

Chapter-14

d and f Block Elements

Transition Elements:

The elements of “d” or “f” block which form one or more stable ions with partially filled d or f orbitals are called transition elements. As they have properties between s-block and p-block so they are called transition elements. They are divided into two categories:

- a) **Main transition elements or outer transition metals:** d-block elements are called main or outer transition elements.
- They have partially filled (n-1) d orbitals in ground state.
 - They are further divided into
 - 1st transition series or 3d series which consist of $_{21}\text{Sc}$ to $_{29}\text{Cu}$
 - 2nd transition series or 4d series which consist of $_{39}\text{Y}$ to $_{47}\text{Ag}$
 - 3rd transition series or 5d series which consist of $_{57}\text{La}$ to $_{79}\text{Au}$
 - 4th transition series or 6d series which consist of $_{89}\text{Ac}$ to $_{109}\text{Mt}$ (Mettnerium)
- b) **Inner transition elements or metals:** f-block elements are called inner transition elements.
- They have partially filled (n-2) f orbitals in ground state
 - They consist of two horizontal rows at the bottom of periodic table called lanthanides and actinides. Both lanthanides and actinides belong to group III-B. Lanthanides belong to 6th period while actinides belong to 7th period.

General Characteristics:

Distinguishing Properties of Transition Metals:

1. They are hard metals and have high melting and boiling points.
2. They are good conductor of heat and electricity.
3. They show variable oxidation states and valences.
4. Their compounds are mostly coloured in solid state as well as in aqueous state.
5. Some of these form paramagnetic compounds.
6. They form complexes or coordination compounds.
7. They form alloys.
8. These elements and some of their compounds act as solid catalysts.
9. They are hard metals.
10. They are good conductor of heat and electricity due to having free electrons of valence shell.
11. Their general electronic configuration is $ns^{1-2}, (n-1) d^{1-10}$.

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Some important General Characteristics

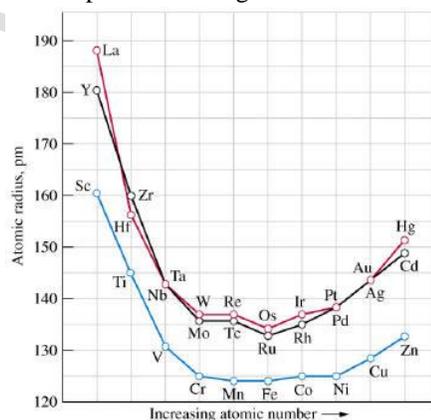
1. **Electronic configuration:**

The most occurring transition metals are that of 3d series. Their electronic configuration is:
Their general electronic configuration is $ns^{1-2}, (n-1) d^{1-10}$

${}_{21}\text{Sc} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$	Non-transition metal
${}_{22}\text{Ti} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$	Transition metals
${}_{23}\text{V} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$	
${}_{24}\text{Cr} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$	
${}_{25}\text{Mn} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$	
${}_{26}\text{Fe} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$	
${}_{27}\text{Co} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$	
${}_{28}\text{Ni} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$	Non-transition metal
${}_{29}\text{Cu} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$	
${}_{30}\text{Zn} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$	

2. **Atomic and Ionic Radii:**

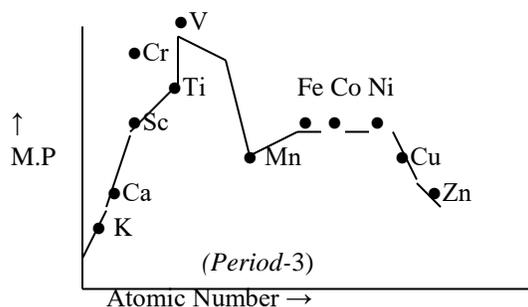
The atomic radii across period, decrease rapidly at the start then remains almost same and then for last elements it increases. This increase is probably due to the filled 3 d orbitals give more shielding to outer shell so atomic radii increases. Changes in ionic radii across period are irregular.



3. **Melting and Boiling Points:**

Melting and boiling points of transition metals are very high due to strong binding forces among their atoms.

M.P & B.P increase in a series up to middle of the series and then decreases up to end of the series. This is due to the reason that up to middle of series number of unpaired electrons increase so binding forces increases thus MP & BP increase, the unpaired d electrons also participate in binding. Then onward pairing of electrons take place so binding forces decrease thus MP & BP decrease.



4. **Binding Energy:**

Transition metals are hard having high mechanical strength due to strong metallic bonding. The strength of metallic bond increases with increasing number of unpaired d-electrons. From group III-B to VII-B number of unpaired d-electrons increases and then from VIII-B to I-B to II-B decreases. Thus binding energy increases from left to right in the period up middle and then decreases.

5. **Oxidation states:**

They show variable oxidation states and this is due to the reason that beside outer s-electrons d-electrons also participate in bonding. In series up to middle, number of oxidation states increases and then decreases as can be seen in 3-d series.

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

Oxidation numbers in parenthesis are uncommon. Highest oxidation state i.e 8, is of Os (Osmium) of 5-d series and also Ru (Ruthenium) of 4-d series has (+8) but it is rare.

6. **Colour:**

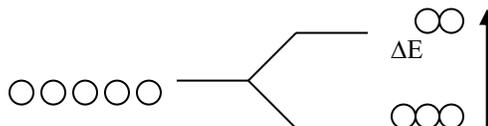
The compounds of transition metals are mostly coloured. The colour is due to d-d transition. The d-orbitals during bonding split up into two energy levels, one set has high energy than the other. The electrons present in low energy

d-orbitals jumps to higher energy d-orbital by absorbing some visible radiations and transmit other that gives different colours

to the ions e.g. Ti^{3+} ions absorb yellow light

and transmit other 6 so it appears violet. Cu^{2+} absorbs red light and transmit other so it appears blue.

Co^{2+} absorb blue and green light and transmit other so it appears pink.



Ion	Outer configuration	Number of unpaired electrons	Colour
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple or violet
Ti^{4+}	$3d^0$	0	Colourless
Cr^{3+}	$3d^3$	3	Dark green
Mn^{2+}	$3d^5$	5	Light pink
Fe^{2+}	$3d^6$	4	Dirty green
Fe^{3+}	$3d^5$	5	Brown
Co^{2+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Zn ²⁺	3d ¹⁰	0	Colourless
------------------	------------------	---	------------

7. **Magnetic Properties:**

Substances which are attracted by external magnetic field are called paramagnetic and phenomenon is called paramagnetism.

Substances which are strongly attracted by magnetic field are called ferromagnetic and the phenomenon is called ferromagnetism.

Substances which are repelled by external magnetic field are called diamagnetic and the phenomenon is called diamagnetism.

Paramagnetic behaviour is due to the presence of unpaired electrons in the atom, ion or molecule of the substance. The attraction is due to interaction of magnetic field generated by spinning electrons and external magnetic field. In diamagnetic substances the electrons are paired and their electrons have opposite spin which cancel the effect of each other.

Ni²⁺ has 2 unpaired electrons so it is paramagnetic

Cu²⁺ has 1 unpaired electron so it is paramagnetic

Fe²⁺ has 4 unpaired electrons so it is paramagnetic

Fe³⁺ has 5 unpaired electrons so it is ferromagnetic

Mn²⁺ has 5 unpaired electrons so it is ferromagnetic

Cu⁺ has no unpaired electrons so it is diamagnetic

Most of transition metals have unpaired electrons in their d-orbitals. Due to spin motion of electrons, magnetic moment is generated. The magnetic moments of unpaired electrons are in same direction so they will reinforce each other and thus substance will act as tiny magnet and is called paramagnetic.

On other hand if electrons are paired their spins are in opposite directions and cancel each other's effect so substance will not be attracted by magnetic field and will be slightly repelled, such substance is called diamagnetic.

The substances which have more number of unpaired electrons will be strongly attracted by magnetic field and are called ferromagnetic. They can be magnetized as they remain permanent magnet even in absence of magnetic field e.g. Iron, cobalt, Nickel.

The magnetic moment is related to number of unpaired electrons and is given as

$$\mu = \sqrt{n(n+2)} \quad \text{where } \mu = \text{magnetic moment}$$

n = number of unpaired electrons

It shows that more is number of unpaired electrons more is magnetic moment.

Magnetic moment is practically measured by Gouy's balance. Its unit is B.M (Bohr magneton).

When n = 1 then $\mu = 1.73$ B.M

When n = 2 then $\mu = 2.83$ B.M

When n = 3 then $\mu = 3.87$ B.M

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

8. **Alloy Formation:**

Due to similarities in their sizes and structure, some transition metals are able to replace one another in the metallic lattice and thus form alloys e.g. steel (alloys of iron with other metals are called steel).

Other examples are brass, bronze etc. They are non-stoichiometric.

Alloy	Composition	Uses
Brass	Cu = 60-80% Zn = 20-40%	Domestic utensils, cartridges, casting, condensers
Bronze	Cu = 75-90% Sn = 10-25%	Statues, coins, bells, blades, machine parts
Steel	Fe = 90-95% C = 0.1-2%	Cutlery, car bodies, bridge, utensils
Stainless Steel	Fe = 73.82%, C = 0.18%, Ni = 8%, Cr = 18%	Utensils, machine parts, nails, anchors
Gold (18carat)	Au = 70-75% Cu = 20-25%	Jewellery, tooth filling, statues, electrical devices

9. **Catalytic properties:**

Transition metals show variable oxidation states, therefore, they form unstable intermediate products with various reactants. These intermediate products decompose to give final products, regenerating the catalyst.

In other cases the finely divided metals or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to closer contact.

Some of examples of these catalysts are

- Finely divide Fe(iron) is used as catalyst in Haber process (formation of ammonia).
- V_2O_5 is used as catalyst in Contact process for oxidation of SO_2 to SO_3 .
- Pt is used as catalyst in Oswald process for oxidation of NH_3 to NO.
- $FeSO_4 + H_2O_2$ (Fenton's reagent) is used as catalyst for oxidation of alcohols to aldehydes.
- Cu is also used as catalyst for oxidation of alcohols to aldehydes.
- Pd is used as catalyst for hydrogenation of phenol to cyclohexanol.
- Pt/PtO (Adam's catalyst) is used as catalyst for reduction.
- $TiCl_4$ (Ziegler Natta catalyst) is used as catalyst for polymerization of ethylene to polythene (Polyethylene).

Coordination Compounds

The compounds in which ligands (electron pair donating species) are attached to transition metal through coordinate covalent bonds are called coordination compounds or complexes.

Complex formation:

Transition elements have great tendency to form coordination compounds or complexes. A compound which has one or more coordinate covalent bonds is called coordination compound or complex.

Transition metals due to having ability of forming vacant hybrid orbitals are capable of forming complexes.

Ligands donate their pairs of electrons to the vacant hybrid orbitals and make coordinate covalent bonds.

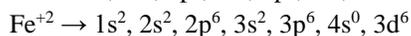
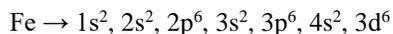
Transition elements have marked tendency to form coordination compounds or complexes. This is due to high positive charge on transition metal cation and availability of vacant hybrid orbitals with them.

e.g. $[Fe(CN)_6]^{4-}$

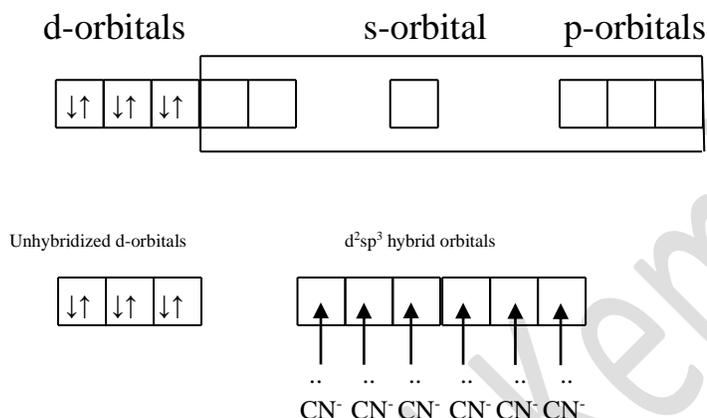
Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)



Due to strong interaction with ligands the unpaired d electrons are paired up and as a result two orbitals of d sub-shell become vacant. Two vacant d-orbitals, one vacant s-orbital and three vacant p-orbitals get hybridized and give six vacant d^2sp^3 hybridized orbitals.



Ligands donate their lone pairs of electrons to the vacant hybrid orbitals of transition metal and thus form coordinate covalent bonds with central transition metal and as a result complex is formed.

Components of complexes Or the terms used in complexes:

Different terms used in study of complexes are

(a) *Central metal atom or ion:*

Transition metal atom or ion to which ligands are attached due to coordinate covalent bonds is called central metal atom or ion respectively.

e.g. (i) In $K_4[Fe(CN)_6]$, Fe is central metal ion

e.g. (ii) In $[Ni(CO)_4]$, Ni is central metal atom

(b) *Ligand:*

The atoms or molecules or anions which make coordinate covalent bonds with central transition metal by donating electron pair(s) to transition metal, are called ligands. The ligands are electron pair donor while transition metal is electron acceptor.

Ligands could be anionic, cationic or neutral.

e.g. (i) In $K_4[Fe(CN)_6]$, CN^- is anionic ligand.

e.g. (ii) In $[Ni(CO)_4]$, CO is neutral ligand.

Ligands could be classified on the basis of number of electron pairs which they donate to the central transition metal, into three types.

(i) Monodentate Ligands:

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

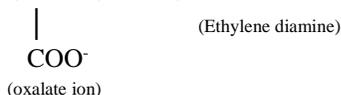
Ligands which donate only one lone pair of electrons to form coordinate covalent bond with central transition metal are called monodentate ligands

e.g. Cl^- , Br^- , NO_2^- , OH^- , CN^- , RCOO^- , CO , NH_3 , H_2O

(ii) Bidentate Ligands:

Ligands which donate two lone pairs of electrons to form coordinate covalent bond with central transition metal are called bidentate ligands.

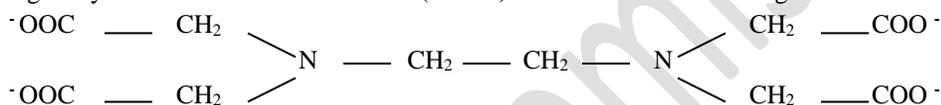
e.g. SO_4^{2-} , CO_3^{2-} , COO^- , $\text{S}_2\text{O}_3^{2-}$, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$



(iii) Polydentate Ligands:

Ligands which donate more than two lone pairs of electrons to form coordinate covalent bond with central transition metal are called polydentate ligands.

e.g. Ethylene diamine tetra acetic acid (EDTA) ion. It is a hexadentate ligand.



(c) *Coordination Number:*

Number of monodentate ligands attached to central transition metal or number of coordinate covalent bonds that are made by transition metal, is called coordination number. Known coordination numbers are 2,3,4,5,6,7,8 and 9.

e.g. (i) In $\text{K}_4[\text{Fe}(\text{CN})_6]$, coordination number of Fe is 6.

e.g. (ii) In $[\text{Ni}(\text{CO})_4]$, coordination number of Ni is 4.

Complexes with 4 and 6 coordination number are very common while complexes with coordination number 5 are less common.

Ag usually shows coordination number 2

Ni, Cu, Pt usually show coordination number 4

Fe, Co usually show coordination number 6

(d) *Coordination Sphere:*

The central metal atom along with ligands is called coordination sphere. It is placed in square brackets. It may be anionic, cationic or neutral e.g. $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ and $[\text{Ni}(\text{CO})_4]$ are anionic, cationic and neutral respectively.

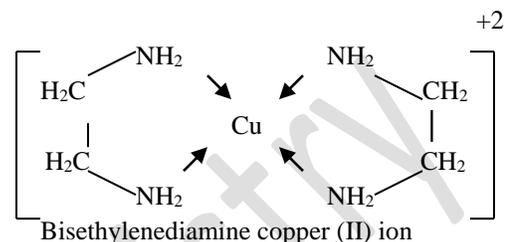
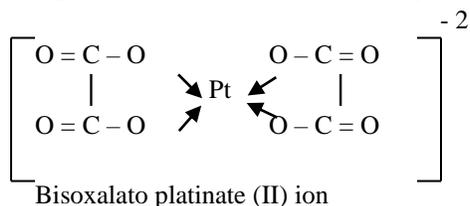
(e) *Charge on Coordination Sphere:*

It is the algebraic sum of the charges present on the central metal ion and ligands e.g. In $[\text{Fe}(\text{CN})_6]^{4-}$ the charge on Fe is +2 and that on each CN is -1, so the charge on coordination sphere is $(+2) + (-1 \times 6) = +2 - 6 = -4$.

(f) *Chelates:*

A complex in which all donor atoms of a bidentate or polydentate ligand get coordinated with the same metal ion such that the complex formed contain one or more rings, such a complex is called chelate.

e.g. (i)



Nomenclature:

IUPAC names of coordination compounds follow following sequence

Cation – ligand – transition metal – anion

- (i) Name of cation is written first if there is any cation.
- (ii) Then name of ligand is written. Prefixes di, tri, tetra, penta are used with the name of monodentate ligand and prefixes bis, tris, tetrakis etc are used with the name of bidentate or polydentate ligands to show the number of ligands. If ligand is anion suffix “O” and for cationic ligand suffix “ium” is used with its name, while no special suffix for neutral ligand just its Latin name is written. If more than one kind of ligands are there then first the negative, then the neutral and at the end the positive ligands are written. If more than one kind of –ve ligands are there then alphabetical order is followed among themselves, Same practice will be followed for +ve and neutral ligands if they are of more than one kind. Prefix μ is used with the names of bridging ligands and they are written after normal ligands.

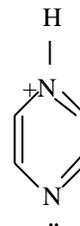
Anionic ligands:

CN^- Cyano	SCN^- Thiocyanato	NO_2^- Nitro	Cl^- Chloro
SO_4^{2-} Sulphato	$\text{S}_2\text{O}_3^{2-}$ Thiosulphato	$\text{C}_2\text{O}_4^{2-}$ Oxalato	OH^- Hydroxo
CO_3^{2-} Carbonato	NH_2^- Amido		

Neutral ligands:

NH_3 Ammine	H_2O Aqua	CO Carbonyl	NO Nitrosyl
$\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ Ethylene diamine (en)			

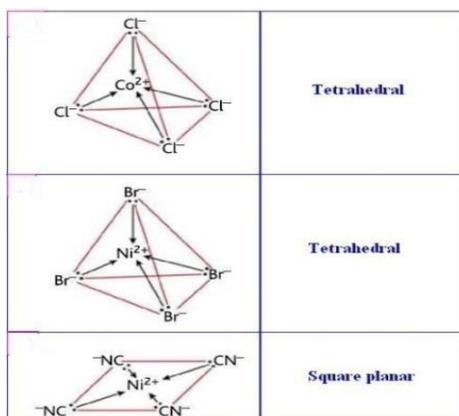
atonic ligands: Hydrazinium N_2H_5^+ or $(:\text{NH}_2 - \text{NH}_3^+)$, Nitrosonium NO^+ , Pyrazinium

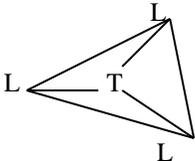
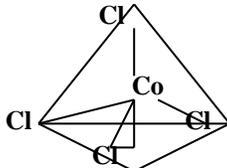
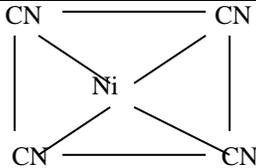
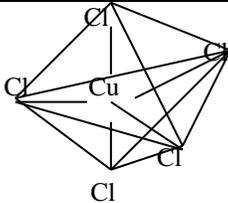
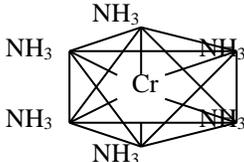


Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)



Coordination Number	Hybridization In Central Atom	Shape	Example	Geometry
2	Sp	Linear	$[\text{Ag}(\text{NH}_3)_2]^{-2}$	$\text{NH}_3 \rightarrow \text{Ag} \leftarrow \text{NH}_3$
3	sp^2	Trigonal planar		
4	sp^3	Tetrahedral	$[\text{CoCl}_4]^{-2}$	
4	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{-2}$	
5	dsp^3	Trigonal Bipyramidal	$[\text{CuCl}_5]^{-3}$	
6	$d^2 sp^3$	Octahedral	$[\text{Cr}(\text{NH}_3)_6]^{+2}$	

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Chemistry of Some Important Transition Metals

Vanadium:

It was discovered in 1801 in Mexico by Anders Manuel del Rio but was considered as form of chromium. Later it was rediscovered in 1830 by Swedish chemist Nils Gabriel Sefström.

The element was named after Vanadis, goddess of beauty and love in Scandinavian mythology.

Characteristics:

(i) Symbol = V (ii) Atomic Number = 23 (iii) Luster = Silvery white (iv) Group = V- B

(v) Period = 3rd

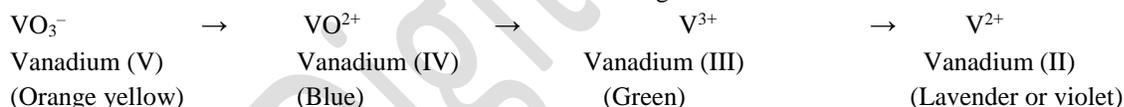
(vi) Melting point = 2188K or 1915°C

(vii) Boiling point = 3623K or 3350°C

(viii) Electronic configuration = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$

(ix) *Oxidation states:*

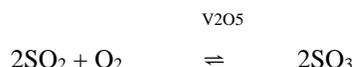
- Vanadium shows +2, +3, +4 and +5 oxidation state in its compounds.
- The compounds with lower oxidation state are ionic, good reducing agent and coloured.
- The compounds in higher oxidation state are generally colourless due to vacant orbitals.
- When compounds having higher oxidation state are reduced by some suitable reducing agent, changes occur in their oxidation states and thus colours changes.



- Vanadium also show +1, 0, -1 oxidation states e.g. oxidation state of vanadium is +1 in $[V(dipy)_3]^+$, zero in $[V(CO)_6]$ and -1 in $[V(CO)]^-$

(x) *As Catalyst:*

In past during manufacturing of sulphuric acid by contact process platinum was used as catalyst. But now platinum is replaced by vanadium pentaoxide (V_2O_5).



It is used as catalyst when substances are oxidized by oxygen. It is also used as catalyst in oxidation of alcohols and hydrogenation of olefins (alkenes).

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Chromium:

Chromium is a shiny metal. Chromium was discovered in 1797 by French chemist Louis Nicolas Vauquelin. It is given the name as chromium which is from Greek word chroma meaning colour. This name is due to its coloured compounds.

Occurrence:

It is 21st most abundant element on earth crust. Its important minerals are Chromite or chrome iron stone ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$), chrome ochre (Cr_2O_3), Crocite or Lead chromate (PbCrO_4).

Characteristics:

- (i) Symbol = Cr (ii) Atomic Number = 24 (iii) Luster = Brilliant silvery white (iv) Group = VI-B
 (v) Period = 3rd
 (vi) Melting point = 2173K or 1900°C (vii) Boiling point = 2963K or 2690°C
 (viii) Electronic configuration = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
 (ix) it is resistant to corrosion.

(x) Oxidation states:

- The compounds of chromium in which it has +2, +3 and +6 oxidation number are stable.
- Oxidation state +2: Compounds in which oxidation state is +2 (Cr^{2+}) are called chromous compounds. e.g. CrCl_2 , CrS , $\text{CrSO}_4\cdot 7\text{H}_2\text{O}$, CrCO_3 etc. These compounds are unstable and thus they on exposure to air oxidize to corresponding stable Cr^{3+} compounds. These compounds are strong reducing agents.
- Oxidation state +3: Compounds in which oxidation state is +3 (Cr^{3+}) are called chromic compounds. e.g. Cr_2O_3 , CrCl_3 , $\text{Cr}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ etc. These compounds are most stable. These compounds are either produced by the oxidation of Cr^{2+} compounds or by reduction of Cr^{6+} compounds.
- Oxidation state +6: Compounds in which oxidation state is +6 (Cr^{6+}) are strong oxidizing agents. Examples of Cr^{6+} compounds are CrO_3 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc.
- The acidic character of oxides increases with increasing oxidation number. Covalent character also increases with increasing oxidation number.

Oxide	CrO	Cr_2O_3	CrO_3
Oxidation number	+2	+3	+6
Nature	Basic	Amphoteric	Acidic
Covalent character	Ionic	Intermediate*	Covalent

* Cr_2O_3 partly ionizes.

Chromate – Dichromate equilibrium:

This is dynamic equilibrium. According to Le-Chatelier's principle, on addition of acid equilibrium will shift to the right and on addition of base equilibrium will shift to the left.

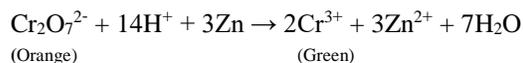
Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

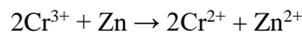
Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Reduction of Dichromate (VI) ions:

Dichromate (VI) ions reduce to chromium (III) ions when treated with Zinc and dilute acid (HCl or H₂SO₄).

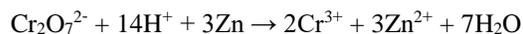


Chromium (III) further reduces by zinc to chromium (II)

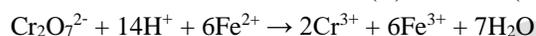
**Potassium dichromate (VI) as an oxidizing agent:**

Acidified potassium dichromate solution acts as a strong oxidizing agent.

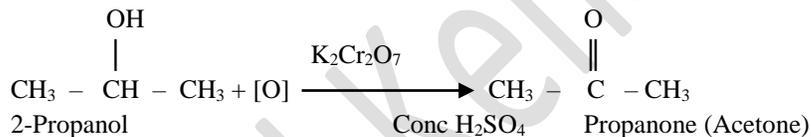
e.g (i) Acidified potassium dichromate solution oxidizes zinc to zinc (II) ion.



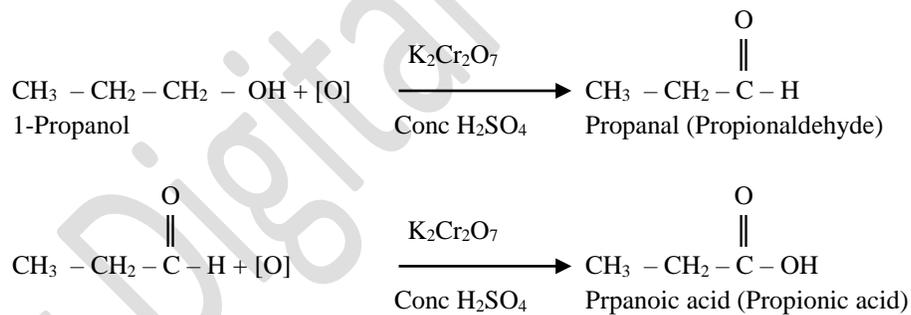
e.g (ii) Acidified potassium dichromate solution oxidizes Fe (II) ion to Fe (III) ion.



e.g (iii) Acidified potassium dichromate solution oxidizes secondary alcohol to corresponding ketone.

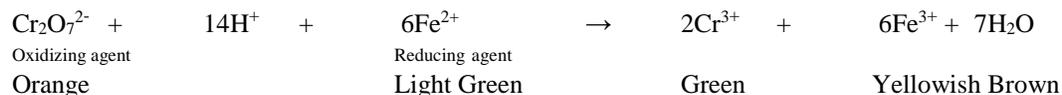


e.g (iv) Acidified potassium dichromate solution oxidizes primary alcohol to corresponding aldehyde which in turn oxidizes to corresponding carboxylic acid.

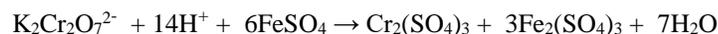


e.g. (v) As an oxidizing agent it redox titration (volumetric analysis):

Potassium dichromate is used in estimation of Fe²⁺ compounds. Fe²⁺ compounds are reducing agents so they need oxidizing agent for their estimation and potassium dichromate is an oxidizing agent so it is used for their estimation.



Or



Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Using following formula amount of Iron (II) compound is determined.

$$\frac{K_2Cr_2O_7}{M_1V_1} = \frac{FeSO_4}{M_2V_2}$$

$$\frac{\quad}{n_1} = \frac{\quad}{n_2}$$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{6}$$

Uses of Chromium and its important compounds:

- Chromium is used in chrome plating. Plating of chromium protects the metal from corrosion and give it attractive luster.
- Uses of $K_2Cr_2O_7$:
 - (i) It is used as oxidizing agent for organic compounds.
 - (ii) It is used in oxidation reduction titration.
 - (iii) It is used in tanning of hide called chrome tanning.
- Uses of K_2CrO_4 :
 - (i) It is used as indicator in argentometric titration ($AgNO_3$ titration) as an indicator. It produce pink precipitate of Ag_2CrO_4 at the end point.
 - (ii) It is used to prepare pigments.

Manganese:

Manganese was discovered in 1774 by Swedish chemist John Gottlieb Gahn. Its name is derived from Latin word magnes meaning magnet. Its principal ore pyrolusite is paramagnetic.

Occurrence:

It is 12th most abundant element on earth crust. Its important minerals and ores are pyrolusite (principal ore) while other ores are rhodochrosite, franklinite and manganite.

Characteristics:

- (i) Symbol = Mn (ii) Atomic Number = 25 (iii) Luster = Silvery white (iv) Group = VII-B
 (v) Period = 3rd
 (vi) Melting point = 1518K or 1245°C (vii) Boiling point = 2334K or 2061°C
 (viii) Electronic configuration = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
 (ix) In Free State it exists only in meteors

(x) Oxidation states:

- It shows +2, +3, +4, +6 and +7. It has highest oxidation state in 3-d series which is +7.

Free Online Chemistry Lectures → [Digital Chemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Chemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

- Oxidation state +2: The most stable oxidation state of manganese is +2. Mn^{2+} ions are stable due to half filled d-orbital ($4s^0, 3d^5$). Mn^{2+} ion exist as pale pink coloured $[Mn(H_2O)_6]^{2+}$. The compounds of Mn^{2+} are called manganous compounds. e.g. MnO , $MnCO_3$, $MnSO_4$, $MnCl_2$.
- Oxidation state +3: The compounds of Mn^{3+} are called manganic compounds. Mn^{3+} ion is quite unstable in aqueous solution and readily changes to Mn^{2+} ion. Some compounds of Mn^{3+} are $H_2Mn_2O_4$, $Mn_2(SO_4)_3$.
- Oxidation state +4: Compounds showing +4 oxidation state are limited in number. e.g. MnO_2 .
- Oxidation state +6: examples of compound showing +6 oxidation state are potassium manganate K_2MnO_4 , manganic acid H_2MnO_4 .
- Oxidation state +7: Compounds showing +7 oxidation state are strong oxidizing agents. e.g. Mn_2O_7 , $KMnO_4$. Mn_2O_7 is an unstable oxide.

Potassium permanganate ($KMnO_4$) as oxidizing agent:

e.g. (i) $KMnO_4$ oxidizes alkenes to their corresponding diols (glycols) both in acid medium as well as in alkaline medium. Colour change depends on medium.

Reaction in acid medium: $5CH_2 = CH_2 + 2MnO_4^- + 2H_2O + 6H^+ \rightarrow 5HO - CH_2 - CH_2 - OH + 2Mn^{2+}$
Intense purple light pink

Reaction in alkaline medium: The manganate (VII) ions are first reduced to manganate (VI) ions. Solution colour turns green due to manganate (VI) ions.

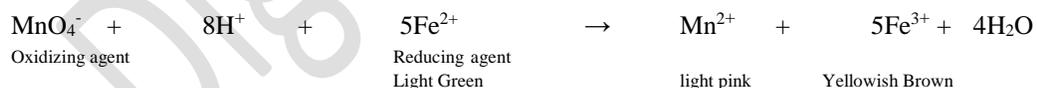


Then further reduction occurs and insoluble manganese (IV) oxide is produced.



e.g. (ii) As oxidizing agent it redox titration (volumetric analysis):

Potassium permanganate is used in estimation of Fe^{2+} compounds. Fe^{2+} compounds are reducing agents so they need oxidizing agent for their estimation and potassium permanganate is an oxidizing agent so it is used for their estimation.



Or $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

Using following formula the amount of Iron (II) compound is determined.

$$\frac{KMnO_4}{M_1 V_1} = \frac{FeSO_4}{M_2 V_2}$$

n₁ n₂

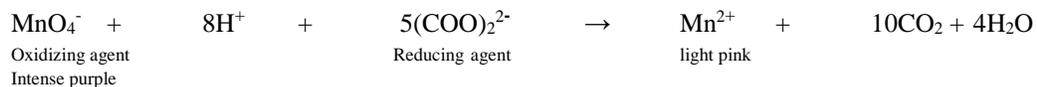
$$\frac{M_1 V_1}{1} = \frac{M_2 V_2}{5}$$

Potassium permanganate is also used in estimation of oxalic acid. Oxalic acid is reducing agent so it need oxidizing agent for its estimation and potassium permanganate is an oxidizing agent so it is used for estimation of oxalic acid.

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)



Or $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5(\text{COOH})_2 \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}$

Using following formula the amount of Iron oxalic acid is determined.

$$\frac{\text{KMnO}_4}{M_1 V_1} = \frac{\text{Oxalic acid}}{M_2 V_2}$$

$$\frac{M_1 V_1}{1} = \frac{M_2 V_2}{5}$$

Uses of Manganese and its important compounds:

- Manganese is used in making steel. Its presence in steel makes the steel tough.
- Uses of KMnO_4 :
 - (i) It is used as oxidizing agent for organic compounds.
 - (ii) It is used as disinfectant.
 - (iii) It is used for sterilization of water. In market it is called pinky.
 - (iv) It is used in oxidation reduction titration.
 - (v) Alkaline aqueous solution of KMnO_4 called Baeyer's reagent is used for detection of carbon carbon double and triple bond.

Iron:

It is an important and useful metal. It was known to ancient Egyptians since 4000 BC. But its extraction started since 2000 BC. In India its extraction started since 600 BC. It belongs to group VIII-B of periodic table.

Occurrence:

After Aluminum it is most abundant metal on the earth crust. It is fourth most abundant element on earth crust. In Free State it exists only in meteors. Broken piece of rock that comes from stars and burn in earth's atmosphere is called meteor. It is found in the rocks, mineral, soils, plants and animals etc.

Some important ores of iron are:

1. Magnetite (Ferrous ferric oxide) Fe_3O_4 . It is found in Chaghi (Baluchistan), Chitral
2. Haematite (Ferric oxide) Fe_2O_3 (red). It is found in Mazazri tang (Kohat), Langrial(Hazara) and huge deposits of low grade ore are found in Kalabagh.
3. Limonite (Hydrated ferric oxide) $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (brown).
4. Siderite (Ferrous carbonate) FeCO_3 .
5. Iron Pyrite (Ferrous sulphide) FeS
6. Copper Pyrite (Fool's Gold) CuFeS_2 .

Characteristics:

- (i) Symbol = Fe (ii) Atomic Number = 26 (iii) Luster = Grayish white (iv) Group = VIII-B
 (v) Period = 3rd

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

(vi) Melting point = 1808K or 1535°C (vii) Boiling point = 3023K or 2750°C

(viii) Electronic configuration = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

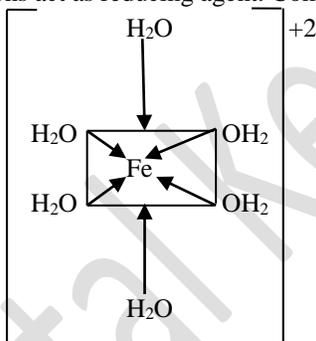
(xi) Commercial forms of Iron:

Iron is available commercially in following three forms. They differ in their carbon contents.

1. Pig iron or Cast iron. It contains 2.5 – 4.5 % carbon.
2. Wrought iron. It contains 0.12 – 0.25 % carbon.
3. Steel. It contains 0.1 – 1.5 % carbon.

(x) Oxidation states:

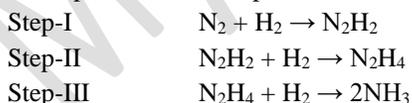
- Iron shows +2, +3, +4, +5 and +6 oxidation states. But the most common oxidation states of iron are +2 and +3.
- Oxidation state +2: Iron in +2 oxidation state is called ferrous ion. Ferrous ion is light or pale green in colour. It get oxidized even on exposure to air and also get oxidized even traces of dissolved oxygen are present in the solution. Ferrous ions act as reducing agent. Complexes of Fe^{2+} are octahedral in geometry. e.g.



- Oxidation state +3: Iron in +3 oxidation state is called ferric ion. Ferric ion is yellow or yellowish brown in colour in solution due to formation of complex ion $[Fe(H_2O)_5(OH)]^{2+}$. When potassium ferrocyanide is added to solution containing ferric ions Prussian blue precipitate of ferric ferro cyanide $Fe_4[Fe(CN)_6]_3$ is produced. Ferric ferro cyanide is used in making blue prints and is also used as bluing agent in laundry.

Iron as catalyst in Haber's process:

In Haber process ammonia is produced by the reaction of nitrogen and hydrogen in presence of iron catalyst. Reaction takes place in three steps.



Dissociation of nitrogen triple is very difficult and highly endothermic so the reaction does not proceed easily without using catalyst. In first step N_2H_2 is produced which is very unstable so it dissociates as soon as it is produced.

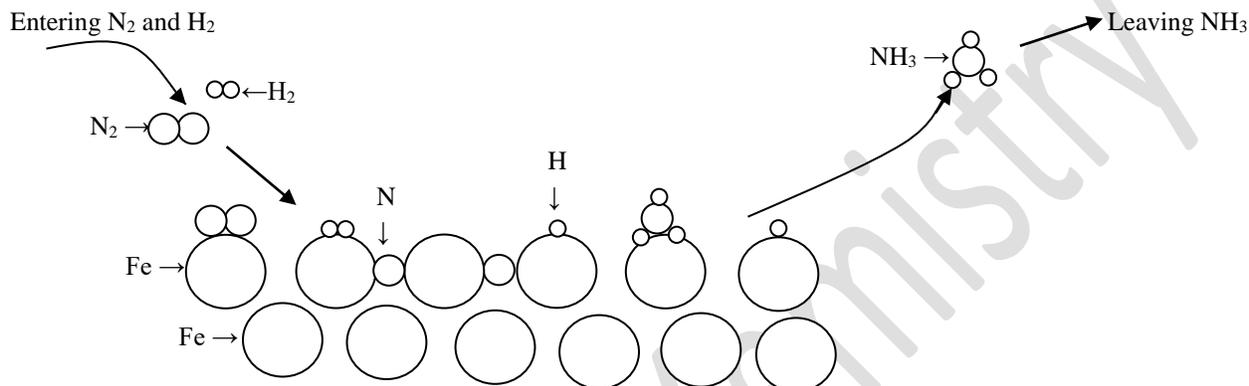
H_2 and N_2 get adsorbed on surface of iron. H_2 immediately dissociates into H-atoms. However N_2 takes time to dissociate into N-atoms and nitrogen atoms then lock into the surface of catalyst.

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

H-atoms migrate across the surface of catalyst and reach to nitrogen atoms and react with them producing ammonia molecules that still attached with surface of catalyst. The ammonia molecules then detach from the surface of catalyst in the form of gas.

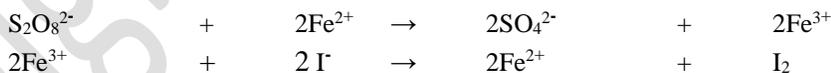


Iron as catalyst in reaction of Persulphate ions and iodide ions:

Persulphate ion is a powerful oxidant. Iron (II) ions and Iron (III) ions act as catalysts in the reaction of persulphate and iodide ions.



When Fe^{2+} act as catalyst:



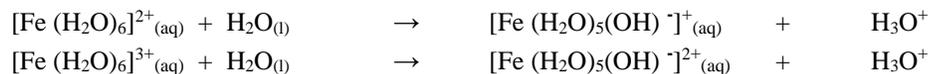
When Fe^{3+} act as catalyst:



Reactions of hexa aqua iron (II) ions and hexa aqua iron (III) ions:

Reaction with water:

Reaction of both ions hexa aqua iron (II) ions and hexa aqua iron (III) ions with water produce acidic solution having pH less than 7. These are not oxidation reduction reactions as oxidation state of iron remains same.



Fe^{3+} (ferric) ions give more acidic solution than Fe^{2+} (ferrous) ions

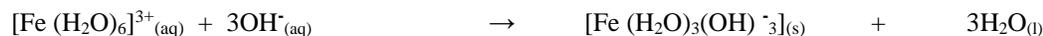
Free Online Chemistry Lectures → [Digital Chemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Chemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Reaction with alkaline solution:

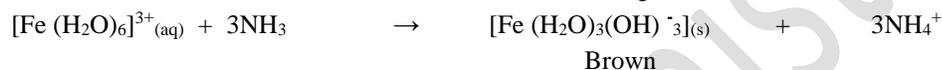
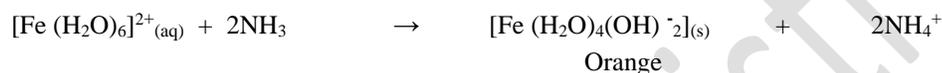
Reaction of hexa aqua iron (III) ions with alkali produces precipitate of trihydroxo triaqua iron (III). This is not oxidation reduction reaction as oxidation state of iron remains same.



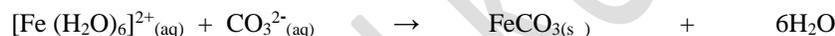
While hexa aqua iron (II) does not interact with alkali as reaction is energetically favourable.

Reaction with ammonia:

In these reactions ammonia removes protons (H^+) from hexa aqua complex. These are not oxidation reduction reactions as oxidation state of iron remains same.

**Reaction with carbonate ions:**

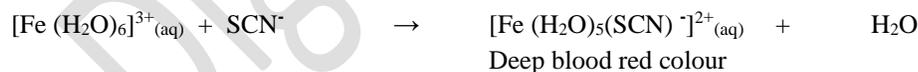
Hexa aqua iron (II) ions on reaction with carbonate ions produce precipitate of iron(II) carbonate. As hexa aqua iron (II) ions are not strongly enough acidic so they cannot liberate CO_2 gas from carbonate and simply produce precipitate of iron (II) carbonate.



Hexa aqua iron (III) ions being more acidic, they on reaction with carbonate ions produce precipitate of trihydroxo triaqua iron (III) along with liberation of CO_2 gas.

**Reaction with thiocyanate ions (identification test for iron (III) ions):**

Hexa aqua iron (III) ions on reaction with NaSCN or KSCN or NH_4SCN , produce blood red colour solution. Thus this reaction could be used as identification test for Iron (III) ions.

**Copper:**

It is an important and useful metal. It belongs to group I-B which consist of copper, silver and gold. These three metals are called coin age metal as in past they were used to make currency coins.

Copper objects are found among the remains of many ancient civilization including Egypt, Asia Minor, China, Southern Europe, Cyprus etc. The name copper is derived from Cyprus.

Occurrence:

Some important ores of copper are:

1. Malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
2. Azurite $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
3. Chalcocite Cu_2S
4. Copper pyrite CuFeS_2

Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

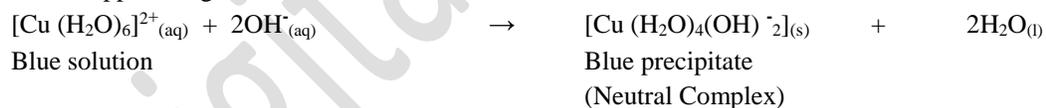
Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Characteristics:

- (i) Symbol = Cu (ii) Atomic Number = 29 (iii) Luster = Brownish red (iv) Group = I-B
 (v) Period = 3rd
 (vi) Melting point = 1356K or 1083°C (vii) Boiling point = 2868K or 2595°C
 (viii) Electronic configuration = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$
 (xi) *Oxidation states:*
- Copper shows +1, +2, +3 and +4 oxidation states. But the most common oxidation states of copper are +1 and +2.
 - Oxidation state +1: Copper in +1 oxidation state is called cuprous ion. Cuprous ions are usually colourless and diamagnetic. e.g. of copper (I) compounds are Cu_2O , CuCl , CuBr etc. They are stable at moderate temperatures.
 - Oxidation state +2: Copper in +2 oxidation state is called cupric ion. Cupric ions are blue in colour. e.g. of copper (II) compounds are CuO , CuF_2 , CuCl_2 , CuCO_3 , CuSO_4 etc.
 - Oxidation state +3: e.g. of copper (III) compounds are potassium cuprate (KCuO_2), K_3CuF_6 etc.
 - Oxidation state +4: e.g. of copper (IV) compound is Cs_2CuF_6
 - Yttrium barium copper oxide ($\text{YBa}_2\text{Cu}_3\text{O}_7$) has both Cu (II) and Cu(III) centers.

Reactions of hexa aqua copper (II) ions:**Reaction with alkaline solution i.e. (OH⁻) ions:**

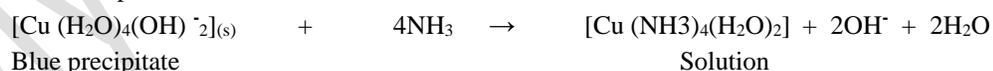
Reaction of hexa aqua copper (II) ions with alkali produces precipitate of dihydroxo tetra aqua copper (II). This is not oxidation reduction reaction as oxidation state of copper remains same. Hydroxide ions remove H^+ ions from water that is attached to copper as ligand.

**Reaction with ammonia:**

In this reaction ammonia removes protons (H^+) from hexa aqua complex. This is not oxidation reduction reaction as oxidation state of copper remains same.



The precipitate dissolves in presence of excess ammonia.

**Reaction with carbonate ions:**

Hexa aqua copper (II) ions on reaction with carbonate ions produce precipitate of copper (II) carbonate. As hexa aqua copper (II) ions are not strongly enough acidic so they cannot liberate CO_2 gas from carbonate and simply produce precipitate of copper (II) carbonate.



Free Online Chemistry Lectures → [Digital Kemistry YouTube Channel](#)

Chemistry Notes → www.mydigitalkemistry.com

Join Digital Kemistry Academy, WhatsApp number: +92-3336753424 (only text for details)

Uses of Copper and its important compounds:

- Uses of Copper:
 - (i) It used for making cooking utensils.
 - (ii) It is used in making calorimeters.
 - (iii) It is used for making electrical appliances, coils, wires etc.
 - (iv) It is used in electroplating.
 - (v) It is used for making alloys.
- Uses of Copper (I) oxide (cuprous oxide, Cu_2O):
 - (i) It is used as a colouring material in glass industry.
 - (ii) It is used as colouring material for pottery.
 - (iii) It is also used in manufacturing of anti rust paints.
- Uses of Copper (II) oxide (cupric oxide, CuO):
 - (i) It is used as a colouring material in glass industry.
 - (ii) It is used as colouring material for pottery.
 - (iii) It is used in the detection of carbon and hydrogen in the organic compounds.
 - (iv) It is used in refining of petroleum. It removes sulphur impurities from petroleum.
- Uses of CuSO_4 :
 - (i) It is used in detection of water produced in combustion of organic compounds and thus hydrogen in the compounds.

CuSO_4	+	$5\text{H}_2\text{O}$	→	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Anhydrous copper sulphate				Hydrated copper sulphate (Blue vitriol)
White				Blue
 - (ii) It is used as fungicide. It is sprayed on wines and potatoes.
 - (iii) It is used in electroplating as electrolyte.
 - (iv) It is used in dyeing and calico printing.
 - (v) It is used in Daniel cell as an electrolyte.
 - (vi) It is used in medicines.