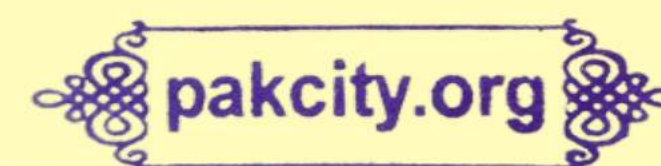
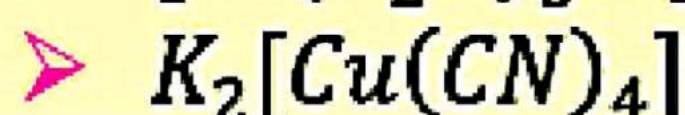
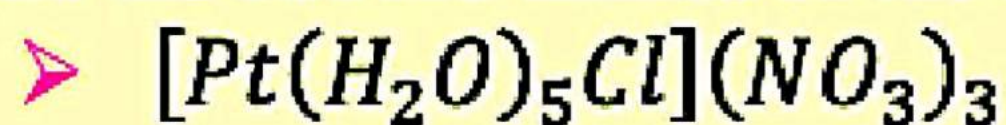
Look at the following examples:

- (i) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
Tetraamminecopper (II) sulphate
- (ii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3$
Tetraaquodichlorochromium (III) nitrate
- (iii) $\text{K}_4[\text{Fe}(\text{CN})_6]$
Potassiumhexacyanoferrate (II)
- (iv) $[\text{Pt}(\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2)_3]\text{Cl}_4$
Trisethylenediamineplatinum (IV) chloride
- (v) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
Triaminetrinitrocobalt (III)
- (vi) $[\text{Zn}(\text{OH})_4]^{-2}$
Tetrahydroxozincate (II) ion
- (vii) $[\text{Cu}(\text{en})_2]^{+2}$
Bisethylenediaminecopper (II) ion



Self-Assessment

Write the IUPAC names of the following complexes.



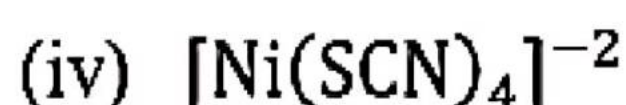
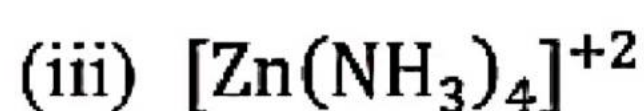
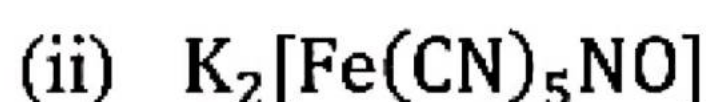
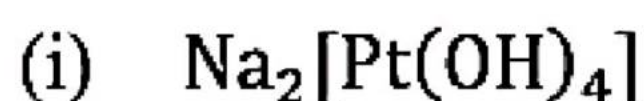
1. pentaquachloroplatinum(IV)nitrate

2. tetraamminechromium(III)ion

3. potassiumtetracyanocuprate(II)

4. hexafluoroaluminate(III)ion

1. Write the IUPAC names of the following:



Answers:

(i) sodiumtetrahydroxoplatinate(II)

(ii) potassiumpentacyanonitrosylferrate(III)

(iii) tetraamminezinc(II)ion

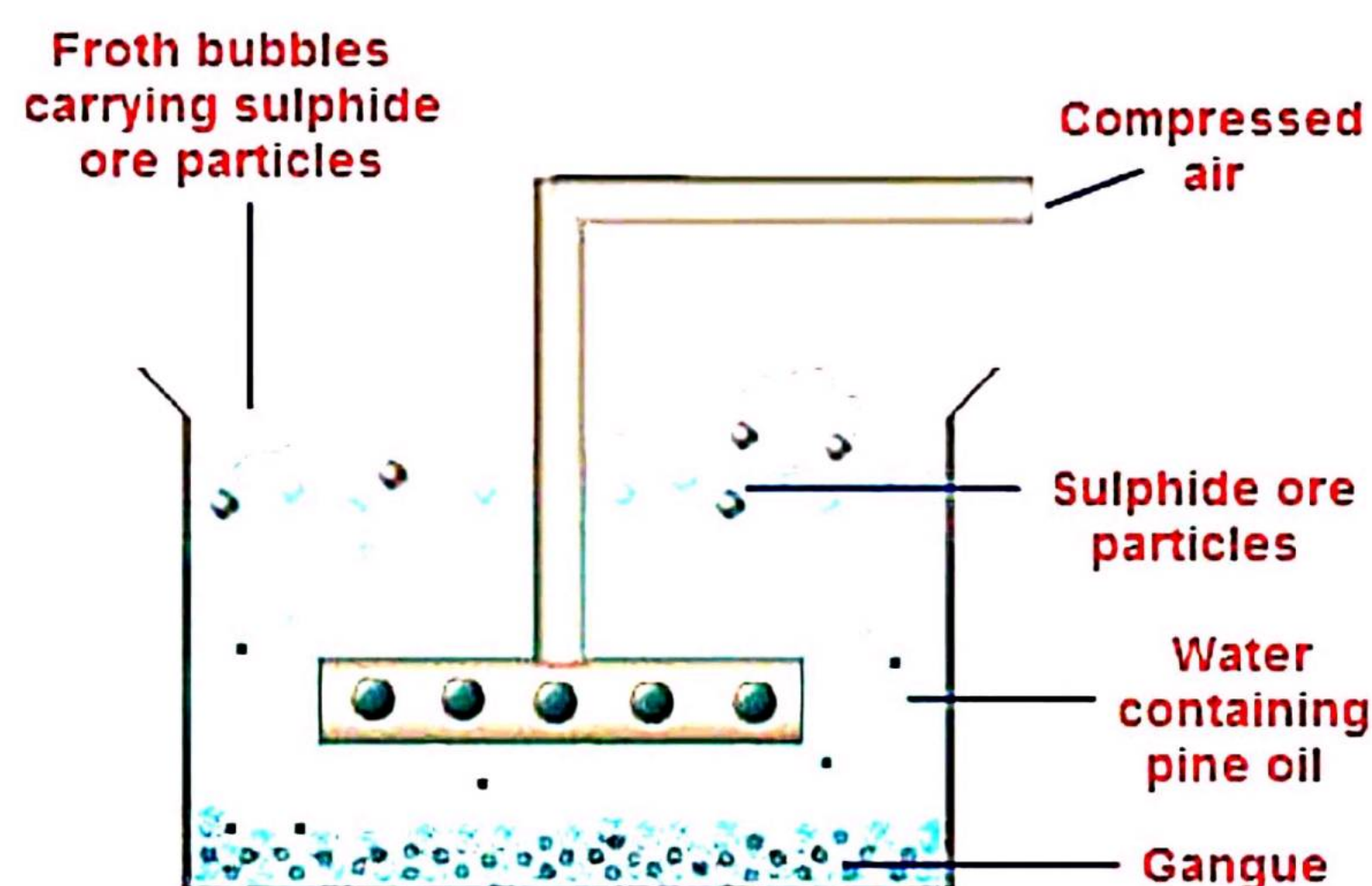
(iv) tetrathiocyanonickelate(II)ion

Metallurgy of Copper

The chief ore of copper metal is copper pyrite or chalcopyrite having chemical formula $CuFeS_2$. This ore contains 6% $CuFeS_2$ and 94% gangue particles or impurities. There are five steps for the extraction of 100% pure copper metal from its chalcopyrite ore.

STEP#1 (CONCENTRATION OF THE ORE)

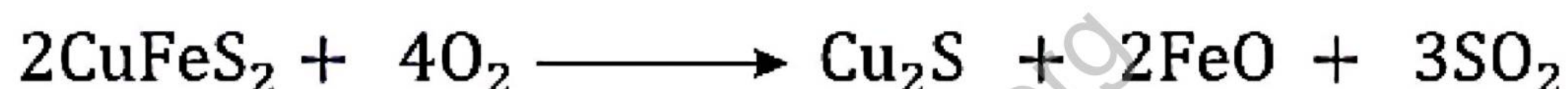
First of all, the gangue particles from copper pyrite ore are removed. It's done by means of froth floatation process. The crushed copper pyrite ore is mixed with a mixture of water and pine oil. Air is introduced into the mixture so that the gangue particles settle down while copper pyrite ore is deposited at the top.



STEP#2 (ROASTIN OF CONCENTRATED ORE)

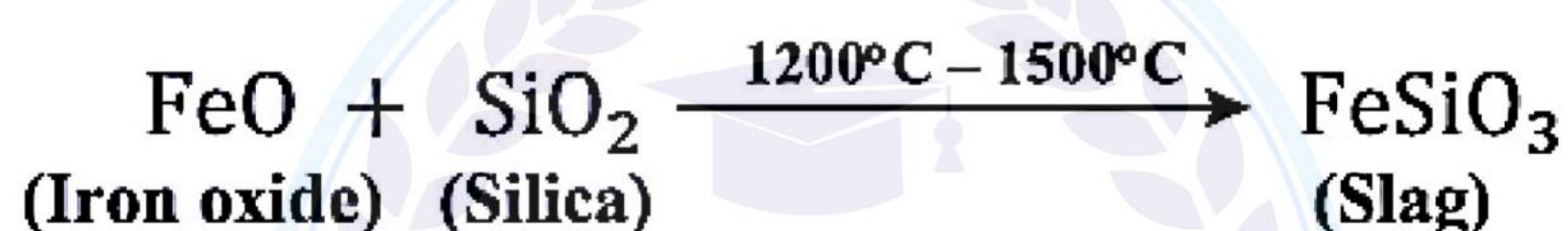


In this step the concentrated copper pyrite ore is heated at high temperature in a kiln or reverberatory furnace. Copper pyrite ore is thermally decomposed into cuprous sulphide (Cu_2S), ferrous oxide (FeO) and Sulphur dioxide gas (SO_2).



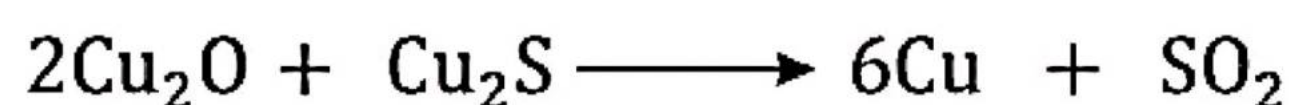
STEP#3 (SMELTING OF ROASTED PYRITE ORE)

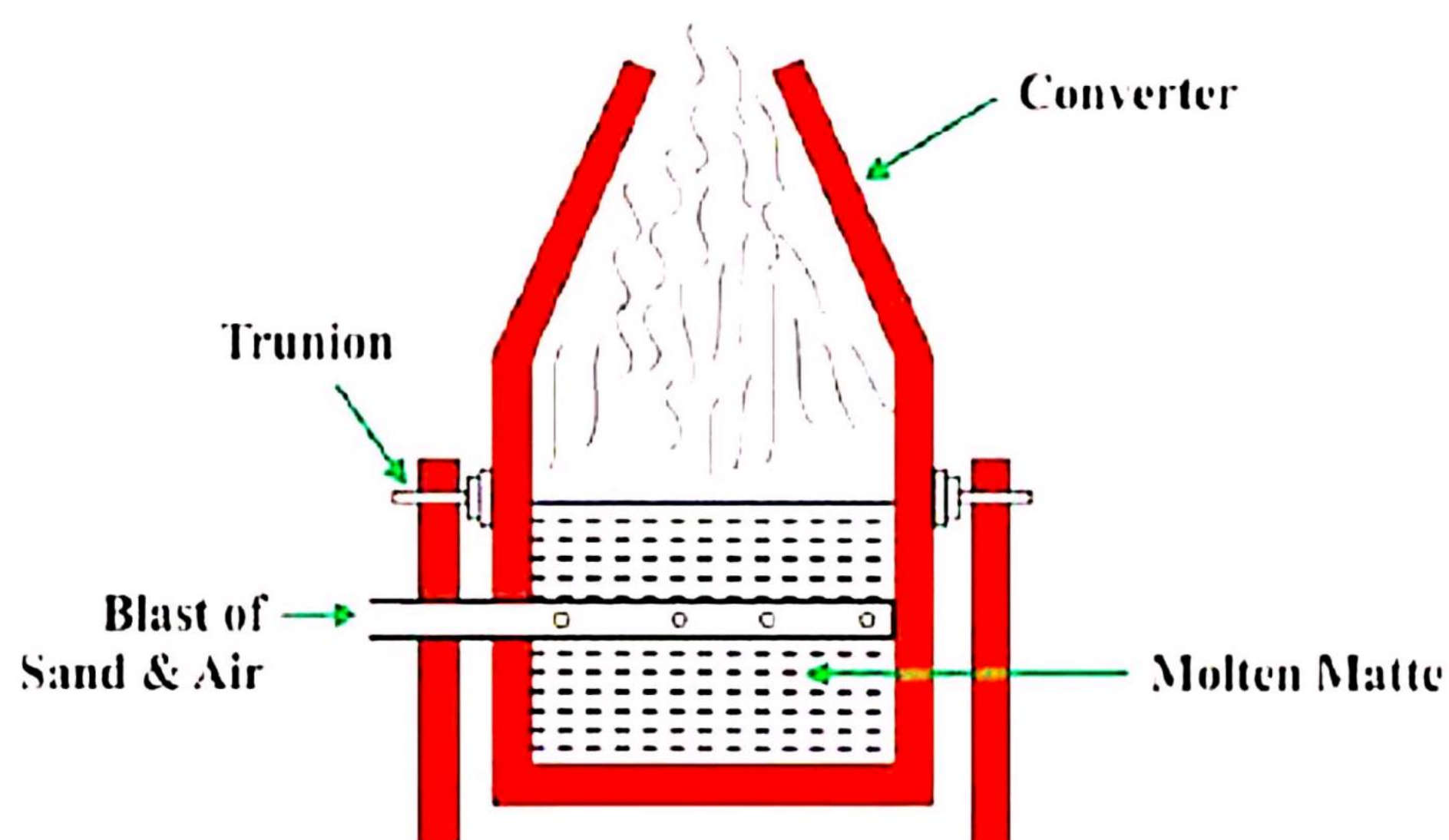
Roasted copper pyrite ore is then introduced into a blast furnace along-with silica (SiO_2) and coal. Hot air is blown inside the furnace by means of tuyeres. The temperature inside furnace reaches to 1200°C to 1500°C . At this temperature, ferrous oxide reacts with silica to form ferrous silicate which is also known as slag. The slag remains at the top of molten matte (Cu_2S). Slag is removed from the top and it can be used for making roads.



STEP#4 (BESSEMERIZATION OF MATTE)

Matte (Cu_2S) is then transferred into Bessemer converter in which matte reacts with oxygen gas to form a mixture of cuprous oxide (Cu_2O) and Sulfur dioxide gas (SO_2). Cuprous oxide finally reacts with cuprous sulphide to produce blister copper which is 99% pure. Due to the evolution of SO_2 gas from copper, blisters are formed on its surface. Hence, it's known as blister copper. Blister copper contains 1% impurities that's why it is not suitable for making wires as it the impurities produces resistance in the flow of electric current.



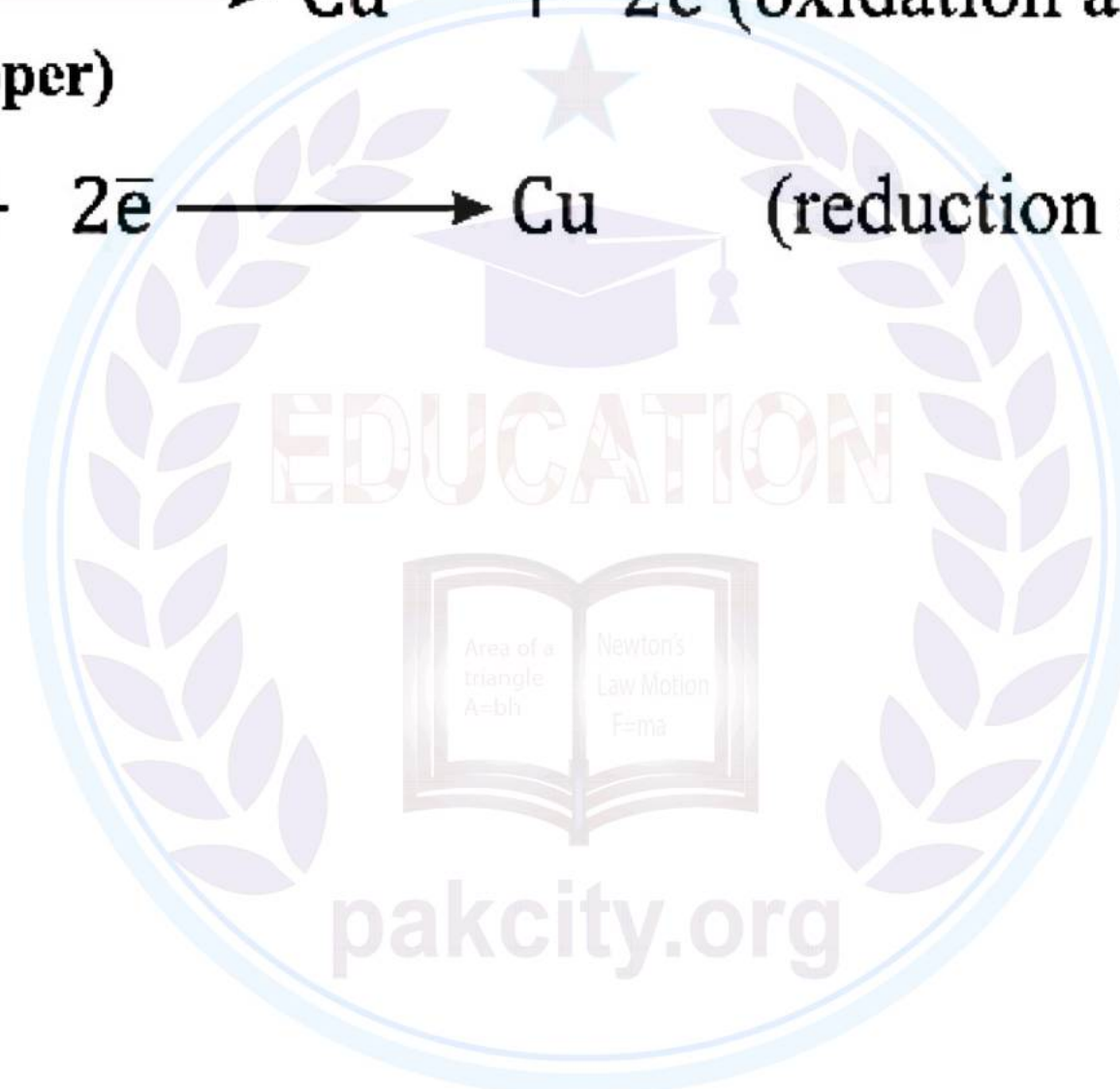
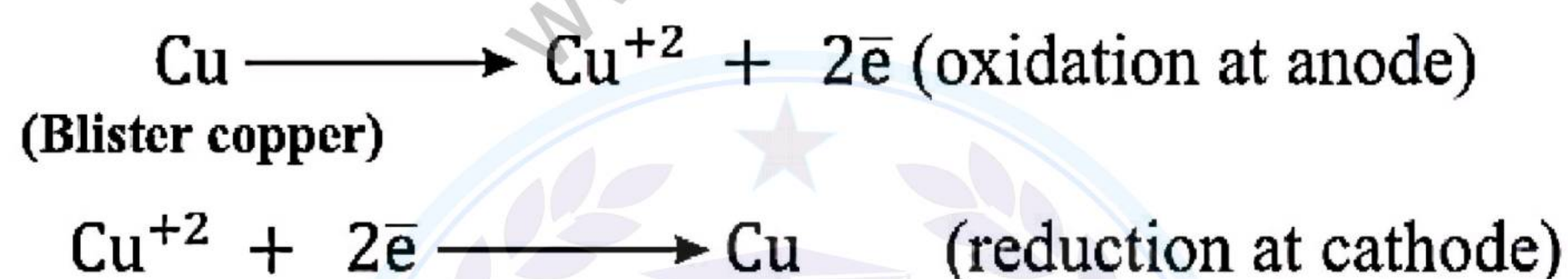


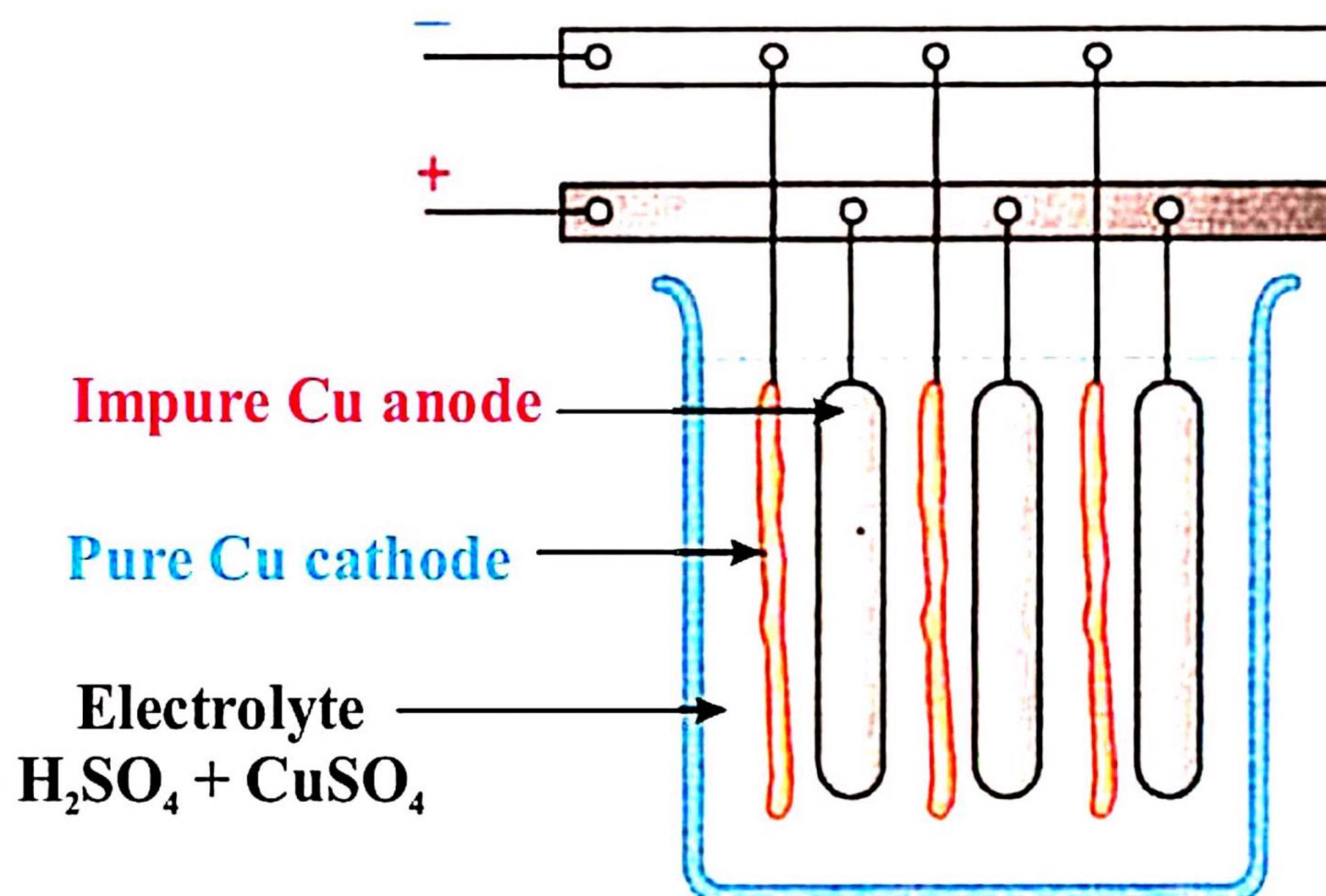
STEP#5 (ELECTROLYTIC REFINING OF BLISTER COPPER)



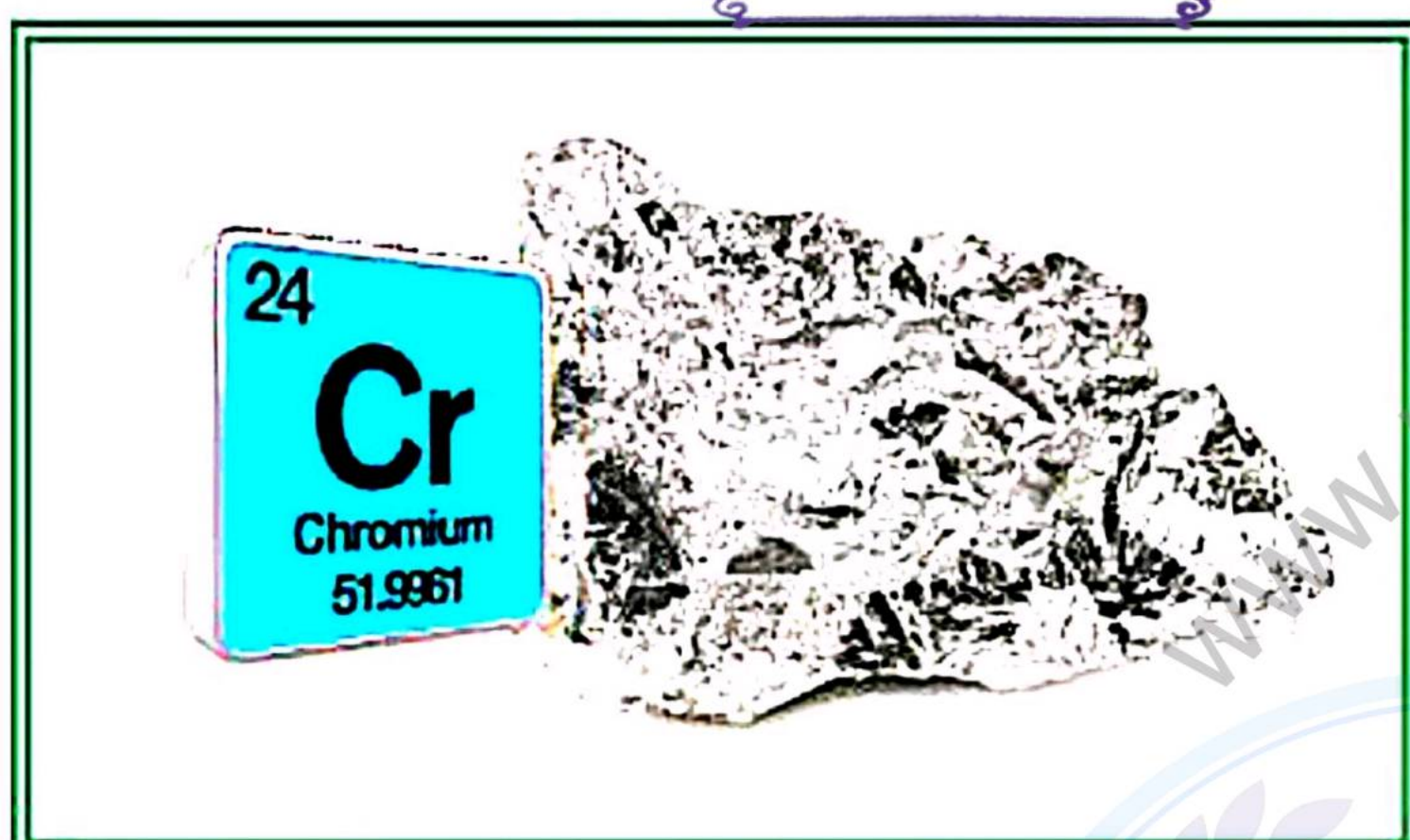
The impurities of blister copper can be removed by electrolytic method. The electrolytic cell used for this purpose is made up of blister copper anode and pure copper cathode. Copper sulphate solution is used as electrolyte.

When an electric current of 1.3 volts is passed through the cell, copper metal is oxidized at anode to form Cu^{+2} ions by the loss of two electrons. Cu^{+2} ions are reduced into pure copper metal at cathode by the gain of two electrons. The impurities of blister copper are deposited below anode as anode mud. In this manner, 100% pure copper metal is produced which can be used for making wires.





Chromium



Chromium is a transition metal and it belongs to 3d series. It has a silvery grey color and metallic luster.

Chromium reacts with dilute hydrochloric acid to liberate hydrogen gas.



Chromium reacts with oxygen to form chromium oxide.



Chromium reacts with steam at high temperatures to form chromium oxide with the liberation of hydrogen.



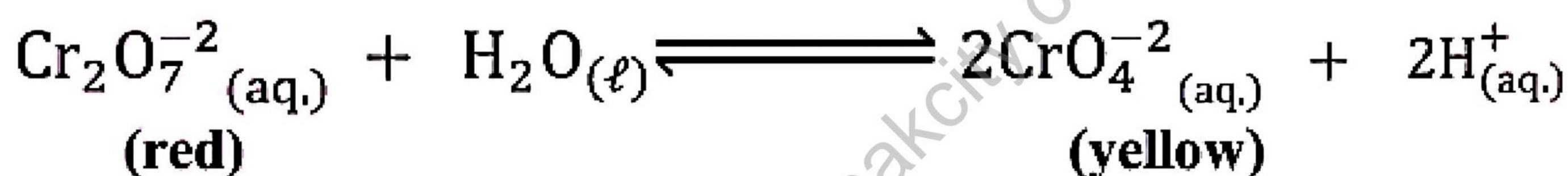
Chromium is used to make stainless steel, chrome plating and pigments.

Chemistry of Potassium dichromate



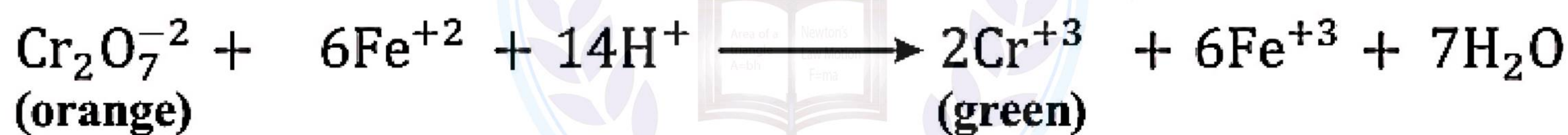
Potassium dichromate is a red crystalline solid that is highly soluble in water.

If it dissolves in water a chromate and dichromate equilibrium is formed which shows an orange – red color.

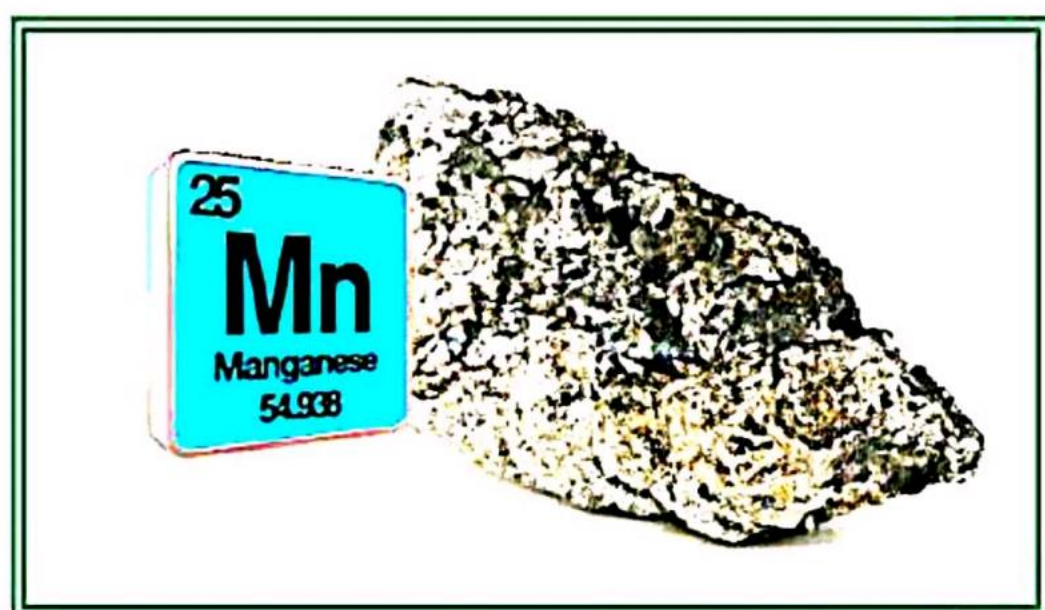


This equilibrium between chromate and dichromate ions is pH sensitive. When an acid is added, the equilibrium shifts to the left, resulting in the formation of a red dichromate solution. On the other hand if a base is added, the equilibrium shifts to the right, leading to the formation of a yellow chromate solution.

Potassium dichromate is used as an oxidizing agent in various chemical reactions since it possesses the highest oxidation state of chromium (+6).

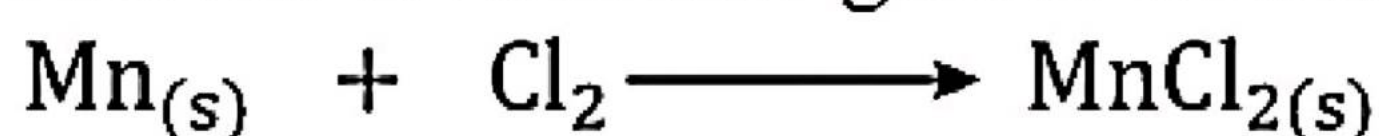


Manganese

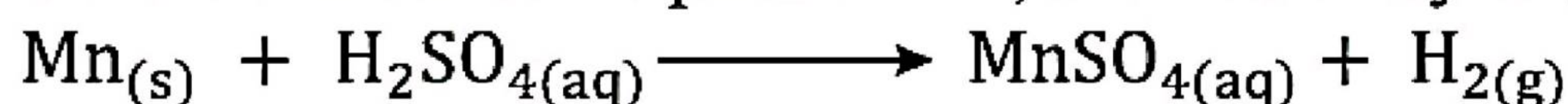


Manganese is an outer transition element belonging to 3d series. Its symbol is "Mn".

Manganese reacts with chlorine to form manganese chloride.



Manganese when dissolves in dilute sulphuric acid, it liberates hydrogen gas.



Chemistry of Potassium Permanganate

The formula of potassium permanganate is KMnO_4 . It is a deep purple crystalline solid. It is highly soluble in water. Mn has +7 oxidation state in potassium permanganate. Due to the highest oxidation state of manganese, KMnO_4 is an oxidizing agent in acidic, basic and neutral medium.

The reaction of potassium permanganate with ferrous sulphate and Mohr's salt is given as;



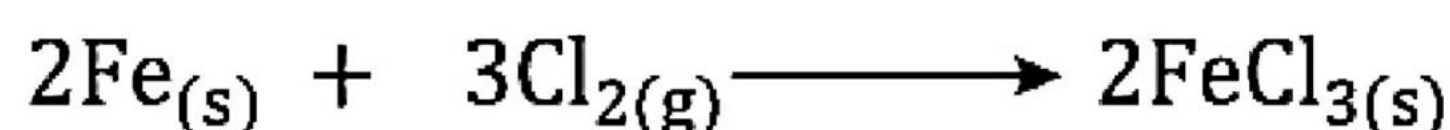
Iron

Iron is an outer transition metal belonging to 3d series. Its symbol is Fe because it is called Ferrum in Latin language. It's the fourth most abundant element in Earth crust. Red color of blood is due to Hemoglobin and it contains iron as well.

When iron is exposed to air, it oxidizes and forms an oxide film on its surface which is rusting of iron.



When it reacts with excess of chlorine, it forms ferric chloride.



Steel

Steel is a widely used alloy comprised primarily of iron combined with some other elements. By the inclusion of carbon and other alloying elements in steel enhances its mechanical, thermal and chemical properties compared with simple iron.

There are several types of steel each characterized by unique compositions and properties suited for specific applications.

Type of Steel	Applications
Carbon Steel	Construction tools, machinery, pipes, tubes, automotive etc.
Stainless Steel	Kitchen appliances, Cutlery and Medical equipment
Tool Steel	Cutting and drilling equipment
Alloy Steel	Fry pan, Toaster etc



Table 2.4 Commercial applications of some common transition elements

Transition Elements	Commercial Applications
Titanium	In making artificial joints, bone plates, screws and dental implants.
Vanadium	Use in batteries, as a catalyst and as a pigment in glass making
Iron	Building and bridge construction and tool making.
Copper	In making copper wires, alloys and sanitary works.
Zinc	Galvanizing, alloying and also use in batteries
Platinum	In making jewellery and also serves as a catalyst.
Mercury	Use in thermometers, B.P. apparatus, and amalgam formation

Multiple Choice Questions

- (i) Zn^{+2} ion is colourless because:
 (a) Its undergoes d-d transition of electron
 (b) Its 3d orbitals have all unpaired electrons
(c) Its 3d orbitals have all paired electrons
 (d) Its d orbitals split up into t_{2g} and e_g
- (ii) The coordination number of cobalt in $\text{Na}_4[\text{Co}(\text{C}_2\text{O}_4)_3]$ is:
 (a) 3 (b) 4
(c) 6 (d) 7
- (iii) An example of a bidentate ligand among the following is:
 (a) OH^- **(b) $\text{C}_2\text{O}_4^{2-}$**
 (c) Cl^- (d) CN^-
- (iv) A highly paramagnetic ion among the following is:
 (a) Fe^{+2} **(b) Fe^{+3}**
 (c) Co^{+2} (d) Cr^{+3}

- (v) The highest oxidation state of chromium is:
(a) +4 (b) +5
(c) +6 (d) +7
- (vi) The element is not used for electroplating:
(a) Zinc (b) Tin
(c) Chromium **(d) Manganese**
- (vii) The steel is typically used in making Fry pans:
(a) Carbon steel (b) Stainless steel
(c) Tool Steel **(d) Alloy Steel**
- (viii) The step which involved in the extraction of copper from chalcopryrite ore in the elimination of gangue impurities is:
(a) Concentration (b) Roasting
(c) Smelting (d) Bessemerization
- (ix) 5d series of outer transition elements is:
(a) Sc to Zn (b) Y to Cd
(c) La to Hg (d) Ac to Cn
- (x) Oxidation of manganese in air gives the following oxide:
(a) MnO (b) MnO₃
(c) Mn₂O₃ **(d) Mn₃O₄**

Short Questions

2. Give reasons for the following:



- (i) Why do transition elements show variable oxidation states?
(ii) Why transition elements have ability to form alloys?
(iii) Why Cu^{+2} ion is blue but Zn^{+2} is colourless?
(iv) Why chromium exists in $4s^1 3d^5$ configuration but not in $4s^2 3d^4$?
(v) Why binding energy of zinc is least in 3d series?

Answers:

- (i) Transition elements show variable oxidation states because they can make bond with ns orbital and (n-1)d orbital as well due to very less energy difference between them.

(ii) Transition elements can form alloys because they have ability to form non-stoichiometric compounds. They have interstitial spaces on their surfaces in which the atoms of other elements adsorb to form alloy,

(iii) d-d transition is possible in Cu^{+2} ions so they absorb light of specific wavelength of red and green color, they release light energy in the form of light having wavelength of blue color. d-d transition is not possible in Zn^{+2} ions because of fully filled d-orbital. That's why they reflect all the light falling on it, hence the compounds of Zinc are white.

(iv) $4s^2, 3d^4$ is unstable electronic configuration of chromium and $4s^1, 3d^5$ stable electronic configuration of chromium.

(v) Binding energy of Zn is least because of its fully filled d sub shell.

3. Write down the balanced chemical equations for the following reactions.

- (i) Reaction of conc. nitric acid with copper
- (ii) Reaction of conc. sulphuric acid with copper
- (iii) Reaction of permanganate with oxalic acid
- (iv) Reaction of dichromate with ferrous sulphate
- (v) Reaction of manganese with dilute sulphuric acid
- (vi) Reaction of iron with chlorine

Answers:

(i)



(ii)



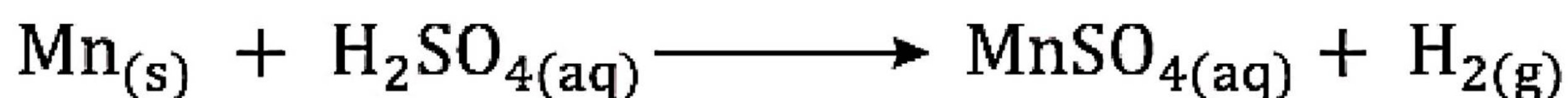
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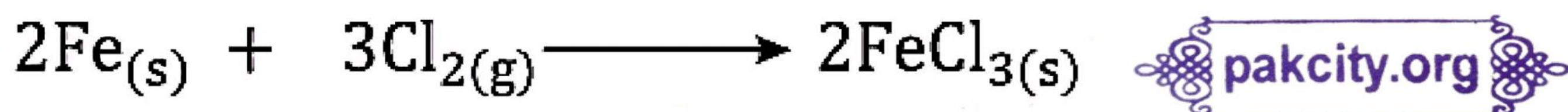
(iv)



(v)



(vi)



4. Why d-block elements are called outer transition elements?

Ans. d-block elements are also called outer transition elements because they are present outside in the periodic table in contrast to inner transition elements which are present inside lanthanum and actinium.

5. Write down the effect of pH changes on dichromate equilibrium in water.

Ans. In acidic medium, dichromate ion is prominent and in basic medium chromate ion is prominent.

6. Melting point of d-block elements increase up to middle of the series and then decrease why?

Ans. d-block elements usually have high melting points due to the covalent bonding formed by the empty or partially filled d-orbitals and unpaired electrons.

Since electrons get paired in the d-orbital after d^5 configuration, the melting point of elements in the d-block increases from d^1 configuration to d^5 configuration and then starts to decrease.

7. Give the composition and applications of stainless steel, brass and bronze.

Ans. Stainless steel is made up of iron, chromium and nickel. It is used to make kitchen utensils, surgical instruments etc.

Brass is an alloy of copper and zinc. It is used to make taps, moving parts of clock, musical instruments, coins etc.

Bronze is an alloy of copper and tin. It is used to make coins, statues, medals etc.

Descriptive Questions

1. Explain the trend of following properties of 3d-series of transition elements.

- (a) Paramagnetic behavior
- (b) Variable oxidation state
- (c) Colour formation.



See the topic of general properties of transition metals

2. How can you define a coordination complex and a chelating ligand? Explain various types of ligands with examples.

See the topic of Co-ordination compounds

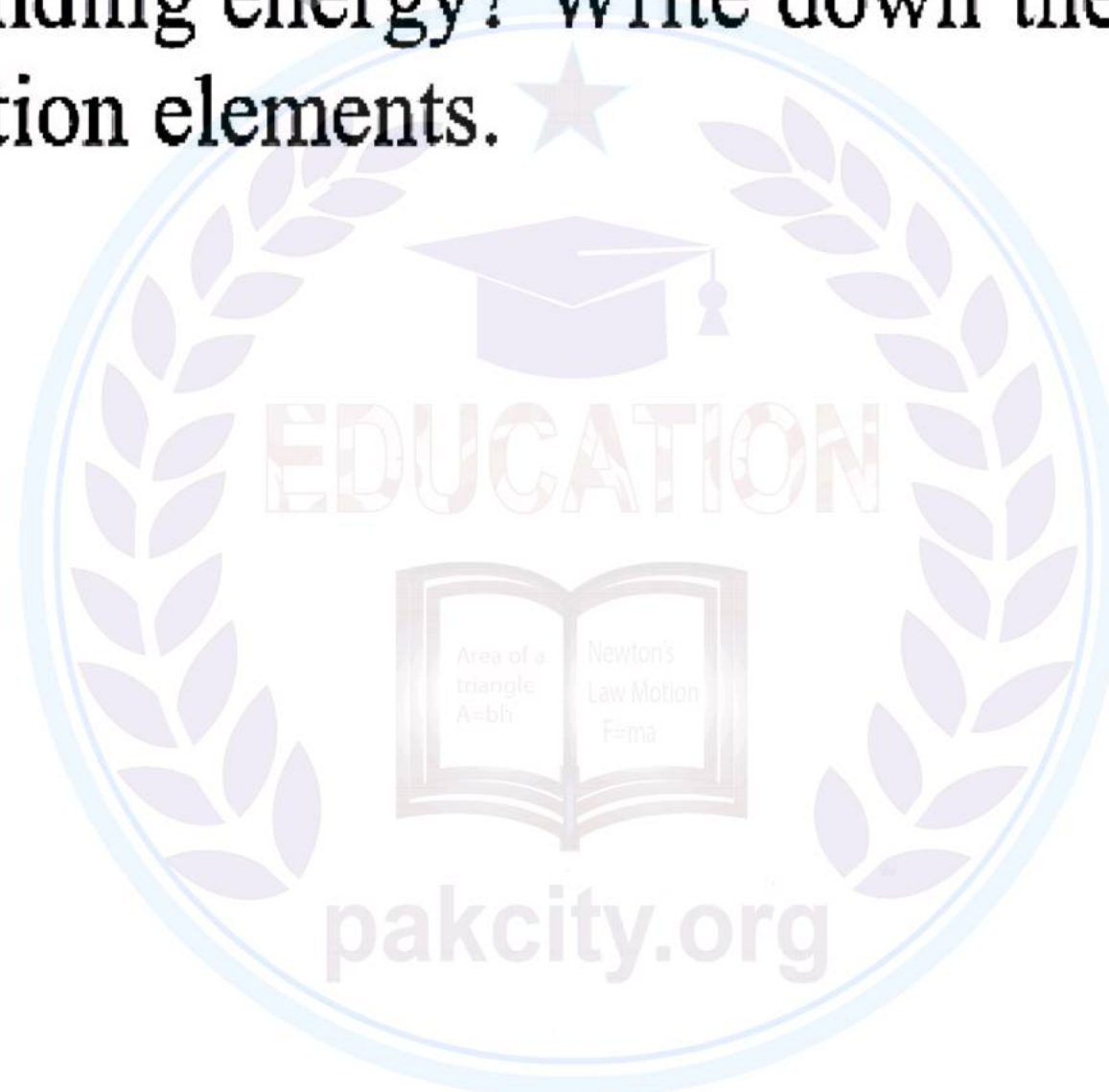
3. Describe how 99.99% pure copper is obtained from its chalcopyrite ore.

See the topic of Metallurgy of Copper

4. Explain why transition elements and their compounds serve as catalysts in many chemical reactions.

See the topic of Catalytic Property of transition element

5. What is meant by binding energy? Write down the trend of binding energy in 3d series of transition elements.



2.1.2 Binding Energy

“The amount of energy required to separate the constituents of a bound system, such as atoms, nuclei, or particles”. It represents the strength of the attractive forces holding the system together.

The d-block elements have partially filled d orbitals, which contribute to their unique properties. Their binding energy is higher than that of other elements due to the strong attraction to their outermost d electrons. The binding energy increases across a period from left to right in the d-block elements due to increasing nuclear charge and decreasing atomic radius. The stronger positive charge attracts the d electrons more, requiring more energy to remove them.

Down a group, the binding energy tends to decrease in the d-block elements. This is because the increasing atomic size and shielding effect reduce the effective nuclear charge felt by the outermost d electrons, making them easier to remove.

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