d and *f*-Block Elements

d-Block elements

A transition element may be defined as an element whose atom in the ground state or ion in common oxidation state has **incomplete sub-shell, has electron 1 to 9**. It is called transition element due to fact that it is lying between most electropositive (*s*-block) and most electronegative (*p*-block) elements and represent a transition from them. The **general electronic configuration** of these element is $(n-1)^{1\,to\,10}\,ns^{0\,to\,2}$.

The definition of transition metal excludes Zn, Cd and Hg because they have complete *d*- orbital. Their common oxidation state is $Zn^{++}, Cd^{++}, Hg^{++}$. They also do not show the characteristics of transition element. Element of group 3 (*Sc*, *Y*, *La* and *Ac*) and group 12 (Zn, Cd, Hg) are called **non typical transition element**.

Table : 19.1 First transition or 3*d* series :

Element	Symbol	At. No.		Electronic configuration
Scandium	*Sc*	21		$[Ar]\,3d^1 4s^2$
Titanium	*Ti*	22		$[Ar]\,3d^2 4s^2$
Vanadium	*V*	23	3*d*-orbitals are filled up	$[Ar]\,3d^3 4s^2$
Chromium	*Cr*****	24		$[Ar]\,3d^5 4s^1$
Manganese	*Mn*	25		$[Ar]\,3d^5 4s^2$
Iron	*Fe*	26		$[Ar]\,3d^6 4s^2$
Cobalt	*Co*	27		$[Ar]\,3d^7 4s^2$
Nickel	*Ni*	28		$[Ar]\,3d^8 4s^2$
Copper	*Cu*****	29		$[Ar]\,3d^{10} 4s^1$
Zinc	*Zn*	30		$[Ar]\,3d^{10} 4s^2$

Table : 19.2 Second transition or 4*d*-series :

Element	Symbol	At. No.		Electronic configuration
Yttrium	*Y*	39		$[Kr]\,4d^1 5s^2$
Zirconium	*Zr*	40		$[Kr]\,4d^2 5s^2$
Niobium	*Nb*****	41		$[Kr]\,4d^4 5s^1$
Molybdenum	*Mo*****	42		$[Kr]\,4d^5 5s^1$
Technetium	*Tc*	43	4*d*-orbitals are filled up	$[Kr]\,4d^5 5s^2$
Ruthenium	*Ru*****	44		$[Kr]\,4d^7 5s^1$
Rhodium	*Rh*****	45		$[Kr]\,4d^8 5s^1$
Palladium	*Pd*****	46		$[Kr]\,4d^{10} 5s^0$
Silver	*Ag*****	47		$[Kr]\,4d^{10} 5s^1$
Cadmium	*Cd*	48		$[Kr]\,4d^{10} 5s^2$

Table : 19.3 Third transition or 5*d*-series :

Element	Symbol	At. No.		Electronic configuration
Lanthanum	*La*	57		$[Xe]\,5d^1 6s^2$
Hafnium	*Hf*	72	5*d*-orbitals are filled	$[Xe]\,4f^{14} 5d^2 6s^2$
Tantalum	*Ta*	73		$[Xe]\,4f^{14} 5d^3 6s^2$

Tungsten	W	74	$[Xe] 4f^{14}5d^46s^2$
Rhenium	Re	75	$[Xe] 4f^{14}5d^56s^2$
Osmium	Os	76	$[Xe] 4f^{14}5d^66s^2$
Iridium	Ir	77	$[Xe] 4f^{14}5d^76s^2$
Platinum	Pt^*	78	$[Xe] 4f^{14}5d^{10}6s^0$
Gold	Au^*	79	$[Xe] 4f^{14}5d^{10}6s^!$
Mercury	Hg	80	$[Xe] 4f^{14}5d^{10}6s^2$

Table : 19.4 Fourth transition or 6d-series :

Element	Symbol	At. No.		Electronic configuration
Actinium	Ac	89		$[Rn] 6d^17s^2$
Rutherfordium	Rf	104		$[Rn] 5f^{14}6d^27s^2$
Hahnium	Ha	105	6d-orbitals are filled up	$[Rn] 5f^{14}6d^37s^2$
Seaborgium	Sg	106		$[Rn] 5f^{14}6d^47s^2$
Bohrium	Bh	107		$[Rn] 5f^{14}6d^57s^2$
Hassium	Hs	108		$[Rn] 5f^{14}6d^67s^2$
Meitnerium	Mt	109		$[Rn] 5f^{14}6d^77s^2$
Ununnilium	Uun	110		$[Rn] 5f^{14}6d^87s^2$
Unununium	Uuu	111		$[Rn] 5f^{14}6d^97s^2$
Unubium	Uub	112		$[Rn] 5f^{14}6d^{10}7s^2$

Elements marked with asterisk have anomalous configurations. These are attributed to factors like nuclear-electron and electron-electron forces and stability of half filled and full filled orbital.

All transition elements are *d* block elements but all *d* block elements are not transition elements.

Physico-Chemical Properties of d-Block Elements

(1) **Atomic radii :** The atomic, radii of 3*d*-series of elements are compared with those of the neighbouring *s* and *p*-block elements.

K	Ca	Sc	Ti	V	Cr	Mn
227	197	144	132	122	117	117
Fe	Co	Ni	Cu	Zn	Ga	Ge
117	116	115	117	125	135	122^*

* in pm units

The atomic radii of transition elements show the following characteristics,

(i) The atomic radii and atomic volumes of *d*-block elements in any series decrease with increase in the atomic number. The decrease however, is not regular. The atomic radii tend to reach minimum near at the middle of the series, and increase slightly towards the end of the series.

Explanation : When we go in any transition series from left, to right, the nuclear charge increases gradually by one unit at each elements. The added electrons enter the same penultimate shell, (inner *d*-shell). These added electrons shield the outermost electrons from the attraction of the nuclear charge. The increased nuclear charge tends to reduce the atomic radii, while the added electrons tend to increase the atomic radii. At the beginning of the series, due to smaller number of electrons in the *d*-orbitals, the effect of increased nuclear charge predominates, and the atomic radii decrease. Later in the series, when the number of *d*-electrons increases, the increased shielding effect and the increased repulsion between the electrons tend to increase the atomic radii. Somewhere in the middle of the series, therefore the atomic radii tend to have a minimum value as observed.

(ii) The atomic radii increase while going down in each group. However, in the third transition series from hafnium (*Hf*) and onwards, the elements have atomic radii nearly equal to those of the second transition elements.

Explanation : The atomic radii increase while going down the group. This is due to the introduction of an additional shell at each new element down the group. Nearly equal radii of second and third transition series elements is due to a special effect called **lanthanide contraction**.

(2) **Ionic radii :** For ions having identical charges, the ionic radii decrease slowly with the increase in the atomic number across a given series of the transition elements.

Elements (m):	Ionic radius,$(M^{2+})/pm$:	$Pm:(M^{3+})/pm$:
Sc	–	81
Ti	90	76
V	88	74
Cr	84	69
Mn	80	66
Fe	76	64
Co	74	63
Ni	72	–
Cu	69	–
Zn	74	–

Explanation : The gradual decrease in the values of ionic radius across the series of transition elements is due to the increase in the **effective nuclear charge**.

(3) **Ionisation energies :** The ionisation energies of the elements of first transition series are given below:

Elements	I_1	I_2	I_3
Sc	632	1245	2450
Ti	659	1320	2721
V	650	1376	2873
Cr	652	1635	2994
Mn	716	1513	3258
Fe	762	1563	2963
Co	758	1647	3237
Ni	736	1756	3400
Cu	744	1961	3560
Zn	906	1736	3838

* in *kJ mol*$^{-1}$

The following generalizations can be obtained from the ionisation energy values given above.

(i) The ionisation energies of these elements are high and in the most cases lie between those of *s*- and *p*-block elements. This indicates that the transition elements are less electropositive than *s*-block elements.

Explanation : Transition metals have smaller atomic radii and higher nuclear charge as compared to the alkali metals. Both these factors tend to increase the ionisation energy, as observed.

(ii) The ionisation energy in any transition series increases in the nuclear with atomic number; the increase however is not smooth and as sharp as seen in the case of *s* and *p*-block elements.

Explanation : The ionisation energy increases due to the increase in the nuclear charge with atomic number at the beginning of the series. Gradually, the shielding effect of the added electrons also increases. This **shielding effect** tends to decrease the attraction due to the nuclear charge. These two opposing factors lead to a rather gradual increase in the ionisation energies in any transition series.

(iii) The first ionisation energies of 5*d*-series of elements are much higher than those of the 3*d* and 4*d* series elements.

Explanation : In the 5*d*-series of transitions elements, after lanthanum (*La*), the added electrons go to the next inner 4*f* orbitals. The 4*f* electrons have poor shielding effect. As a result, the outermost electrons experience greater nuclear attraction. This leads to higher ionisation energies for the 5*d*- series of transition elements.

(4) **Metallic character :** All the transition elements are metals. These are hard, and good conductor of heat and electricity. All these metals are malleable, ductile and form alloys with other metals.

These elements occur in three types *e.g.*, face- centered cubic (*fcc*), hexagonal close-packed (*hcp*) and body-centered cubic (*bcc*), structures.

The transition elements shows both covalent as well as metallic bonding amongst their atoms.

Explanation : The ionisation energies of the transition elements are not very high. The outermost shell in their atoms have many vacant, **partially filled orbitals**. These characteristics make these elements metallic in character. The hardness of these metals, suggests the presence of covalent bonding in these metals. The presence of unfilled *d*-orbitals favour covalent bonding. Metallic bonding in these metals is indicated by the conducting nature of these metals. Therefore, it appears that there exists covalent and metallic bonding in transition elements.

(5) **Melting and boiling points :** The melting and boiling points of transition elements except *Cd* and *Hg*, are very high as compared to the s-block and *p*-block elements. The melting and boiling points **first increase**, pass through maxima and then **steadily decrease** across any transition series. The maximum occurs around middle of the series.

Explanation : Atoms of the transition elements are closely packed and held together by strong metallic bonds which have appreciable covalent character. This leads to high melting and boiling points of the transition elements.

The strength of the metallic bonds depends upon the number of unpaired electrons in the outermost shell of the atom. Thus, greater is the number of unpaired electrons stronger is the metallic bonding. In any transition element series, the number of unpaired electrons first increases from 1 to 5 and then decreases back to the zero .The maximum five unpaired electrons occur at *Cr* (3*d* series). As a result, the melting and boiling points first increase and then decrease showing maxima around the middle of the series.

The low melting points of *Zn, Cd,* and *Hg* may be due to the absence of **unpaired *d*-electrons** in their atoms.

(6) **Enthalpies of atomization :** Transition metals exhibit high enthalpies of atomization.

Explanation : This is because the atoms in these elements are closely packed and held together by strong metallic bonds. The metallic bond is formed as a result of the interaction of electrons in the outermost shell. Greater the number of valence electrons, stronger is the metallic bond.

(7) **Oxidation states :** Most of the transition elements exhibit several oxidation states *i.e.*, they show variable valency in their compounds. Some common oxidation states of the first transition series elements are given below in table,

Outer Ele. Confi. and O. S. for 3d- elements

Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1\,4s^2$	+ 2, + 3
Ti	$3d^2\,4s^2$	+ 2, + 3, + 4
V	$3d^3\,4s^2$	+ 2, + 3, + 4, + 5
Cr	$3d^5\,4s^1$	+ 1, + 2, + 3, + 4, + 5, + 6
Mn	$3d^5 4s^2$	+ 2, + 3, + 4, + 5, + 6, + 7
Fe	$3d^6 4s^2$	+ 2, + 3, + 4, + 5, + 6
Co	$3d^7 4s^2$	+ 2, + 3, + 4
Ni	$3d^8 4s^2$	+ 2, + 3, + 4
Cu	$3d^{10} 4s^1$	+ 1, + 2
Zn	$3d^{10} 4s^2$	+ 2

***Explanation* :** The outermost electronic configuration of the transition elements is $(n - 1)d^{1-10}ns^2$. Since, the energy levels of $(n-1)d$ and ns-orbitals are quite close to each other, hence both the ns and $(n-1)$ d-electrons are available for bonding purposes. Therefore, the number of oxidation states show by these elements depends upon the number of d-electrons it has. For example, Sc having a configuration $3d^1 4s^2$ may show an oxidation state of + 2 (only s-electrons are lost) and + 3 (when d-electron is also lost). The highest oxidation state which an elements of this group might show is given by the total number of ns and $(n -1)$ d-electrons.

The relative stability of the different oxidation states depends upon the factors such as, electronic configuration, nature of bonding, stoichiometry, lattice energies and solvation energies. The highest oxidation states are found in fluorides and oxides because fluorine and oxygen are the most electronegative elements. The highest oxidation state shown by any transition metal is eight. The oxidation state of eight is shown by **Ru and Os**.

An examination of the common oxidation states reveals the following conclusions.

(i) The variable oxidation states shown by the transition elements are due to the participation of **outer ns and inner $(n–1)d$-electrons** in bonding.

(ii) Except scandium, the most common oxidation state shown by the elements of first transition series is +2. This oxidation state arises from the loss of two $4s$ electrons. This means that after scandium, d-orbitals become more stable than the s-orbital.

(iii) The highest oxidation states are observed in fluorides and oxides. The highest oxidation state shown by any transition elements (by Ru and Os) is 8.

(iv) The transition elements in the + 2 and + 3 oxidation states mostly form ionic bonds. In compounds of the higher oxidation states (compound formed with fluorine or oxygen), the bonds are essentially covalent. For example, in permanganate ion MnO_4^-, all bonds formed between manganese and oxygen are covalent.

(v) Within a group, the maximum oxidation state increases with atomic number. For example, iron shown the common oxidation state of + 2 and + 3, but ruthenium and osmium in the same group form compounds in the + 4, + 6 and + 8 oxidation states.

(vi) Transition metals also form compounds in low oxidation states such as +1 and 0. For example, nickle in, nickel tetracarbonyl, $Ni(CO)_4$ has **zero oxidation state**. Similarly Fe in $(Fe(CO)_5$ has **zero oxidation state**.

The bonding in the compounds of transition metals in low oxidation states is not always very simple.

(vii) ***Ionisation energies and the stability of oxidation states*** :The values of the ionisation energies can be used in estimating the relative stability of various transition metal compounds (or ions). For example, Ni^{2+} compounds are found to be thermodynamically more stable than Pt^{2+}, whereas Pt^{4+} compounds are more stable than Ni^{4+} compounds. The relative stabilities of Ni^{2+} relative to Pt^{2+} and that of Pt^{4+} relative to Ni^{4+} can be explained as follows,

The first four ionisation energies of Ni and Pt

Metal	(IE_1+IE_2) $kJmol^{-1}$,	(IE_3+IE_4) $kJmol^{-1}$,	Etotal, $kJ\,mol^{-1}$ (= $IE_1 + IE_2 + IE_3 + IE_4$)
Ni	2490	8800	11290
Pt	2660	6700	9360

Thus, the ionisation of Ni to Ni^{2+} requires lesser energy (2490 $kJ\,mol^{-1}$) as compared to the energy required for the production of Pt^{2+} (2660 $kjmol^{-1}$). Therefore, Ni^{2+} compounds are thermodynamically more stable than Pt^{2+} compounds.

On the other hand, formation of Pt^{4+} requires lesser energy (9360 $kJ\,mol^{-1}$) as compared to that required for the formation of Ni^{4+}(11290 $kJ\,mol^{-1}$). Therefore, Pt^{4+} compounds are more stable than Ni^{4+} compounds.

This is supported by the fact that $[PtCl_6]^{2-}$ complex ion is known, while the corresponding ion for nickel is not known. However, other factors which affect the stability of a compound are,

(a) Enthalpy of sublimation of the metal.

(b) Lattice and the solvation energies of the compound or ion.

(viii) Transition elements like *Sc*, *Y*, *La* and *Ac* do not show variable valency.

(8) **Electrode potentials** (E^o) **:** Standard electrode potentials of some half–cells involving 3*d*-series of transition elements and their ions in aqueous solution are given in table,

Standard electrode potentials for 3*d*-elements

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

The negative values of E^o for the first series of transition elements (except for Cu^{2+}/Cu) indicate that,

(i) These metals should liberate hydrogen from dilute acids i.e., the reactions,

$M + 2H^+ \rightarrow M^{2+} + H_2 (g)$; $2M + 6H^+ \rightarrow 2M^{3+} + 3H_2(g)$
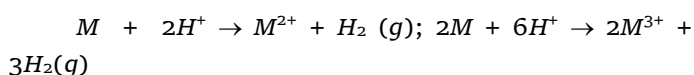
are favourable in the forward direction. In actual practice however, most of these metals react with dilute acids very slowly. Some of these metals get coated with a **thin protective layer** of oxide. Such an oxide layer prevents the metal to react further.

(ii) These metals should act as good reducing agents. There is no regular trend in the E^o values. This is due to irregular variation in the ionisation and sublimation energies across the series.

Relative stabilities of transition metal ions in different oxidation states in aqueous medium can be predicted from the electrode potential data. To illustrate this, let us consider the following,

$M(s) \rightarrow M(g)$; $\Delta H_1 =$ Enthalpy of sublimation, ΔH_{sub}

$M(g) \rightarrow M^+(g) + e^-$; $\Delta H_2 =$ Ionisation energy , IE

$M^+(g) \rightarrow M^+(aq)$; $\Delta H_3 =$ Enthalpy of hydration, ΔH_{hyd}
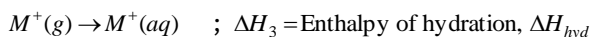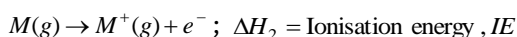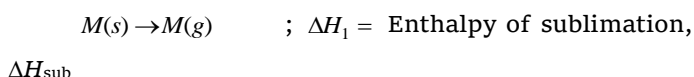
Adding these equations one gets,
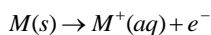
$M(s) \rightarrow M^+(aq) + e^-$

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{sub} + IE + \Delta H_{hyd}$

The ΔH represents the enthalpy change required to bring the solid metal M to the monovalent ion in aqueous medium, M^+(aq).

The reaction, $M(s) \rightarrow M^+$(aq) $+e^-$, will be favourable only if ΔH is negative. More negative is the value is of ΔH, more favourable will be the formation of that cation from the metal. Thus, the oxidation state for which ΔH value is more negative will be stable in the solution.

Electrode potential for a M^{n+}/M half-cell is a measure of the tendency for the reaction, M^{n+}(aq) $+ ne^- \rightarrow M (s)$

Thus, this reduction reaction will take place if the electrode potential for M^{n+}/M half- cell is positive. The reverse reaction, $M(s) \rightarrow M^{n+}$(aq) $+ ne^-$

Involving the formation of M^{n+}(aq) will occur if the electrode potential is negative, *i.e.*, the tendency for the formation of M^{n+}(aq) from the metal M will be more if the corresponding E^o value is more negative. In other words, *the oxidation state for which E^o value is more negative (or less positive) will be more stable in the solution*.

When an elements exists in more than one oxidation states, the standard electrode potential (E^o) values can be used in the predicting the relative stabilities of different oxidation states in aqueous solutions. The following rule is found useful.

The oxidation state of a cation for which $\Delta H = (\Delta H_{sub} + lE + \Delta H_{hyd})$ *or E^o is more negative (for less positive) will be more stable.*

(9) **Formation of coloured ions :** Most of the compound of the transition elements are coloured in the solid state and /or in the solution phase. The compounds of transition metals are coloured due to the presence of unpaired electrons in their *d*-orbitals.

***Explanation* :** In an isolated atom or ion of a transition elements, all the five *d*-orbitals are of the same energy (they are said to be regenerate). Under the influence of the combining anion (*s*), or electron-rich molecules, the five *d*-orbitals split into two (or sometimes more than two) levels of different energies. The difference between the two energy levels depends upon the nature of the combining ions, but corresponds to the energy associated with the radiations in the visible region $(\lambda = 380 - 760 nm)$. Typical splitting for octahedral and tetrahedral geometries are shown in fig.

Promotion of d-electron to a higher level
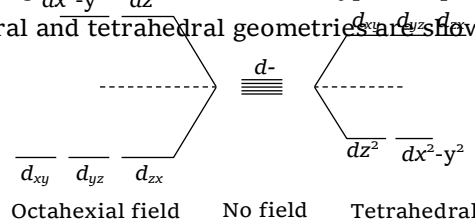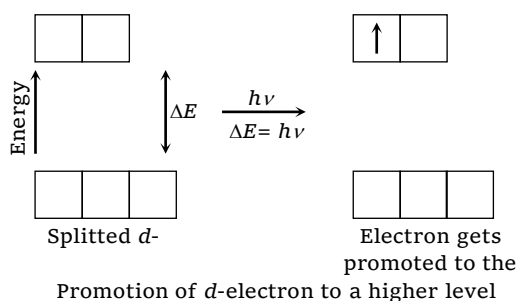
The transition metals in elements form or in the ionic form have one or more unpaired electrons. When visible light falls on the sample, the electrons from the lower energy level get promoted to a higher energy level due to the absorption of light of a characteristic wavelength (or colour). This wavelength (or colour) of the absorbed light depends upon the energy difference of the two levels. Rest of the light gets transmitted. The transmitted light has a colour complementary to the absorbed colour. Therefore, the compound or the solution appears to be of the complementary colour. For example, $Cu(H_2O)_6^{2+}$ ions absorb red radiation, and appear **blue-green** (blue-green is complementary colour to red). Hydrated Co^{2+} ions absorb radiation in the blue-green region, and therefore, appear red in sunlight. Relationship between the colour of the absorbed radiation and that of the transmitted light is given in table

Relationship between the colours of the absorbed and transmitted light: the complementary colours.

Colour of the		Colour of the	
Absorbed light	Transmitted light	Absorbed light	Transmitted light
IR	White	Blue-green	Red
Red	Blue-green	Blue	Orange
Orange	Blue	Indigo	Yellow
Yellow	Indigo	Violet	Yellow-green
Yellow-green	Violet	UV	White
Green	Purple		

However, if radiations of all the wavelengths (or colours) except one are absorbed, then the colour of the substance will be the colour of the transmitted radiation. For example, if a substance absorbs all colours except green, then it would appear green to the eyes.

The transition metal ions which have completely filled d-orbitals are colourless, as there are no vacant d-orbitals to permit promotion of the electrons. Therefore, Zn^{2+} ($3d^{10}$), $Cd^2 + (4d^{10})$ and $Hg^{2+}(5d^{10})$ Sc^{3+}, Ti^{4+}, Cu^+ ions and Zn, Cd, Hg are colourless and diamagnetic. The transition metal ions which have completely empty d-orbitals are also colourless, Thus, Sc^{3+} and Ti^{4+} ions are colourless, unless a coloured anion is present in the compound.

Colours and the outer- electronic configurations of the some important ions of the first transition series elements are given bellow,

Ion	Outer configuration	Number of unpaired electrons	Colour of the ion
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{2+}	$3d^5$	5	Light pink
Mn^{3+}	$3d^4$	4	Violet
Fe^{2+}	$3d^6$	4	Green
Fe^{3+}	$3d^5$	5	Yellow
Co^{3+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^+	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

(10) **Magnetic properties :** Most of the transition elements and their compounds show **paramagnetism**. The paramagnetism first increases in any transition element series, and then decreases. The maximum paramagnetism is seen around the middle of the series. The paramagnetism is described in **Bohr Magneton** (BM) units. The paramagnetic moments of some common ions of first transition series are given below in Table

Explanation : A substance which is attracted by magnetic filed is called paramagnetic substance. The substances which are repelled by magnetic filed are,

called **diamagnetic substances**. Paramagnetism is due to the presence of unpaired electrons in atoms, ions or molecules.

The magnetic moment of any transition element or its compound/ion is given by (assuming no contribution from the orbital magnetic moment).

$$\mu_s = \sqrt{4S(S+1)} \qquad BM = \sqrt{n(n+2)} \quad BM$$

where, S is the total spin $(n \times s)$: n is the number of unpaired electrons and s is equal to ½ (representing the spin of an unpaired electron).

From the equation given above, the magnetic moment (μ_s) increases with an increase in the number of unpaired electrons.

Magnetic moments of some ions of the 3d-*series elements*

Ion	Outer configuration	No. of unpaired electrons	Magnetic moment (BM)	
			Calculated	observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.86
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.95
Fe^{2+}	$3d^6$	4	4.90	5.0-5.5
Co^{2+}	$3d^7$	3	3.87	4.4-5.2
Ni^{2+}	$3d^8$	2	2.84	2.9-3.4
Cu^{2+}	$3d^9$	1	1.73	1.4-2.2
Zn^{2+}	$3d^{10}$	0	0	0

In d-obitals belonging to a particular energy level, there can be at the maximum five unpaired electrons in d^5 cases. Therefore, paramagnetism in any transition series first increases, reaches a maximum value for d^5 cases and then decreases thereafter.

(11) **Formation of complex ions :** Transition metals and their ions show strong tendency for complex formation. The cations of transition elements (d-block elements) form complex ions with certain molecules containing one or more lone-pairs of electrons, viz., CO, NO, NH_3 etc., or with anions such as, F^-, Cl^-, CN^- etc. A few typical complex ions are,

$[Fe(CN)_6]^{4-}, [Cu(NH_3)_4]^{2+}, [Y(H_2O)_6]^{2+}$,

$[Ni(CO)_4], [Co(NH_3)_6]^{3+} [FeF_6]^{3-}$
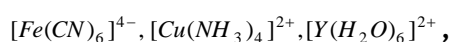
Explanation **:** This complex formation tendency is due to,

(i) Small size and high nuclear charge of the transition metal cations.

(ii) The availability to vacant inner d-orbitals of suitable energy.

(12) **Formation of interstitial compounds :** Transition elements form a few interstitial compounds with elements having small atomic radii, such as hydrogen, boron, carbon and nitrogen. The small atoms of these elements get entrapped in between the void spaces (called interstices) of the metal lattice. Some characteristics of the interstitial compound are,

(i) These are non-stoichiometric compounds and cannot be given definite formulae.

(ii) These compounds show essentially the same chemical properties as the parent metals, but differ in physical properties such as density and hardness. Steel and cast iron are hard due to the formation of interstitial compound with carbon. Some non-stoichimetric compounds are, $VSe_{0.98}$ (Vanadium selenide), $Fe_{0.94}O$ and titanium nitride.

Explanation **:** Interstital compounds are hared and dense. This is because, the smaller atoms of lighter elements occupy the interstices in the lattice, leading to a more closely packed structure. Due to greater electronic interactions, the strength of the metallic bonds also increases.

(13) **Catalytic properties :** Most of the transition metals and their compounds particularly oxides have good catalytic properties. Platinum, iron, vanadium pentoxide, nickel, etc., are important catalysts. Platinum is a general catalyst. Nickel powder is a good catalyst for hydrogenation of unsaturated organic compound such as, hydrogenation of oils some typical industrial catalysts are,

(i) Vanadium pentoxide (V_2O_5) is used in the Contact process for the manufacture of sulphuric acid,

(ii) Finely divided iron is used in the Haber's process for the synthesis of ammonia.

Explanation **:** Most transition elements act as good catalyst because of,

(i) The presence of vacant d-orbitals.

(ii) The tendency to exhibit variable oxidation states.

(iii) The tendency to form reaction intermediates with reactants.

(iv) The presence of defects in their crystal lattices.

(14) **Alloy formation :** Transition metals form alloys among themselves. The alloys of transition metals are hard and high metals are high melting as compared to the host metal. Various steels are alloys of iron with metals such as chromium, vanadium, molybdenum, tungsten, manganese etc.

Explanation : The atomic radii of the transition elements in any series are not much different from each other. As a result, they can very easily replace each other in the lattice and form solid solutions over an appreciable composition range. Such solid solutions are called alloys.

(15) **Chemical reactivity** : The *d*-block elements (transition elements) have lesser tendency to react, *i.e.*, these are less reactive as compared to *s*-block elements.

Explanation : Low reactivity of transition elements is due to,

(i) Their high ionisation energies.

(ii) Low heats of hydration of their ions.

(iii) Their high heats of sublimation.

Chromium containing compounds

Potassium dichromate, ($K_2Cr_2O_7$)

Potassium dichromate is one of the most important compound of chromium, and also among dichromates. In this compound *Cr* is in the hexavalent (+6) state.

Preparation : It can be prepared by any of the following methods,

(i) *From potassium chromate* : Potassium dichromate can be obtained by adding a calculated amount of sulphuric acid to a saturated solution of potassium chromate.

$$\underset{\substack{\text{potassium chromate} \\ (yellow)}}{2K_2CrO_4} + H_2SO_4 \rightarrow \underset{\substack{\text{potassium dichromate} \\ (orange)}}{K_2Cr_2O_7} + K_2SO_4 + H_2O$$
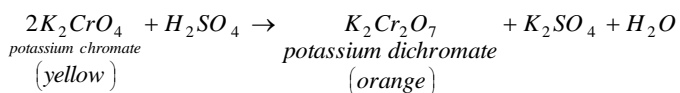
$K_2Cr_2O_7$ Crystals can be obtained by concentrating the solution and crystallisation.

(ii) *Manufacture from chromite ore* : $K_2Cr_2O_7$ is generally manufactured from chromite ore ($FeCr_2O_4$). The process involves the following steps.

(a) *Preparation of sodium chromate* : Finely powdered chromite ore is mixed with soda ash and quicklime. The mixture is then roasted in a reverberatory furnace in the presence of air. Yellow mass due to the formation of sodium chromate is obtained.

$$4FeCr_2O_4 + O_2 \rightarrow 2Fe_2O_3 + 4Cr_2O_3$$

$$4Cr_2O_3 + 8Na_2CO_3 + 6O_2 \rightarrow 8Na_2CrO_4 + 8CO_2(g)$$

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8CO_2(g) + \underset{\text{sodium chromate}}{8Na_2CrO_4}$$
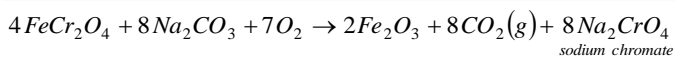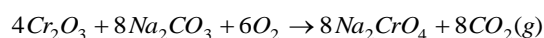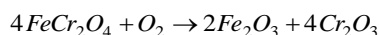
The yellow mass is extracted with water, and filtered. The filtrate contains sodium chromate.

The reaction may also be carried out by using $NaOH$ instead of Na_2CO_3. The reaction in that case is,

$$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$
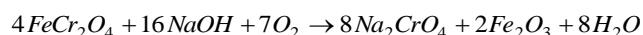
(b) *Conversion of chromate into dichromate* : Sodium chromate solution obtained in step (a) is treated with concentrated sulphuric acid when it is converted into sodium dichromate.

$$\underset{\text{sodium chromate}}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$
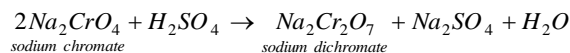
On concentration, the less soluble sodium sulphate, $Na_2SO_4.10H_2O$ crystallizes out. This is filtered hot and allowed to cool when sodium dichromate, $Na_2Cr_2O_7.2H_2O$, separates out on standing.

(c) *Concentration of sodium dichromate to potassium dichromate* : Hot concentrated solution of sodium dichromate is treated with a calculated amount of potassium chloride. When potassium dichromate being less soluble crystallizes out on cooling.

$$\underset{\text{sod .dichromate}}{Na_2Cr_2O_7} + 2KCl \rightarrow \underset{\text{pot .dichromate}}{K_2Cr_2O_7} + 2NaCl$$
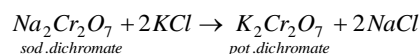
Physical properties

(i) Potassium dichromate forms orange-red coloured crystals.

(ii) It melts at 699 *K*.

(iii) It is very stable in air (near room temperature) and is generally, used as a primary standard in the volumetric analysis.

(iv) It is soluble in water though the solubility is limited.

Chemical properties

(i) *Action of heat* : Potassium dichromate when heated strongly. Decomposes to give oxygen.

$$4K_2Cr_2O_7(s) \xrightarrow{\Delta} 4K_2CrO_4(s) + 2Cr_2O_3(s) + 3O_2$$
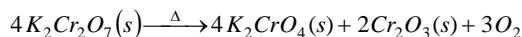
(ii) *Action of acids*

(a) In cold, with concentrated H_2SO_4, red crystals of chromium trioxide separate out.

$$K_2Cr_2O_7(aq) + conc.H_2SO_4 \rightarrow KHSO_4(aq) + 2CrO_3(s) + H_2O$$
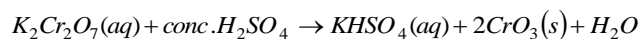
On heating a dichromate-sulphuric acid mixture, oxygen gas is given out.

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$
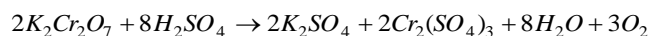
(b) With *HCl*, on heating chromic chloride is formed and Cl_2 is liberated.

$$K_2Cr_2O_{7(aq)} + 14HCl(aq) \rightarrow 2CrCl_{3(aq)} + 2KCl(aq) + 7H_2O + 3Cl_2(g)$$
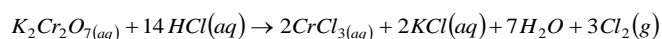
(iii) *Action of alkalies* : With alkalies, it gives chromates. For example, with *KOH*,

$$\underset{orange}{K_2Cr_2O_4} + 2KOH \rightarrow \underset{yellow}{2K_2CrO_4} + H_2O$$
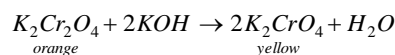
On acidifying, the colour again changes to orange-red owing to the formation of dichromate.

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$
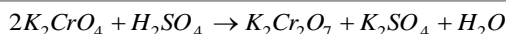
Actually, in dichromate solution, the $Cr_2O_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions.

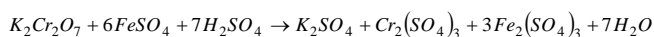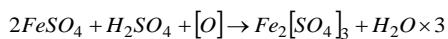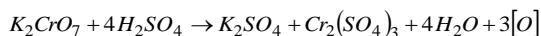$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$
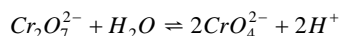
(iv) ***Oxidising nature*** : In neutral or in acidic solution, potassium dichromate acts as an excellent oxidising agent, and $Cr_2O_7^{2-}$ gets reduced to Cr^{3+}. The standard electrode potential for the reaction,
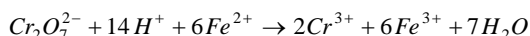
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O \text{ is } +1.31V.$$
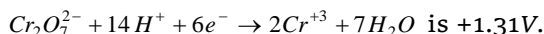
This indicates that dichromate ion is a fairly strong oxidising agent, especially in strongly acidic solutions. That is why potassium dichromate is widely used as an oxidising agent, for quantitative estimation of the reducing agents such as, Fe^{2+}. It oxidises,

(a) *Ferrous salts to ferric salts*

$$K_2CrO_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2[SO_4]_3 + H_2O \times 3$$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

Ionic equation

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

(b) *Sulphites to sulphates and arsenites to arsenates.*

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4] \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Na_2SO_4 + 4H_2O$$

Ionic equation

$$Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$
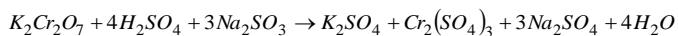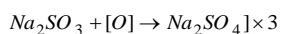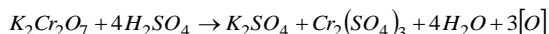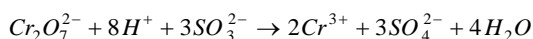
Similarly, arsenites are oxidised to arsenates.

$$Cr_2O_7^{2-} + 8H^+ + 3AsO_3^{3-} \rightarrow 2Cr^{3+} + 3AsO_4^{3-} + 4H_2O$$
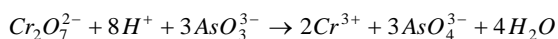
(c) *Hydrogen halides to halogens.*

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2HX + O \rightarrow H_2O + X_2] \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 6HX \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3X_2$$
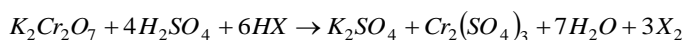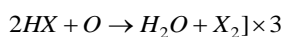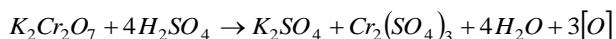
where, X may be Cl, Br, I.

Ionic equation :

$$Cr_2O_7^{2-} + 8H^+ + 6HX \rightarrow 2Cr^{3+} + 3X_2 + 7H_2O$$

(d) *Iodides to iodine*

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2KI + H_2O + [O] \rightarrow 2KOH + I_2] \times 3$$

$$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O] \times 3$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

Ionic equation :

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$$
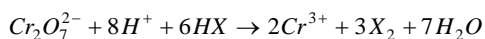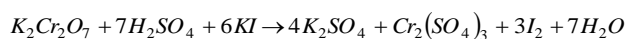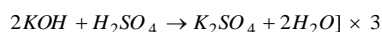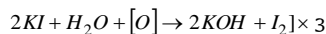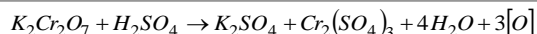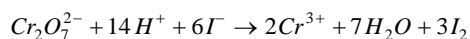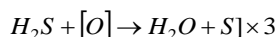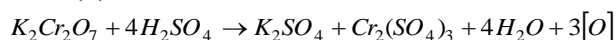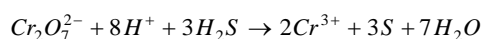
Thus, when KI is added to an acidified solution of $K_2Cr_2O_7$ iodine gets liberated.

(e) *It oxidises H_2S to S.*

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$H_2S + [O] \rightarrow H_2O + S] \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

Ionic equation

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$$
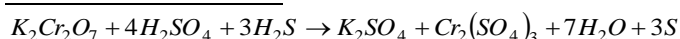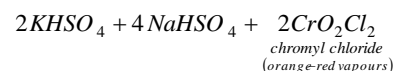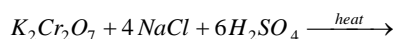
(v) ***Formation of insoluble chromates*** : With soluble salts of lead, barium etc., potassium dichromate gives insoluble chromates. Lead chromate is an important yellow pigment.

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightarrow 2PbCrO_4 + 2KNO_3 + 2HNO_3$$
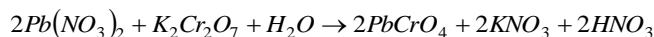
(vi) ***Chromyl chloride test*** : When potassium dichromate is heated with conc. H_2SO_4 in the presence of a soluble chloride salt, the orange-red vapours of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \xrightarrow{heat}$$

$$2KHSO_4 + 4NaHSO_4 + \underset{\substack{chromyl\ chloride \\ (orange\text{-}red\ vapours)}}{2CrO_2Cl_2}$$

Chromyl chloride vapours when passed through water give yellow-coloured solution containing chromic acid.

$$CrO_2Cl_2 + 2H_2O \rightarrow 2HCl + \underset{Chromic\ acid.(yellow\ solution)}{H_2CrO_4}$$
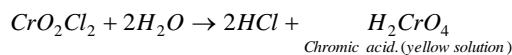
Chromyl chloride test can be used for the detection of chloride ion is any mixture.

Uses : Potassium dichromate is used as,

(i) An oxidising agent

(ii) In chrome tanning

(iii) The raw meterial for preparing large number of chromium compounds

(iv) Primary standard in the volumetric analysis.

Structures of Chromate and Dichromate Ions

Chromates and dichromates are the salts of chromic acid (H_2CrO_4). In solution, these ions exist in equilibrium with each other. Chromate ion has four oxygen atoms arranged tetrahedrally around Cr atom. (see Fig). Dichromate ion involves a $Cr-O-Cr$ bond as shown in Fig.
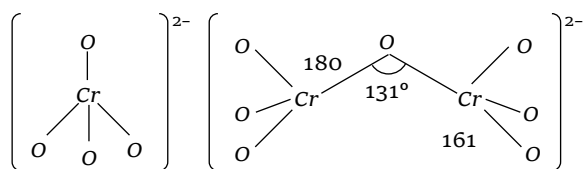
Chromate ion   Dichromate

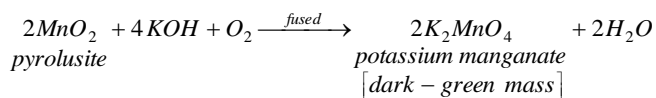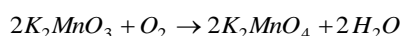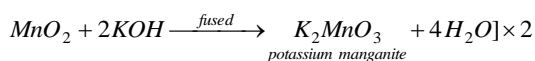The structure of chromate (CrO^{2-}_4) and dichromate

Manganese containing compound

Potassium Permanganate, ($KMnO_4$)

Potassium permanganate is a salt of an unstable acid $HMnO_4$ (permanganic acid). The Mn is an +7 state in this compound.

Preparation : Potassium permanganate is obtained from pyrolusite as follows.
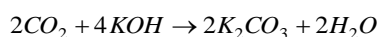
Conversion of pyrolusite to potassium manganate : When manganese dioxide is fused with potassium hydroxide in the presence of air or an oxidising agent such as potassium nitrate or chlorate, potassium manganate is formed, possibly via potassium manganite.

$$MnO_2 + 2KOH \xrightarrow{\text{fused}} \underset{\text{potassium manganite}}{K_2MnO_3} + 4H_2O] \times 2$$

$$2K_2MnO_3 + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$\underset{\text{pyrolusite}}{2MnO_2} + 4KOH + O_2 \xrightarrow{\text{fused}} \underset{\substack{\text{potassium manganate} \\ [\text{dark} - \text{green mass}]}}{2K_2MnO_4} + 2H_2O$$

Oxidation of potassium manganate to potassium permanganate : The potassium manganate so obtained is oxidised to potassium permanganate by either of the following methods.

By chemical method : The fused dark-green mass is extracted with a small quantity of water. The filtrate is warmed and treated with a current of ozone, chlorine or carbon dioxide. Potassium manganate gets oxidised to potassium permanganate and the hydrated manganese dioxide precipitates out. The reactions taking place are,
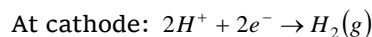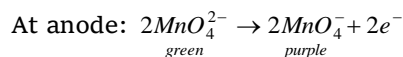
When CO₂ is passed

$$\underset{\text{potassium manganate}}{3K_2MnO_4} + 2H_2O \rightarrow \underset{\text{potassium permangana te}}{2KMnO_4} + MnO_2 \downarrow + 4KOH$$

$$2CO_2 + 4KOH \rightarrow 2K_2CO_3 + 2H_2O$$

When chlorine or ozone is passed

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2(g)$$
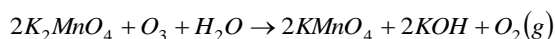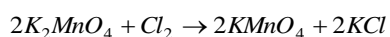
The purple solution so obtained is concentrated and dark purple, needle-like crystals having metallic lustre are obtained.

Electrolytic method : Presently, potassium manganate (K_2MnO_4) is oxidised electrolytically. The electrode reactions are,

At anode: $2MnO^{2-}_4 \underset{\text{green}}{} \rightarrow 2MnO^-_4 \underset{\text{purple}}{} + 2e^-$

At cathode: $2H^+ + 2e^- \rightarrow H_2(g)$

The purple solution containing $KMnO_4$ is evaporated under controlled condition to get crystalline sample of potassium permanganate.

Physical properties

$KMnO_4$ crystallizes as dark purple crystals with greenish luster (m.p. 523 K).

It is soluble in water to an extent of 6.5g per 100g at room temperature. The aqueous solution of $KMnO_4$ has a purple colour.
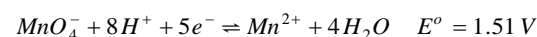
Chemical properties : Some important chemical reactions of $KMnO_4$ are given below,

Action of heat : $KMnO_4$ is stable at room temperature, but decomposes to give oxygen at higher temperatures.

$$2KMnO_4(s) \xrightarrow{\text{heat}} K_2MnO_4(s) + MnO_2 + O_2(g)$$
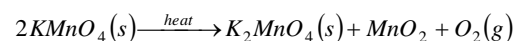
Oxidising actions : $KMnO_4$ is a powerful agent in neutral, acidic and alkaline media. The nature of reaction is different in each medium. The oxidising character of $KMnO_4$ (to be more specific, of MnO^-_4) is indicated by high positive reduction potentials for the following reactions.
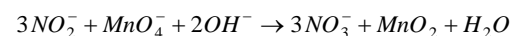
Acidic medium

$$MnO^-_4 + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad E^o = 1.51\,V$$

Alkaline medium

$$MnO^-_4 + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^- \quad E^o = 1.23\,V$$

In strongly alkaline solutions and with excess of MnO^-_4, the reaction is $MnO^-_4 + e^- \rightleftharpoons MnO^{2-}_4 \quad E^o = 0.56\,V$

There are a large number of oxidation-reduction reactions involved in the chemistry of manganese compounds. Some typical reactions are,

In the presence of excess of reducing agent in acidic solutions permanganate ion gets reduced to manganous ion, e.g.,
$$5Fe^{2+} + MnO^-_4 + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$
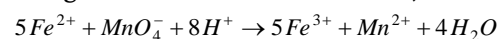
An excess of reducing agent in alkaline solution reduces permanganate ion only to manganese dioxide e.g.,

$$3NO^-_2 + MnO^-_4 + 2OH^- \rightarrow 3NO^-_3 + MnO_2 + H_2O$$

In faintly acidic and neutral solutions, manganous ion is oxidised to manganese oxidised to manganese dioxide by permanganate.
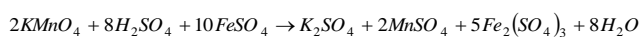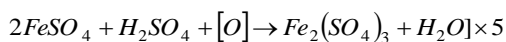
$$2MnO_4^- + 3Mn^{+2} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$
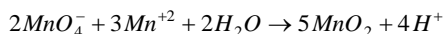
In strongly basic solutions, permangante oxidises manganese dioxide to manganate ion.

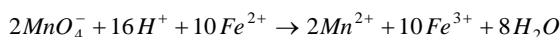$$MnO_2 + 2MnO_4^- + 4OH^- \rightarrow 3MnO_4^{2-} + 2H_2O$$

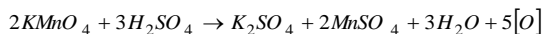In acidic medium, $KMnO_4$ oxidises,

Ferrous salts to ferric salts

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\underline{2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O] \times 5}$$

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

Ionic equation

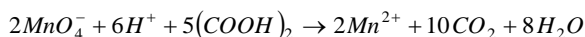$$2MnO_4^- + 16H^+ + 10Fe^{2+} \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$

The reaction forms the basis of volumetric estimation of Fe^{2+} in any solution by $KMnO_4$.
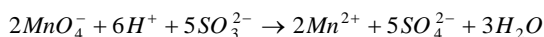
Oxalic acid to carbon dioxide

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\underline{(COOH)_2 + [O] \rightarrow 2CO_2 + H_2O] \times 5}$$

$$\overline{2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O}$$

Ionic equation

$$2MnO_4^- + 6H^+ + 5(COOH)_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Sulphites to sulphates

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\underline{Na_2SO_3 + [O] \rightarrow Na_2SO_4] \times 5}$$

$$\overline{2KMnO_4 + 3H_2SO_4 + 5Na_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 3H_2O}$$

Ionic equation

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$
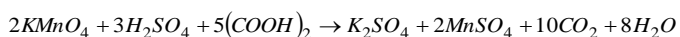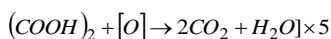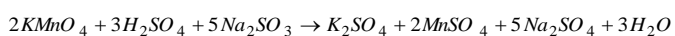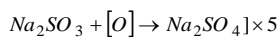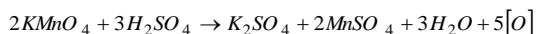
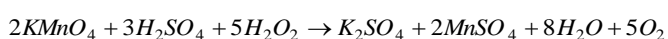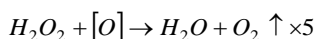### Iodides to iodine in acidic medium

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$2KI + H_2O + [O] \rightarrow I_2 + 2KOH \times 5$$

$$\underline{2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O] \times 5}$$

$$\overline{2KMnO_4 + 8H_2SO_4 + 10KI \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O}$$

Ionic equation

$$2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$
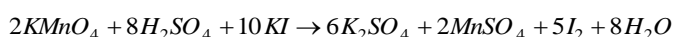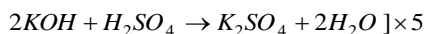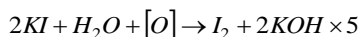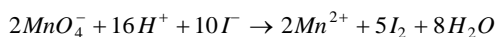
Hydrogen peroxide to oxygen

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\underline{H_2O_2 + [O] \rightarrow H_2O + O_2 \uparrow \times 5}$$

$$\overline{2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2}$$

Manganous sulphate ($MnSO_4$) to manganese dioxide (MnO_2)

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$$

$$MnSO_4 + H_2O + [O] \rightarrow MnO_2 + H_2SO_4 \times 3$$

$$\underline{2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O}$$

$$\overline{2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4}$$

Ionic equation

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

Ammonia to nitrogen

$$2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH + 3[O]$$

$$\underline{2NH_3 + 3[O] \rightarrow N_2(g) + 3H_2O}$$

$$\overline{2KMnO_4 + 2NH_3 \rightarrow 2MnO_2 + 2KOH + 2H_2O + N_2(g)}$$
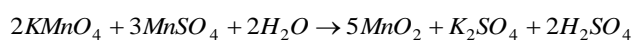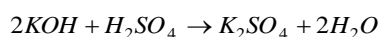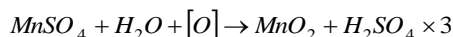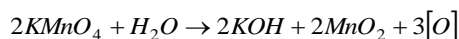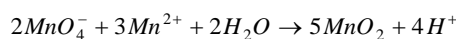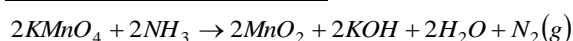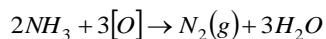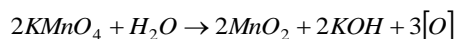
Uses : $KMnO_4$ is used,

(i) As an oxidising agent. (ii) As a disinfectant against disease-causing germs. (iii) For sterilizing wells of drinking water. (iv) In volumetric estimation of ferrous salts, oxalic acid etc. (v) Dilute alkaline $KMnO_4$ solution known as **Baeyer's reagent**.

Structure of Permanganate Ion (MnO_4^-) : Mn in MnO_4^- is in +7 oxidation state. Mn^{7+} exhibits sp^3 hybridisation in this ion. The structure of MnO_4^- is, shown in fig.
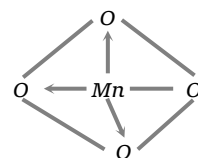

Strucutre of MnO_4^- ion

Iron and its Compounds

(1) **Ores of iron :** Haematite Fe_2O_3, Magnetite (Fe_3O_4), Limonite ($Fe_2O_3.3H_2O$), Iron pyrites (FeS_2), Copper pyrities ($CuFeS_2$) etc.

(2) **Extraction :** Cast iron is extracted from its oxides by reduction with carbon and carbon monoxide in a blast furnace to give pig iron.

Roasting **:** Ferrous oxide convert into ferric oxide.

$$Fe_2O_3.3H_2O \rightarrow Fe_2O_3 + 3H_2O \; ; \; 2FeCO_3 \rightarrow 2FeO + 2CO_2$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$
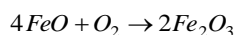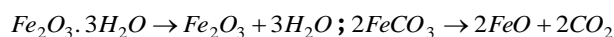
Smelting **:** Reduction of roasted ore of ferric oxide carried out in a blast furnace.

(i) The reduction of ferric oxide is done by carbon and carbon monoxide (between $1473k$ to $1873k$)

$2C + O_2 \rightarrow 2CO$
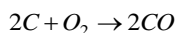
(ii) $Fe_2O_3 + 3CO \xrightleftharpoons{673\ K} 2Fe + 3CO_2$. It is a reversible and exothermic reaction. Hence according to *Le-chatelier* principle more iron will be produced in the furnace at lower temp. $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$
(it is not reversible)

(iii) $FeO + C \xrightarrow[\substack{\text{endothermi c} \\ \text{reaction}}]{1073\ K} Fe + CO$
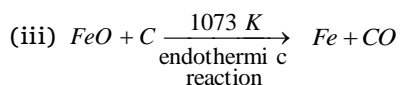
The gases leaving at the top of the furnace contain up to 28% *CO* and are burnt in **cowper's stove** to pre-heat the air for blast

Varieties of iron : The three commercial varieties of iron differ in their carbon contents. These are;

(1) **Cast iron or Pig-iron :** It is most impure form of iron and contains highest proportion of carbon (2.5–4%).

(2) **Wrought iron or Malleable iron :** It is the purest form of iron and contains minimum amount of carbon (0.12–0.25%).

(3) **Steel :** It is the most important form of iron and finds extensive applications. Its carbons content (Impurity) is mid-way between cast iron and wrought iron. *It contains 0.2–1.5% carbon. Steels containing 0.2–0.5% of carbon are known as mild steels, while those containing 0.5–1.5% carbon are known as hard steels.*

Steel is generally manufactured from cast iron by three processes, *viz*, (i) Bessemer Process which involves the use of a large pear-shaped furnace (vessel) called Bessemer converter, (ii) L.D. process and (iii) open hearth process, Spiegeleisen (an alloy of *Fe, Mn* and *C*) is added during manufacture of steel.

Heat treatment of steels **:** Heat treatment of steel may be defined as the process of carefully heating the steel to high temperature followed by cooling to the room temperature under controlled conditions. Heat treatment of steel is done for the following two purposes,

(i) To develop certain special properties like hardness, strength, ductility etc. without changing the chemical composition.

(ii) To remove some undesirable properties or gases like entrapped gases, internal stresses and strains. The various methods of heat treatment are,

(a) *Annealing :* It is a process of heating steel to redness followed by slow cooling.

(b) *Quenching or hardening :* It is a process of heating steel to redness followed by sudden cooling by plunging the red hot steel into water or oil.

(c) *Tempering :* It is a process of heating the hardened or quenched steel to a temperature much below redness (473–623K) followed by slow cooling.

(d) *Case-hardening :* It is a process of giving a thin coating of hardened steel to wrought iron or to a strong and flexible mild steel by heating it in contact with charcoal followed by quenching in oil.

(e) *Nitriding :* It is a process of heating steels at about $700\ ^oC$ in an atmosphere of ammonia. This process imparts a hard coating of iron nitride on the surface of steel.

***Properties of steel* :** The properties of steel depend upon its carbon contents. With the increase in carbon content, the hardness of steel increases while its ductility decreases.

(i) Low carbon or soft steels contain carbon upto 0.25%.

(ii) Medium carbon steels or mild steels contain 0.25–0.5% carbon.

(iii) High carbon or hard steels contains 0.1 – 1.5 percent carbon.

(iv) Alloy steels or special steels are alloys of steel with Ni, Cr, Co, W, Mn, V etc., For example

(a) Stainless steel (*Fe* = 73%, *Cr* = 18%, *Ni* = 8% + *C*) is resistant to corrosion and is used for making ornamental pieces, cutlery etc.

(b) Invar (*Fe* = 64%, *Ni* = 36%) has small coefficient of expansion and is used for making metre scales, pendulum rods and watches.

(c) Manganese steel (*Fe* = 86%, *Mn* 13% + carbon) is very hard and resistant to wear and hence is used for making rock drills, safes etc.

(d) Tungsten steel (*Fe* = 94%, *W* = 5% + carbon) is quite hard and is used for making high speed cutting tools.

(e) Permalloy (*Fe* = 21%, *Ni* = 78% + carbon) is strongly magnetised by electric current but loses magnetism when current is cut off. It is used for making electromagnets, ocean cables etc.

Properties of iron

(1) Dry or moist air has no action on pure iron but impure iron when exposed to moist air is covered with a layer of rust $Fe_2O_3 + Fe(OH)_3$. However, finely divided pure iron burns in air or oxygen forming Fe_3O_4 (magnetic oxide of iron).

$3Fe + 2O_2 \rightarrow Fe_3O_4$
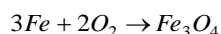
(2) Iron decomposes steam at red heat

$3Fe + 4H_2O \xrightarrow[\text{Steam}]{\text{Red heat}} Fe_3O_4 + 4H_2$
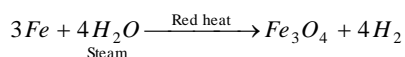
(3) **Action of acids** : Iron reacts with dil. *HCl* and dil. H_2SO_4 liberating hydrogen. with hot conc. H_2SO_4 , it gives SO_2, with dil. HNO_3, it gives NH_4NO_3 and moderately conc. HNO_3 reacts with iron forming NO_2.
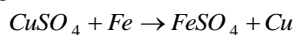
Cold conc. HNO_3 makes iron passive due to the deposit of a thin layer of iron oxide (Fe_3O_4) on the surface.
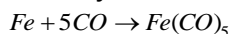
Hot conc. HNO_3 reacts with iron liberating NO.

$$Fe + 4HNO_3(\text{hot conc.}) \rightarrow Fe(NO_3)_3 + NO + 2H_2O$$
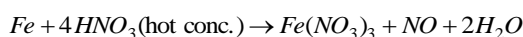
(4) Iron does not react with alkalies.

(5) It displaces less electropositive metals (*e.g.*, *Cu*, *Ag* etc.) from their salts

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

(6) Finely divided iron combines with *CO* forming penta carbonyl
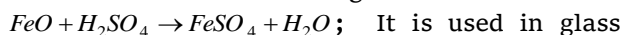
$$Fe + 5CO \rightarrow Fe(CO)_5$$

(7) Iron does not form amalgam with *Hg*.

(8) Iron is the most abundant and most widely used transition metal.

Compounds of iron

(1) **Oxides of Iron :** Iron forms three oxides FeO, Fe_2O_3 (Haematite), Fe_3O_4 (magnetite also called magnetic oxide or load stone).

(i) ***Ferrous oxide,*** *FeO* : It is a black powder, basic in nature and reacts with dilute acids to give ferrous salts.

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O\ ;\quad \text{It is used in glass}$$

industry to impart green colour to glass.

(ii) ***Ferric oxide*** Fe_2O_3 : It is a reddish brown powder, not affected by air or water; amphoteric in nature and reacts both with acids and alkalis giving salts. It can be reduced to iron by heating with *C* or *CO*.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO\ ;\quad Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

It is used as red pigment to impart red colour to external walls and as a polishing powder by jewellers.

(iii) ***Ferrosoferricoxide*** $Fe_3O_4(FeO.Fe_2O_3)$: It is more stable than FeO and Fe_2O_3, magnetic in nature and dissolves in acids giving a mixture of iron (II) and iron (III) salts.

$$Fe_3O_4 + 4H_2SO_4 \text{ (dil) } \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O$$
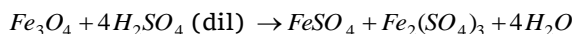
(2) **Ferrous sulphide** FeS : It is prepared by heating iron filing with sulphur. With dilute H_2SO_4, it gives H_2S. $\quad FeS + H_2SO_4 \text{ (dil) } \rightarrow FeSO_4 + H_2S \uparrow$

(3) **Ferric chloride** $FeCl_3$: (i) ***preparation*** : It is prepared by treating $Fe(OH)_3$ with HCl

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$$
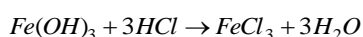
The solution on evaporation give yellow crystals of $FeCl_3.6H_2O$

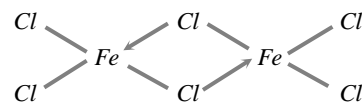(ii) ***Properties*** : (a) Anhydrous $FeCl_3$ forms reddish-black deliquescent crystals.

(b) $FeCl_3$ is hygroscopic and dissolves in H_2O giving brown acidic solution due to formation of HCl

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$
$$\text{(Brown)}$$
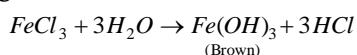
(c) Due to oxidising nature Fe^{3+} ions $FeCl_3$ is used in etching metals such as copper
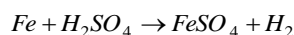
$$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}(aq)$$
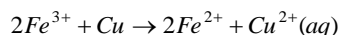
(d) In vapour state $FeCl_3$ exists as a dimer, Fe_2Cl_6
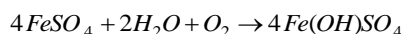

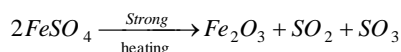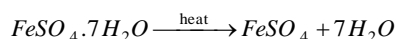(e) $FeCl_3$ is used as stypic to stop bleeding from a cut.

(4) **Ferrous sulphate,** $FeSO_4, 7H_2O$ (Green vitriol) : It is prepared as follow ,

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

(i) One pressure to moist air crystals become brownish due to oxidation by air.

$$4FeSO_4 + 2H_2O + O_2 \rightarrow 4Fe(OH)SO_4$$

(ii) On heating, crystals become anhydrous and on strong heating it decomposes to Fe_2O_3, SO_2 and SO_3 .

$$FeSO_4.7H_2O \xrightarrow{\text{heat}} FeSO_4 + 7H_2O$$
$$2FeSO_4 \xrightarrow[\text{heating}]{\text{Strong}} Fe_2O_3 + SO_2 + SO_3$$

(iii) It can reduce acidic solution of $KMnO_4$ and $K_2Cr_2O_7$

(iv) It is generally used in double salt with ammonium sulphate.

$$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \rightarrow \underset{\text{Mohr's salt}}{FeSO_4.(NH_4)_2SO_4.6H_2O}$$
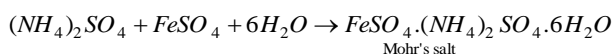
Mohr's salt is resistant to atmospheric oxidation.

(v) It is used in the ring test for nitrate ions where it gives brown coloured ring of compound $FeSO_4.NO$.

$$FeSO_4 + NO \rightarrow FeSO_4.NO$$
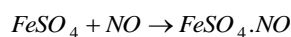
(vi) $FeSO_4$ is used in manufacture of blue black ink.

(vii) $FeSO_4 + H_2O_2$ is known as a name of **Fenton's reagent.**

(5) **Mohr's salt** $FeSO_4.(NH_4)_2SO_4.6H_2O$: It is a double salt and is prepared by crystallising a solution containing equivalent amounts of $FeSO_4.7H_2O$ and $(NH_4)_2SO_4$. It may be noted that Mohr's salt contains only Fe^{2+} ions without any trace of Fe^{3+} ions. In contrast $FeSO_4.7H_2O$ always contains some Fe^{3+} ions due to aerial oxidation of Fe^{2+} ions. Mohr salt is, therefore, used as a primary standard in volumetric analysis since a standard solution of Fe^{2+} ions can be obtained directly by weighing a known amount of the Mohr salt.

It acts as a reducing agent and as such reduces acidified $KMnO_4$ and $K_2Cr_2O_7$ solutions.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$
$\underset{\text{(From mohrs salt)}}{}$
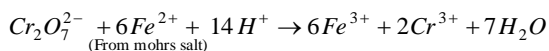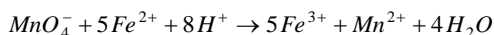
Copper and its Compounds

(1) **Ores :** Copper pyrites (chalcopyrite) $CuFeS_2$, Cuprite (ruby copper) Cu_2O, Copper glance (Cu_2S), Malachite $[Cu(OH)_2.CuCO_3]$, Azurite $[Cu(OH)_2.2CuCO_3]$

(2) **Extraction :** Most of the copper (about 75%) is extracted from its sulphide ore, copper pyrites.

Concentration of ore : Froth floatation process.

Roasting : Main reaction :

$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$.

Side reaction : $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$.

Smelting : $FeO + SiO_2 \rightarrow FeSiO_3$(slag)

$Cu_2O + FeS \rightarrow FeO + Cu_2S$

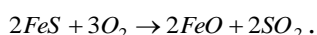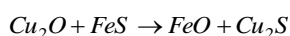The mixture of copper and iron sulphides melt together to form '**matte**' $(Cu_2S + FeS)$ and the slag floats on its surface.

Conversion of matte into Blister copper (Bessemerisation) : Silica is added to matte and a hot blast of air is passed $FeO + SiO_2 \rightarrow FeSiO_3$(slag). Slag is removed. By this time most of iron sulphide is removed. $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

Blister copper : Which contain about 98% pure copper and 2% impurities (*Ag*, *Au*, *Ni*, *Zn* etc.)

Properties of copper : It has reddish brown colour. It is highly malleable and ductile. It has high electrical conductivity and high thermal conductivity. Copper is second most useful metal (first being iron). It undergoes displacement reactions with lesser reactive metals e.g. with *Ag*. It can displace *Ag* from $AgNO_3$. The finally divided *Ag* so obtained is black in colour.
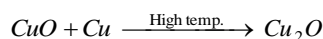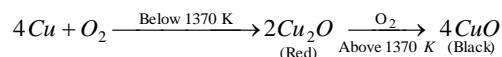
Copper shows oxidation states of +1 and +2. Whereas copper (I) salts are colourless, copper (II) salts are blue in colour. *Cu* (I) salts are less stable and hence are easily oxidised to *Cu* (II) salts $(2Cu^+ \rightarrow Cu^{2+} + Cu)$. This reaction is called **disproportionation.**

(1) In presence of atmospheric CO_2 and moisture, copper gets covered with a green layer of basic copper carbonate (green layer) which protects the rest of the metal from further acton.
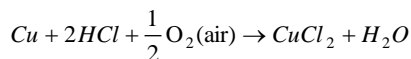
$$Cu + O_2 + CO_2 + H_2O \rightarrow \underset{\text{(green layer)}}{Cu(OH)_2CuCO_3}$$
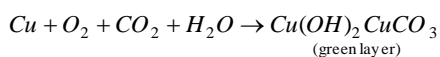
(2) In presence of oxygen or air, copper when heated to redness (below 1370*K*) first forms red cuprous oxide which changes to black cupric oxide on
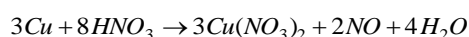
further heating. If the temperature is too high, cupric oxide changes back to cuprous oxide

$$4Cu + O_2 \xrightarrow{\text{Below 1370 K}} \underset{\text{(Red)}}{2Cu_2O} \xrightarrow[\text{Above 1370 } K]{O_2} \underset{\text{(Black)}}{4CuO}$$

$$CuO + Cu \xrightarrow{\text{High temp.}} Cu_2O$$

(3) **Action of acids.** Non oxidising dil. acids such as HCl, H_2SO_4 have no action on copper. However, copper dissolves in these acids in presence of air.

$$Cu + 2HCl + \frac{1}{2}O_2(\text{air}) \rightarrow CuCl_2 + H_2O$$

With dil. HNO_3, Cu liberates NO (nitric oxide)

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

With conc. HNO_3, copper gives NO_2

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

With hot conc. H_2SO_4, copper gives SO_2

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

Compounds of Copper

(1) **Halides of copper :** Copper (II) chloride, $CuCl_2$ is prepared by passing chlorine over heated copper. Concentrated aqueous solution of $CuCl_2$ is dark brown but changes first to green and then to blue on dilution.

On heating, it disproportionates to copper (I) chloride and chlorine

$$2CuCl_2 \xrightarrow{\text{Heat}} 2CuCl + Cl_2$$
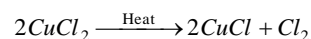
It is used as a catalyst in the **Daecon's process** for the manufacture of chlorine.

Copper (I) chloride, $CuCl$ is a white solid insoluble in water. It is obtained by boiling a solution of $CuCl_2$ with excess of copper turnings and conc. HCl.

$$CuCl_2 + Cu \xrightarrow{\text{HCl}} 2CuCl$$
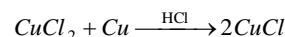
It dissolves in conc. HCl due to the formation of complex $H[CuCl_2]$

$$CuCl + HCl \rightarrow H[CuCl_2]$$
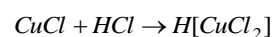
It is used as a catalyst alongwith NH_4Cl in the preparation of synthetic rubber.

(2) **Cuprous oxide** Cu_2O : It is a reddish brown powder insoluble in water but soluble in ammonia solution, where it forms diammine copper (I) ion. $Cu^+ + 2NH_3 \rightarrow [Cu(NH_3)_2]^+$. It is used to impart red colour to glass in glass industry.

(3) **Cupric oxide** CuO : It is dark black, hygroscopic powder which is reduced to Cu by hydrogen, CO etc. It is used to impart light blue colour to glass. It is prepared by heating copper nitrate.

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

(4) **Copper sulphate** $CuSO_4.5H_2O$ (Blue vitriol) **:** It is prepared by action of dil H_2SO_4 on copper scrap in presence of air. $2Cu + 2H_2SO_4 + O_2 \text{(air)} \rightarrow CuSO_4 + 2H_2O$

(i) On heating this blue salt becomes white due to loss of water of crystallization.

$$\underset{Blue}{CuSO_4.5H_2O} \xrightarrow{503\ K} \underset{White}{CuSO_4} + 5H_2O$$

At about 1000 K, $CuSO_4$ decomposes to give CuO and SO_3.

$$CuSO_4 \xrightarrow{1000\ K} CuO + SO_3$$

(ii) It gives a deep blue solution of tetrammine copper (II) sulphate with NH_4OH.

$$Cu_2SO_4 + 4NH_4OH, \rightarrow \underset{Blue\ colour}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

(iii) With KCN it first gives yellow precipitate of $CuCN$ which decomposes of give $Cu_2(CN)_2$. $Cu_2(CN)_2$ dissolves in excess of KCN to give $K_3[Cu(CN)_4]$

$$2CuSO_4 + 4KCN \rightarrow Cu_2(CN)_2 + 2K_2SO_4 + (CN)_2$$

(iv) With KI it gives white ppt. of Cu_2I_2

$$4KI + 2CuSO_4 \rightarrow 2K_2SO_4 + \underset{White\ ppt.}{Cu_2I_2} + I_2$$

(v) With $K_4[Fe(CN)_6], CuSO_4$ gives a reddish brown ppt. of $Cu_2[Fe(CN)_6]$

$$2CuSO_4 + K_4[Fe(CN)_6] \rightarrow \underset{Reddish\ brown\ ppt.}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

Uses *:* For electroplating and electrorefining of copper. As a mordant in dyeing. For making Bordeaux mixture (11 parts lime as milk of lime + 16 parts copper sulphate in 1,000 parts of water). It is an excellent fungicide. For making green pigments containing copper carbonate and other compounds of copper. Like Verdigris which is $Cu(CH_3COO)_2Cu(OH)_2$ *i.e.* basic copper acetate and is used as a green pigment in paints. As a fungicide in starch paste for book binding work.

(5) **Cupric sulphide** CuS : It is prepared as follows : $Cu(NO_3)_2 + H_2S \rightarrow \underset{Black\ ppt.}{CuS} + 2HNO_3$.

(6) **Basic copper carbonates :** Because of lower solubility of the hydroxide, the normal carbonate does not exist. Two basic copper carbonates occur in nature viz **malachite** $CuCO_3.Cu(OH)_2$ which has a fine green colour, and **azurite,** $2CuCO_3, Cu(OH)_2$ which is deep blue in colour.

Malachite is prepared by heating a mixture of $CuSO_4$ solution and limestone in a sealed tube at 423 – 443 K

$$2CuSO_4 + 2CaCO_3 + H_2O \xrightarrow{423-443K} \underset{Malachite}{CuCO_3Cu(OH)_2}$$

$$+2CaSO_4 + CO_2$$

At lower temperature *azurite* is formed

$$3CuSO_4 + 3CaCO_3 + H_2O \xrightarrow{<423\ K} \underset{Azurite}{2CuCO_3.Cu\ (OH)_2}$$

$$+3CaSO_4 + CO_2$$

On heating, both decompose to give black cupric oxide, water and CO_2.

They are used as green and blue painter's pigments under the name '**malachite green**' and **azurite blue**'.

Silver and its Compounds

(1) **Ores :** Argentite (silver glance) Ag_2S, Horn silver *(AgCl)*, Ruby silver (Pyrargyrite) $3Ag_2S.Sb_2S_3$.

(2) **Extraction :** *Cyanide process or Mac Arthus-Forrest cyanide process* **:** This method depends on the fact that silver, its sulphide or chloride, forms soluble complex with alkali cyanides in the silver. This implies that silver compounds will dissolve in solution of alkali cyanides in the presence of blast of air.

$$4Ag + 8NaCN + 2H_2O + O_2 \underset{air}{\rightleftharpoons} 4Na[Ag(CN)_2] + 4NaOH$$

or $4Ag + 8CN^- + 2H_2O + O_2 \rightleftharpoons 4[Ag(CN)_2]^- + 4OH^-$

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

$$AgCl + 2NaCN \rightleftharpoons Na[Ag(CN)_2] + NaCl.$$

The reaction with the sulphide is reversible and accumulation of Na_2S must be prevented. A free excess of air is continuously passed through the solution which oxidizes Na_2S into sulphate and thiosulphate.

$$2Na_2 + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$

$$Na_2S_2O_3 + 2NaOH + 2O_2 \rightarrow 2Na_2SO_4 + H_2O$$

$$2Na[Ag(CN)_2] + 4NaOH + Zn \rightarrow Na_2ZnO_2 +$$

$$4NaCN + 2H_2O + 2Ag$$

(3) **Extraction of Ag from argentiferrous lead (PbS + Ag₂S)– Parke's Process :** It is based upon the following facts (i) Molten *Zn* and *Pb* are immiscible, zinc forms the upper layer (ii) *Ag* is more soluble in molten *Zn* (iii) *Zn-Ag* alloy solidifies earlier than molten *Pb* (IV) *Zn* being volatile can be separated from *Ag* by distillation. *Ag* is purified by cupellation.

Properties of Silver: Silver is a white lustrous metal, best conductor of heat and electricity. Being soft, it is alloyed. The silver alloy used for making jewellery contain 80% *Ag* and 20% *Cu*. The composition of a silver alloy is expressed as its purity i.e. the amount of *Ag* present in 1000 parts of the alloy *Ag* does not react with dilute *HCl* or dil. H_2SO_4 and aqua regia but reacts with dil. HNO_3 and conc. HNO_3
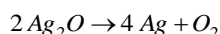
forming NO and NO_2 respectively. Chlorine also reacts with Ag to form $AgCl$.

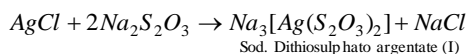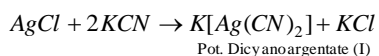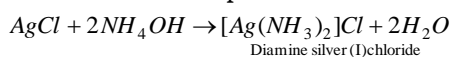$$2\,Ag + Cl_2 \rightarrow 2\,AgCl$$

Hot conc. H_2SO_4 reacts with Ag forming SO_2 like Cu

Compounds of Silver:

(1) **Silver oxide** (Ag_2O) **:** It is unstable and decomposes into Ag and O_2 on slow heating.
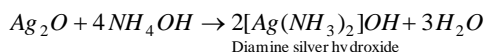
$$2\,Ag_2O \rightarrow 4\,Ag + O_2$$

(2) **Silver halides (*AgF, AgCl, AgBr* and *Agl*) :** Only AgF is soluble in H_2O. $AgCl$ is insoluble in H_2O but dissolves in NH_4OH, $Na_2S_2O_3$ and KCN solutions. $AgBr$ is partly soluble whereas Agl is completely insoluble in NH_4OH. Except AgF, all the remaining three silver halides are photosensitive.

$$AgCl + 2NH_4OH \rightarrow \underset{\text{Diamine silver (I)chloride}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$AgCl + 2KCN \rightarrow \underset{\text{Pot. Dicyanoargentate (I)}}{K[Ag(CN)_2]} + KCl$$

$$AgCl + 2Na_2S_2O_3 \rightarrow \underset{\text{Sod. Dithiosulphato argentate (I)}}{Na_3[Ag(S_2O_3)_2]} + NaCl$$

(3) **Silver nitrate (*AgNO₃*) :** Silver nitrate ($AgNO_3$) is called lunar caustic silver nitrate on *heating above* its m.p. (485 K) decomposes to silver nitrite but on heating to red heat gives silver.

$$2\,AgNO_3 \xrightarrow{\text{Above 485 K}} 2\,AgNO_2 + O_2$$

$$2\,AgNO_3 \xrightarrow{\text{Red heat}} 2\,Ag + 2NO_2 + O_2$$
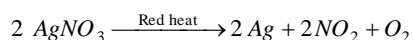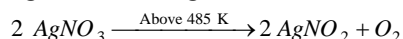
When treated with *alkali*, $AgNO_3$ forms *silver oxide* which in case of NH_4OH dissolves to form complex ion.

$$2\,AgNO_3 + 2NaOH \rightarrow Ag_2O + 2NaNO_3 + H_2O$$

$$2\,AgNO_3 + 2NH_4OH \rightarrow Ag_2O + 2NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \rightarrow \underset{\text{Diamine silver hydroxide}}{2[Ag(NH_3)_2]OH} + 3H_2O$$
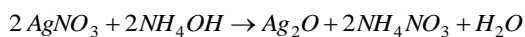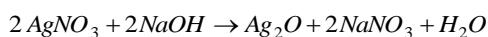
$AgNO_3$ reacts with iodine in two ways

$$6\,AgNO_3 \text{ (excess)} + 3l_2 + 3H_2O \rightarrow AglO_3 + 5AgI + 6HNO_3$$

$$5\,AgNO_3 + 3l_2 \hspace{3cm} \text{(excess)}$$
$$+\,3H_2O \rightarrow HIO_3 + 5Agl + 5HNO_3$$
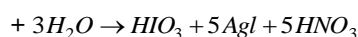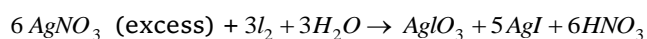
In contact with organic matter (skin, cloth, paper etc.) $AgNO_3$ is reduced to metallic silver (black)

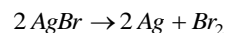$$2\,AgNO_3 + H_2O \rightarrow 2\,Ag + 2HNO_3 + [O] \rightarrow \text{oxidises}$$
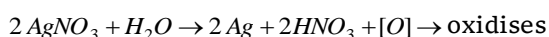
organic matter

$AgNO_3$ gives different coloured ppt. with different anions like $Cl^-, Br^-, I^-, S^{2-}, S_2O_3^{2-}, CrO_4^{2-}, PO_4^{3-}$ etc.

$AgNO_3$ is used in the preparation of ink and hair dyes.

Photography : The photographic plate is coated with a colloidal gelatinised solution of $AgBr$. During exposure, $AgBr$ is reduced to metallic silver.

$$2\,AgBr \rightarrow 2\,Ag + Br_2$$

The exposed film is developed. The developer used is an alkaline solution of hydroquinone or quinol which reduces some of the exposed $AgBr$ to black silver.

$$\underset{\text{Quinol}}{C_6H_4(OH)_2} + 2\,AgBr \rightarrow 2\,Ag + \underset{\text{Quinone}}{C_6H_4O_2} + 2\,HBr$$
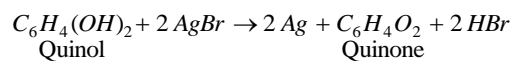
The film is finally fixed by dipping in a solution of sodium thiosulphate or hypo which removes unchanged $AgBr$ as complex ion.

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$
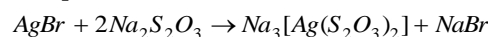
After taking a print of the photograph it is finally toned by dipping in a dilute solution of gold chloride to impart a beautiful golden colour or it is dipped in potassium chloro platinate K_2PtCl_6 solution to get a shining grey tinge.

$$AuCl_3 + 3\,Ag \rightarrow 3\,AgCl + Au$$
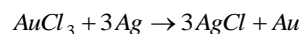
Gold and its Compounds

(1) **Occurrence of gold :** Gold is mainly found in native state either as vein gold, placer gold or alluvial gold. It is also present to a small extent in the combined state as sulphide, telluride and arsenosulphide. It is considered to be the king of metal.
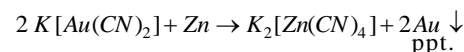
Some important ores of gold are:

(i) Calaverite, $AuTe_2$ (ii) Sylvanite, $AuAgTe_2$ and

(iii) Bismuth aurite, $BiAu_2$

(2) **Extraction of gold :** (i) *Mac-Arthur-Forest Cyanide process* : The powdered gold ore, after concentration by *Froth-floatation process*, is roasted to remove easily oxidisable impurities of tellurium, arsenic and sulphur. The roasted ore is then treated with a dilute solution of KCN in presence of atmospheric oxygen when gold dissolves due to the formation of an aurocyanide complex.

$$4\,Au + 8\,KCN + 2\,H_2O + O_2 \rightarrow \underset{\text{Solution}}{4\,K[Au(CN)_2]} + 4\,KOH$$
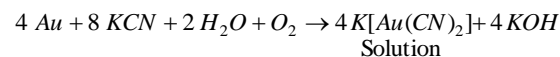
The metal is then extracted by adding zinc dust.

$$2\,K[Au(CN)_2] + Zn \rightarrow K_2[Zn(CN)_4] + \underset{\text{ppt.}}{2\,Au \downarrow}$$

(ii) *Plattner's chlorine process* : The roasted ore is moistened with water and placed in wooden vats with false perforated bottoms. It is saturated with current of chlorine, gold chloride thus formed is leached with water and the solution is treated with a reducing agent such as $FeSO_4$ or H_2S to precipitate gold.
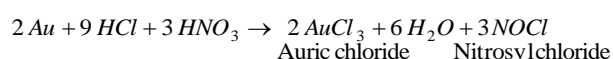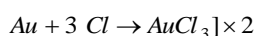
$$AuCl_3 + 3FeSO_4 \rightarrow Au\downarrow + FeCl_3 + Fe_2(SO_4)_3$$

$$2\,AuCl_3 + 3H_2S \rightarrow 6HCl + 3S + 2Au\downarrow$$
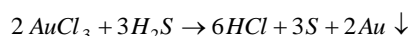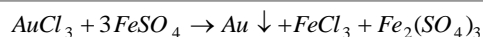
The impure gold thus obtained contains impurities of Ag and Cu. The removal of Ag and Cu from gold is called parting. This is done by heating impure gold with conc. H_2SO_4 (or HNO_3) when Ag and Cu dissolve leaving behind Au.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O$$
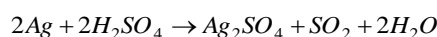
Properties of Gold: Gold is a yellow, soft and heavy metal. Gold and Ag are called noble metals since they are not attacked by atmospheric oxygen. However, Ag gets tarnished when exposed to air containing traces of H_2S. Gold is malleable, ductile and a good conductor of heat and electricity.

Pure gold is soft. It is alloyed with Ag or Cu for making jewellery. Purity of gold is expressed in terms of carats. Pure gold is 24 carats. Gold '14 carats' means that it is an alloy of gold which contains 14 parts by weight of pure gold and 10 parts of copper per 24 parts by weight of the alloy. Thus the percentage of gold in '14 carats" of gold is $= \dfrac{100}{24} \times 14 = 58.3\%$.

Most of the jewellery is made from 22 carat gold (91.66% pure gold). Gold is quite inert. It does not react with oxygen, water and acids but dissolves in aqua regia

$$3HCl + HNO_3 \rightarrow NOCl + 2H_2O + 2Cl]\times 3$$

$$Au + 3\,Cl \rightarrow AuCl_3]\times 2$$

$$\underset{\text{Auric chloride}}{2\,Au + 9\,HCl + 3\,HNO_3 \rightarrow} \; \underset{\text{Nitrosyl chloride}}{2\,AuCl_3 + 6\,H_2O + 3\,NOCl}$$

Oxidation states of gold: The principal oxidation states of gold are + 1 and + 3 though + 1 state is more stable than + 3.

Compounds of gold

(1) **Auric chloride, $AuCl_3$:** It is prepared by passing dry Cl_2 over finely divided gold powder at 573 K

$$2\,Au + 3Cl_2 \xrightarrow{573\,K} 2\,AuCl_3$$
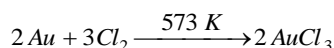
It is a red coloured crystalline solid soluble in water and decomposes on heating to give gold (I) chloride and Cl_2

$$AuCl_3 \xrightarrow{\text{Heat}} AuCl + Cl_2$$
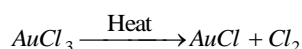
It dissolves in conc. HCl forming chloroauric acid

$$AuCl_3 + HCl \rightarrow H[AuCl_4]$$

Chloroauric acid is used in photography for toning silver prints and as an antidote for snake poisoning.

(2) **Aurous sulphide, Au_2S :** It is prepared when H_2S is passed through an acidified solution of potassium aurocyanide, $K[Au(CN)_2]$

$$2K[Au(CN)_2] + H_2S \rightarrow Au_2S + 2KCN + 2HCN$$
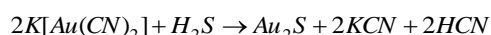
It is a dark brown solid, not attached by dilute mineral acids and hence is probably the most stable gold compound.

Zinc and its Compounds

(1) **Occurrence of zinc:** Zinc does not occur in the native form since it is a reactive metal. The chief ores of zinc are (i) Zinc blende (ZnS) (ii) Calamine or zinc spar ($ZnCO_3$) and (iii) Zincite (ZnO)

(2) **Extraction of zinc :** Zinc blende, after concentration by Froth floatation process, is roasted in air to convert it into ZnO. In case of calamine, ore is calcined to get ZnO. The oxide thus obtained is mixed with crushed coke and heated at 1673 K in fire clay retorts (Belgian Process) when ZnO gets reduced to metallic zinc. Being volatile at this temperature, the metal distils over and is condensed leaving behind Cd, Pb and Fe as impurities. The crude metal is called spelter. The metal may be refined either by electrolysis or by fractional distillation.
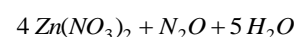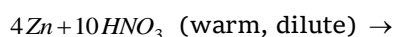
Properties of Zn : Zinc is more reactive than mercury. It is a good conductor of heat and electricity. Zinc readily combines with oxygen to form ZnO. Pure zinc does not react with non-oxidising acids (HCl or H_2SO_4) but the impure metal reacts forming Zn^{2+} ions and evolving H_2 gas.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$$
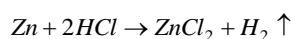
Hot and conc. H_2SO_4 attacks zinc liberating SO_2 gas

$$Zn + 2H_2SO_4 \rightarrow ZnSO_4 + SO_2 + 2H_2O$$

Zinc also reacts with both dilute (hot and cold) HNO_3 and conc. HNO_3 liberating nitrous oxide (N_2O), ammonium nitrate (NH_4NO_3) and nitrogen dioxide (NO_2) respectively.

$$4Zn + 10HNO_3 \text{ (warm, dilute)} \rightarrow$$
$$4\,Zn(NO_3)_2 + N_2O + 5\,H_2O$$

$$4Zn + 10HNO_3 \text{ (cold very dilute)} \rightarrow$$
$$4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Zn + 4HNO_3 \text{ (hot and conc.)} \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

Zinc dissolves in hot concentrated $NaOH$ forming the soluble sod. Zincate

$$Zn + 2NaOH + 2H_2O \rightarrow Na_2[Zn(OH)_4] + H_2$$
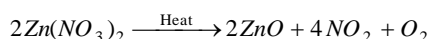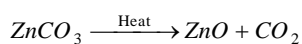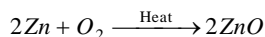
or $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
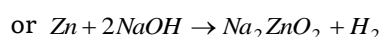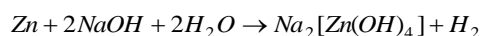
(3) **Special varieties of zinc.** (i) *Zinc dust* : It is prepared by melting zinc and then atomising it with a blast of air.

(ii) *Granulated zinc* : It is prepared by pouring molten zinc into cold water.

Both these varieties of zinc are used as reducing agents in laboratory.
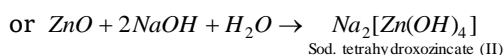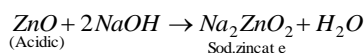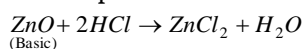
Compounds of zinc

(1) **Zinc oxide (Zinc white or Chinese white), ZnO** : It is obtained by burning zinc in air or by heating zinc carbonate or zinc nitrate.

$$2Zn + O_2 \xrightarrow{\text{Heat}} 2ZnO$$

$$ZnCO_3 \xrightarrow{\text{Heat}} ZnO + CO_2$$

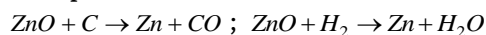$$2Zn(NO_3)_2 \xrightarrow{\text{Heat}} 2ZnO + 4NO_2 + O_2$$

It is a white powder but becomes yellow on heating and again white on cooling.

It is insoluble in water and is very light and hence commonly known as **philosopher's wool**.

It is amphoteric in nature.

$$\underset{\text{(Basic)}}{ZnO + 2HCl} \rightarrow ZnCl_2 + H_2O$$

$$\underset{\text{(Acidic)}}{ZnO + 2NaOH} \rightarrow \underset{\text{Sod.zincate}}{Na_2ZnO_2} + H_2O$$

or $ZnO + 2NaOH + H_2O \rightarrow \underset{\text{Sod. tetrahydroxozincate (II)}}{Na_2[Zn(OH)_4]}$

It is reduced both by carbon and H_2 and is used as a white paint

$$ZnO + C \rightarrow Zn + CO \; ; \; ZnO + H_2 \rightarrow Zn + H_2O$$

(2) **Zinc chloride, $ZnCl_2$** : It is obtained when Zn metal, ZnO or $ZnCO_3$ is treated with dil. HCl. It crystallizes as $ZnCl_2.2H_2O$ and becomes anhydrous on heating. $ZnCl_2$ is highly deliquescent and is highly soluble in H_2O and also readily dissolves in organic solvents like acetone, alcohol, ether etc. its aqueous solution is acidic due to hydrolysis.

$$ZnCl_2 + H_2O \rightarrow Zn(OH)Cl + HCl$$
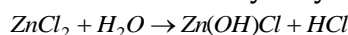
Anhydrous $ZnCl_2$ is used as a Lewis acid catalyst in organic reactions. Mixed with moist zinc oxide, it is used for filling teeth and its solution is used for preserving timber. Anhydrous $ZnCl_2$ used as a Lucas reagent with conc. HCl.

(3) **Zinc sulphide, ZnS** : It is a white solid. It is soluble in dil. HCl and thus does not get precipitated by H_2S in the acidic medium.

$$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S .$$
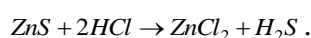
It is a constituent of lithopone $(ZnS + BaSO_4)$

(4) **Zinc sulphate, $ZnSO_4.7H_2O$** : It is commonly known as white vitriol and is obtained by the action of dil. H_2SO_4 on zinc metal, ZnO or $ZnCO_3$. On heating, it first loses six molecules of water of crystallization at

373 K. At 723 K, it becomes anhydrous and on further heating, it decomposes.

$$ZnSO_4.7H_2O \xrightarrow{373\,K} ZnSO_4.H_2O \xrightarrow{723\,K}$$

$$2ZnSO_4 \xrightarrow{1073\,K} 2ZnO + 2SO_2 + O_2$$
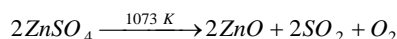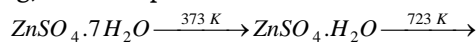
It is used to prepare lithopone $(BaSO_4 + ZnS)$, a white paint and also in galvanising iron.

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$$
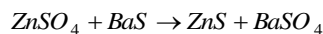
It is also used as an eye lotion.

Mercury and its compounds

(1) **Occurrence and extraction of mercury : Cinnabar (HgS)** is the only important ore of Hg. It is concentrated by froth floatation method and mercury is extracted from this ore by heating it in air at 773-873 K (auto reduction).
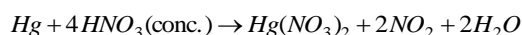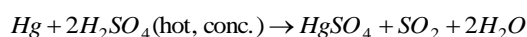
$$HgS + O_2 \xrightarrow{273-873\,K} Hg + SO_2$$
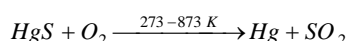
The mercury vapours thus obtained are condensed to give liquid metal. Hg thus obtained contains impurities of Zn, Sn and Pb. These are removed by treating the impure metal with dil HNO_3 , mercurous nitrate, $Hg_2(NO_3)_2$ thus formed react with metals present as impurities forming their nitrates which pass into solution leaving behind pure mercury. However, it is best purified by distillation under reduced pressure.

$$6Hg + 8HNO_3(dil.) \xrightarrow{\text{warm}} 3Hg_2(NO_3)_2 + 4H_2O + 2NO$$

$$Zn + Hg_2(NO_3)_2 \rightarrow Zn(NO_3)_2 + 2Hg$$
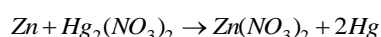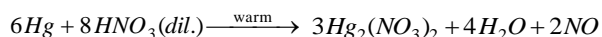
Similar reaction is given by Pb and Sn.

Properties of mercury : Mercury is less reactive than Zn. It is a liquid at room temperature and has low thermal and electrical conductivity. Mercury forms dimeric mercury (I) ions, Hg_2^{+2} in which the two atoms are bonded by a covalent bond. It is slowly oxidised to HgO at about its boiling point. Hg does not react with dil. HCl or dil. H_2SO_4 but reacts with hot concentrated H_2SO_4 to form $HgSO_4$, it reacts with both warm dil. and conc. HNO_3 evolving NO and NO_2 respectively.

$$Hg + 2H_2SO_4(\text{hot, conc.}) \rightarrow HgSO_4 + SO_2 + 2H_2O$$

$$Hg + 4HNO_3(\text{conc.}) \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$
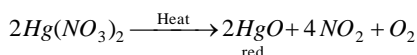
Hg does not react with steam or water hence can't form any hydroxide.

Compounds of mercury
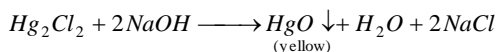
(1) **Mercuric oxide, HgO** : It is obtained as a red solid by heating mercury in air or oxygen for a long time at 673 K

$$2Hg + O_2 \xrightarrow{\ 673\,K\ } 2HgO(red)$$
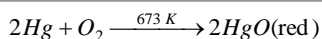
or by heating mercuric nitrate alone or in the presence of Hg

$$2Hg(NO_3)_2 \xrightarrow{\ Heat\ } 2HgO + 4NO_2 + O_2$$
$$\qquad\qquad\qquad\quad red$$

When $NaOH$ is added to a solution of $HgCl_2$, yellow precipitate of HgO are obtained.

$$Hg_2Cl_2 + 2NaOH \longrightarrow HgO\downarrow + H_2O + 2NaCl$$
$$\qquad\qquad\qquad\qquad (yellow)$$

Red and yellow forms of HgO differ only in their particle size. On heating to 673 K, yellow form changes to red form.

$$HgO \xrightarrow{\ 673\,K\ } HgO$$
$$yellow \qquad\qquad red$$
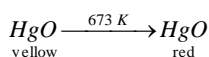
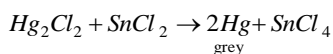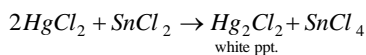It is used in oil paints or as a mild antiseptic in ointments.

(2) **Mercuric chloride, HgCl₂ :** It is obtained by treating Hg with Cl_2 or by heating a mixture of $NaCl$ and $HgSO_4$ in presence of small amount of MnO_2 (which oxidises any Hg(I) salts formed during the reaction).

$$HgSO_4 + 2NaCl \xrightarrow[MnO_2]{\ Heat\ } HgCl_2 + Na_2SO_4$$
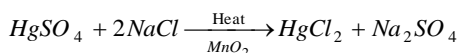
It is a white crystalline solid and is commonly known as **corrosive sublimate**. It is a covalent compound since it dissolves in organic solvents like ethanol and ether.

It is extremely poisonous and causes death. Its best antidote is white of an egg.

When treated with stannous chloride, it is first reduced to white ppt. of mercurous chloride and then to mercury (black).
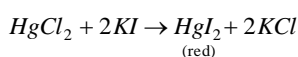
$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$
$$\qquad\qquad\qquad white\ ppt.$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$$
$$\qquad\qquad\qquad\qquad grey$$

With ammonia it gives a white ppt. known as infusible white ppt.

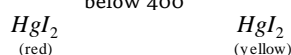$$HgCl_2 + 2NH_3 \rightarrow Hg(NH_2)Cl + NH_4Cl$$
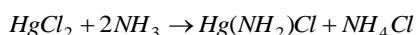
A dilute solution of $HgCl_2$ is used as an antiseptic.
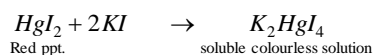
(3) **Mercuric iodide, HgI₂ :** It is obtained when a required amount of KI solution is added to a solution of $HgCl_2$.

$$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$$
$$\qquad\qquad\quad (red)$$

Below 400 K, HgI_2 is red but above 400 K, it turns yellow.

$$HgI_2 \underset{below\ 400}{\overset{above\ 400}{\rightleftharpoons}} HgI_2$$
$$(red) \qquad\qquad\qquad (yellow)$$

HgI_2 readily dissolves in excess of KI solution to form the $(HgI_4)^{2-}$ complex ion.

$$HgI_2 + 2KI \rightarrow K_2HgI_4$$
$$Red\ ppt. \qquad\quad soluble\ colourless\ solution$$
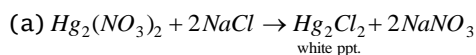
An alkaline solution of $K_2[HgI_4]$ is called Nessler's reagent and is used to test NH_4^+ ions.

It gives a brown ppt. of $NH_2 - Hg - O - Hg - I$ (Iodide of Millon's base) with NH_4^+ ions.

$$2K_2[HgI_4] + NH_3 + 3KOH \rightarrow NH_2.HgO.HgI + 7KI + 2H_2O$$
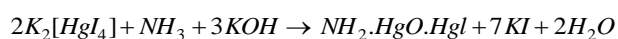
It is used in ointments for treating skin infections.

(4) **Mercurous chloride, Hg₂Cl₂ :** It is obtained as under :

(a) $Hg_2(NO_3)_2 + 2NaCl \rightarrow Hg_2Cl_2 + 2NaNO_3$
$$\qquad\qquad\qquad\qquad\qquad white\ ppt.$$

(b) $HgCl_2 + Hg \xrightarrow{\ Heat\ in\ an\ iron\ retort\ } Hg_2Cl_2$ (condenses on cooling)

It is purified by sublimation.

Mercurous chloride is also called calomel. It is a white powder insoluble in H_2O. On heating, it decomposes to give $HgCl_2$ and Hg.

$$Hg_2Cl_2 \xrightarrow{\ Heat\ } HgCl_2 + Hg$$
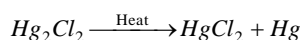
It dissolves in chlorine water forming mercuric chloride.

$$Hg_2Cl_2 + Cl_2 \rightarrow 2HgCl_2$$
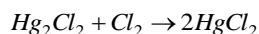
With ammonia, it turns black due to the formation of a mixture of finely divided black Hg and mercuric amino chloride.

$$Hg_2Cl_2 + 2NH_3 \rightarrow \underbrace{Hg + NH_2HgCl}_{(black)} + NH_4Cl$$
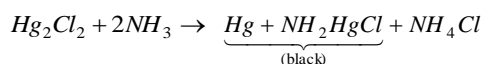
It is used to prepare standard calomel electrode and as a purgative in medicine.

(5) **Mercuric sulphide, HgS :** The solubility product of HgS is lower than that of ZnS and hence it gets precipitated as black solid when H_2S is passed through an acidic solution of any mercury (II) salt.

$HgCl_2 + H_2S \rightarrow HgS + 2HCl$

It is insoluble in water and *HCl* but dissolves in aqua regia (1 part conc. HNO_3 + 3 parts conc. *HCl*)

$$3HCl + HNO_3 \rightarrow \underset{\text{Nitrosylchloride}}{NOCl} + 2H_2O + \underset{\text{Nascent chlorine}}{2[Cl]}$$
$$\underset{\text{Aqua regia}}{}$$

$$HgS + 2|Cl| \rightarrow \underset{\text{(Soluble)}}{HgCl_2} + S \downarrow$$

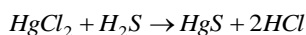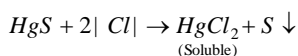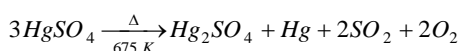On sublimation, its colour changes to red and hence it is used as a red pigment.

(6) **Mercuric sulphate, $HgSO_4$:** It is obtained when *HgS* is treated with conc. H_2SO_4.

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + SO_2 + 2H_2O$$

It is a white solid which decomposes on heating to give mercurous sulphate.

$$3HgSO_4 \xrightarrow[675\,K]{\Delta} Hg_2SO_4 + Hg + 2SO_2 + 2O_2$$

It is used as a catalyst in the hydration of alkynes to give aldehydes or ketones. It is also used as a cosmetic under the name **Vermillon** and in ayurvedic medicine as **makardhwaj**.

(7) **Amalgams :** Mercury forms alloys commonly known as amalgams, with all metals except iron and platinum. Hence it is transported in iron containers.

(8) **Alloy of transition metal :** See in table discuss earlier in metallurgy.

Lanthanides and Actinides

Lanthanides and actinides are collectively called *f*-block elements because last electron in them enters into *f*-orbitals of the antepenultimate (*i.e.*, inner to penultimate) shell partly but incompletely filled in their elementary or ionic states. The name inner transition, elements is also given to them because they constitute transition series with in transition series (*d*-block elements) and the last electron enters into antepenultimate shell (*n*-2)*f*. In addition to incomplete *d*-subshell, their *f*-subshell is also incomplete. Thus, these elements have three incomplete outer shells i.e., (*n*–2), (*n*–1) and *n* shells and the general electronic configuration of *f*-block elements is (*n*–2)f^{1-14} (*n*–1)$d^{0-10}ns^2$.

(1) **Lanthanides :** The elements with atomic numbers 58 to 71 *i.e.* cerium to lutetium (which come immediately after lanthanum Z = 57) are called lanthanides or *lanthanones or rare earths*. These elements involve the filling of 4 *f*-orbitals. Their general electronic configuration is, $[Xe]4f^{1-14}5d^{0-10}6s^2$. Promethium (*Pm*), atomic number 61 is the only synthetic (man made) radioactive lanthanide.

Properties of lanthanides

(i) These are highly dense metals and possess high melting points.

(ii) They form alloys easily with other metals especially iron. e.g. **misch metal** consists of a rare earth element (94–95%), iron (upto 5%) and traces of *S*, *C*, *Ca* and *Al*, pyrophoric alloys contain *Ce* (40–5%), *La* + neodymium (44%), *Fe* (4–5%), *Al* (0–5%) and the rest is *Ca*, *Si* and *C*. It is used in the preparation of ignition devices e.g., trace bullets and shells and flints for lighters and cigarette.

(iii) *Oxidation state* : Most stable oxidation state of lanthanides is +3. Oxidation states + 2 and + 4 also exist but they revert to +3 e.g. $Sm^{2+}, Eu^{2+}, Yb^{2+}$ lose electron to become +3 and hence are good reducing agents, where as $Ce^{4+}, Pr^{4+}, Tb^{4+}$ in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4 *f* and 5 *d* subshells and thus the number of oxidation states is limited.

(iv) *Colour* : Most of the trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. This is due to the partly filled *f*-orbitals which permit *f*–*f* transition. The elements with *xf* electrons have a similar colour to those of (14 – *x*) electrons.

(v) *Magnetic properties* : All lanthanide ions with the exception of Lu^{3+}, Yb^{3+} and Ce^{4+} are paramagnetic because they contain unpaired electrons in the 4 *f* orbitals. These elements differ from the transition elements in that their magnetic moments do not obey the simple "**spin only**" formula $\mu_{eff} = \sqrt{n(n+2)}$ B.M. where *n* is equal to the number of unpaired electrons. In transition elements, the orbital contribution of the electron towards magnetic moment is usually quenched by interaction with electric fields of the environment but in case of lanthanides the 4*f*-orbitals lie too deep in the atom for such quenching to occur. Therefore, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions and a more complex formula

$$\mu_{eff} = \sqrt{4S(S+1)+L(L+1)} \text{ B.M.}$$

which involves the orbital quantum number *L* and spin quantum number *S*.

(vi) *Complex formation* : Although the lanthanide ions have a high charge (+3) yet the size of their ions is very large yielding small charge to size ratio *i.e.*, low charge density. As a consequence, they have poor tendency to form complexes. They form complexes

mainly with strong chelating agents such as EDTA, β - diketones, oxine etc. *No* complexes with π -bonding ligands are known.

(vii) ***Lanthanide contraction*** : The regular decrease in the size of lanthanide ions from La^{3+} to Lu^{3+} is known as lanthanide contraction. It is due to greater effect of the increased nuclear charge than that of the screening effect.

Consequences of lanthanide contraction

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange

(b) Each element beyond lanthanum has same atomic radius as that of the element lying above it in the group (e.g. *Zr* 145 *pm*, *Hf* 144 *pm*); *Nb* 134 *pm*, *Ta* 134 *pm* ; *Mo* 129 *pm*, *W* 130 *pm*).

(c) The covalent character of hydroxides of lanthanides increases as the size decreases from La^{3+} to Lu^{3+}. However basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic. Similarly, the basicity of oxides also decreases in the order from La^{3+} to Lu^{3+}.

(d) Tendency to form stable complexes from La^{3+} to Lu^{3+} increases as the size decreases in that order.

(e) There is a slight increase in electronegativity of the trivalent ions from *La* to *Lu*.

(f) Since the radius of Yb^{3+} ion (86 pm) is comparable to the heavier lanthanides *Tb*, *Dy*, *Ho* and *Er*, therefore they occur together in natural minerals.

(2) **Actinides :** The elements with atomic numbers 90 to 103 i.e. thorium to lawrencium (which come immediately after actinium, *Z* = 89) are called actinides or actinones. These elements involve the **filling of 5 *f*-orbitals**. Their general electronic configuration is, $[Rn]5f^{1-14}6d^{0-1}7s^2$.

They include three naturally occuring elements thorium, protactinium and uranium and eleven transuranium elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or man made elements. All actinides are radioactive.

Properties of actinides

(i) ***Oxidation state*** : The dominant oxidation state of actinides is +3 which shows increasing stability for the heavier elements. *Np* shows +7 oxidation state but this is oxidising and is reduced to the most stable state +5. *Pu* also shows states upto +7 and *Am* upto +6 but the most stable state drops to *Pu* (+4) and *Am* (+3). *Bk* in +4 state is strongly oxidising but is more stable than *Cm* and *Am* in 4 state due to f^7 configuration. Similarly, *No* is markedly stable in +2 state due to its f¹⁴

configuration. When the oxidation number increases to + 6, the actinide ions are no longer simple. The high charge density causes the formation of oxygenated ions e.g., UO_2^{2+}, NpO_2^{2+} etc. The exhibition of large number of oxidation states of actinides is due to the fact that there is a very small energy gap between 5*f*, 6*d* and 7*s* subshells and thus all their electrons can take part in bond formation.

(ii) ***Actinide contraction*** : There is a regular decrease in ionic radii with increase in atomic number from *Th* to *Lr*. This is called actinide contraction analogous to the lanthanide contraction. It is caused due to imperfect shielding of one 5*f* electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

(iii) ***Colour of the ions*** **:** Ions of actinides are generally coloured which is due to *f – f* transitions. It depends upon the number of electrons in 5 *f* orbitals.

(iv) ***Magnetic properties*** **:** Like lanthanides, actinide elements are strongly paramagnetic. The magnetic moments are lesser than the theoretically predicted values. This is due to the fact that 5*f* electrons of actinides are less effectively shielded which results in quenching of orbital contribution.

(v) ***Complex formation*** **:** Actinides have a greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms. They form complexes even with π-bonding ligands such as alkyl phosphines, thioethers etc, besides EDTA, β-diketones, oxine etc. The degree of complex formation decreases in the order.

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$$
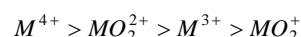
Where *M* is element of actinide series. There is a high concentration of charge on the metal atom in MO_2^{2+} which imparts to it relatively high tendency towards complex formation.

T Tips & Tricks

✍ Iron pyrites is also known as Fool's gold ($CuFeS_2$).

✍ *Ni* can be extracted by or ford process.

✍ Chromium oxide is also known as chrome green.

✍ Cr_2O_3/C_5H_5N or solution of chromic oxide in pyridine is known as Collin's reagent.

✍ $Cr_2O_3.2H_2O$ is also known as Guignet's green.

✍ Zn, Cd and Hg are not expected to form covalent bond amongst themselves, hence they have relatively lower melting point.

✍ The +2 oxidation state become more stable while the +3 state become less stable from left to right in the periodic table.

✍ For the first four element of a transition series higher oxidation states are more stable than lower oxidation state. For next five-element lower oxidation state are more stable than higher oxidation state.

✍ Many transition metal compound are isomorphous *e.g.* $FeSO_4.7H_2O$ and $ZnSO_4.7H_2O$ because of almost equal ionic sizes of these metals.

✍ Lightest transition metal is Sc and heaviest and densest transition element is osmium.

✍ Mercurous ion exist as dimer Hg_2^{2+} and not as Hg^+ and this explains its diamagnetic nature.

✍ Pt, Pd and Ir are inert metal.

✍ $TiCl_4$ and TiO_2 are used in smoke screens.

✍ Mo is used in X-ray tube, Ta in analytic weight and instrument used in surgery of veins.

✍ Fe^{2+} is green and Fe^{3+} is yellow.

✍ Fe^{3+} is powerful oxidizing agent than Fe^{2+} ion.

✍ Iron carbide or cementite is Fe_3C.

✍ Kipp's base is $FeS + H_2SO_4$.

✍ Copper dissolves in an aqueous solution of $FeCl_3$.

✍ $CuSO_4$ reacts only with KI does not react with KCl, KBr or KF.

✍ $CuCl_2$ and $CuBr_2$ are covalent and exist as polymer while CuF_2 is an ionic solid.

✍ All silver halide except AgF are insoluble in water.

✍ Ag, Au and Cu are known as coinage metals.

✍ Fulminating gold is $Au(NH_2) = NH$ or N_2H_3.

✍ Purple of cassius is a colloidal solution of gold.

✍ Mercuric salts are more stable than mercurous salts.

✍ All the elements of f-block are in group 3 of the periodic table.

✍ Schweitzer reagent is $[Cu(NH_3)_4]SO_4$.

✍ Etard reagent is CrO_2Cl_2.

✍ Barfoed's reagent is $Cu(CH_3COO)_2 + CH_3COOH$.

✍ Milon's reagent is the solution of mercuric and mercurous nitrate.

✍ Zeigler natta catalyst is $TiCl_4 + (C_2H_5)_3Al$.

✍ Lindlar's catalyst is $Pd/BaSO_4$.

✍ Wilkinson's catalyst is $[Ph_3P]_3RhCl$.

✍ Adam catalyst is Pt/PtO.

✍ Brown's catalyst is Nickel boride (P-2 catalyst).