

TRANSITION ELEMENTS



Dr. T. Geetha

Assistant Professor

Department of Chemistry

St. Mary's College, Thrissur



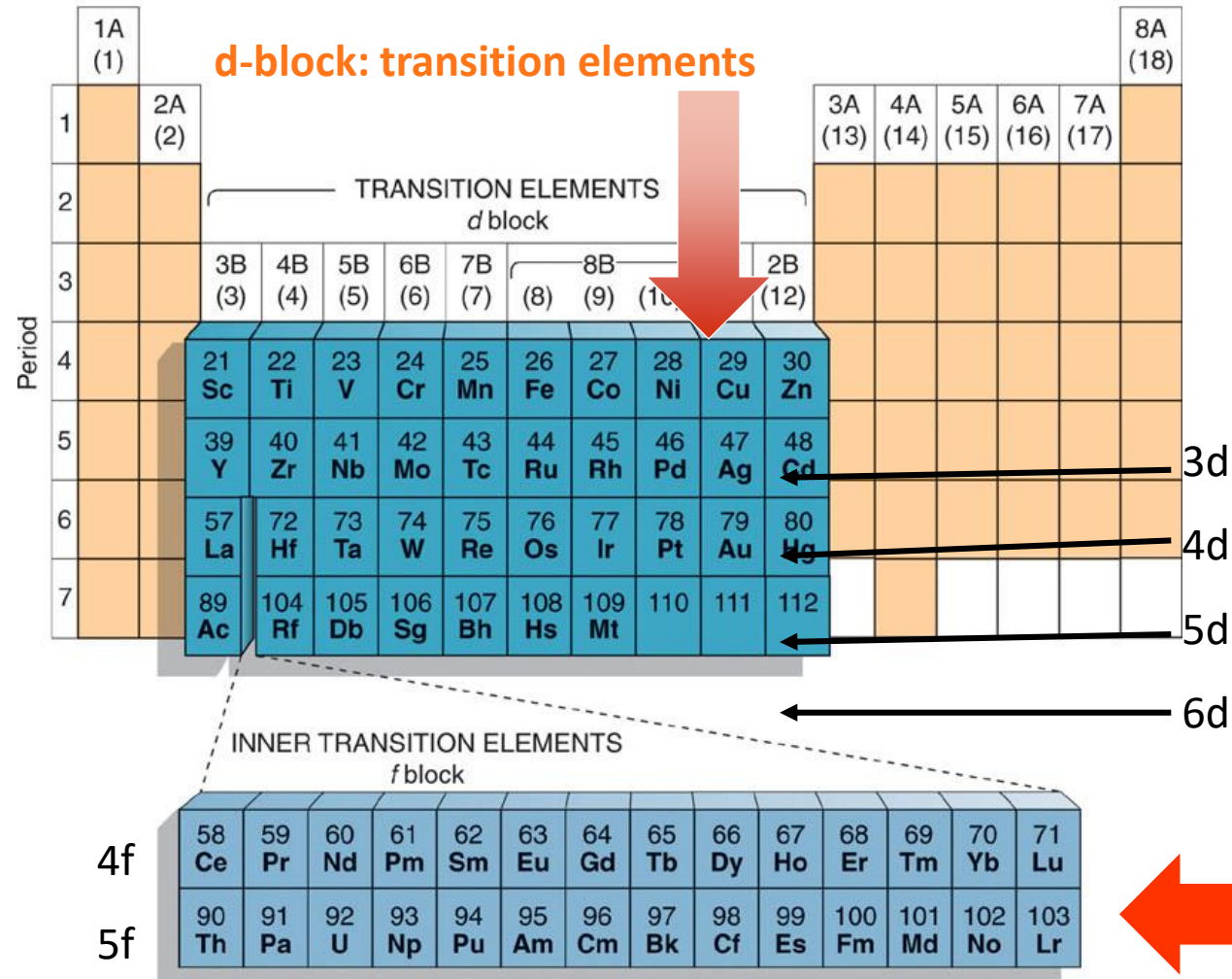
Transition Elements

- ❖ **Partially filled d orbital** in its atom in the ground state or in any one of its oxidation state
- ❖ General Electronic configuration **$(n-1) d^{1-10}ns^{1-2}$**
- ❖ **Zn , Cd & Hg – Group 12 - pseudo transition elements – filled d orbital $(n-1) d^{10}ns^2 / (n-1) d^{10}$**

What is a transition metal?



**“an element with valance d- or f-electrons”
ie. a d-block or f-block metal**





biological activity

color

magnetic behavior

geometry

What's interesting about Transition Metal Complexes??

coordination number

oxidation states

medical applications



Sc Ti V Cr Mn Fe Co Ni Cu Zn

The 3d series

- Starts from **Scandium** & ends in **Zinc**
- Atomic no. - **(21-30)**
- **Electronic configuration: $[\text{Ar}]3d^14s^2$ to $[\text{Ar}]3d^{10}4s^2$**



Scandium, Sc; 3B(3)



Titanium, Ti; 4B(4)



Vanadium, V; 5B(5)



Chromium, Cr; 6B(6)



Manganese, Mn; 7B(7)



Iron, Fe; 8B(8)



Cobalt, Co; 8B(9)



Copper, Cu; 1B(11)



Nickel, Ni; 8B(10)



Zinc, Zn; 2B(12)

Orbital Occupancy of the Period 4 Transition Metals



Element	Partial Orbital Diagram			Unpaired Electrons
	4s	3d	4p	
Sc	↑↓	↑		1
Ti	↑↓	↑ ↑		2
V	↑↓	↑ ↑ ↑		3
Cr	↑	↑ ↑ ↑ ↑ ↑		6
Mn	↑↓	↑ ↑ ↑ ↑ ↑		5
Fe	↑↓	↑↓ ↑ ↑ ↑ ↑		4
Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑		3
Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑		2
Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		1
Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		0

Extra stability of half filled & completely filled orbital

The number of unpaired electrons increases in the first half of the series and decreases in the second half, when pairing begins.



The 4d series

- Starts from **Yttrium** & ends in **Cadmium** – (39-48)
- Electronic configuration: $[\text{Kr}]4d^{15}5s^2$ to $[\text{Kr}]4d^{10}5s^2$
- Mo - stability of half filled shell
- Ag - stability of completely filled shell
- Other anomalies explained by
 - nuclear electron attraction
 - Shielding of electron
 - Inter electronic repulsion etc.



The 4d series

Element	Atomic Number	Symbol	Electronic configuration
Yttrium	39	Y	[Kr] 4d ¹ 5s ²
Zirconium	40	Zr	[Kr] 4d ² 5s ²
Niobium	41	Nb	[Kr] 4d ⁴ 5s ¹
Molybdenum	42	Mo	[Kr] 4d ⁵ 5s ¹
Technetium	43	Tc	[Kr] 4d ⁵ 5s ²
Ruthenium	44	Ru	[Kr] 4d ⁷ 5s ¹
Rhodium	45	Rh	[Kr] 4d ⁸ 5s ¹
Palladium	46	Pd	[Kr] 4d ¹⁰ 5s ⁰
Silver	47	Ag	[Kr] 4d ¹⁰ 5s ¹
Cadmium	48	Cd	[Kr] 4d ¹⁰ 5s ²



The 5d series



- Starts from Lanthanum & ends in Mercury (57-80)
- Electronic configuration: $[\text{Xe}]5d^16s^2$ to $[\text{Xe}]4f^{14}5d^{10}6s^2$
- Lanthanide elements (*4f series*) lies between La & Hf
- Au - stability of completely filled shell
- Pt - $5d^96s^1$ – no simple explanation



The 5d series

Element	Atomic Number	Symbol	Electronic configuration
Lanthanum	57	La	[Xe] 5d ¹ 6s ²
Hafnium	72	Hf	[Xe] 4f ¹⁴ 5d ² 6s ²
Tantalum	73	Ta	[Xe] 4f ¹⁴ 5d ³ 6s ²
Tungstun	74	W	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
Rhenium	75	Re	[Xe] 4f ¹⁴ 5d ⁵ 6s ²
Osmium	76	Os	[Xe] 4f ¹⁴ 5d ⁶ 6s ²
Iridium	77	Ir	[Xe] 4f ¹⁴ 5d ⁷ 6s ²
Platinum	78	Pt	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹
Gold	79	Au	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Mercury	80	Hg	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²



Ac Rf Db Sg Bh Hs Mt Ds Rg Uub

The 6d series

- Starts from **Actinium** & ends in **Copernicium** (89-112)
- **Electronic configuration: [Rn]6d¹7s² to [Rn] 5f¹⁴6d¹⁰7s²**
- **Actinides elements (*5f series*) lies between Ac & Rf**
- **Rg - stability of completely filled shell 6d¹⁰7s¹**



The 6d series

Element	Symbol	At. No.	Electronic configuration
Actinium	Ac	89	[Rn] 6d ¹ 7s ²
Rutherfordium	Rf	104	[Rn] 5f ¹⁴ 6d ² 7s ²
Hahnium	Ha	105	[Rn] 5f ¹⁴ 6d ³ 7s ²
Seaborgium	Sg	106	[Rn] 5f ¹⁴ 6d ⁴ 7s ²
Bohrium	Bh	107	[Rn] 5f ¹⁴ 6d ⁵ 7s ²
Hassium	Hs	108	[Rn] 5f ¹⁴ 6d ⁶ 7s ²
Meitnerium	Mt	109	[Rn] 5f ¹⁴ 6d ⁷ 7s ²
Ununnilium	Uun	110	[Rn] 5f ¹⁴ 6d ⁸ 7s ²
Unununium	Uuu	111	[Rn] 5f ¹⁴ 6d ⁹ 7s ²
Unubium	Uub	112	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ²



Properties of the Transition Metals

All transition metals are **metals**, whereas main-group elements in each period change from metal to nonmetal

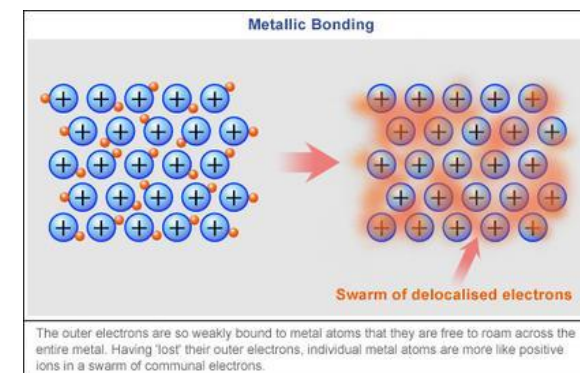
Many transition metal compounds are **colored** and **paramagnetic**, whereas most main-group ionic compounds are colorless and diamagnetic

The **properties** of transition metal compounds are **related to the electron configuration** of the metal ion



Metallic character

- All transition elements are metallic in nature
- Metallic & covalent bonding
- Valence s electron – metallic bond
- $(n-1) d$ electron- covalent bond
- Lustre & ductility,
- malleability, high tensile strength
- thermal & electrical conductivity
- Hard & brittle – partially filled d orbital - covalent bonding between metal atom through orbital overlap
- Zn, Cd & Hg – completely filled $(n-1)d$ orbital – lack covalent bonding through orbital overlap - lower hardness & brittleness



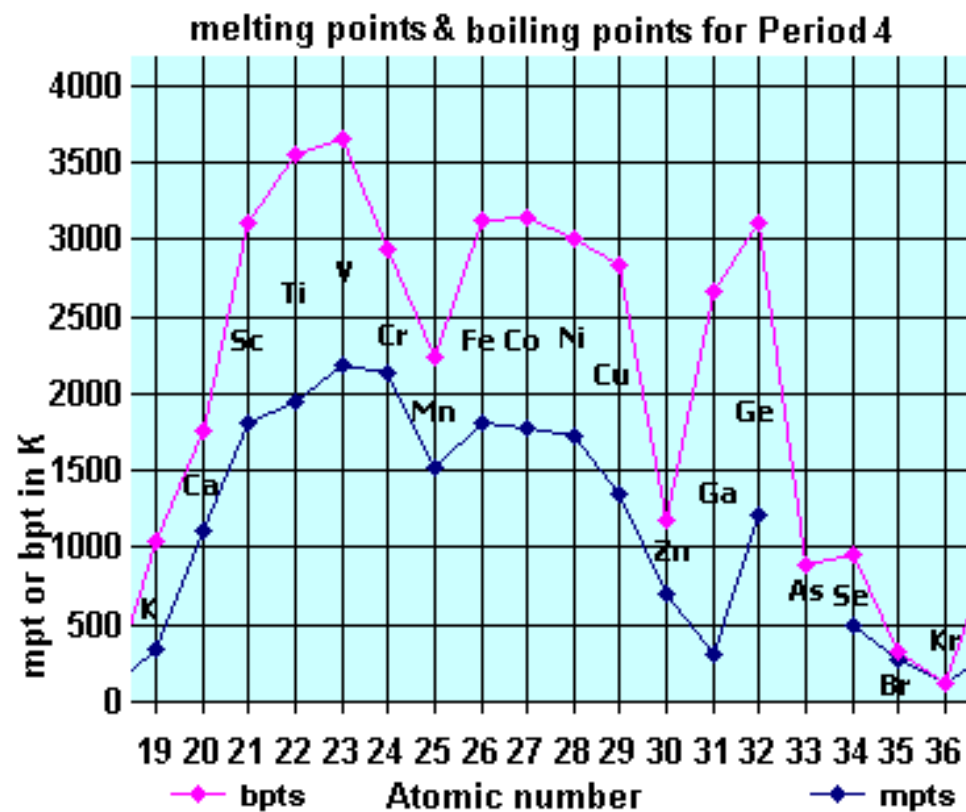


Melting & Boiling Point

- Melting & Boiling point higher than S Block element
- Reason - valence & covalent Bond
- Expected trend – increases with increasing no. of unpaired d electron
- **Anomalies – Mn** – low M. Pt. - inherent stability of $3d^5 4s^2$ - lowers participation of these electrons in interatomic metallic & covalent bond
- **Zn, Cd & Hg** — no partially filled d orbital for covalent bonding – low M. P & B. P



Melting & Boiling Point





Melting & Boiling Point

- 4d & 5d - larger, more diffuse, more penetrating than 3d orbital
- Reduced mutual repulsion between electron – stronger bond
- Extensive metal Metal- metal covalent bond
- M.P. & B.P. increases as we move down a group in transition metal

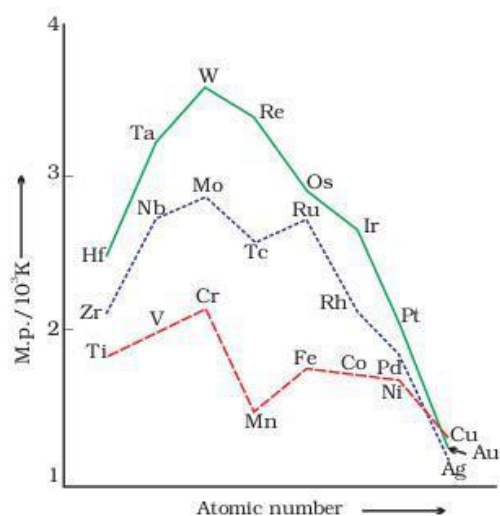
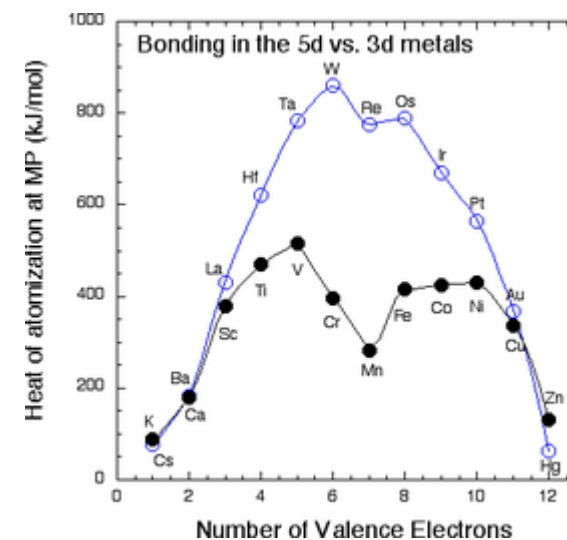


Fig. 8.1: Trends in melting points of transition elements

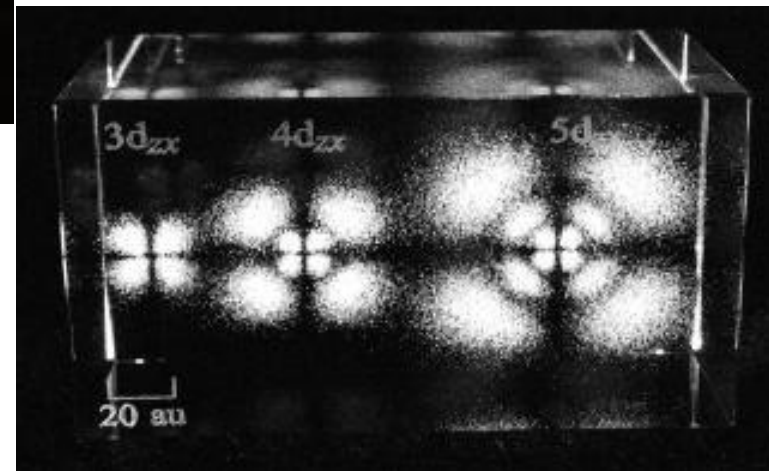




Relative size of d orbitals



3d, 4d, 5d



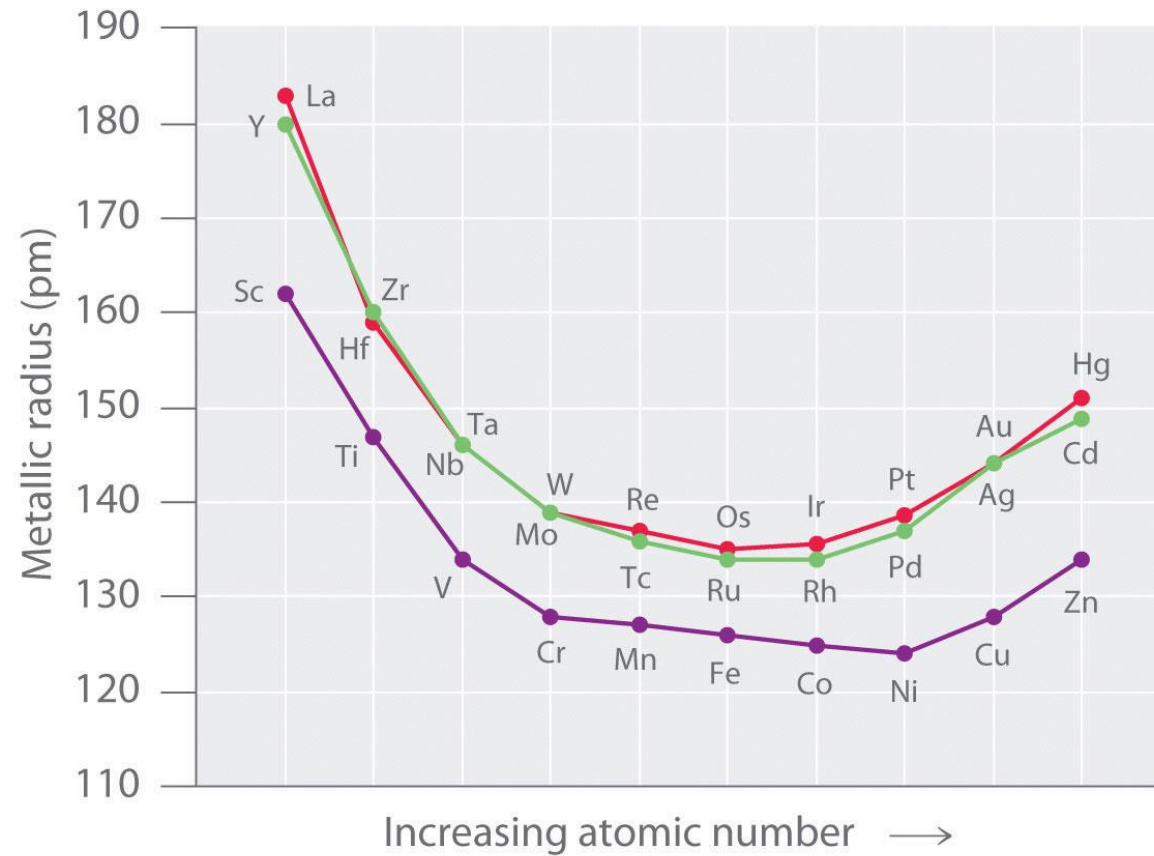


Atomic & Ionic radii

- Atomic & ionic radii **decreases on moving from left to right**
- Atomic no. increases - Addition of new electrons in d subshell
 - effective nuclear charge increases
 - shielding of d electron ineffective
- electrostatic **attraction between nucleus & outermost electron increases**
- Towards end of series – slight increase in radii
- Atomic radii increases down a group
- radii of 4d & 5d series nearly identical – lanthanide contraction

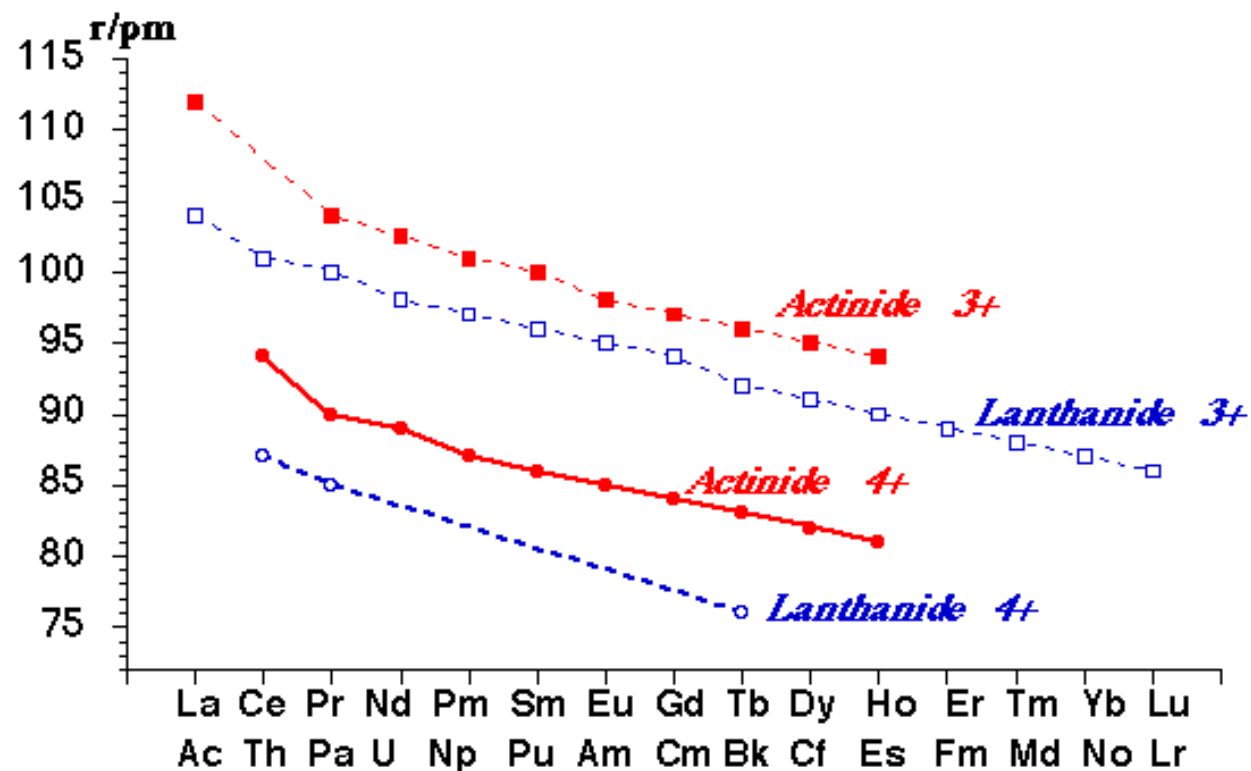


Atomic radii





Ionic radii





Lanthanide Contraction

As the atomic number increases, each succeeding element adds

- ❑ one electron in the 4f orbital
- ❑ one proton in the nucleus
- ❑ 4f electrons are ineffective in screening the outer electrons from the nucleus causing imperfect shielding
- ❑ gradual increase in the nucleus attraction for the outer electrons
- ❑ gradual decrease in size occur

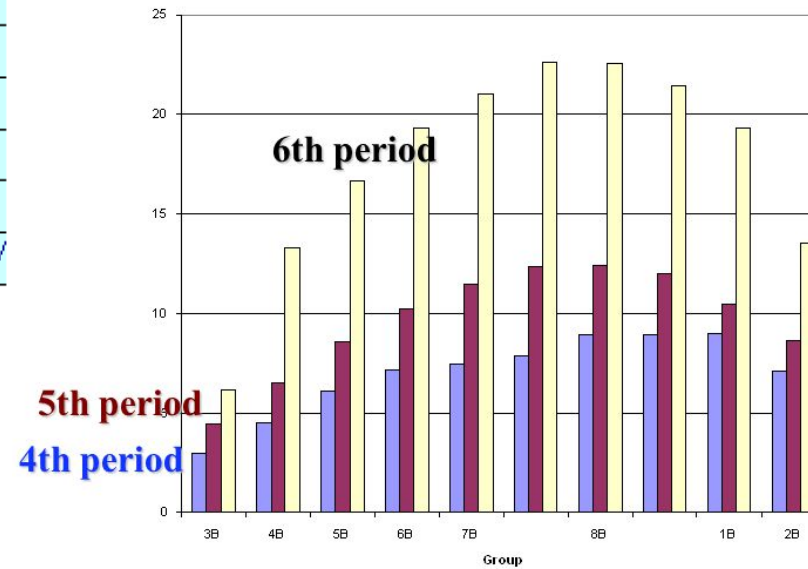
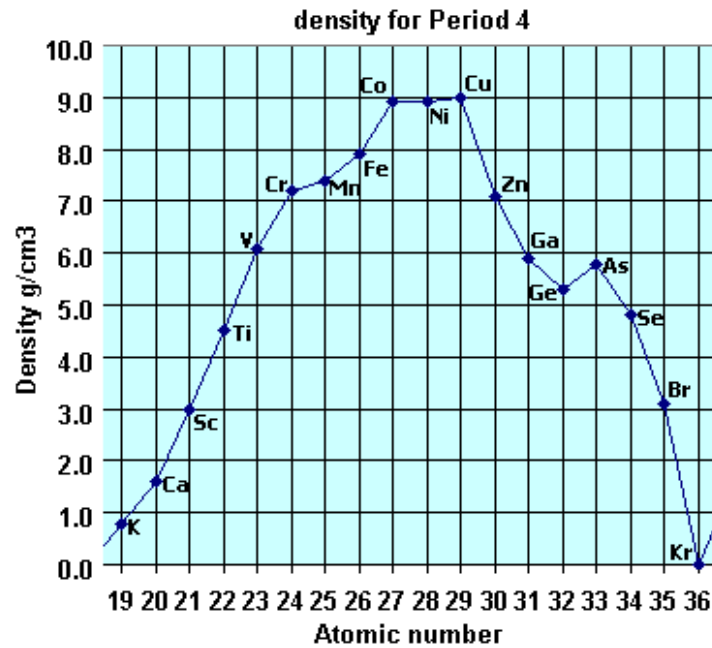


Density

- Increase in density across a series
 - Dec. in atomic radii – dec. in volume – inc. in atomic mass
- Density **higher than s & p block element**
- Density of **5d series > 4d series**
- Atomic mass increases considerably on moving from second to third row but atomic size is nearly the same – lanthanide contraction – increase in density



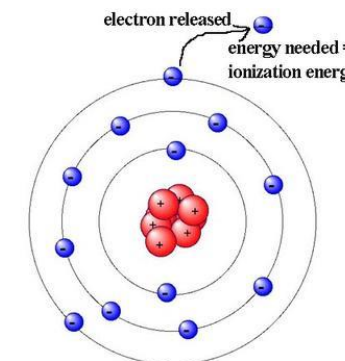
Density



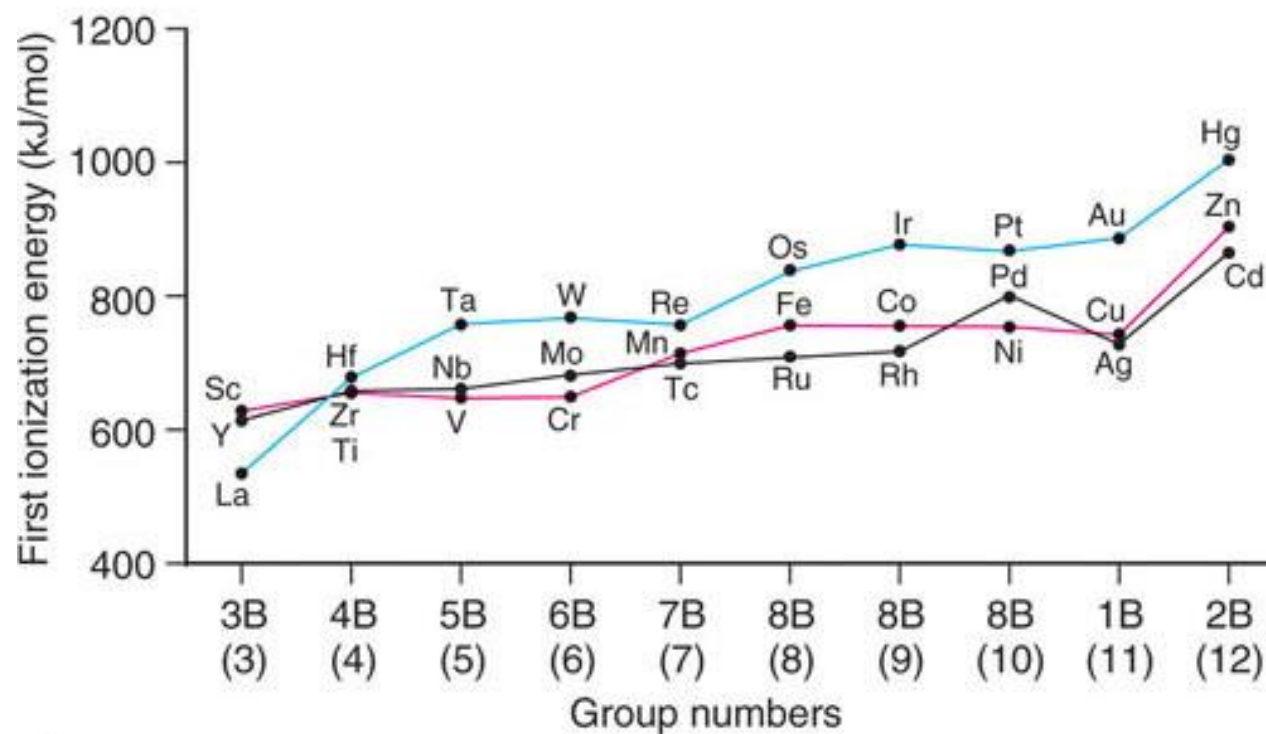


Ionization energy

- Ease with which an electron can be removed from an isolated gaseous atom
- Ionization energy **fairly high**
- **Intermediate between S & P** block element
- Ionization energy **increases along a series**
 - increase in the nuclear charge - shielding effect of the added electrons increases - decrease the attraction due to the nuclear charge-opposing factors - gradual increase in the ionisation energies



1st ionization energy



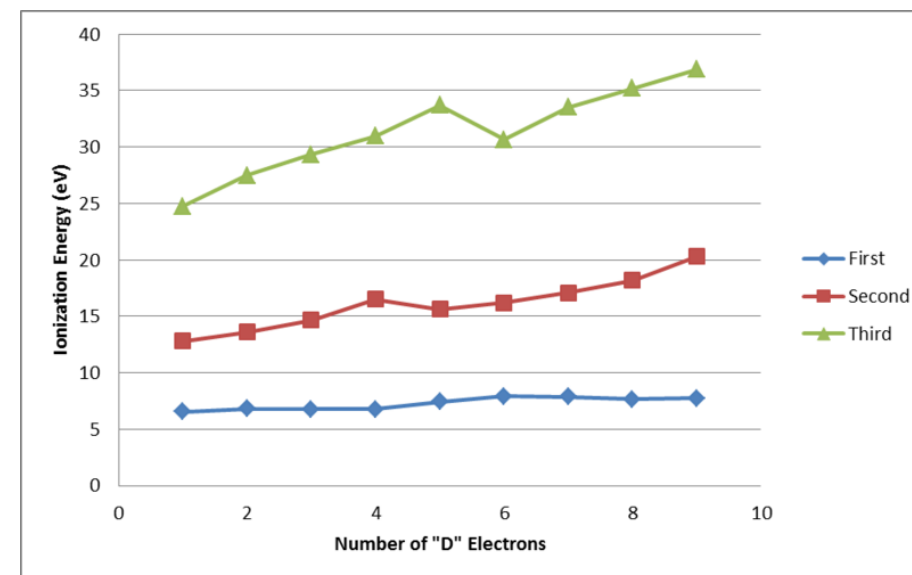
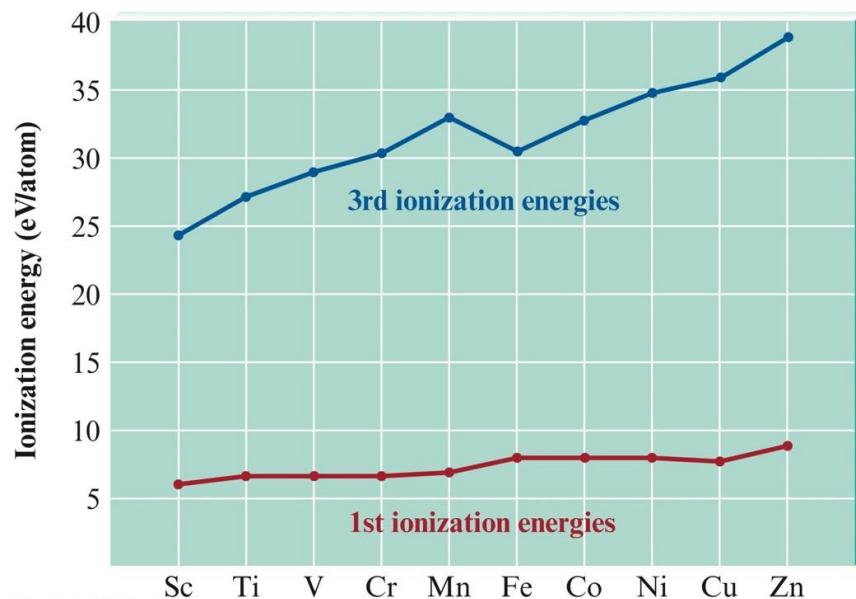
1st ionization energy



- **energy needed to remove 4s electron** - 4s electrons the outermost electrons – higher energy - removed first
- **5d-series much higher than 3d and 4d series** -5d-series elements after lanthanum (La) - electrons go inner 4f orbital - poor shielding effect - outermost electrons experience greater nuclear attraction - higher ionization energies for the 5d- series
- **Values for Zn, Cd & Hg** – sudden increase – additional stability due to complete filling of d sub shell



IInd & IIIrd Ionization energy





IInd & IIIrd ionization energy

- **IInd ionization energy – Cr & Cu higher** – outer electronic configuration of singly charged Cr & Cu Ion - d^5 & d^{10} - extra stability of half filled & fully filled orbital
- **IIIrd ionization energy** – markedly higher - energy required to remove a 3d electron (both 4s electrons have been removed - greater difficulty for the removal of an electron from Mn^{2+} (d^5) and Zn^{2+} (d^{10}) ions - marked difference between third ionization enthalpies of Fe and Mn



Oxidation state

➤ Variable oxidation state

- (n-1)d & ns electron – comparable energy – participate in bonding
- Varying no. of (n-1)d electron participate in bonding
- Highest oxidation state observed in combination with F & O – Mn_2O_7
- Lower oxidation state - ns electron participate in bonding
 - ionic bond
- Higher oxidation state – ns & (n-1)d electron take part in bonding
 - covalent bond - charge on cation increases
 - size decreases – polarizing power increases
 - increases tendency of cation to share electron
- VCl_2 , MnCl_2 - Ionic; VCl_4 , MnCl_4 – Covalent

Oxidation state



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

Orbital Occupancy of the Period 4 Transition Metals



Element	Partial Orbital Diagram			Unpaired Electrons
	4s	3d	4p	
Sc	↑↓	↑		1
Ti	↑↓	↑ ↑		2
V	↑↓	↑ ↑ ↑		3
Cr	↑	↑ ↑ ↑ ↑ ↑		6
Mn	↑↓	↑ ↑ ↑ ↑ ↑		5
Fe	↑↓	↑↓ ↑ ↑ ↑ ↑		4
Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑		3
Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑		2
Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		1
Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		0

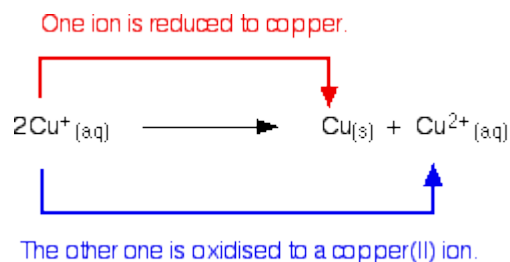
Extra stability of half filled & completely filled orbital

The number of unpaired electrons increases in the first half of the series and decreases in the second half, when pairing begins.



Oxidation state

- **+2** - Most **common** oxidation state
- **+3** - oxidation state shown by **all elements except Cu & Zn**
- **+1** - oxidation state shown by **Cu**
 - unstable in aq. solution – disproportionation
 - stability of Cu^{2+} in aq. solution- **higher hydration enthalpy** of Cu^{2+}





Oxidation state

➤ For the first Five elements

- minimum oxidation state = no. of electron in the outer s subshell
- Maximum oxidation state = sum of outer s & d electron

➤ For the rest

- minimum oxidation state = no. of electron in the outer s subshell
- Maximum oxidation state – rarely higher than +2 or +3

➤ Elements with greatest no. of oxidation state – middle of series

➤ Elements with highest oxidation state – middle of series

➤ Mn – maximum oxidation state & highest in 1st series (+2 to +7)



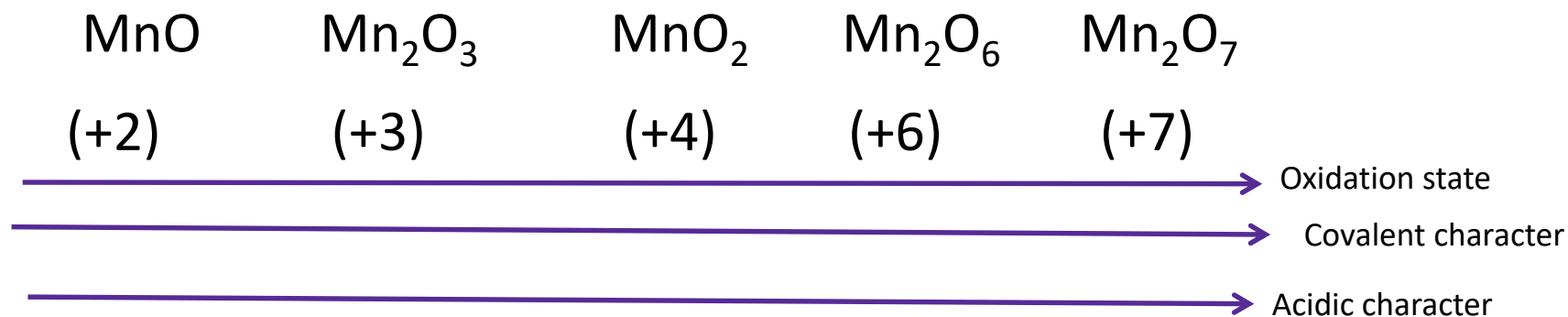
Oxidation state

- **Elements in the beginning of series** - fewer oxidation state – fewer d electron – Sc (+3), Sc(+2)- rare; Ti(+2), Ti (+3), Ti(+4) – more stable
- **Elements towards end of series** - fewer oxidation state – Too many d electron - fewer d orbital with unpaired electron – Zn (+2), Cu(+2), Cu (+1) only
- **Oxidation state of elements differ by unity** – V(+2), V(+3), V(+4), V(+5)
- **Highest oxidation state** in 3d series – (+7) - Mn
4d series – (+8) - Ru
5d series – (+8) – Os
- **Oxidation state of metal - Zero** – Ni(CO)₄, Fe(CO)₅ & Cr(CO)₆



Oxidation state

- **Among Group 4 to 10** – higher oxidation state favoured by heavier members – Group 6 – Cr, Mo & W - , Mo (+6) & W (+6) more stable than Cr(+6) – $\text{Cr}_2\text{O}_7^{2-}$ - strong oxidizing agent in acidic medium – MoO_3 & WO_3 are not
- **P block elements** - Lower oxidation state favoured by heavier members – inert pair effect
- **Higher oxidation state** – covalent character – increase in acidity of oxides & halides



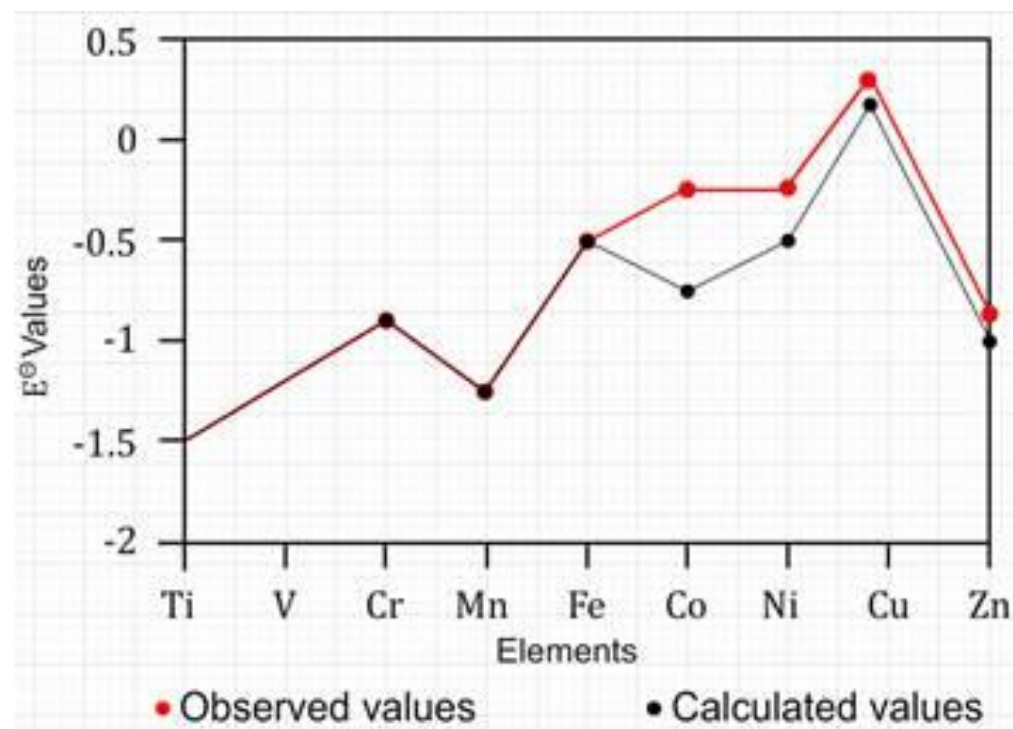


Reducing property & Electrode potential

- **more negative the reduction potential for M^{n+}/M couple – greater reducing potential – greater tendency of metal M to undergo oxidation**
- **$E^0_{M^{2+}/M}$ values for all 3d transition metals except Cu are negative**
- **All 3d metals except Cu will reduce H^+ & displace H_2 from dil. acid**
- **Some react too slowly**
- **Some coated with adherent protective layer of oxides – protect from attack by acids**
- **Less negative E^0 , lower reducing character – across series**



Reducing property & Electrode potential

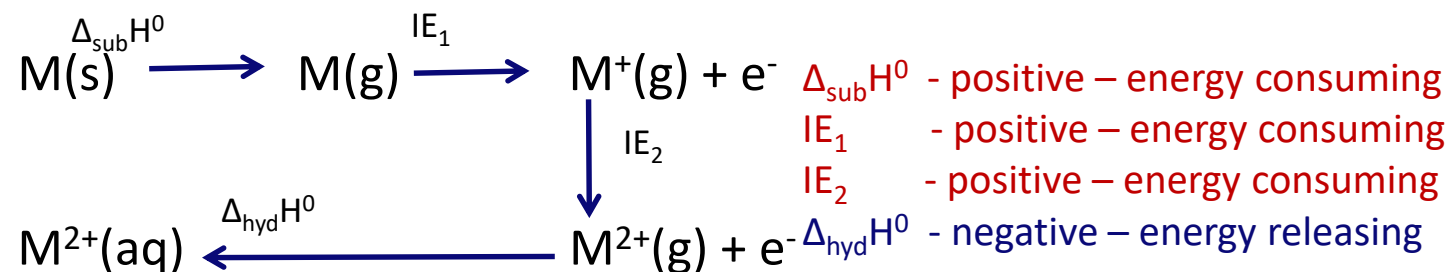




Factors determining E^0 Values & reducing character

➤ Value of $E^0_{M^{2+}/M}$ determined by

- Enthalpy of sublimation – $\Delta_{\text{sub}}H^0$
- First ionization energy – IE_1
- Second ionization energy- IE_2
- Enthalpy of Hydration - $\Delta_{\text{hyd}}H^0$



Lower the value of $\Delta_{\text{sub}}H^0$, IE_1 , IE_2 ; More negative value of $\Delta_{\text{hyd}}H^0$
- More negative the value of $E^0_{M^{2+}/M}$ - More reducing the metal



E^0 Values & reducing character

- In general across a series –
 - First & second ionization enthalpy increases
 - Less negative $E^0_{M^{2+}/M}$ values – lower reducing character

Anomalies

- Mn higher reducing property than Cr – higher stability of half filled d^5 configuration of Mn^{2+}
- Zn higher reducing property than expected – higher stability of half filled d^{10} configuration of Zn^{2+}
- Ni higher reducing property than expected – most negative value for the $\Delta_{hyd}H^0$ for Ni^{2+} in the first transition series
- Cu – only positive value for $E^0_{M^{2+}/M}$ in 1st transition series – tendency to oxidize to M^{2+} least - $[\Delta_{sub}H^0 + IE_1 + IE_2] > \Delta_{hyd}H^0$



Magnetic property

Diamagnetic:

unaffected by a magnetic field
no unpaired electrons

Paramagnetic:

influenced by a magnetic field
unpaired electrons

Transition metals and their compounds are often paramagnetic

⇒ Have unpaired d-electrons - Eg. Ti^{2+} Mn^{2+}

Magnetic property

Magnetic properties of transition metal

Sc	Ti	V	Cr	Mn	Fe	Co	Zn
$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^{10}$

Greater the no. of unpaired e⁻ – more paramagnetic the ion

Paramagnetic

Spin cancel Net spin

Paramagnetism
↓
Unpaired electron
↓
Net magnetic effect
(Attract by magnetic field)

Strong diamagnetic materials

pyrolytic graphite Bismuth

Diamagnetic

Spin cancel Spin cancel

Diamagnetism
↓
Paired electron
↓
No Net magnetic effect
(Repel by magnetic field)

Click [here](#) levitation on bismuth Click [here](#) levitation



Magnetic property

- **Unpaired electron** -
- magnetic moment = spin angular momentum + orbital angular momentum
- For 3d series - magnetic moment = spin angular momentum
 - Contribution of orbital angular momentum quenched by fields associated with surrounding ligands
- **Magnetic momentum $\mu = \sqrt{n(n+2)}$ (spin only formula)**
 - n = no. of unpaired electron
 - Unit - Bohr Magneton (BM)
 - A single 1s electron has a magnetic moment of 1.73 BM (1 BM = 9.2732×10^{-24} A m²).



Magnetic property

Ion	Configuration	Unpaired electron	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	2.76
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	5.96
Fe ²⁺	3d ⁶	4	4.90	5.3-5.5
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	1.8-2.2
Zn ²⁺	3d ¹⁰	0	0	0



Formation of coloured ion

- transition metal ions are **coloured** due to **d-d transitions**
- energy absorbed in **excitation** of an electron from a lower energy d orbital to a higher energy d orbital corresponds to the frequency which generally lies in the visible region
- The colour observed corresponds to the complementary colour of the light absorbed
- The frequency of light absorbed is determined by the nature of ligand



Formation of coloured ion

- In the presence of ligand – **degeneracy** of d orbital **lost**
- d orbital **split** into different levels
- Electron from lower energy d orbital **excited** to higher energy orbital
- Absorption of light correspond to visible region
- Colour observed – **complementary colour** of light absorbed
- d-d transition in symmetrical **octahedral** environment – not allowed – forbidden – colour **not intense**
- **Laporte rule** - applies to centrosymmetric molecules (those with an inversion centre - those that only involve a redistribution of electrons within a given subshell are forbidden ($\Delta\ell = 0$))
- **tetrahedral** - lacks centre of symmetry - d-d transition allowed – **intensely coloured**



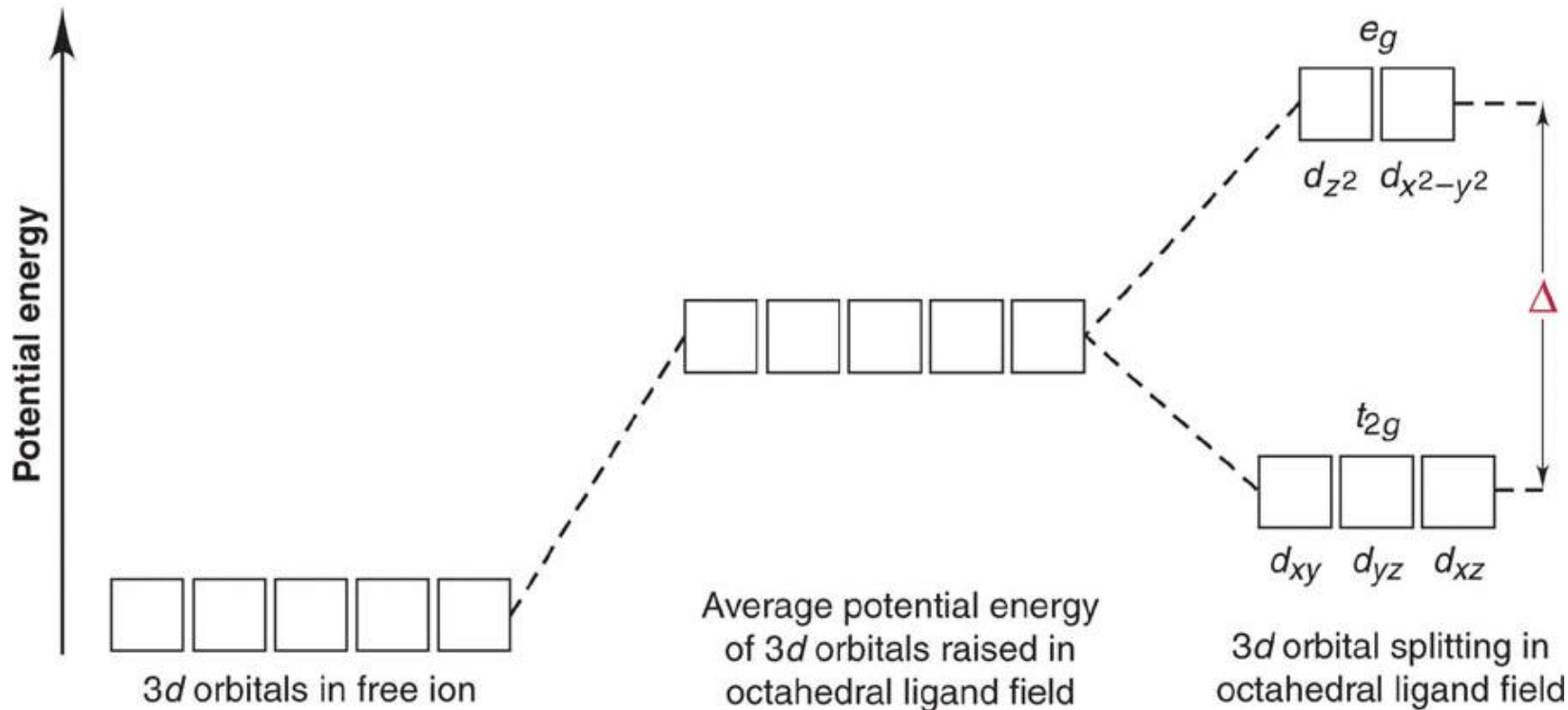
Formation of coloured ion

Relation Between Absorbed and Observed Colour

Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520



Splitting of d-orbital energies by an octahedral field of ligands



Δ is the splitting energy



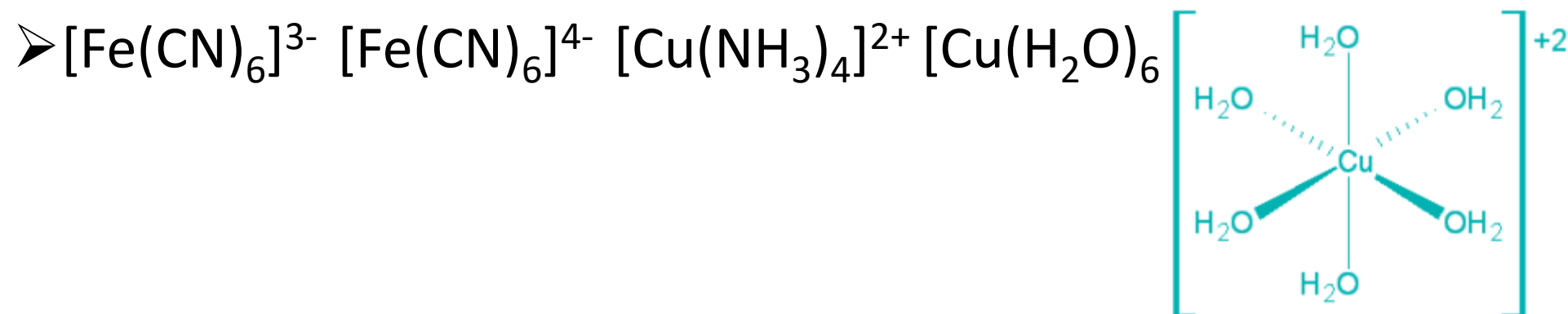
Colour of aquated first row ion

Ion	Configuration	Unpaired electron	Colour
Sc ³⁺ Ti ⁴⁺	3d ⁰	0	Colourless
Ti ³⁺ V ⁴⁺	3d ¹	1	Blue /purple
V ³⁺	3d ²	2	green
V ²⁺ Cr ³⁺	3d ³	3	violet
Mn ³⁺	3d ⁴	4	violet
Mn ²⁺ /Fe ³⁺	3d ⁵	5	Pink/ yellow
Fe ²⁺ /Co ³⁺	3d ⁶	4	Green/ Pink
Co ²⁺	3d ⁷	3	pink
Ni ²⁺	3d ⁸	2	Green
Cu ²⁺	3d ⁹	1	Blue
Zn ²⁺ Cu ⁺	3d ¹⁰	0	Colourless



Complex formation

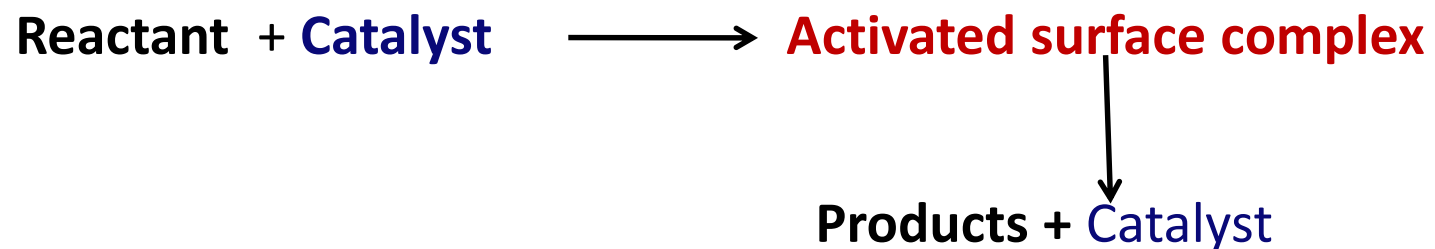
- Large no. of complexes
- Capacity to accept electron pair from ligand
 - Small size of transition metal
 - High ionic charge – high charge density – easier to accept electron
 - d orbital available for bonding





Catalytic properties

- show **catalytic activity**
 - ability to exhibit multiple oxidation states
 - to form complexes,
 - alloys and interstitial compounds
 - Chemisorb reactant molecule



- Pathway causes
 - Increase in conc of reactant at catalyst surface
 - Lowers activation energy – weakening of bonds in reactant



Catalytic properties

- heterogeneous catalyst used in car exhausts- **Pt/Rh alloy** supported on a ceramic matrix and converts the mixture of O_2 , CO, NO_x and hydrocarbons in the exhaust gases to H_2O , CO_2 , and N_2
- **V_2O_5** - Contact process - manufacture of sulphuric acid,
- **finely divided iron** - Haber's process - manufacture of NH_3
- **Ni** - hydrogenation of oils



Non stoichiometric compound

- Form Bertholides
 - do not correspond to ideal chemical formula
 - different elements are in non integral atomic ratio- $\text{VH}_{0.56}$, $\text{TaH}_{0.76}$,
 - Do not correspond to normal oxidation state of component element
 - Due to defect in crystal lattice & variable valency of metal
 - Small atoms like H, N etc trapped in voids
 - Hard, inert, high M.Pt. than metal
 - Most have formula – WO_{3-x} , Co_{1-x}O x- positive smaller than 1



Non stoichiometric compound



- Metal deficiency defect – FeO crystal – Fe^{2+} ion lost – electrical neutrality maintained by converting Fe^{2+} to Fe^{3+}



- Metal excess defect – Excess Zn $2+$ ion trapped in interstitial site – electrically neutral - free electron in neighboring site – absorb light – yellow colour



Alloy formation

- Homogenous substitutional solid solution
- distribution – random or ordered
- Alloy formation favoured between
 - Comparable metallic radii
 - Comparable electronegativity
 - Cu/Au, Ag/Au, Cu/Ni
- Alloys -hard – high mp - useful



Difference 1st & other row elements

- Atomic size – 1st row lower – 2nd & 3rd row similar
- Reactivity - 1st row – more reactive
- Stability of oxidation state - 1st row - +2 & +3 more important
 - - 2nd & 3rd row - higher oxidation state
- Coordination no. - 1st row - rarely greater than 6
 - - 2nd & 3rd row - many complexes with coordination no. greater than 6
- Type of complex - 1st row - high spin complexes more
 - - 2nd & 3rd row - high spin complexes few, more low spin complexes



Reference

- B.R. Puri, L.R. Sharma and K.C. Kalia, Principles of Inorganic Chemistry, 31 st Edition, Milestone Publishers and Distributors, New Delhi, 2013
- P.L. Soni and Mohan Katyal, Textbook of Inorganic Chemistry, 20th Edition, S. Chand and Sons, New Delhi, 2013
- Wahid U. Malik, G.D. Tuli and R.D. Madan, Selected Topics in Inorganic Chemistry, S. Chand and Co., New Delhi, 2010 (Reprint)
- J.E. Huheey, E.A. Keitler and R.L. Keitler, Inorganic Chemistry – Principles of Structure and Reactivity, 4 th Edition, Pearson Education, New Delhi, 2013

Thank You