d-BLOCK ELEMENTS

No. of lectures – 12
Term - 1

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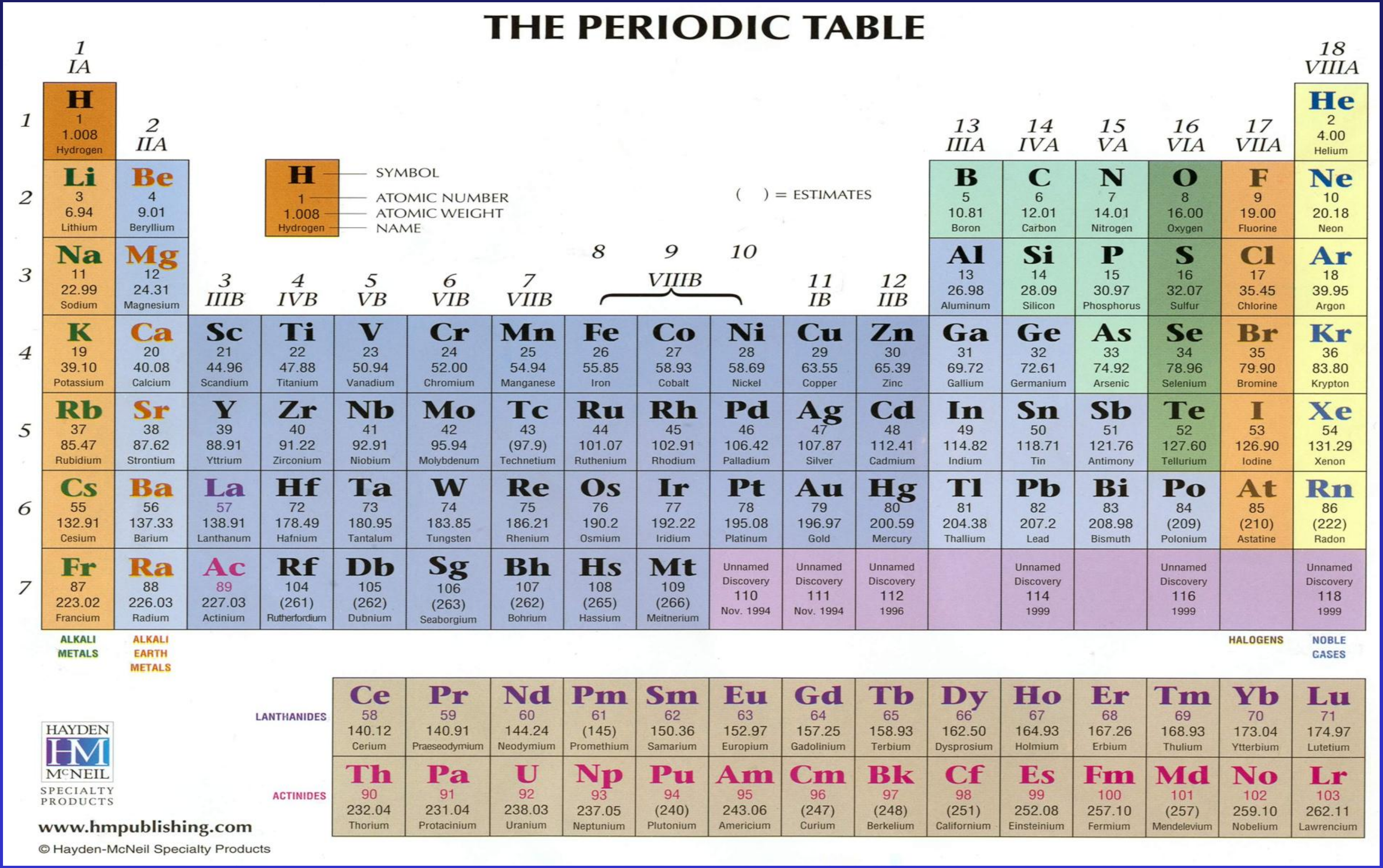
INTRODUCTION OF D-BLOCK ELEMENTS



THE PERIODIC TABLE

H	
H	SYMBOL
1	ATOMIC NUMBER
1.008	ATOMIC WEIGHT
Hydrogen	NAME

( ) = ESTIMATES

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	**H** 1 1.008 Hydrogen																	**He** 2 4.00 Helium
2	**Li** 3 6.94 Lithium	**Be** 4 9.01 Beryllium											**B** 5 10.81 Boron	**C** 6 12.01 Carbon	**N** 7 14.01 Nitrogen	**O** 8 16.00 Oxygen	**F** 9 19.00 Fluorine	**Ne** 10 20.18 Neon
3	**Na** 11 22.99 Sodium	**Mg** 12 24.31 Magnesium											**Al** 13 26.98 Aluminum	**Si** 14 28.09 Silicon	**P** 15 30.97 Phosphorus	**S** 16 32.07 Sulfur	**Cl** 17 35.45 Chlorine	**Ar** 18 39.95 Argon
4	**K** 19 39.10 Potassium	**Ca** 20 40.08 Calcium	**Sc** 21 44.96 Scandium	**Ti** 22 47.88 Titanium	**V** 23 50.94 Vanadium	**Cr** 24 52.00 Chromium	**Mn** 25 54.94 Manganese	**Fe** 26 55.85 Iron	**Co** 27 58.93 Cobalt	**Ni** 28 58.69 Nickel	**Cu** 29 63.55 Copper	**Zn** 30 65.39 Zinc	**Ga** 31 69.72 Gallium	**Ge** 32 72.61 Germanium	**As** 33 74.92 Arsenic	**Se** 34 78.96 Selenium	**Br** 35 79.90 Bromine	**Kr** 36 83.80 Krypton
5	**Rb** 37 85.47 Rubidium	**Sr** 38 87.62 Strontium	**Y** 39 88.91 Yttrium	**Zr** 40 91.22 Zirconium	**Nb** 41 92.91 Niobium	**Mo** 42 95.94 Molybdenum	**Tc** 43 (97.9) Technetium	**Ru** 44 101.07 Ruthenium	**Rh** 45 102.91 Rhodium	**Pd** 46 106.42 Palladium	**Ag** 47 107.87 Silver	**Cd** 48 112.41 Cadmium	**In** 49 114.82 Indium	**Sn** 50 118.71 Tin	**Sb** 51 121.76 Antimony	**Te** 52 127.60 Tellurium	**I** 53 126.90 Iodine	**Xe** 54 131.29 Xenon
6	**Cs** 55 132.91 Cesium	**Ba** 56 137.33 Barium	**La** 57 138.91 Lanthanum	**Hf** 72 178.49 Hafnium	**Ta** 73 180.95 Tantalum	**W** 74 183.85 Tungsten	**Re** 75 186.21 Rhenium	**Os** 76 190.2 Osmium	**Ir** 77 192.22 Iridium	**Pt** 78 195.08 Platinum	**Au** 79 196.97 Gold	**Hg** 80 200.59 Mercury	**Tl** 81 204.38 Thallium	**Pb** 82 207.2 Lead	**Bi** 83 208.98 Bismuth	**Po** 84 (209) Polonium	**At** 85 (210) Astatine	**Rn** 86 (222) Radon
7	**Fr** 87 223.02 Francium	**Ra** 88 226.03 Radium	**Ac** 89 227.03 Actinium	**Rf** 104 (261) Rutherfordium	**Db** 105 (262) Dubnium	**Sg** 106 (263) Seaborgium	**Bh** 107 (262) Bohrium	**Hs** 108 (265) Hassium	**Mt** 109 (266) Meitnerium	Unnamed Discovery 110 Nov. 1994	Unnamed Discovery 111 Nov. 1994	Unnamed Discovery 112 1996		Unnamed Discovery 114 1999		Unnamed Discovery 116 1999		Unnamed Discovery 118 1999
	ALKALI METALS	ALKALI EARTH METALS															HALOGENS	NOBLE GASES

LANTHANIDES	**Ce** 58 140.12 Cerium	**Pr** 59 140.91 Praeseodymium	**Nd** 60 144.24 Neodymium	**Pm** 61 (145) Promethium	**Sm** 62 150.36 Samarium	**Eu** 63 152.97 Europium	**Gd** 64 157.25 Gadolinium	**Tb** 65 158.93 Terbium	**Dy** 66 162.50 Dysprosium	**Ho** 67 164.93 Holmium	**Er** 68 167.26 Erbium	**Tm** 69 168.93 Thulium	**Yb** 70 173.04 Ytterbium	**Lu** 71 174.97 Lutetium
ACTINIDES	**Th** 90 232.04 Thorium	**Pa** 91 231.04 Protacinium	**U** 92 238.03 Uranium	**Np** 93 237.05 Neptunium	**Pu** 94 (240) Plutonium	**Am** 95 243.06 Americium	**Cm** 96 (247) Curium	**Bk** 97 (248) Berkelium	**Cf** 98 (251) Californium	**Es** 99 252.08 Einsteinium	**Fm** 100 257.10 Fermium	**Md** 101 (257) Mendelevium	**No** 102 259.10 Nobelium	**Lr** 103 262.11 Lawrencium

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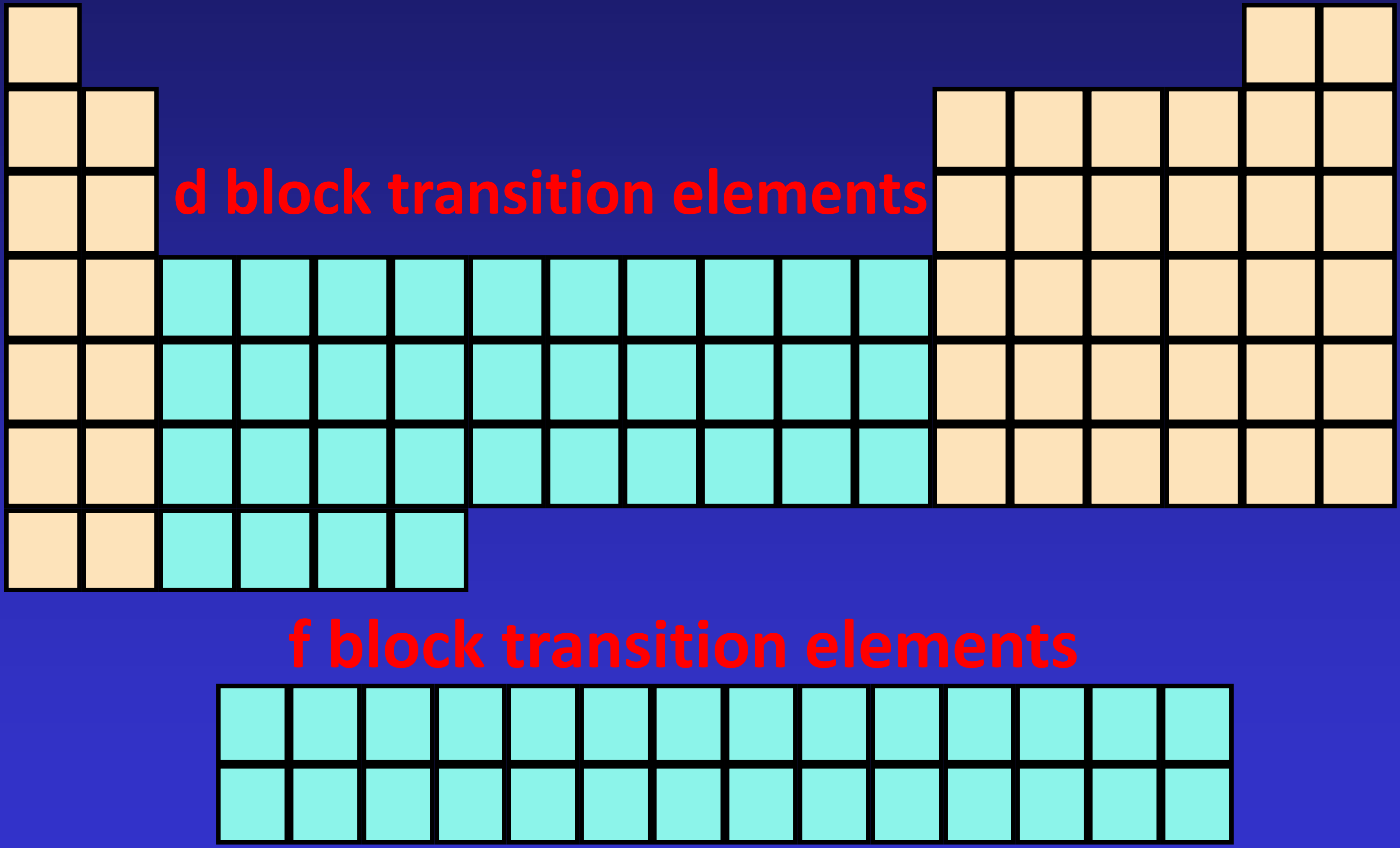
Periodic Table



d block transition elements

f block transition elements

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d-Block Transition Elements

IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Most have partially occupied d sub-shells in common oxidation states

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What is a transition metal?

an element which forms at least one ion with a partially filled d orbital(s).

Why are they called d-block elements?

Their last electron enters the d-orbital

- Most d-block elements are also called transition metals. This is because they exhibit characteristics that ranges from s -block to p – block.
- Zinc group and Scandium group are *NOT* considered as transition metals, are called Non-typical Transition elements
- The d block consists of three horizontal series in periods 4, 5 & 6
  - 10 elements in each series
- **Electronic Configuration**
  - Across the 1st row of the d block (Sc to Zn) each element
    - has 1 more electron and 1 more proton
    - Each "additional" electron enters the 3d sub-shell
    - The core configuration for all the 1st series of transition elements is [Ar] $3d^{1-10}\,4s^2$

General configuration - [Inert gas] $(n-1)d^{1-10}\,ns^2$

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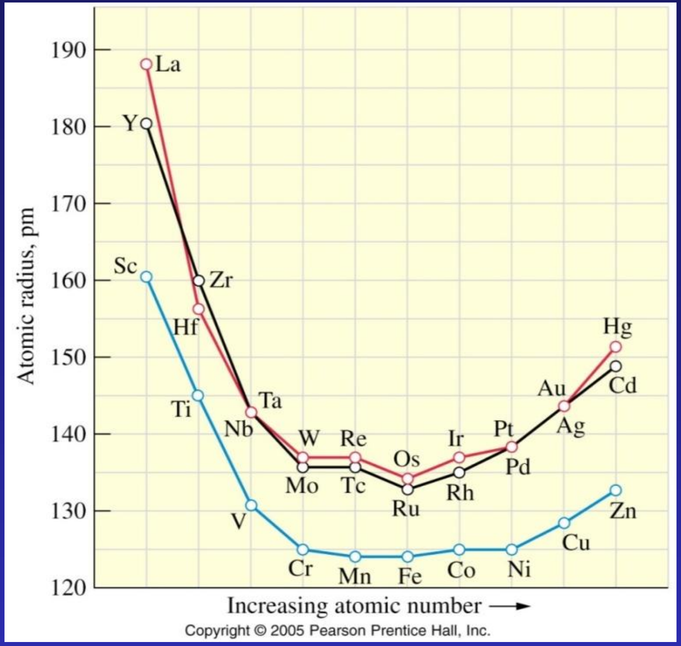
Electronic Arrangement

Element	Z		3d					4s
Sc	21	[Ar]	↑					↑↓
Ti	22	[Ar]	↑	↑				↑↓
V	23	[Ar]	↑	↑	↑			↑↓
Cr	24	[Ar]	↑	↑	↑	↑	↑	↑
Mn	25	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	26	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	27	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	28	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	29	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	30	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Trends in properties



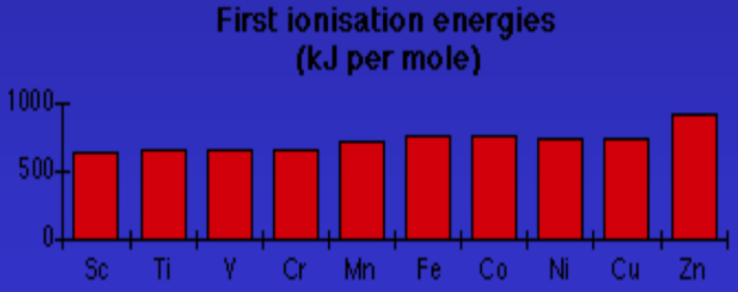
1. Atomic and Ionic radii

Decreases across the series as the atomic no. Increases, due to increase in nuclear charge.

a) From Sc to Cr - regular expected decrease
Increased nuclear attraction

b) From Cr to Ni - almost same size
nuclear attraction = inter electronic repulsion

c) Ni to Zn – Marginal increase
nuclear attraction < inter electronic repulsion



2. Ionization Potential

Follows the trend inversely to Changes in the atomic radii;
However Zn group has very high value due to d10 configuration

3. Variable Oxidation States

- D-block elements exhibit variable oxidation states.
- This means that they can form two or more different types of cations.
- Examples: Iron can form both Fe^{2+} and Fe^{3+}
  - Manganese shows Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{6+} and Mn^{7+}

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

Oxidation States of TM's

- **Nature of bonds – Ionic and covalent**
  - Lower OS's found in ionic compounds
    - E.g. compounds containing Cr^{3+}, Mn^{2+}, Fe^{3+}, Cu^{2+} ions
  - TM's in higher OS's usually covalently bound to electronegative element such as O or F
    - E.g VO_3^-, vanadate(V) ion; MnO_4^-, manganate(VII) ion
    - Simple ions with high OS's such as V^{5+} & Mn^{7+} *are not formed*

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Oxidising and reducing nature

- lower oxidation states are highly reducing
  - E.g. V^{2+}(aq) & Cr^{2+}(aq) strong reducing agents
- higher oxidation states are oxidising in nature
  - E.g. Co^{3+} is a strong oxidising agent,
  - $KMnO_4$ - OS +7, $K_2Cr_2O_7$ - OS +6 are oxidising agents

Acidic and basic nature

- Higher oxidation states are acidic in nature
- Lower oxidation states become increasingly basic

via amphoteric nature

- ✓ H_2CrO_4 is strong acid – Cr OS +6
- ✓ Mn_2O_3 – basic (+3), MnO_2 – amphoteric(+4), $KMnO_4$ – acidic(+7)

Formation of coloured ions

The compounds of the d-block metal ions are usually colored, except, those of d^0 and d^{10} metal ions. The colors are due to:

Electronic transitions of d-electrons within the d sub-shell. These are known as d→d transitions. When light passes through these compounds, electrons from a lower energy d-orbital absorb a photon of energy and are promoted to higher energy d-orbitals. The energy absorbed is equivalent to the energy difference between the two sets of orbitals. Electron while returning from the excited state gives away the energy which falls in visible range of spectrum and the substance appears coloured.

Since light of a certain frequency is absorbed, the light that comes out looks coloured because it lacks some colour.

The colour of the compound is the complementary of the one that was absorbed

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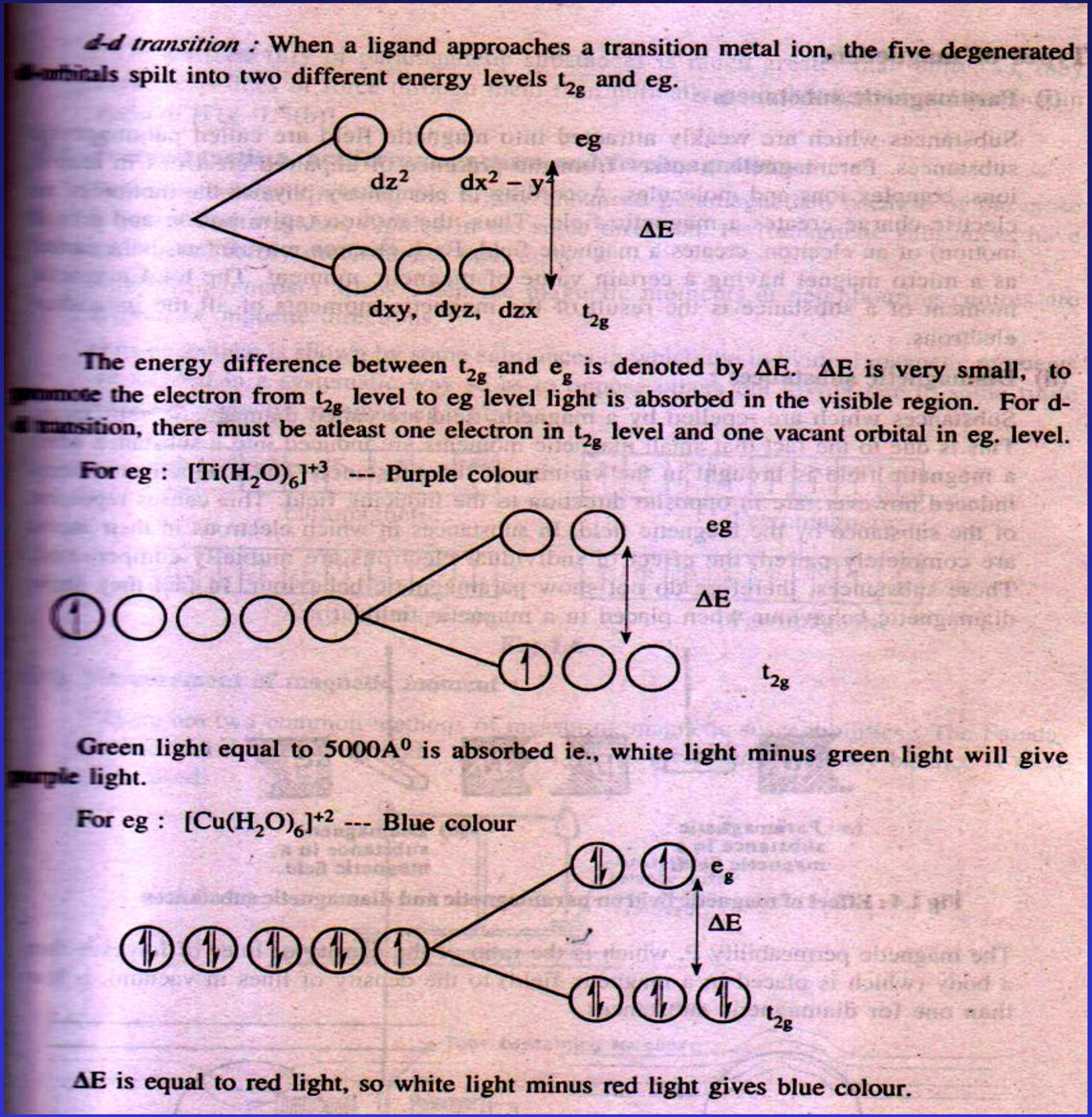

d-d transition : When a ligand approaches a transition metal ion, the five degenerated d-orbitals spilt into two different energy levels t_{2g} and eg.

The energy difference between t_{2g} and e_g is denoted by ΔE. ΔE is very small, to promote the electron from t_{2g} level to eg level light is absorbed in the visible region. For d-d transition, there must be atleast one electron in t_{2g} level and one vacant orbital in eg. level.

For eg : $[Ti(H_2O)_6]^{+3}$ --- Purple colour

Green light equal to $5000A^0$ is absorbed ie., white light minus green light will give purple light.

For eg : $[Cu(H_2O)_6]^{+2}$ --- Blue colour

ΔE is equal to red light, so white light minus red light gives blue colour.

Magnetic behaviour

Electron is a micromagnet, moves

1. On its axis – Spin moment
2. In the orbitals – Orbital moment

Total magnetic moment = Spin moment + Orbital moment

$$\mu_{(S + L)} = \sqrt{4S(S+1) + L(L+1)}$$

Orbital moment is negligible,

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

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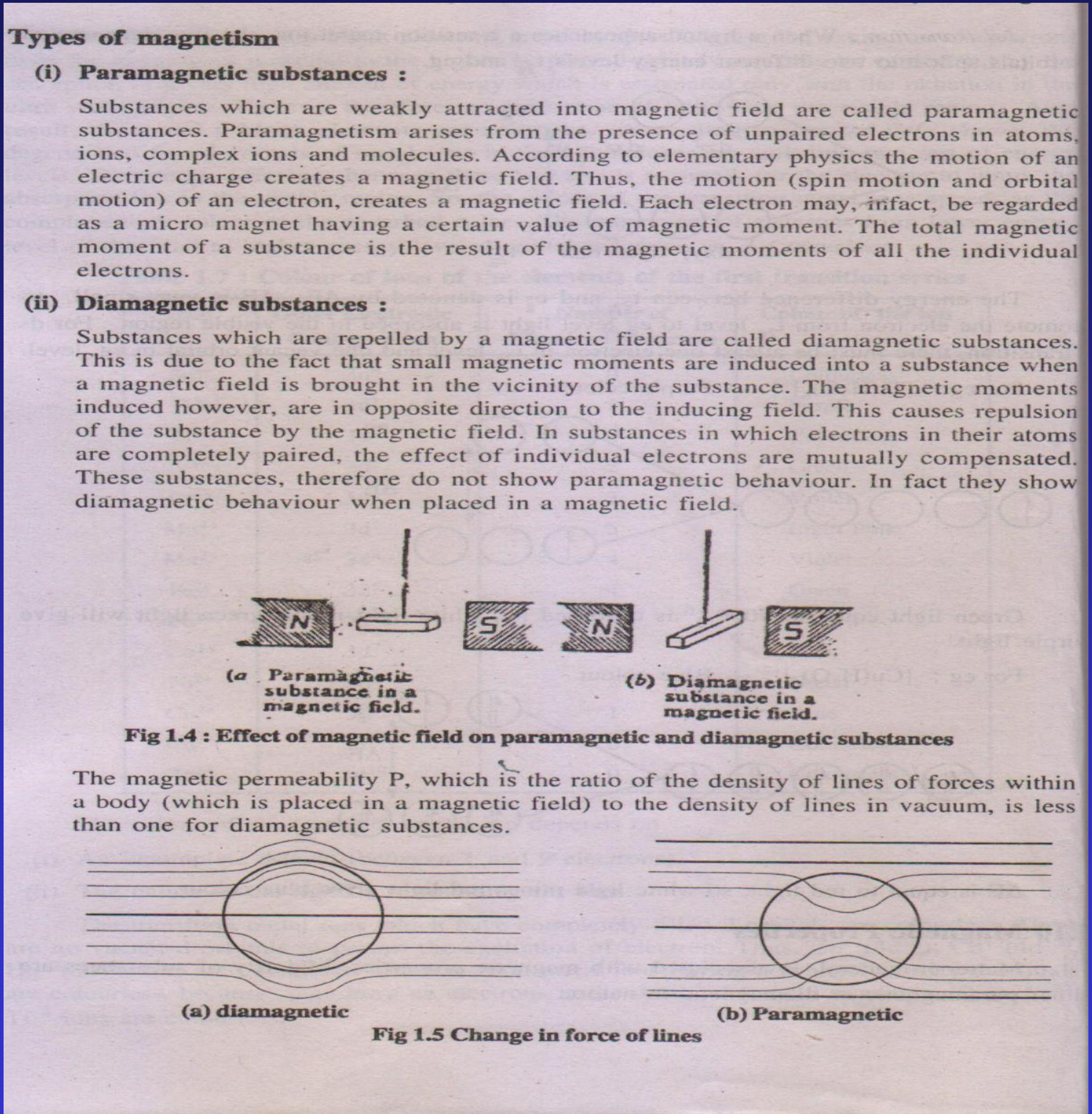


Types of magnetism

(i) Paramagnetic substances :

Substances which are weakly attracted into magnetic field are called paramagnetic substances. Paramagnetism arises from the presence of unpaired electrons in atoms, ions, complex ions and molecules. According to elementary physics the motion of an electric charge creates a magnetic field. Thus, the motion (spin motion and orbital motion) of an electron, creates a magnetic field. Each electron may, infact, be regarded as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the result of the magnetic moments of all the individual electrons.

(ii) Diamagnetic substances :

Substances which are repelled by a magnetic field are called diamagnetic substances. This is due to the fact that small magnetic moments are induced into a substance when a magnetic field is brought in the vicinity of the substance. The magnetic moments induced however, are in opposite direction to the inducing field. This causes repulsion of the substance by the magnetic field. In substances in which electrons in their atoms are completely paired, the effect of individual electrons are mutually compensated. These substances, therefore do not show paramagnetic behaviour. In fact they show diamagnetic behaviour when placed in a magnetic field.

(a) Paramagnetic substance in a magnetic field.

(b) Diamagnetic substance in a magnetic field.

Fig 1.4 : Effect of magnetic field on paramagnetic and diamagnetic substances

The magnetic permeability P, which is the ratio of the density of lines of forces within a body (which is placed in a magnetic field) to the density of lines in vacuum, is less than one for diamagnetic substances.

(a) diamagnetic

(b) Paramagnetic

Fig 1.5 Change in force of lines

Measurement of magnetic moment :

There are two common methods of measuring magnetic susceptibilities : The Faraday method and the Gouy method. However, the Gouy method by Gouy balance is more often used.

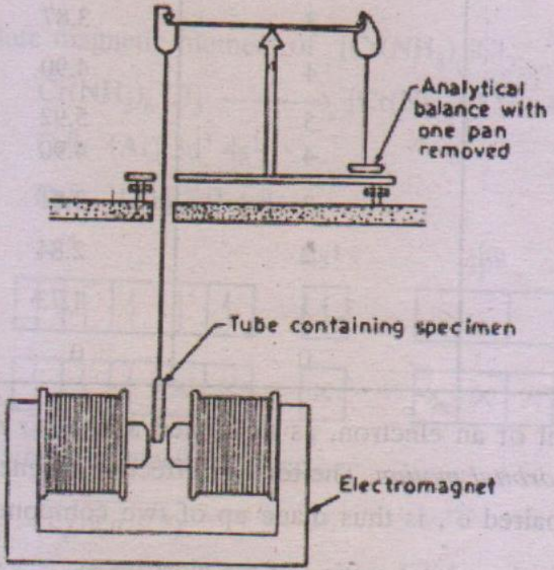
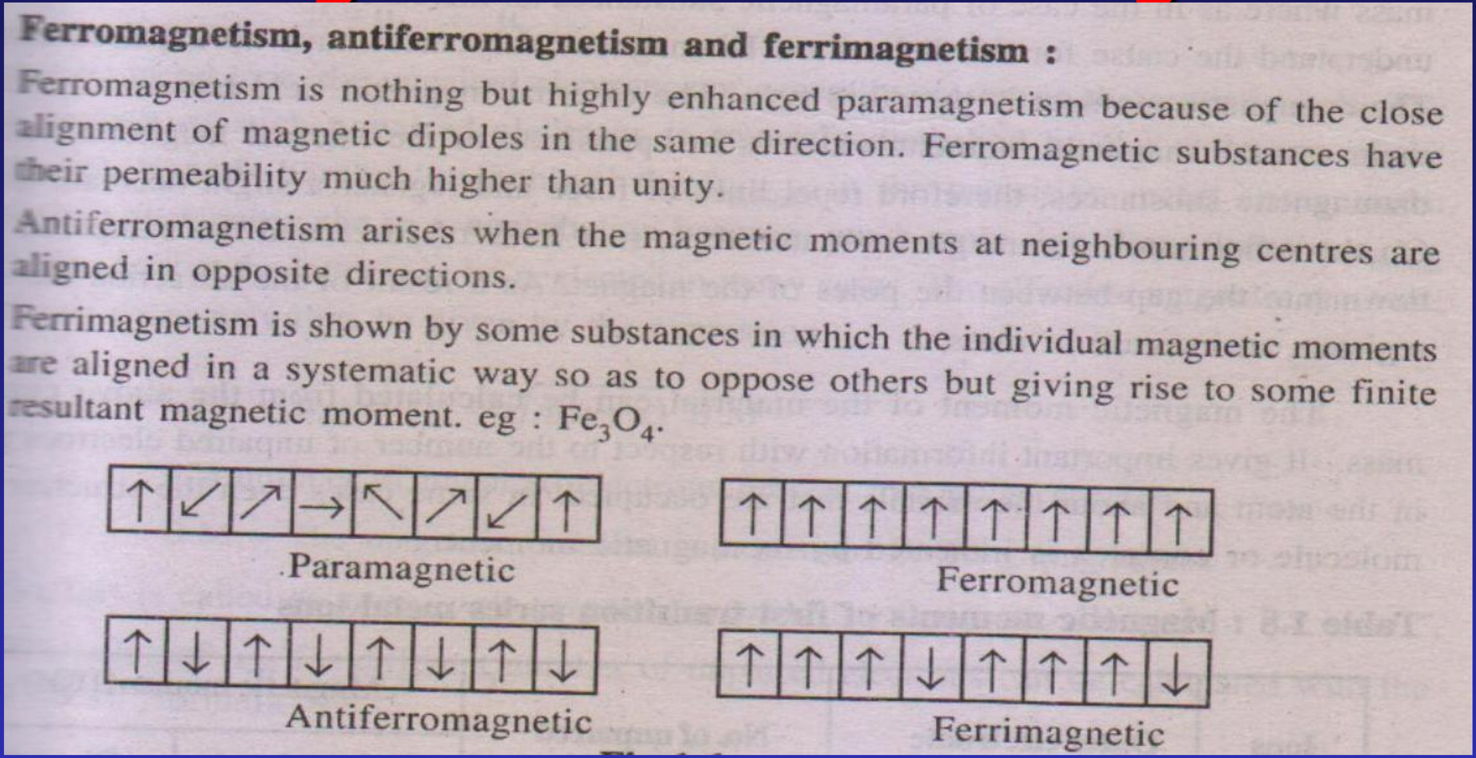


Fig 1.7 - Gouy's magnetic balance

ble 1.8 : Magnetic moments of first transition series metal ions

Ions	Outer electronic 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	2.76
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	5·0 - 5·5
Co^{2+}	$3d^7$	3	3.81	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

Ferromagnetism and Paramagnetism



Ferromagnetism, antiferromagnetism and ferrimagnetism :

Ferromagnetism is nothing but highly enhanced paramagnetism because of the close alignment of magnetic dipoles in the same direction. Ferromagnetic substances have their permeability much higher than unity.

Antiferromagnetism arises when the magnetic moments at neighbouring centres are aligned in opposite directions.

Ferrimagnetism is shown by some substances in which the individual magnetic moments are aligned in a systematic way so as to oppose others but giving rise to some finite resultant magnetic moment. eg : Fe_3O_4.

↑ ↙ ↗ → ↖ ↗ ↙ ↑

Paramagnetic

↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑

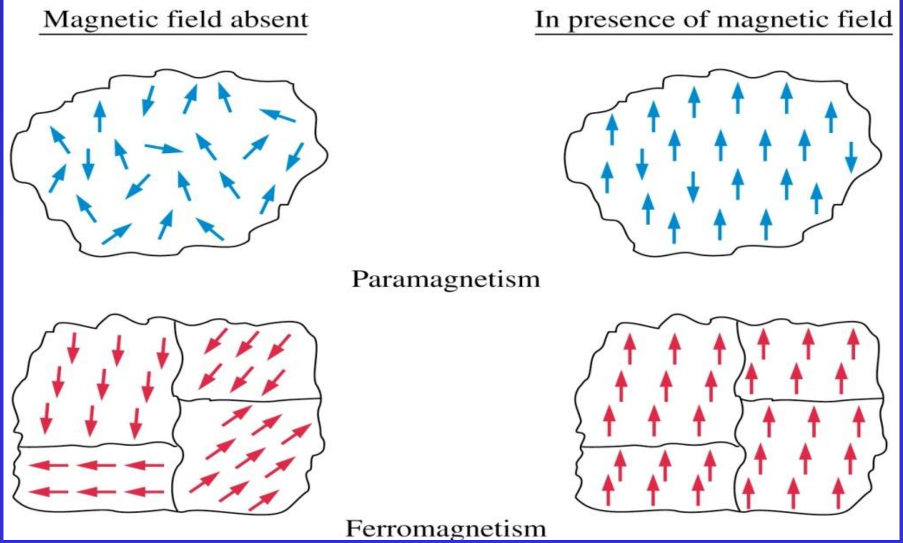
Ferromagnetic

↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓

Antiferromagnetic

↑ ↑ ↑ ↓ ↑ ↑ ↑ ↓

Ferrimagnetic



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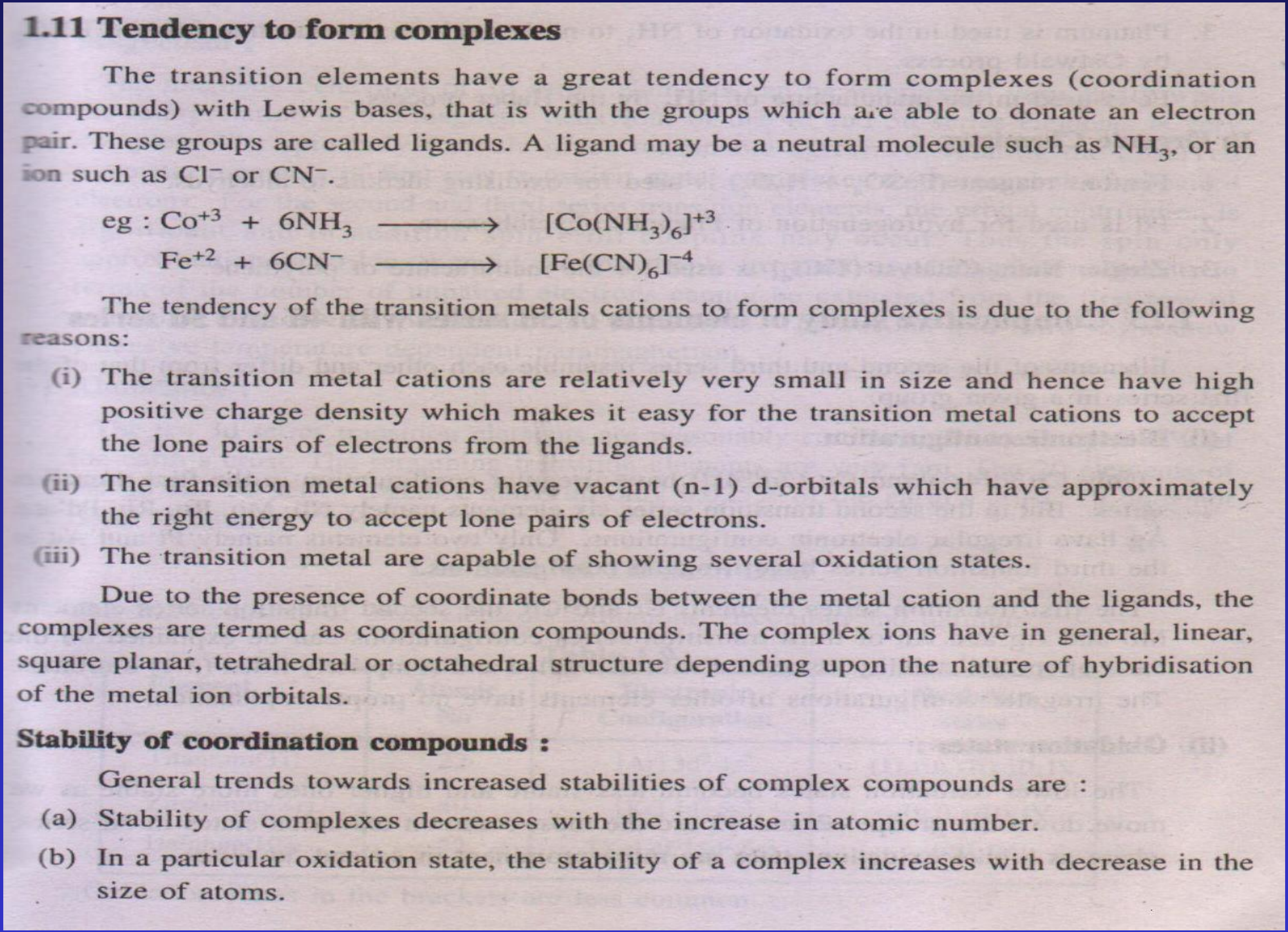


1.11 Tendency to form complexes

The transition elements have a great tendency to form complexes (coordination compounds) with Lewis bases, that is with the groups which are able to donate an electron pair. These groups are called ligands. A ligand may be a neutral molecule such as NH_3, or an ion such as Cl^- or CN^-.

$$\text{eg : } Co^{+3} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{+3}$$

$$Fe^{+2} + 6CN^- \longrightarrow [Fe(CN)_6]^{-4}$$

The tendency of the transition metals cations to form complexes is due to the following reasons:

(i) The transition metal cations are relatively very small in size and hence have high positive charge density which makes it easy for the transition metal cations to accept the lone pairs of electrons from the ligands.

(ii) The transition metal cations have vacant (n-1) d-orbitals which have approximately the right energy to accept lone pairs of electrons.

(iii) The transition metal are capable of showing several oxidation states.

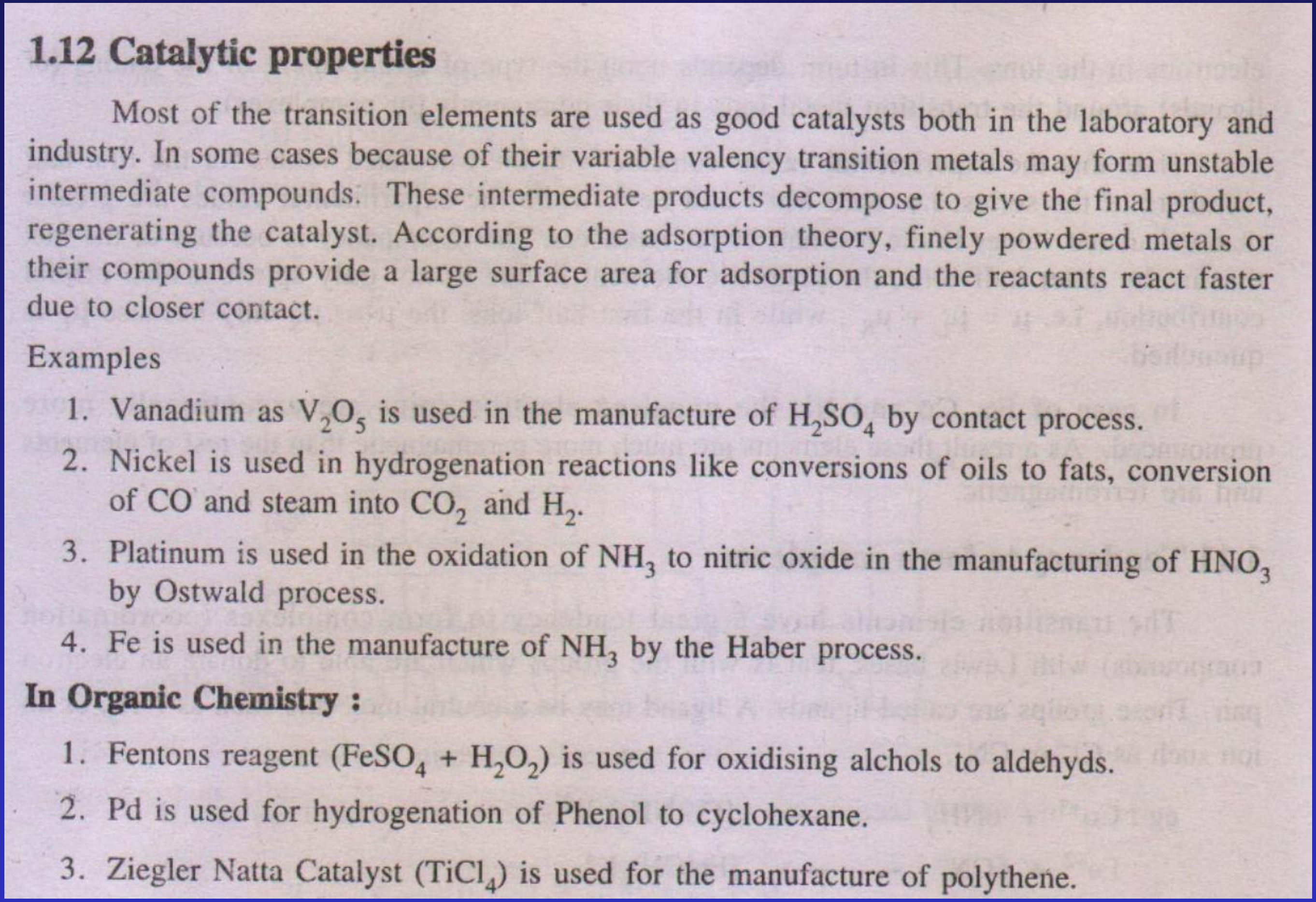
Due to the presence of coordinate bonds between the metal cation and the ligands, the complexes are termed as coordination compounds. The complex ions have in general, linear, square planar, tetrahedral or octahedral structure depending upon the nature of hybridisation of the metal ion orbitals.

Stability of coordination compounds :

General trends towards increased stabilities of complex compounds are :

(a) Stability of complexes decreases with the increase in atomic number.

(b) In a particular oxidation state, the stability of a complex increases with decrease in the size of atoms.



1.12 Catalytic properties

Most of the transition elements are used as good catalysts both in the laboratory and industry. In some cases because of their variable valency transition metals may form unstable intermediate compounds. These intermediate products decompose to give the final product, regenerating the catalyst. According to the adsorption theory, finely powdered metals or their compounds provide a large surface area for adsorption and the reactants react faster due to closer contact.

Examples

1. Vanadium as V_2O_5 is used in the manufacture of H_2SO_4 by contact process.
2. Nickel is used in hydrogenation reactions like conversions of oils to fats, conversion of CO and steam into CO_2 and H_2.
3. Platinum is used in the oxidation of NH_3 to nitric oxide in the manufacturing of HNO_3 by Ostwald process.
4. Fe is used in the manufacture of NH_3 by the Haber process.

In Organic Chemistry :

1. Fentons reagent ($FeSO_4 + H_2O_2$) is used for oxidising alchols to aldehyds.
2. Pd is used for hydrogenation of Phenol to cyclohexane.
3. Ziegler Natta Catalyst ($TiCl_4$) is used for the manufacture of polythene.

Titanium Triad

titanium 22 Ti 47.867	Titanium	[Ar] $3d^2 4s^2$	Quite unreactive
zirconium 40 Zr 91.224	Zirconium	[Kr] $4d^2 5s^2$	Fairly inactive element
hafnium 72 Hf 178.49	Hafnium	[Xe] $4f^{14} 5d^2 6s^2$	Not very reactive
rutherfordium 104 Rf [261]	Rutherfordium	[Rn] $5f^{14}\ 6d^2 7s^2$	Highly radioactive

Oxidation States

M^{4+}	M^{3+}	M^{2+}
1. Most stable –d^0 Config	Fairy stable	Unstable
2. Covalent, Tetrahedral	Reducing agents	strongly reducing
3. Diamagnetic	Paramagnetic (1 e)	Paramagnetic
4. Colourless	Coloured	Coloured

M^{3+} and M^{2+} undergo disproportionation to give higher and lower O.S.

$2\ Ti\ Cl_2 \rightarrow Ti\ Cl_4 + Ti$

$2\ Ti\ Cl_3 \rightarrow Ti\ Cl_4 + Ti\ Cl_2$

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Oxides

1. Normal oxides

MO_2 : 1. Stable and insoluble in water

2. Basic nature of oxides increases down the group

TiO_2 : Amphoteric $\quad TiO_2 + \underset{\text{Conc.}}{H_2SO_4} \rightarrow \underset{\text{Titanyl sulphate}}{TiOSO_4} + H_2O$

$$TiO_2 + 2\,NaOH \rightarrow \underset{\text{Sodium titanate}}{Na_2TiO_3.n\,H_2O}$$

ZrO_2 : Basic, **HfO_2** : More Basic, on heating becomes refractory and are used as pigments

2. Oxygenyl ions :

1. Titanyl ion, TiO^{2+} is unstable and polymerises to form chains
2. Ziroconyl ion, ZrO^{2+} is stable

3. Peroxides :

on heating with H_2O_2 peroxides are obtained .

General formula - $M(OH)_3\,OOH$ when M=Ti, Zr,

.

Halides

1. Ti & Zr give all the tetrahalides, MX4

2. Hf given only HfF_4 & $HfCL_4$

3. Tetrafluorides are ionic while other are covalent.

4. Except MF_4 others undergo hydrolysis and fume in moist air

$$TiX_4 \rightarrow Ti(OH)_4 \rightarrow TiO_2 . 2H_2O$$

5. Tetrahalides are electron pair acceptors and given six coordinated complex ions

$$TiF_4 + 2\,NaF \rightarrow Na_2[TiF_6]$$

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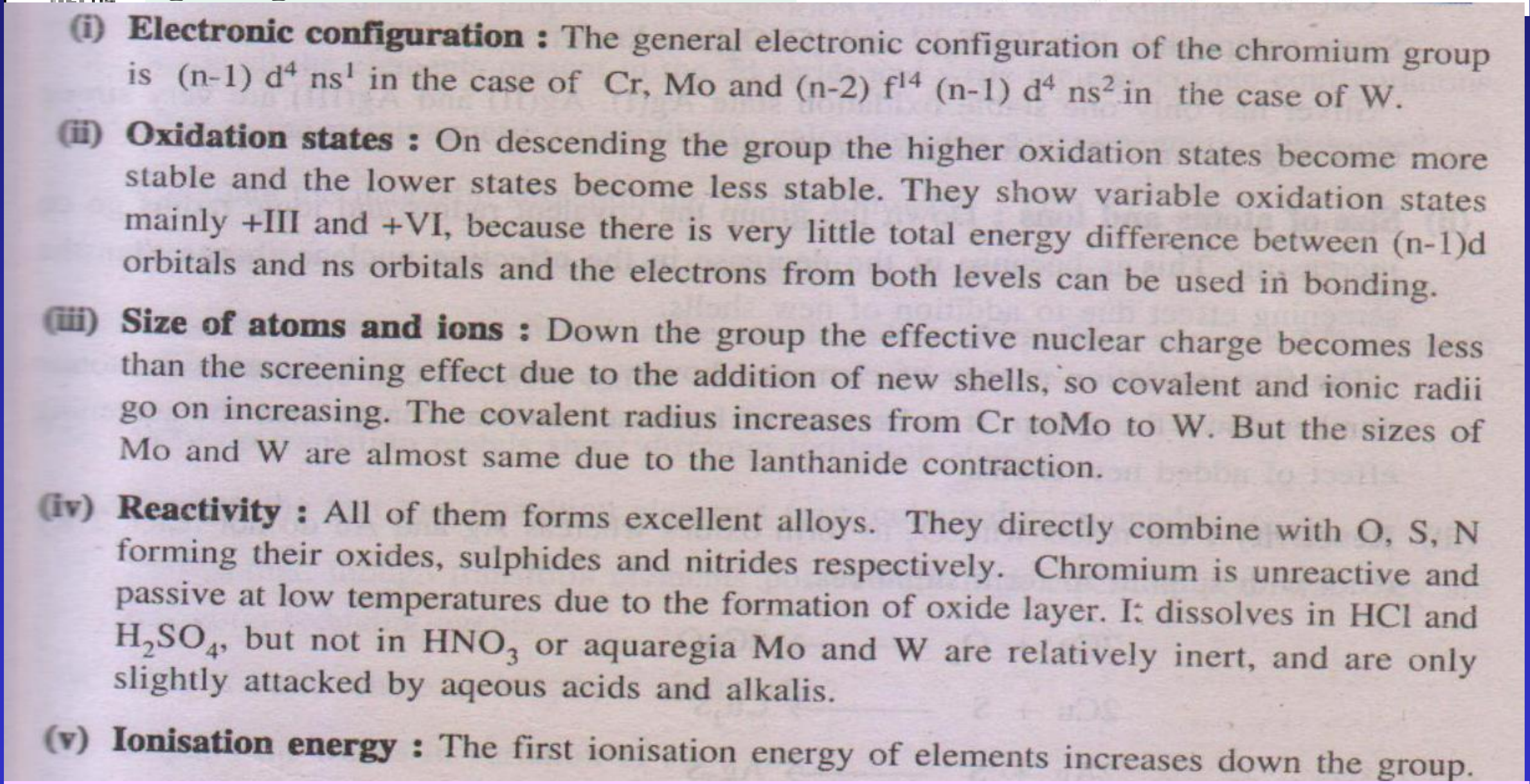
Chromium Triad

chromium 24 Cr 51.996	[Ar] $3d^5 4s^1$	Cr: +2, +3, +6
molybdenum 42 Mo 95.94	[Kr] $4d^5 5s^1$	Mo: +2, +3, +4, +5, +6
tungsten 74 W 183.84	[Xe] $4f^{14}\,5d^5 6s^1$	W: +2, +3, +4, +5, +6



(i) **Electronic configuration :** The general electronic configuration of the chromium group is $(n-1)\ d^4\ ns^1$ in the case of Cr, Mo and $(n-2)\ f^{14}\ (n-1)\ d^4\ ns^2$ in the case of W.

(ii) **Oxidation states :** On descending the group the higher oxidation states become more stable and the lower states become less stable. They show variable oxidation states mainly +III and +VI, because there is very little total energy difference between (n-1)d orbitals and ns orbitals and the electrons from both levels can be used in bonding.

(iii) **Size of atoms and ions :** Down the group the effective nuclear charge becomes less than the screening effect due to the addition of new shells, so covalent and ionic radii go on increasing. The covalent radius increases from Cr toMo to W. But the sizes of Mo and W are almost same due to the lanthanide contraction.

(iv) **Reactivity :** All of them forms excellent alloys. They directly combine with O, S, N forming their oxides, sulphides and nitrides respectively. Chromium is unreactive and passive at low temperatures due to the formation of oxide layer. It dissolves in HCl and H_2SO_4, but not in HNO_3 or aquaregia Mo and W are relatively inert, and are only slightly attacked by aqeous acids and alkalis.

(v) **Ionisation energy :** The first ionisation energy of elements increases down the group.

(vi) All are coloured and paramagnetic

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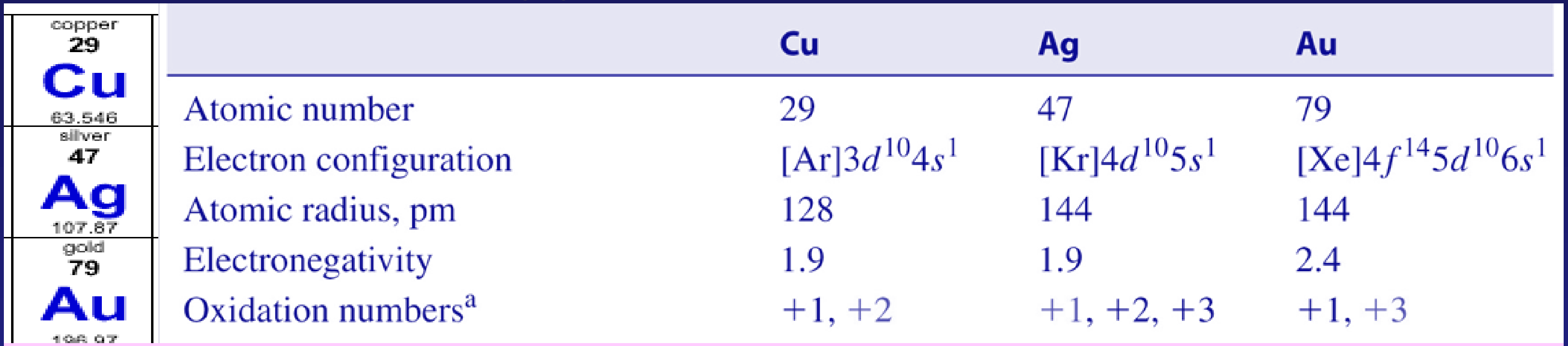
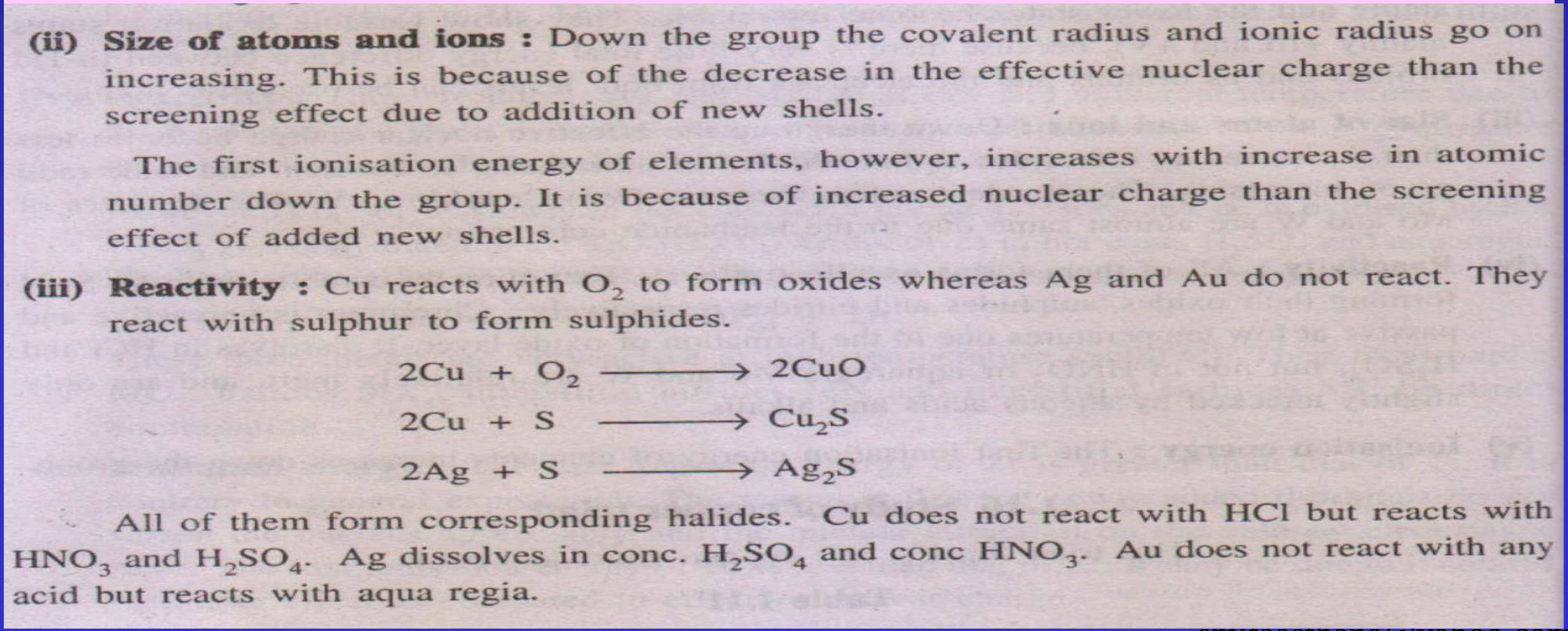
Copper Triad



	Cu	Ag	Au
Atomic number	29	47	79
Electron configuration	$[Ar]3d^{10}4s^1$	$[Kr]4d^{10}5s^1$	$[Xe]4f^{14}5d^{10}6s^1$
Atomic radius, pm	128	144	144
Electronegativity	1.9	1.9	2.4
Oxidation numbers[a]	+1, +2	+1, +2, +3	+1, +3

(i) Oxidation states

- s and d electrons are involved in bonding
- For Copper +2, Silver +1 and Gold +3 are Most stable O.S.
- Cu +1 Disproportionate in water - $Cu_2 Cl_2 \rightarrow Cu + CuCl_2$
- Cu^{3+} is known in some complexes - $[CuF_6]^{3-}$
- Ag^{2+} and Ag^{3+} are strong O.A.



(ii) Size of atoms and ions : Down the group the covalent radius and ionic radius go on increasing. This is because of the decrease in the effective nuclear charge than the screening effect due to addition of new shells.

The first ionisation energy of elements, however, increases with increase in atomic number down the group. It is because of increased nuclear charge than the screening effect of added new shells.

(iii) Reactivity : Cu reacts with O_2 to form oxides whereas Ag and Au do not react. They react with sulphur to form sulphides.

$$2Cu + O_2 \longrightarrow 2CuO$$

$$2Cu + S \longrightarrow Cu_2S$$

$$2Ag + S \longrightarrow Ag_2S$$

All of them form corresponding halides. Cu does not react with HCl but reacts with HNO_3 and H_2SO_4. Ag dissolves in conc. H_2SO_4 and conc HNO_3. Au does not react with any acid but reacts with aqua regia.

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