

UNIT - I

A] Chemistry of Elements of Transition series

Introduction:-

The elements in which last electrons enters in $(n-1)d$ sub orbital are called d-block elements. These elements are called as transition elements, because these elements are present between s-block elements (metals) and p-block elements (Non-metals).

viz \rightarrow namely These elements are classified into four series viz 3d, 4d, 5d, 6d series corresponding to the filling of 3d, 4d, 5d & 6d orbitals, respectively.

- First Transition series:

It is also called as 3d series because last electron enters in 3d sub orbital. It includes elements from scandium $[Z=21]$ to zinc $[Z=30]$.

- Second Transition series:

It is also called as 4d series because last electron enters in 4d sub orbital. It includes elements from yttrium $(Z=39)$ to cadmium $(Z=48)$.

- Third Transition series:

It is also called as 5d series. It includes elements from Lanthanum $(Z=57)$, Hafnium $(Z=72)$ to mercury $(Z=80)$.

- Fourth Transition series:

It is also called as 6d series. It includes elements from Actinium $(Z=89)$, Rutherfordium $(Z=104)$ to Copernicium $(Z=112)$.

General Characteristics of d-block Elements

- ① The general outermost electronic configuration of transition elements is $(n-1)d^{1-10} ns^{0,1,2}$.
- ② Transition elements are metals and shows properties of malleability, ductility and metallic luster.
- ③ They are good conductor of heat and electricity.
- ④ They have high M.P. and B.P.
- ⑤ They shows variable oxidation states.
- ⑥ Generally their compounds are coloured.
- ⑦ They form complexes.
- ⑧ Their compounds shows paramagnetic property because they contain unpaired electrons.
- ⑨ The metals and their compounds have catalytic property.
- ⑩ They forms alloys and organometallic comds.

Comparative Study of First transition series Elements (3d-series Elements)

The first transition series elements belongs to 4th period and 3-12 groups. In first transition series elements last electron enters in 3d orbitals. Their outermost (valance) electronic configuration is $3d^{1-10} 4s^{1-2}$. The 3d series contain 10 elements from Scandium (Z=21) to zinc (Z=30).

① Electronic configuration

Subshell arrangement

The general outermost E.C. of 3d series elements is $3d^{1-10} 4s^{1-2}$. In this series element last electron enters in 3d sub orbitals. The electronic configuration of 3d series elements is

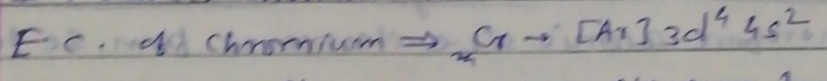
Sc Ti V Cr Mn Fe Co Ni Cu Zn
 Chromium Iron Nickel

S.No	Element	Symbol	At. No.	E.C.	EC in terms of inert gas
1	Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	[Ar] $3d^1 4s^2$
2	Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$	[Ar] $3d^2 4s^2$
3	Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	[Ar] $3d^3 4s^2$
4	Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	[Ar] $3d^5 4s^1$
5	Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	[Ar] $3d^5 4s^2$
6	Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	[Ar] $3d^6 4s^2$
7	Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$	[Ar] $3d^7 4s^2$
8	Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$	[Ar] $3d^8 4s^2$
9	Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	[Ar] $3d^{10} 4s^1$
10	Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	[Ar] $3d^{10} 4s^2$

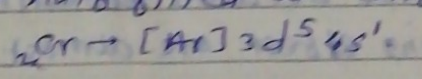
The irregularity is observed in E.C. of Chromium (Z=24) and Copper (Z=29). This irregular E.C. is called as anomalous configuration. This can be explained on the basis of ~~concept~~ rule of extra stability of half filled ($3d^5$) and completely filled ($3d^{10}$) orbitals.

According to the rule extra stability, if orbitals are half filled ($3d^5$) or completely filled ($3d^{10}$) then they get extra stability or their E.C. is relatively more stable than other configuration.

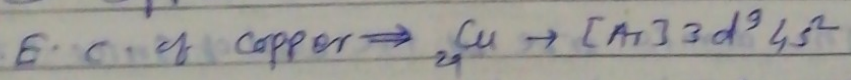
eg. ~~Iron~~ ① Chromium



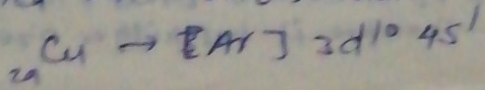
In case of Chromium, one electron from 4s orbital is transferred (excited) to 3d orbital and achieve more stable ~~to~~ half filled $3d^5$ configuration.



eg. ② Copper



but in case copper, one electron from 4s orbital is transferred to 3d orbital and achieve more stable completely filled $3d^{10}$ configuration.



② Atomic and Ionic size

def:- The distance between centre of nucleus and last orbit electron (valance electron) in an atom or ion is called as Atomic size or ionic size. It is measured in pm.

As we go left to right in 3d series elements, Atomic and ionic size decreases but decrease in atomic size is not regular.

3d series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At size (pm)	144	132	122	117	117	117	116	115	117	125
	Decreases				const.				Increase	

It is observed that, atomic size decreases from Scandium to Chromium, from Chromium to copper remain almost constant and in case of zinc atomic size increases. This can be explain as

④ From Sc to Cr atomic size decreases because from Sc to Cr, at. no. increases, nuclear charge increase therefore at. size decrease, but at the same time electron (σ is added in 3d orbital (inner orbital) successively, provides shielding effect. As no. of 3d-electron increases, shielding effect increases. But it is observed that increase in effective nuclear charge is more than shielding effect therefore atomic size decreases from Sc to Cr.

⑤ From Cr to Cu, atomic ~~radii~~ radii remain almost constant because effective nuclear charge and shielding effect are almost constant. Therefore there is no change in atomic ~~radii~~ radii from Cr to Cu.

⑥ The atomic size at the end of series (Zn) is higher. This is due to interelectronic repulsion (i.e. electron-electron repulsion in 3d-orbitals) and crowding of electrons takes place. This repulsion is higher in zinc. Therefore it has higher size in the 3d series.

③ Ionisation

Ionisation

def:- The

remove

is call

A

IT

M

n

The

S-b

Ionisation

is

one

and

IE

IE

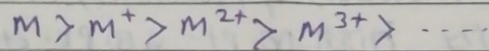
T

at

+

S

The same trend is observed in ionic radii.
In general, for the 4^{th} elements, ionic radii decreases with increase in the charge on cation.

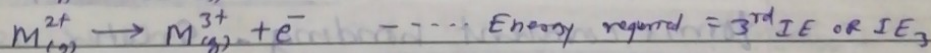
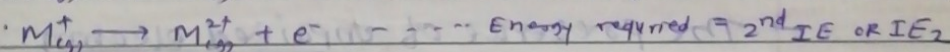
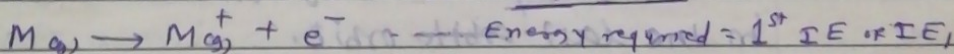


③ Ionisation Energy or Ionisation potential or Ionisation enthalpy:

Def:- The minimum amount of energy required to remove the electron from least orbit of neutral atom is called as ionisation energy.

~~As we go from Sc to Zn in 3d series, Ionisation energy increases but increase in Ionisation energy is not regular.~~

It is measured in KJ mol^{-1}



The IP or IE value of d-block elements lies between s-block and p-block elements.

Ionisation energy depends upon size, ~~high~~ smaller is the size, higher is the ionisation energy.

As we go from Sc to Zn in 3d series, ionisation energy ~~decreases~~ increases but increase in Ionisation energy is not regular due to decrease in atomic size and increase in ~~ionisation~~ nuclear charge.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE ₁ (KJmol ⁻¹)	632	650	659	662	716	762	758	738	744	906
IE ₂	1245	1320	1376	1635	1523	1564	1647	1756	1901	1736

The 2nd IE value also increases with increase in atomic number. The value of Cr & Cu are higher than neighbouring elements. This is due to most stable electronic configuration of Cr & Cu.

↓ (Half filled) (Completely filled)

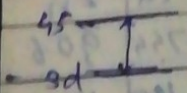
④ Metallic Nature

- All transition elements are metals and shows the properties of metals like, good conductor of heat and electricity, malleability, ductility, metallic luster, high density, High M.Pt., B.Pt. etc.
- Transition metals have Hexagonal closed packed (HCP), Cubic closed packed (CCP), and Body centred cubic (BCC) structure, which are the characteristic property of true metals.
- The metallic character of transition elements depends upon low ionisation energy and presence of vacant orbitals in outermost orbit.
- This favors the formation of metallic bonds and shows metallic character. The metallic bonding is due to the presence of one or more unpaired electrons in the last orbit.
- The presence of unpaired electrons in d-orbitals forms covalent bonding. Greater is the number of unpaired d-electrons, greater is the covalent bond and more strong is the bond.

④ ⑤ Cr, Mo, W are very hard metals because they contain more no. of unpaired e⁻s. ~~(4 electrons)~~ while Mn, Zn, Cd, Hg are soft metals as they don't have any unpaired electrons.

⑤ Oxidation state:

- Transition elements shows variable oxidation state because energy gap between 3d and 4s orbital is small. (In general (n-1)d & ns orbital gap is small)
- The variable o.s. is related to electronic configuration.
- The most common oxidation state of element is +2 (except Sc, which shows +3 o.s.)



① Minimum oxidation state

- All 3d elements shows +2 o.s. by the loss of two electrons from ns^2 level.
- Cr and Cu also shows +1 o.s. by the loss of one electron from ns^1 level.

② Maximum oxidation state

Transition elements shows +2 to +7 o.s.

eg ① Scandium

The outermost E.C. of Sc = $3d^1 4s^2$. It shows +2, +3 by the loss of ns^2 and $(n-1)d^1$ electrons. 0.s. but +3 o.s. is most stable

② Titanium

The outermost E.C. of Ti = $3d^2 4s^2$. It shows +2, +3 +4 o.s. by losing ns^2 , ns^2 & $(n-1)d^1$ and ns^2 & $(n-1)d^2$ electrons respectively.

③ Vanadium: +2 +3 +4 +5

④ Chromium: +2 +3 +4 +5 +6

⑤ Manganese: +2 +3 +4 +5 +6 +7

⑥ Iron: +2 +3 +4 +5 +6 (Fe²⁺, Ferric, Fe³⁺ ~~and~~ Ferric and Fe⁺⁶ as ferrate)

~~⑦ In Cobalt and Nickel~~

⑦ Cobalt: +2 +3 +4

⑧ Nickel: +2 +3 +4

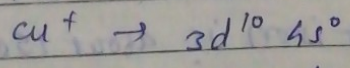
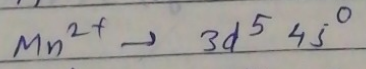
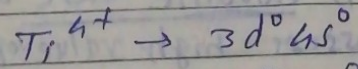
⑨ Copper: +1 +2

⑩ Zinc: +2

③ Relative stability of oxidation state

According to the rule of extra stability if ~~the~~ o.s. like $3d^0$, $3d^5$, $3d^{10}$ are extra stable

eg



④ Nature of compounds (Ionic or covalent):

The transition elements can form ionic compound in lower o.s. (like +2, +3) ~~and~~ and covalent compounds in higher o.s.

- The elements in higher o.s. i.e. +4 and above are good oxidising agent.
eg. $K_2Cr_2O_7$, $KMnO_4$, CrO_2Cl_2 are good oxidising agent.

(6) Magnetic properties

The transition element shows different behavior when they placed in magnetic field. are

- (i) Paramagnetism
- (ii) Diamagnetism.
- (iii) Ferromagnetism.

(i) Paramagnetism

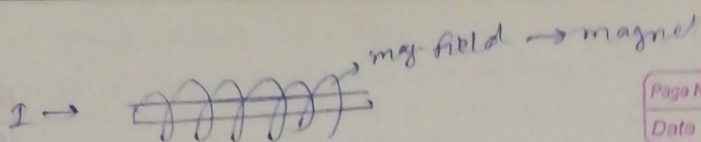
- The substance which contain one or more unpaired electron is called as paramagnetic substance and such property is called as paramagnetism.
- These substances are weakly attracted by magnetic field.
- They have definite magnetic moment.

(ii) Diamagnetism:

- The substance which does not contain unpaired electron is called as **diamagnetic** substance. and such property is called as diamagnetism.
- These substances are repelled by magnetic field
- They have zero magnetic moment.

(iii) Ferromagnetism:

- Ferromagnetism is extreme case of Paramagnetism.
- These substances possess high value of magnetic permeability.
eg permeability of iron is about 1500 times.
- These substances have high degree of magnetization in magnetic field.



Page No.	
Date	

Magnetic moment (M)

Flow of electron is called as current. (or electric current)
 - When current is passed through a wire coiled around core, a field is produced which behaves as a magnet. Such field is called magnetic moment.

The electron can spin in ~~two~~ two ways

- ① orbital motion → which is due to the motion of electron around the nucleus. It produces definite magnetic moment called as orbital magnetic moment
- ② spin motion → which is due to the motion of electron around its own axis. It also produces definite magnetic moment called as spin magnetic moment.

$$\text{The total mag. moment} = \mu_{\text{total}} = \mu_{\text{orbital}} + \mu_{\text{spin}}$$

In case of ~~3d~~ transition elements, (3d series elements) the unpaired electrons are present in 3d orbitals, which are valence shell orbitals. When they (metals) interact with ligand, the orbital motion of electrons is suppressed or quenched and therefore magnetic moment ~~is~~ arises due to spin motion of electrons only.

$$\therefore \mu_{\text{total}} = \mu_{\text{effective}} = \mu_{\text{spin}}$$

- In such case, the magnetic moment depends upon no. of unpaired electrons and can be calculated by the formula.

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

Where n is no. of unpaired electron

B.M is Bohr magneton, unit of magnetic moment.

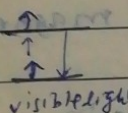
eg In $\text{Mn}^{2+} (3d^5)$, no. of unpaired electron = 5

$$\begin{aligned} \mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} \\ &= \sqrt{35} \\ &= \sqrt{35} \times 9.27 \times 10^{-24} \text{ J T}^{-1} \\ &= 5.92 \text{ B.M.} \end{aligned}$$

No. of Unpaired e^- s in 3d-orbitals	magnetic moment in BM
0	0
1	1.73
2	2.84
3	3.89
4	4.90
5	5.92

(7) Colour of salts:

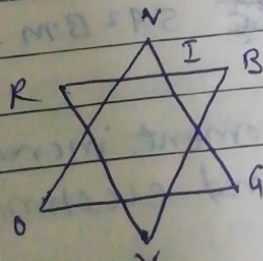
- The compounds of transition elements are colourless in solid or in solution form.
- The colour of the transition element compounds depends upon number of unpaired electrons in d-orbital and absorption of visible light. (400-750nm)
- The compounds which does not contain unpaired electrons are colourless or white.
- When white light is fall on a solution of compounds there are three possibilities



- If the light (radiation) is completely absorbed, then substance appears a black.
- If the radiation is completely transmitted then, substance appears a ~~black~~ white.
- If substance absorbed some amount of light and some amount of light is transmitted then, it appears colour.

The colour of transmitted light is complementary colour of absorbed light.
The complementary colour can be identified using Munsell colour wheel.

[The opposite placed colour are complementary]

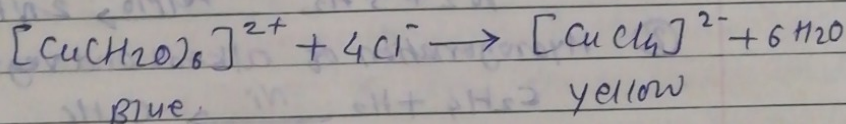


- Transition metals are coloured due to d-d transition OR transfer of electron from ligand to metal i.e. charge transfer which provide intense colour.
- the transition metal compound containing d¹ to d⁹ configuration shows colour. The d⁰ & d¹⁰ configuration are colourless.

extra shot - MnO_4^- ion has intense purple colour due to charge transfer. In MnO_4^- , the electrons are transfer from oxygen to metal and reduces the o.s. of metal from Mn^{7+} to Mn^{4+} . Other examples of ^{colour due to} charge transfer are $Cr_2O_7^{2-}$, CrO_4^{2-} , Cu_2O & $Ni-DMG$.

- The colour also depends upon ligand and geometry of complex.

eg. when $CuSO_4$ dissolved in water, it forms blue ~~colour~~ colour solution of $[Cu(H_2O)_6]^{2+}$ which has octahedral geometry. But when this solution is treated with conc. HCl, it turns yellow. This change is due to formation of complex $[CuCl_4]^{2-}$, which has tetrahedral geometry.



⑧ Catalytic properties

- The substance which increase the rate of reaction but does not take part in the reaction is called as catalyst. and such property is called catalytic property.
- Transition metals and their compounds shows Catalytic properties.
- The role of catalyst during the reaction can be explain by two theories

① Intermediate compound formation theory:

Transition metal shows variable O.S. The catalyst

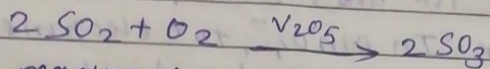
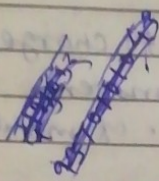
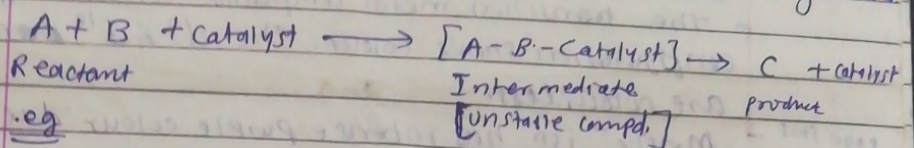
Ligand: The species which can donate lone pair of electrons and forms coordinate bond is ligand.

- Ligand may be +ve charge or neutral or -ve charge species.
- Ligands are electron rich species.

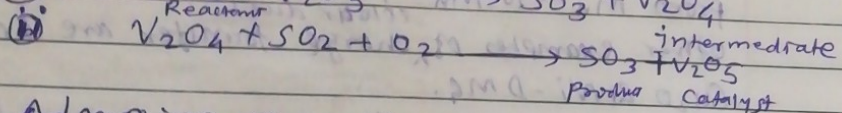
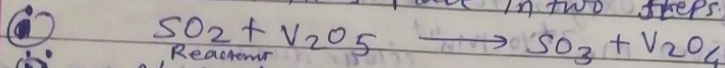
Date

(12)

Combine with one of the reactant and forms a intermediate compound. These intermediate decomposed to give final product and catalyst is regenerated.



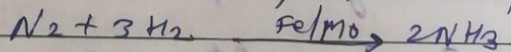
This reaction takes place in two steps.



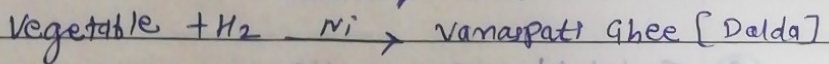
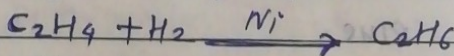
(8) Adsorption theory:

According to this theory, reactant molecule adsorbed on the surface of finely divided catalyst. The reactant molecules get activated and undergoes reaction to form product. The product molecules get desorbed and gain the new reactant molecules and get adsorbed and process is continues.

eg. Manufacturing of NH_3 by Haber's process

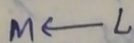


(2) Hydrogenation of alkene and vegetable oil

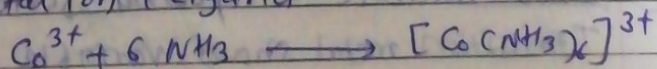
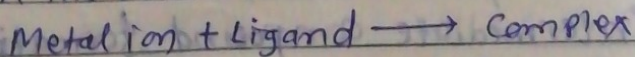


(9) Complex formation Reaction:

When metal ion combine with ligands, their compound is formed called as complex compound or coordination compound.



The complexes are stable, do not lose their identity in solution, do not give the test of each ions in the solution.



During the formation of complex, ligand donate lone pair of electron to the metal ion and forms coordinate bond.

The number of ligands attached to the metal ion is called as coordination number, and geometry of complex is related to coordination number.

eg tetrahedral or square planar (C.N. = 4), octahedral (C.N. = 6)

The stability of complex depends upon

(i) Smaller size and high positive charge density of metal ion.

(ii) metal ion must contain vacant d-orbital to accept electron donated by ligands

(iii) Metal ion shows variable o.s.

(iv) Due to splitting of d-orbitals, the additional stabilization energy is available called as crystal field stabilization energy.

extra shot

Generally, stability of complexes increases with increase in d , n and decrease in ionic size

(i) The transition metal with lower or zero o.s. forms stable complex with ligand, like CO, NO, C_6H_6 due to formation of π -bond due to back bonding

(ii) The highly electronegative and basic ligands like F^- , Cl^- , NH_3 can form stable complex with metal even in higher o.s.

Introduction to 4d and 5d Transition series

(A) 4d-Elements (OR) second Transition series:

The Elements in which last electron enters in 4d sub orbitals are called 4d series elements or second transition series elements. There are ten elements starting from Yttrium, ($Z = 39$) to Cadmium ($Z = 48$)

S.No	Element	Symbol	At No	Electronic Configuration	E.C. in terms of inert gas
1	Yttrium	Y	39	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^1 4f^0 5s^2$	[Kr] $4d^1 5s^2$
2	Zirconium	Zr	40	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^2 4f^0 5s^2$	[Kr] $4d^2 5s^2$
3	Niobium	Nb	41	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^4 4f^0 5s^1$	[Kr] $4d^4 5s^1$
4	Molybdenum	Mo	42	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^5 4f^0 5s^1$	[Kr] $4d^5 5s^1$
5	Technetium	Tc	43	————— " ———— $4d^5 5s^2$	[Kr] $4d^5 5s^2$
6	Ruthenium	Ru	44	————— " ———— $4d^7 5s^1$	[Kr] $4d^7 5s^1$
7	Rhodium	Rh	45	————— " ———— $4d^8 5s^1$	[Kr] $4d^8 5s^1$
8	Palladium	Pd	46	————— " ———— $4d^{10} 5s^0$	[Kr] $4d^{10} 5s^0$
9	Silver	Ag	47	————— " ———— $4d^{10} 5s^1$	[Kr] $4d^{10} 5s^1$
10	Cadmium	Cd	48	————— " ———— $4d^{10} 5s^2$	[Kr] $4d^{10} 5s^2$

① There are irregularities in $Mo = 4d^5 5s^1$ and $Ag = 4d^{10} 5s^1$ due to ~~extra stability~~ half filled and completely filled orbitals and get extra stability.

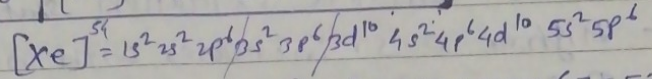
② There is abnormal configuration in Nb, Ru, Rh & Pd which can be explain on the basis of interaction such as (i) electron-electron repulsion (ii) nucleus-electron attraction (iii) shielding effect. but it is not easy to explain accurately.

(B) 5d-elements (OR) Third transition series:

The elements in which last electron enters in 5d sub orbital are ^{called as} 5d series elements or third transition series elements. There are ten elements starting from Lanthanum (Z=57) and from Hafnium (Z=72) to mercury (Z=80).

S.No	Element	Symbol	At No.	E.C. in terms of inert gas
1	Lanthanum	La	57	[Xe] $4f^0 5d^1 6s^2$
2	Hafnium	Hf	72	[Xe] $4f^{14} 5d^2 6s^2$
3	Tantalum	Ta	73	[Xe] $4f^{14} 5d^3 6s^2$
4	Tungsten	W	74	[Xe] $4f^{14} 5d^4 6s^2$
5	Rhenium	Re	75	[Xe] $4f^{14} 5d^5 6s^2$
6	Osmium	Os	76	[Xe] $4f^{14} 5d^6 6s^2$

7	Iridium	Ir	77	$[Xe] 4f^{14} 5d^7 6s^2$
8	Platinum	Pt	78	$[Xe] 4f^{14} 5d^9 6s^1$
9	Gold	Au	79	$[Xe] 4f^{14} 5d^{10} 6s^1$
10	Mercury	Hg	80	$[Xe] 4f^{14} 5d^{10} 6s^2$



- Third transition series start with Lanthanum (Z=57) in which last electron enters in 5d orbital.
 - In between La and Hf, there are 14 elements called as lanthanides in which 4f orbitals are successively filled to its capacity of 14 electrons. and then addition of electron takes into 5d orbital at Hf and continue upto Hg.

Again here we find that there are abnormalities in the configuration of some elements which can be explain in terms of extra stability of half and completely filled d-orbitals and factors like (i) electron-electron repulsion (ii) nuclear electron repulsion (iii) shielding effect. but it is not easy to explain accurately.

msml Comparison of 4d & 5d Elements with 3d Elements

(i) Atomic and ionic radii

Similarities:- in 4d & 5d series elements, As we go left to right, atomic or ionic radii decrease and for the last ^{elements} increase due to inter electronic repulsion similar with 3d series elements.

Differences:-

As we go top to bottom, i.e. from 3d → 4d → 5d series, the radii are expected to increase. But it is observed that atomic radii increases from 3d → 4d but from 4d → 5d, atomic radii remains almost const. due to Lanthanide contraction. [Decrease in atomic and ionic radii.]

② oxidation state:

Similarities

- All transition ~~series~~ elements of 3d, 4d & 5d series shows variable oxidation state.
- Higher O.S. increases with increase 'm at. no.
- The maxim O.S. 'm 4d series is +8 by Ru and in 5d series is by Os. and 3d series is +7 by Mn.

The higher O.S. of 4d & 5d series elements are more stable than of 3d metals.

The ^{last} element of 3d, 4d, 5d ~~elements~~ ^{series} does not shows variable O.S.

eg Zn (3d series) shows +2 O.S. only

Cd (4d series) shows +2 O.S. only

Hg (5d series) shows +1 & +2 O.S. only.

③ Magnetic properties:

- The magnetic properties of transition elements depends upon unpaired electrons.

- Generally, 4d & 5d series elements forms low spin complexes while 3d series elements forms high spin complexes.

- Generally, 4d & 5d series elements forms diamagnetic complexes whereas 3d series elements forms paramagnetic complexes.

④ Colour:

The colour depends upon transfer of electrons from one energy level to another energy level by the absorption of visible light.

The colour of 4d & 5d series elements is similar to 3d series due to partly filled d-orbitals.

== x ==