

Unit - VI

Chemistry of d-Block Elements

The d-block elements are defined as the elements which having partly filled d sub-shell in their elementary form or as ions.

The d-block elements are also called 'transition elements' because their properties are intermediate between those of s & p-block elements.

They generally contain two electrons in their ns orbital while their penultimate shell is being expanded from eight to eighteen electrons by the addⁿ of ten d-e^s. These elements are therefore called d-block elements.

Zn, Cd & Hg have completely filled (n-1)d subshell in their elementary form as well as in an ions. So, according to defⁿ these elements cannot included in the d-block elements.

The d-block elements consist of three rows called first, second & third T.S.

Electronic configuration :

First transition series

Atomic Number	Elements	Electronic configuration
21	Sc	$[Ar] 3d^1 4s^2$
22	Ti	$[Ar] 3d^2 4s^2$
23	V	$[Ar] 3d^3 4s^2$
24	Cr	$[Ar] 3d^5 4s^1$
25	Mn	$[Ar] 3d^5 4s^2$
26	Fe	$[Ar] 3d^6 4s^2$
27	Co	$[Ar] 3d^7 4s^2$
28	Ni	$[Ar] 3d^8 4s^2$
29	Cu	$[Ar] 3d^{10} 4s^1$
30	Zn	$[Ar] 3d^{10} 4s^2$

Second transition series :-

At. No.	Elements	Electronic configuration
39	Y	$[\text{Kr}] 4d^1 5s^2$
40	Zr	$[\text{Kr}] 4d^2 5s^2$
41	Nb	$[\text{Kr}] 4d^4 5s^1$
42	Mo	$[\text{Kr}] 4d^5 5s^1$
43	Tc	$[\text{Kr}] 4d^5 5s^2$
44	Ru	$[\text{Kr}] 4d^7 5s^1$
45	Rh	$[\text{Kr}] 4d^8 5s^1$
46	Pd	$[\text{Kr}] 4d^9 5s^1$
47	Ag	$[\text{Kr}] 4d^{10} 5s^1$
48	Cd	$[\text{Kr}] 4d^{10} 5s^2$

Third transition series

57	La	$[\text{Xe}] 5d^1 6s^2$
72	Hf	$[\text{Xe}] 5d^2 6s^2$
73	Ta	$[\text{Xe}] 5d^3 6s^2$
74	W	$[\text{Xe}] 5d^4 6s^2$
75	Re	$[\text{Xe}] 5d^5 6s^2$
76	Os	$[\text{Xe}] 5d^6 6s^2$
77	Ir	$[\text{Xe}] 5d^7 6s^2$
78	Pt	$[\text{Xe}] 5d^8 6s^2$
79	Au	$[\text{Xe}] 5d^{10} 6s^1$
80	Hg	$[\text{Xe}] 5d^{10} 6s^2$

② General characteristics of d-block elements

1) Atomic & Ionic radii

The atomic & ionic radii of almost all the transition metals are small & they are almost same in a series.

The atomic radius or the ionic radius slightly decreases with an increase in the atomic number in each series.

2) Atomic volumes & densities :-

Atomic volumes of the d-block elements are much lower than those of the s & p block elements of the neighbouring groups.

The reason is that the inner orbitals get filled, the increased nuclear charge pulls the e^- inward. The molar volume, decreases. As a result of decrease in molar volume, there is corresponding increase in density. That's why the densities of the transition elements are quite high. Most of these elements have densities greater than 5 g/cm^3 .

Sc, Ti & V with densities 3.01, 4.51 & 4.47 respectively are the only exceptions.

3) Metallic character:-

All the transition elements are metals, because they possess only two e^- in their outermost shell, which can be readily lost. They are lustrous, malleable as well as ductile. (except Hg)

- They are less metallic than alkali & alkaline earth metals. Transition elements form strong metallic bonds. In the series, on moving from left to right, the strength of the metallic bond first increases & then decreases.

e.g. In 3d-series it is strongest for V & Cr but weakest in case of Zn

- All the transition metals are good conductor of heat & electricity. Cu, Ag & Au are the best.

4) melting & Boiling Points :-

The m.p. & B.P. of transition elements are very high i.e. above 900°C . This is due to strong interatomic attraction & strong metallic bonds in them.

In transition series, the m.p. first increases & then decreases.

The m.p. of Zn, Cd & Hg are relatively low i.e. 419.5 , 320.9 & -38.4°C respectively because of weak metallic bonding in them.

5) Ionisation Energies :-

It gives an idea of the ease with which an e^- can be removed from its isolated gaseous atom.

Ionisation energies increase as we move from left to right across a transition series. The values, in most cases, lie in between those of s & p block elements.

e.g. In the 1st transition series I.E. of Sc, Ti, V & Cr are fairly close to one another, while values of Fe, Co, Ni & Cu are almost similar. This is due to the effect of increasing nuclear charge which would tend to pull the outer e^- charge cloud inward with increasing force.

In the 1st transition series the addition of increasing number of d- e^- s increases the screening effect & hence shields the outer s e^- from the inward pull of the +ve nucleus. Thus the effect of increasing nuclear charge & expansion of d subshell tend to oppose each other. On account of these counter effects, the I.E. increases rather slowly on moving along the period.

The value for Zn is higher. This is due to additional stability of the atom.

6) Reactivity :-

Transition elements are less reactive than s-block elements. The low reactivity is due to high ionisation energy, high heat of sublimation & low heat of hydration. Au, Pt, Ag etc are called noble metals because of their low reactivity.

7) Oxidation States :-

All transition elements, except the first & last member of the each series, exhibit a variety of oxidation state. The variation in the oxidⁿ state is due to the involvement of incomplete d-orbital in addition to the $\bar{e}$ s of the outermost s-orbital.

- moreover, there is only a slight energy difference betⁿ $(n-1)d$ & ns orbitals & so $\bar{e}$ s from both the energy level can be used for bonding.
- All these elements have two $ns \bar{e}$. so generally they exhibit an oxidⁿ state of +2, by the loss of these two $\bar{e}$.
- In addⁿ they also utilize one or more $(n-1)d$ electrons for bonding & so exhibit oxidⁿ state of +3 or more.

The variation in oxidⁿ state depends upon the number of d-e^s taking part in the bond formⁿ.

It varies from +2 to +7.

e.g. i) Mn = [Ar] 3d⁵ 4s² ⇒ +2, +3, +4, +6, +7, +5 oxidⁿ state

8) Electronegativity & electropositivity:

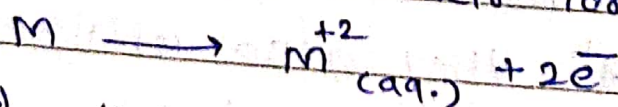
d-block elements are highly electropositive.

They have low electro^{-ve} values, but their electro^{-vity} values are more than s-block elements & electropositive character is less than that of s-block elements, because transition elements have smaller atomic size.

9) Reducing Properties:-

- The reducing property of a metal depends on its tendency to form ions.

- All d-block elements except copper have standard potential considerably more -ve than that of the standard hydrogen electrode i.e. zero. Hence these are oxidised easily to their ions in aq. solⁿ.



They should, therefore be good reducing agents. However, they are not as good reducing agents as the metal of gr. 1, 2 & 13.

The transition metals have less tendency to form ion because of their high I.E., high heats of sublimation & low heats of hydration of their ions. Therefore they are not good reducing agent as the metals of 1, 2 & 13 gr.

10) Tendency to form complexes :-

All the transition elements form the co-ordination complex readily. This is due to

- i) small size of the metal ions
- ii) large ionic or nuclear charge.
- iii) available of various oxidⁿ state.
- iv) available of d-orbitals.
- v) low basicity of the metal ions
- vi) high Lewis acid nature of e^- pair accepting tendency of the metal ion.

The tendency of the formⁿ of complexes increases gradually from left to right.

11) Colour :-

Transition metal ions are generally coloured due to the presence of unpaired d- e^- , which absorb light from the visible region & thus move to higher energy level. ($\lambda^{\nu} = 3800-7600 \text{ \AA}^{\circ}$)

- Therefore one of the colours of the visible spectrum is absorbed by the transition metal ion gets the complementary colour.
- The transition metal ion with completely filled d-orbitals are colourless.
e.g. Zn^{2+} , Cd^{2+} , Hg^{2+} are colourless
 $\Rightarrow$ unpaired e^-

Ti^{3+} - Purple - 1

V^{4+} , Cu^{2+} - Blue - 1

Co^{2+} , V^{2+} - Pink - 3

V^{3+} , Ni^{2+} - Green - 2

Cr^{3+} - Green - 3

Cr^{2+} - Blue - 4

Mn^{3+} - Violet - 4

Fe^{2+} - Green - 4

Fe^{3+} - Yellow - 5

Mn^{2+} - Pink - 5

- The colour of the transition metal ion arises due to d-d transition / e^- excitation

12) Magnetic Properties :-

majority of the substance are either paramagnetic or diamagnetic. only few are ferromagnetic. A paramagnetic substance is one which is attracted into magnetic field & diamagnetic

substance is one which is repelled by a magnetic field.

- Paramagnetism arises from the presence of unpaired e^- in atoms, ions, complex ion or molecules.

The unpaired e^- gives rise to a magnetic field on account of its spin & because of the angular momentum.

In the transition metal ions, the unpaired e^- are generally present in the outer orbitals. The orbital motion of such unpaired e^- is disturbed by the e^- of the surrounding ligands thereby 'quenching' the orbital angular momentum in the transition metal compounds. Therefore in such cases the l_{spin} contribution becomes much more significant than the ~~$l_{orbital}$~~ $l_{orbital}$.

$$\therefore \mu_{eff} = \mu_{spin} = \sqrt{n(n+2)}$$

where, $n = \text{no. of unpaired } e^-$

The magnetic moment is expressed in Bohr magneton.

A Bohr magneton (B.M.) is given by

$$1 \text{ B.M.} = \frac{eh}{4\pi mc}$$

$h = \text{Planks const}$, $e = \text{electronic charge}$

$c = \text{velocity of light}$, $m = \text{mass of } e^-$

no. of unpaired e^-	0	1	2	3	4	5
in (B.M.) magnetic moment	0	1.73	2.84	3.87	4.90	5.92

13) Catalytic Property :-

most of the transition metals & their compounds have good catalytic properties.

	catalyst	Reaction
1)	Fe + Mo	- Haber Process for NH_3
2)	Pt or V_2O_5	- contact Process for H_2SO_4
3)	Pt	- Ostwald Process for HNO_3
4)	Ni	- Hydrogenation of oil
5)	$\text{FeSO}_4 + \text{H}_2\text{O}_2$	- For oxid ⁿ of alcohols to aldehydes
6)	Mg TiCl_4 (Ziegler Natta catalyst)	- For mkt of Polyethene.

① Comparison of second & third transition series with First T.S. elements :-

For this it is helpful to divide the elements of the three series into groups of three elements each.

e.g. Scandium group - Sc, Y, La

Titanium group - Ti, Zr, Hf

Vanadium group - V, Nb, Ta & so on

Zinc group - Zn, Cd, Hg.

The elements of the 1st transition series have considerably different properties from those of the elements of the 2nd & 3rd T.S. The main points of difference are as follows

1) Ionic radius :-

The ionic radii of the elements of 2nd & 3rd T.S. are larger than those of the 1st T.S. in each group. This is due to increased number of e^- & higher principal quantum no. in the element of the 2nd T.S.

Due to the lanthanide contraction, there is very little difference in the ionic radii of the elements of 2nd & 3rd T.S. in given group.

e.g. ①	Ni ²⁺	Pd ²⁺	Pl ²⁺	②	Co ³⁺	Rh ³⁺	Ir ³⁺
	0.63	0.78	0.74 Å		0.69	0.81	0.82 Å

2) co-ordination number :-

co-ordination numbers 7 & 8 are quite common for the 1st few members of 2nd & 3rd T.S., these co-ordⁿ numbers are quite rare for the elements of 1st T.S.

3) metal-metal bonding :-

The 2nd & 3rd T.S. elements have greater tendency to form the compounds containing M-M bond than the 1st T.S.

e.g. i) $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ & $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ V does not form
ii) $[\text{Ti}_2\text{Cl}_8]^{2-}$ & $[\text{Re}_2\text{Cl}_8]^{2-}$ Mn does not form

4) oxidation state :-

The lower oxidⁿ state, especially +2 & +3 of the elements of 1st T.S. are of relatively little importance for most of the elements of 2nd & 3rd T.S.

The higher oxidⁿ state is generally more stable for the elements of the 2nd & 3rd T.S than for the 1st T.S.

e.g. RuO_4 , WCl_6 , PtF_6 are quite stable whereas FeO_4 , CrCl_6 , NiF_6 are not known.

① Compounds of Rhodium & Iridium :-

A) Rhodium

Rhodium occurs only $10^{-7}\%$ of the earth crust. It occurs generally alloyed with platinum.

Properties :-

- It is silvery-white metal, soft & ductile
- It is inert & dissolves only in hot conc. H_2SO_4
- The chief oxidⁿ state of Rh is +3.

Compounds of Rhodium

- 1) The highest oxidⁿ state of rhodium is +6 & this exhibits in RhF_6 . This compound is unstable & highly reactive.
- 2) The compounds of Rh(V) are very rare & are unstable. RhF_5 is actually a cyclic tetramer in which four RhF_6 octahedra form a ring through Rh-F-Rh bonds.
- 3) The compound RhF_4 is unstable. Another comp. of Rh(IV) is RhO_2 which is formed by the oxidⁿ of an aq. solⁿ of Rh(III) compounds by strong oxidising agent such as $NaBiO_3$ in the presence of an alkali.

4) The halocomplexes of Rh(IV) are slightly more stable than the simple Rh(IV) compounds.
e.g. $K_2[RhCl_6]$ & $K_2[RhF_6]$ are slightly more stable than RhF_4 & RhO_2 .

5) The +3 oxidⁿ state of Rh is more stable than any other oxidⁿ state of the metal. All the trihalides are known & are found to be quite stable. e.g. RhX_3 , $RhCl_3 \cdot 3H_2O$ (octahedral)
- Rh(III) complexes are also very stable. most of these are diamagnetic in character.

6) Pentahalide & heptahalide complex ions such as $[RhBr_5]^{2-}$ & $[RhBr_7]^{4-}$ are known, yet these are not very stable.

7) Wilkinson's catalyst :-

The complex $[RhCl(PPh_3)_3]$ is known as Wilkinson's catalyst. It is square planar structure & is red-violet in colour. It is obtained by refluxing $RhCl_3 \cdot 3H_2O$ with PPh_3 . It is used as a catalyst in the oxo process in which CO & H_2 are added to the end double bond of alkenes forming aldehydes which on oxidⁿ gives carboxylic acid & on reduction gives alcohols.

8) The carbonyls $[Rh_6(CO)_6]$, $[Rh_4(CO)_{12}]$ contain Rh in zero oxidⁿ state whereas the complex anion $[Rh(CO)_4]^-$ contains Rh in -1 oxidⁿ state.

B) Iridium :

It occurs in nature as an alloy of osmium & ruthenium.

Properties :-

- It is a silvery-white metal which is brittle but fairly hard.
- It is used as an additive to Pt for hardening.
- It is extremely resistant to attack of acids.
- In bulk state it does not dissolve even in aqua regia.
- It dissolves in mixture of conc. HCl & sod. chlorate at 150°C .
- It combines with chlorine at red heat to give the trichloride IrCl_3 & with fluorine at 600°C to give the hexafluoride, IrF_6 .

Compounds of Iridium :-

- The highest oxidⁿ state of Ir is +6.
- The compound IrF_6 is known but is quite unstable.
- The +4 oxidⁿ state of Ir is quite stable. The tetrahalides of Ir are known.
- Ir is heated in current of oxygen to form IrO_2 (+4).

e.g. $[\text{IrCl}_6]^{2-}$, $[\text{IrCl}_3(\text{H}_2\text{O})_3]^+$, $[\text{IrCl}_4(\text{H}_2\text{O})_2]$ etc.

- All the halides of Ir(III) are insoluble in water.
- The +2 oxidⁿ state of Ir is not very common although IrCl_2 is known.
-  Vaska's compound :- $\text{trans} [\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ is yellow in colour & has the capability of co-ordinating aerial O_2 .
- The yellow coloured Vaska's compound turns orange when it takes up oxygen. When flushed with hydrogen, it releases oxygen & again turns yellow.
- $[\text{Ir}(\text{PF}_3)_4]^-$ & $[\text{Ir}_4(\text{CO})_{12}]$ contain Ir in -1 & zero oxidⁿ state respectively.

c) Palladium :-

It occurs alloyed with other metals such as gold, copper, iron & nickel in South Africa, Russia & Columbia.

The chief source is Sudbury nickel ore.

Properties :-

- Silvery-white metal
- malleable & ductile.
- m.p. 1552°C
- dissolves in dil. HNO_3 to form $\text{Pd}(\text{NO}_3)_2$ i.e. Palladous nitrate & with dil. H_2SO_4 Palladous sulphate

$\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

Compounds of Palladium :-

- Pd (CO) compounds :- It shows zero oxidⁿ state in it's complexes formed by 6 donor & π acceptor ligands. e.g. $[\text{Pd}(\text{CO})(\text{PPh}_3)_3]$

- Pd (II) compounds :- Palladium forms large number of compounds in which it has the oxidⁿ state +2. These are

a) Palladous oxide (PdO) :-

- It is obtained by heating spongy Pd at 800°C in oxygen. or by heating palladous nitrate ($\text{Pd}(\text{NO}_3)_2$)

- It is black powder & insoluble in acids & even in aqua regia.

- It is a strong oxidising agent.

b) Palladous hydroxides $\text{Pd}(\text{OH})_2$:-

- It is obtained as ppt on heating solⁿ of $\text{Pd}(\text{NO}_3)_2$

- It dissolves readily in acids

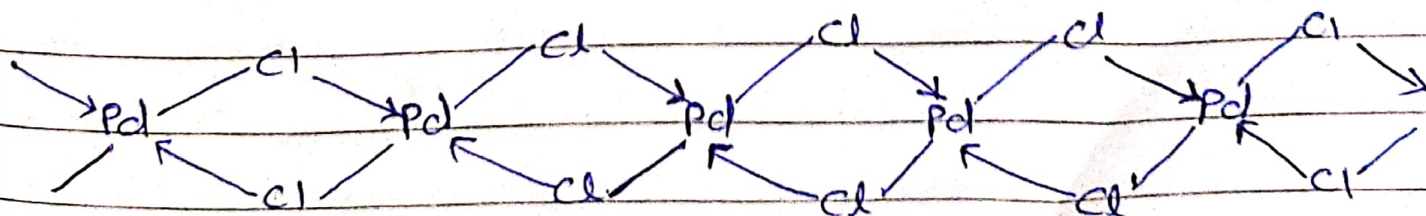
- It starts decomposing when heated above 550°C.

c) Palladous chloride PdCl_2 :-

- It is obtained by heating Pd in chlorine.

- It is dark red solid & soluble in water.

- PdCl_2 exist as a chain polymer in the solid state



d) Palladous nitrate $\text{Pd}(\text{NO}_3)_2$:-
- It is obtained by dissolving Pd or $\text{Pd}(\text{OH})_2$ in dil. HNO_3 . The soln on evaporation yields brown deliquescent Prism-like structure.

e) Palladous cyanide $\text{Pd}(\text{CN})_2$:-
- obtained by ppt on adding KCN to a soln of PdCl_2 . The ppt dissolves on adding excess of KCN to give the complex compound $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$.

- Palladium (III) compounds :- Pd(III) compounds are uncommon. Amongst the few compounds known PdF_3 is important. This is formed by heating Pd in a current of fluorine at 500°C . The complex compounds $\text{Na}_3[\text{PdF}_6]$ & $\text{Na}[\text{PdF}_4]$ though unstable, are known to exist.

- Palladium (IV) compounds :- Very few compounds of Pd(IV) are known. PdO_2 is stable only in the hydrated form. Amongst the halogens only fluorine forms the tetrahalide PdF_4 .

The complexes of Pd(IV) are more stable than Pd(IV) compounds.

e.g. $\text{Na}_2[\text{PdX}_6]$, $\text{Pd}[\text{X}_4(\text{NH}_3)_2]$

D) Platinum :-

It occurs $5 \times 10^{-7} \%$ in the earth crust.

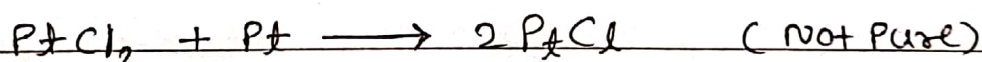
- Pt is white metal with a silvery lustre.
- It's m.p. is 1769°C
- It has very high density of 21.4 g/cc .
- It is malleable & ductile.
- It is more reactive than Os & Ir.

Compounds of Platinum.

i) Platinum (0) :- $\text{Pt}[\text{C}(\text{CO})_2(\text{PPh}_3)_2]_2$

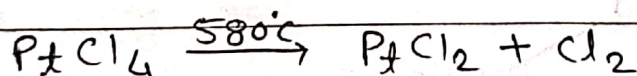
ii) Platinum (I) :- PtCl

It is obtained by heating Pt (II) chloride with Platinum at $581-583^\circ\text{C}$.



iii) Platinum (II) :- PtCl_2

Prepⁿ:-



It is green grey Powder insoluble in water.

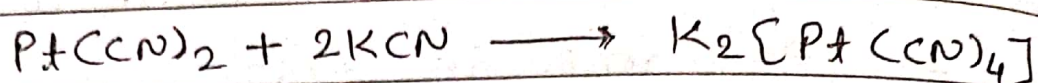
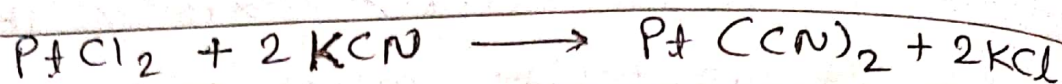
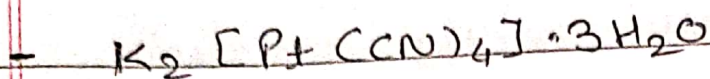
It dissolves in HCl forming $[\text{PtCl}_4]^{2-}$ complex



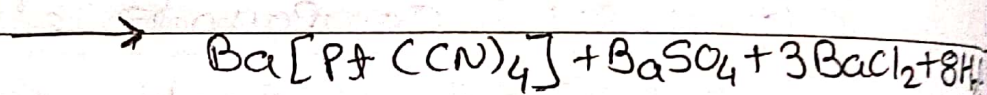
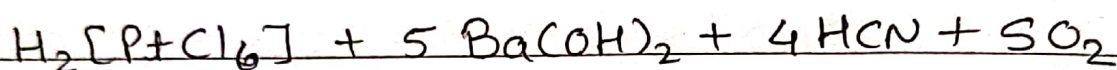
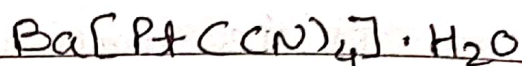
Most of the tetrachloroplatinate (II) complexes are soluble in water yielding red solⁿ

- $[\text{PtCl}_4]^{2-}$ is diamagnetic

- It has square planar geometry.



- Barium tetracyanoplatinate (II)

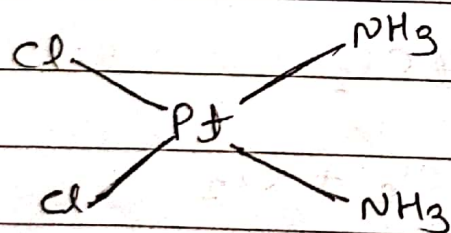


dimagnetic

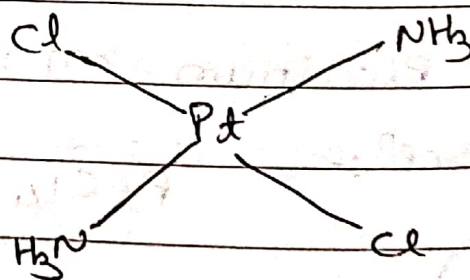
(Square Planar)

- Diamminedichloro Platinum (II) -

This exists in two isomeric forms.



cis



trans

- The cis isomer commonly known as cis Platin it is used in the treatment of cancer.

- platinum (II) iodide (PtI_2) :-

It is obtained as a black insoluble powder



→ compounds & complexes of Pt (IV)

a) Platinum (IV) chloride $PtCl_4$:-

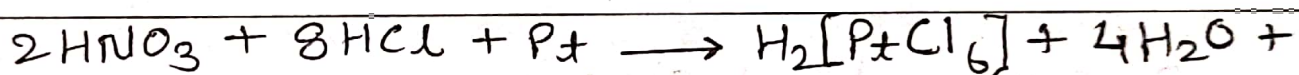
It is obtained by heating chloroplatinic acid in a current of chlorine at $370^\circ C$



It is reddish brown, crystalline solid, readily soluble in water.

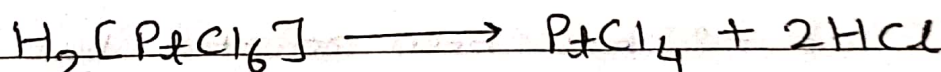
b) chloroplatinic acid $H_2[PtCl_6]$:-

It is prepared by the action of aqua regia

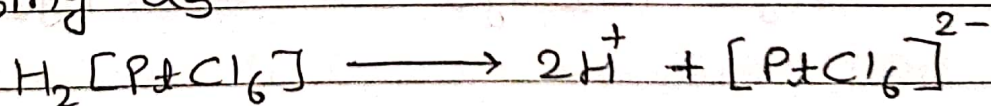


on heating in chlorine at $360-370^\circ C$

it decomposes into Pt (IV) chloride.



Chloroplatinic acid is a strong dibasic acid, ionising as



E) Silver :-

It's ores are

- argentite (silver glance), Ag_2S
- horn silver, AgCl
- Pyrargyrite (Ruby silver) $\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$

Properties :- It is white lustrous metal,

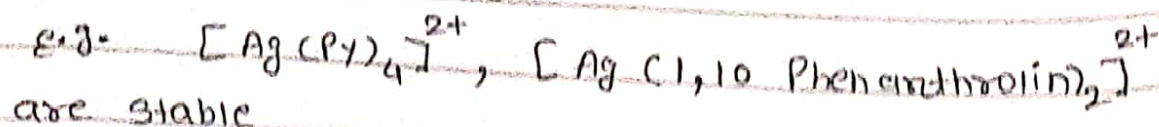
- Highly malleable & ductile
- Best conductor of heat & electricity
- It has density of 10.5 g/cc & melts 960.8°C

① Compounds of silver :-

- a) - The normal oxidⁿ state of silver is +1.
- Few compounds in which silver is in oxidⁿ state of +2 have been reported but these are highly unstable.



- Another compound of Ag(II) is AgF_2 . This is also unstable & is a powerful oxidising agent.
- However, some complexes of Ag(II) are more stable than its salts.



- Ag(III) is less common. $\text{Na}[\text{AgF}_4]$

f) Gold :

Properties :- - It is a yellow metal.

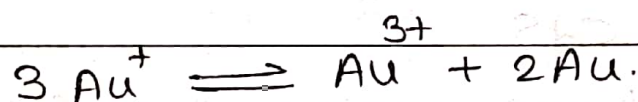
- highly malleable & ductile

- specific gravity 19.3

- very good conductor of heat & electricity.

① compounds of gold :-

Gold commonly exhibits oxidⁿ states of +1 & +3. The +3 oxidⁿ state is more stable. Au(I) ion is unstable & it undergoes disproportionation in solⁿ



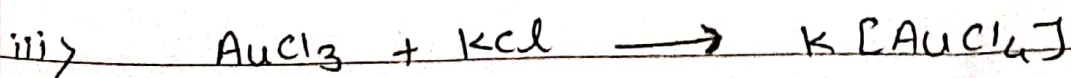
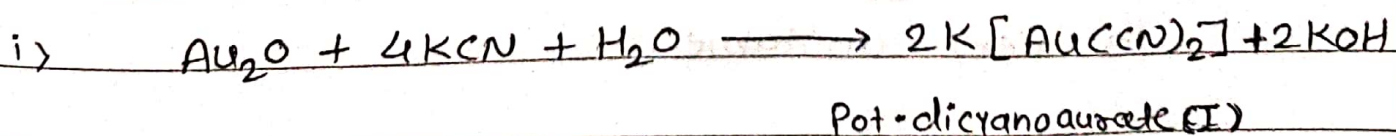
- Au(III) compound is AuCl_3

- The only compound of Au(V) is AuF_5 . This is dark red polymeric solid which is diamagnetic.

- Gold in -1 oxidⁿ state :-

when Au & Cs are fused together in equal proportion it forms salt with the composition $\text{Cs}^+ \text{Au}^-$.

- complexes of gold :-



Chloroauric acid

- (n) Cadmium - It does not occur free in nature.
- Zinc ores such as calamine or zinc blende contain 2-3% of cadmium.

② Properties:-

- It is a soft, bluish white metal.
- It is malleable & ductile. It is much less reactive.

③ Compounds of cadmium:-

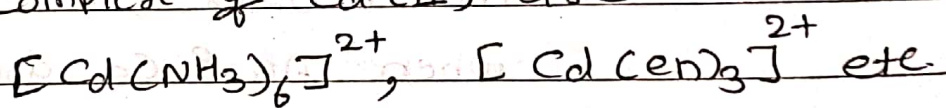
The usual oxidⁿ state of Cd is +2.

e.g. CdS

- Cd forms number of complexes such as $[\text{Cd}(\text{NH}_3)_4]^{2+}$, $[\text{Cd}(\text{CN})_4]^{2-}$, $[\text{CdI}_4]^{2-}$

- $[\text{CdCl}_5]^{3-}$ - trigonal bipyramidal

- octahedral complex of Cd(II) are



- Cd(I) - The Cd-Cd bond is much weaker than Hg-Hg bond.

∴ Hg_2^{2+} ion is quite stable whereas Cd_2^{2+} ion is very unstable.

H) mercury :-

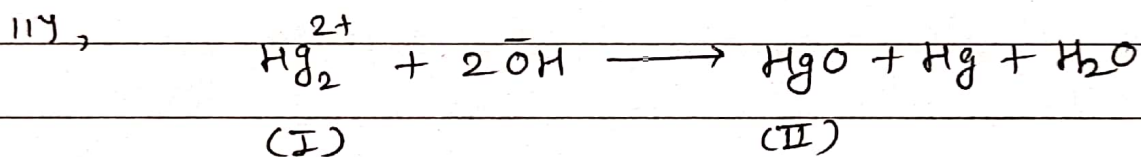
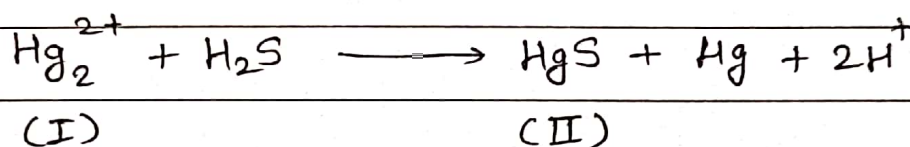
ore - cinnabar (Spain & Italy)

Properties :-

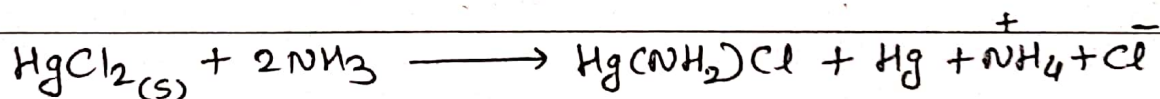
- It is silvery-white metal & liquid at R.T.
- It freezes at -38.4°C & boils at 357°C

Compounds of Hg :-

It shows +1 & +2 oxidⁿ state.



Hg(I) salts are very little soluble in water.



- compound containing Hg_3 & Hg_4 units:-

