D BLOCK ELEMENTS

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Synopsis:

Definition of D-Block elements

Transition elements.

General and Physical properties of elements

Atomic & Ionic size

Ionization Enthalpy

Oxidation states

Coloured ions

Catalytic properties

Magnetic properties

Formation of complex compounds

Formation of interstitial compounds

THE PERIODIC TABLE

H 1 1.008 Hydrogen	— SYMBOL — ATOMIC NUMBER — ATOMIC WEIGHT — NAME

( ) = ESTIMATES

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	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 Praseodymium	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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Definition of d-block elements

- **d-block elements:**
  The elements of periodic table belonging to **group 3 to 12** are known as d-Block elements. because in these elements last electron enters in d sub shell or d orbital .

- The d -block elements lies in between s- and p-block elements in the long form of periodic table

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10

3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7*s*	2	2	2	2	2	2	2	2	1	2
6*d*	1	2	3	4	5	6	7	8	10	10

Transition Elements

A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states. i.e.

A transition element should have partially filled (n-1) d orbital.

Electronic Configuration

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]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Table 9.1 Outer electron configurations of the transition elements (ground state)

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10
2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10
3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

How are d - Block Elements & Transition elements different?

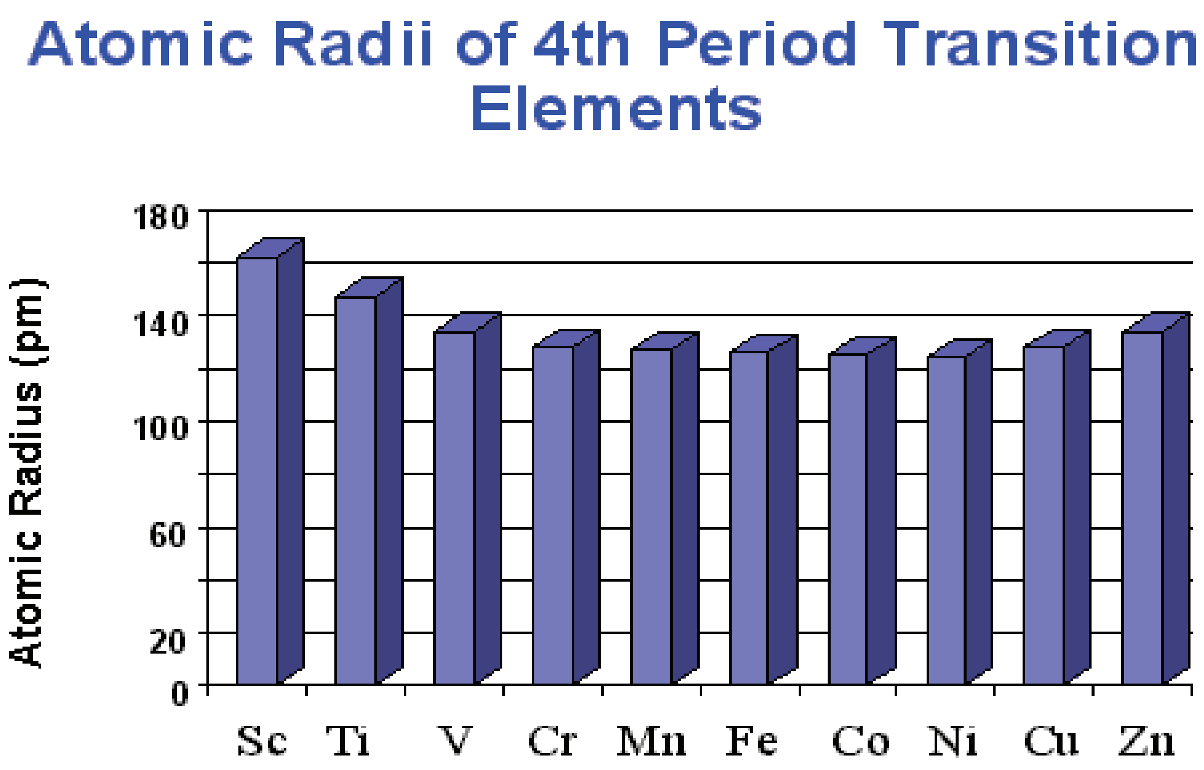
All d block elements are not transition elements but all transition elements are d-block elements

All d block elements are not transition elements because d block elements like Zinc have full d^{10} configuration in their ground state as well as in their common oxidation state.which is not according to definition of transition elements.

General & physical Properties of d-Block Elements

- physical properties
- Atomic & Ionic size
- Ionization Enthalpy
- Oxidation States of d-Block Elements
- Coloured Ions
- Catalytic properties
- Magnetic properties
- Formation of Complex Compounds
- Formation of Interstitial Compounds

ATOMIC & IONIC SIZE



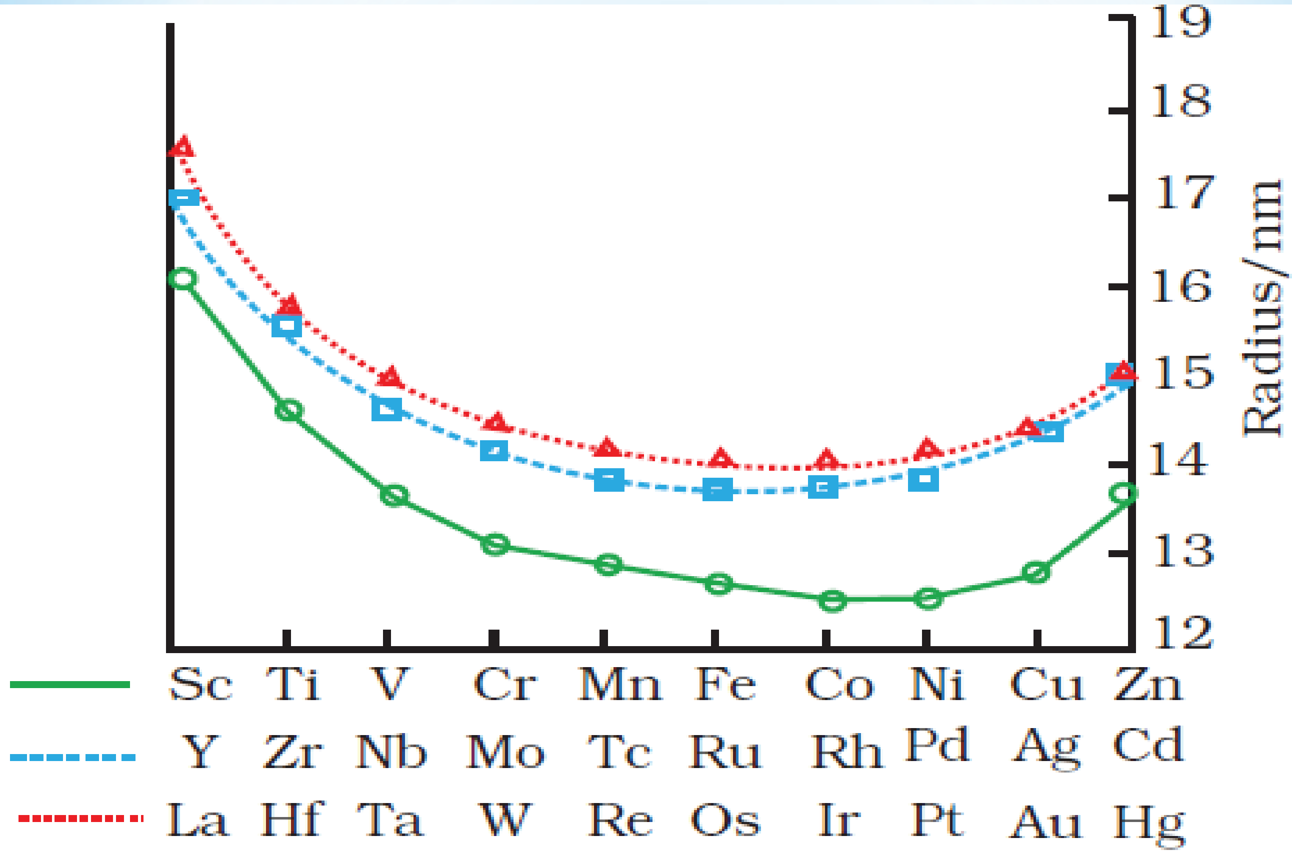


Fig. 8.3: *Trends in atomic radii of transition elements*

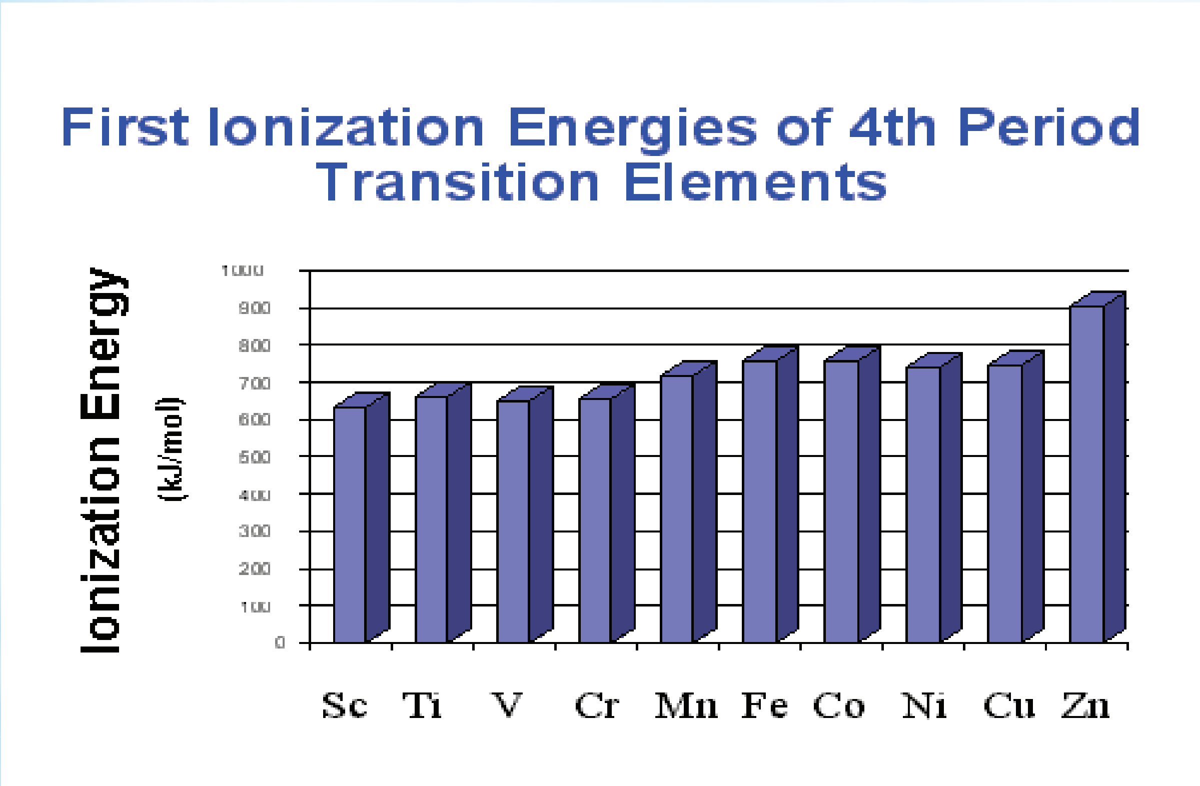
- Along the rows nuclear charge increases but the penultimate d-sub shell has poor shielding effect so atomic and ionic size remain almost same .

- The radii of the third (5*d*) *series are virtually the* same as those of the corresponding members of the second series.

- This phenomenon is associated with the intervention of the *4f orbital*, *the filling of 4f* before 5*d orbital results in a regular decrease in atomic radii called* Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number.

- The net resultof the lanthanoid contraction is that the second and the third *d series* exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm)

IONIZATION ENTHALPIES



IE_2 :V < Cr > Mn and Ni < Cu > Zn

IE_3 : Fe << Mn

- Due to an increase in nuclear charge which accompanies the filling of the inner *d-orbitals* , There is an increase in ionization enthalpy along each series of the transition elements from left to right.

- However, many small variations occur.

oxidation states

- Transition elements have **variable oxidation states** ,due to very small energy difference between (n-1)d & ns sub-shell electrons from both the sub-shell take part in bonding

Table 8.3: Oxidation States of the first row Transition Metals (the most common ones are in bold types)

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

- The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.

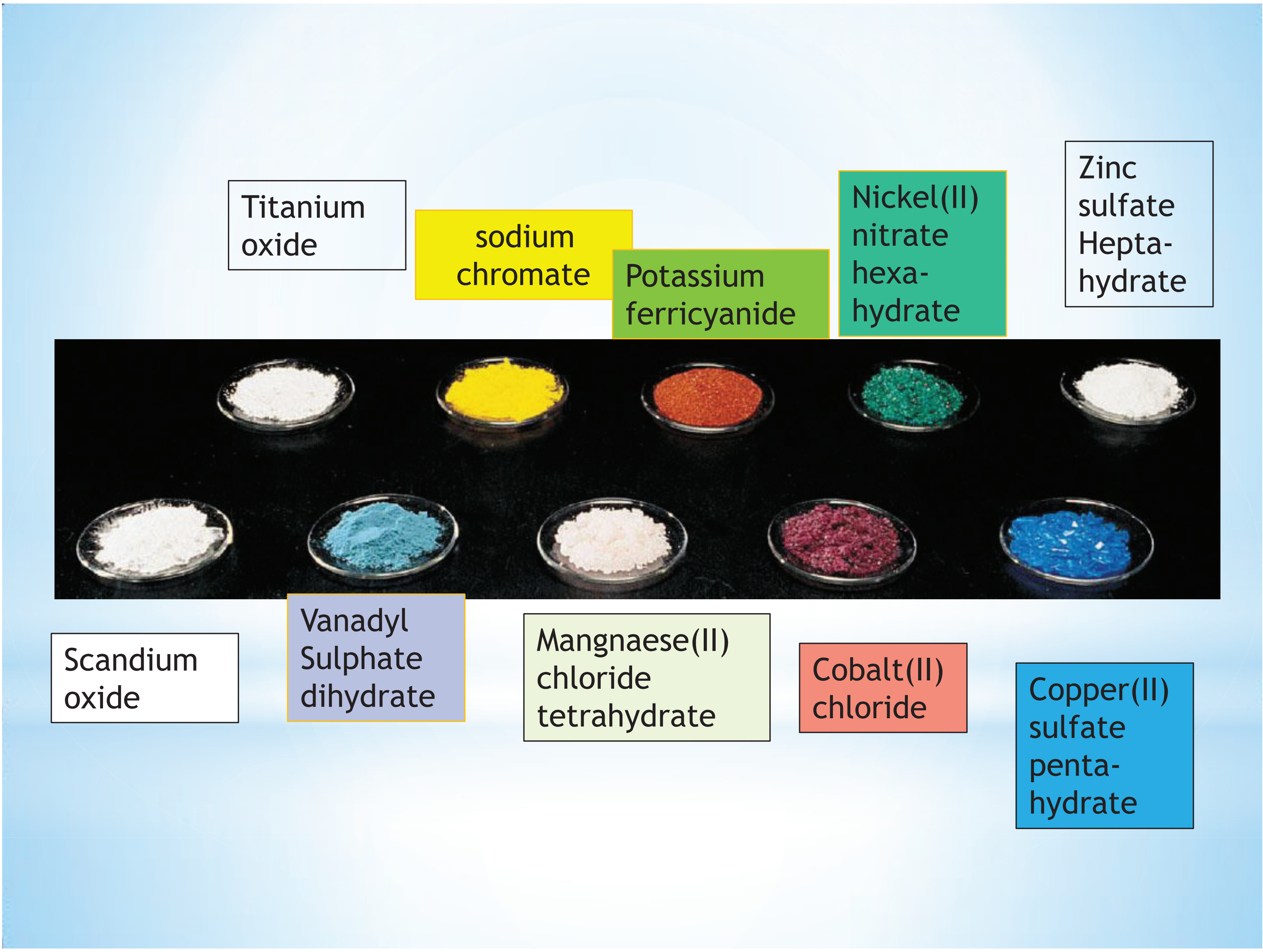
- Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding.

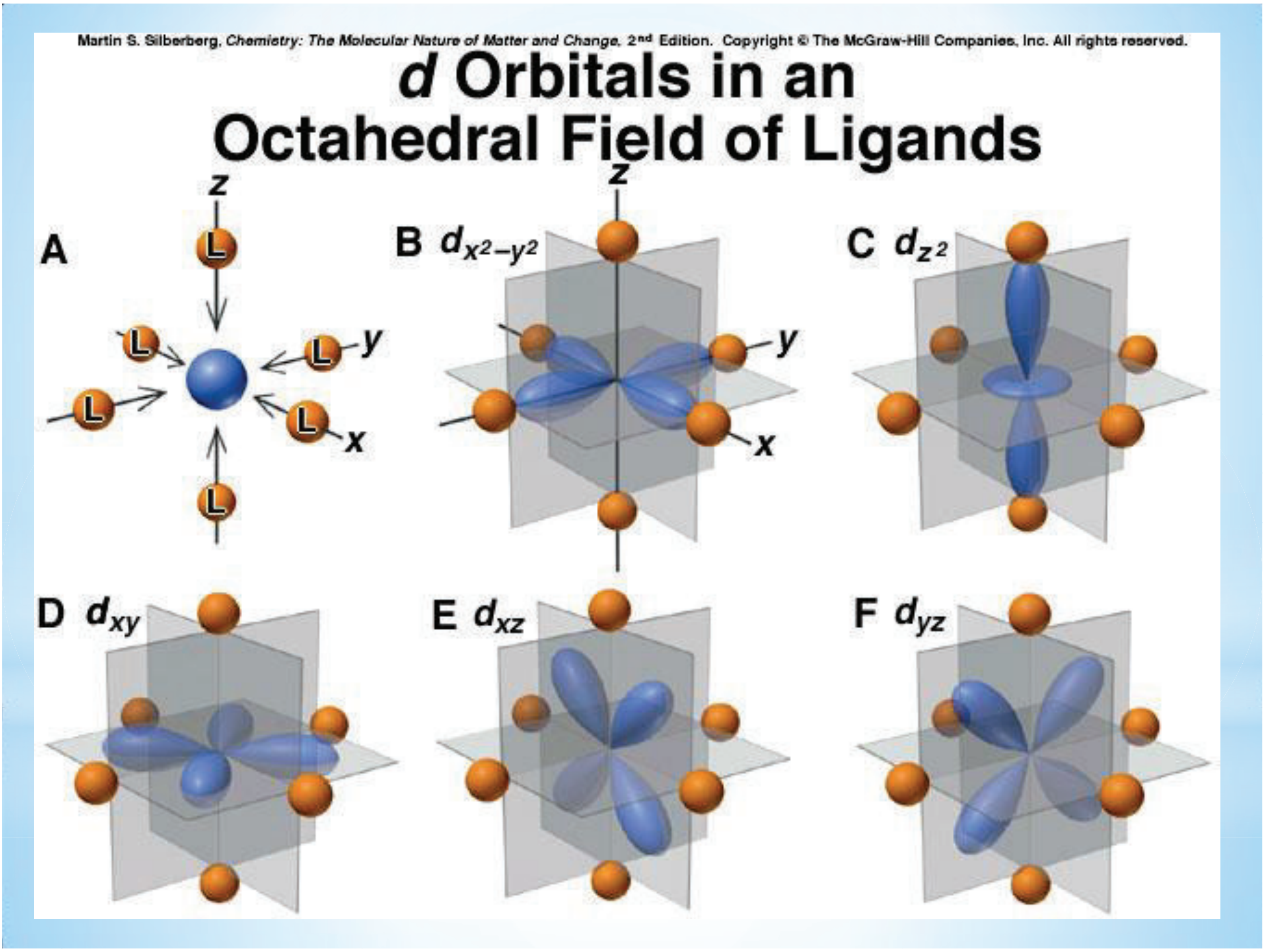
*For example, in Ni(CO)4 and Fe(CO)5, the oxidation state of nickel and iron is zero.

COLOURED IONS

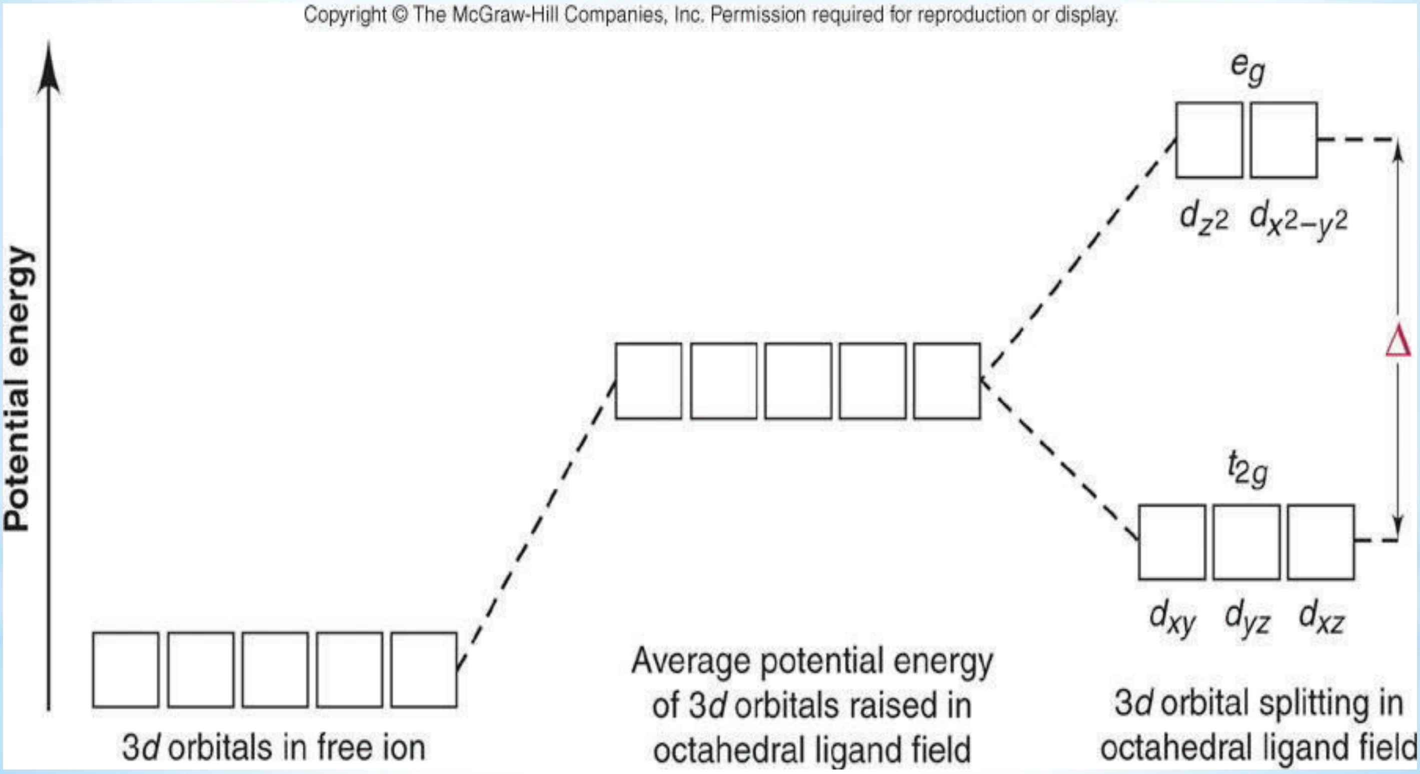
Most of the transition metal compounds (ionic as well as covalent) are coloured both in solid state & in aqueous state.

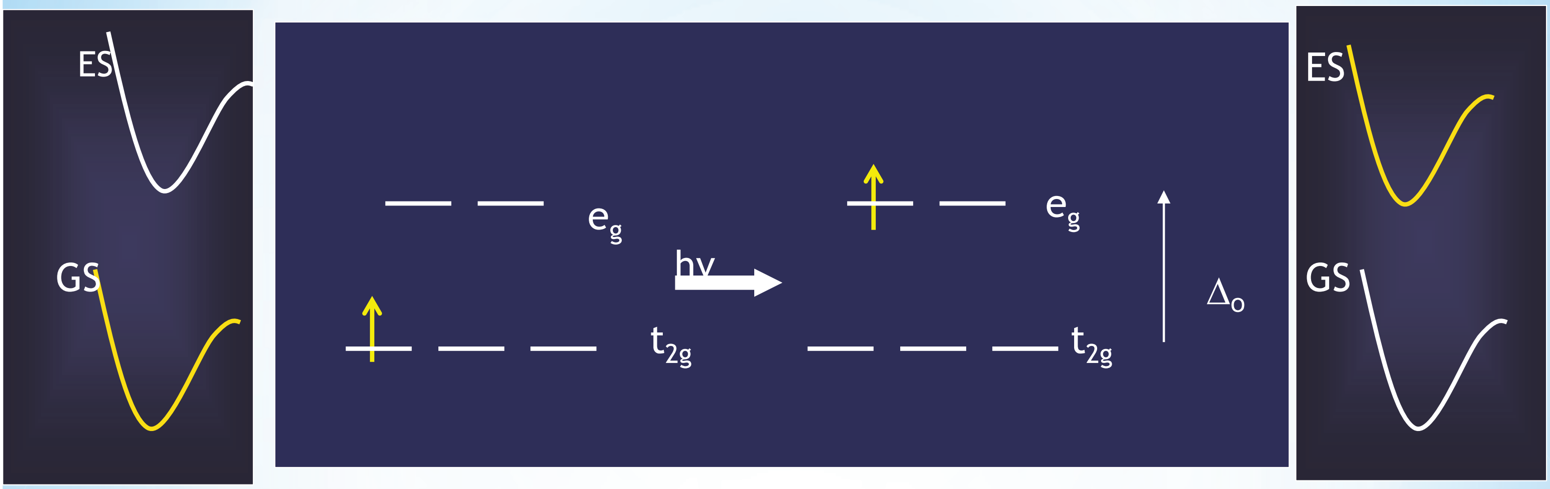
Generally the elements/ions having unpaired electrons produce coloured compound.


Titanium oxide
sodium chromate
Potassium ferricyanide
Nickel(II) nitrate hexa-hydrate
Zinc sulfate Hepta-hydrate
Scandium oxide
Vanadyl Sulphate dihydrate
Mangnaese(II) chloride tetrahydrate
Cobalt(II) chloride
Copper(II) sulfate penta-hydrate


Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.
d Orbitals in an Octahedral Field of Ligands
A
B $d_{x^2-y^2}$
C d_{z^2}
D d_{xy}
E d_{xz}
F d_{yz}
L
x
y
z

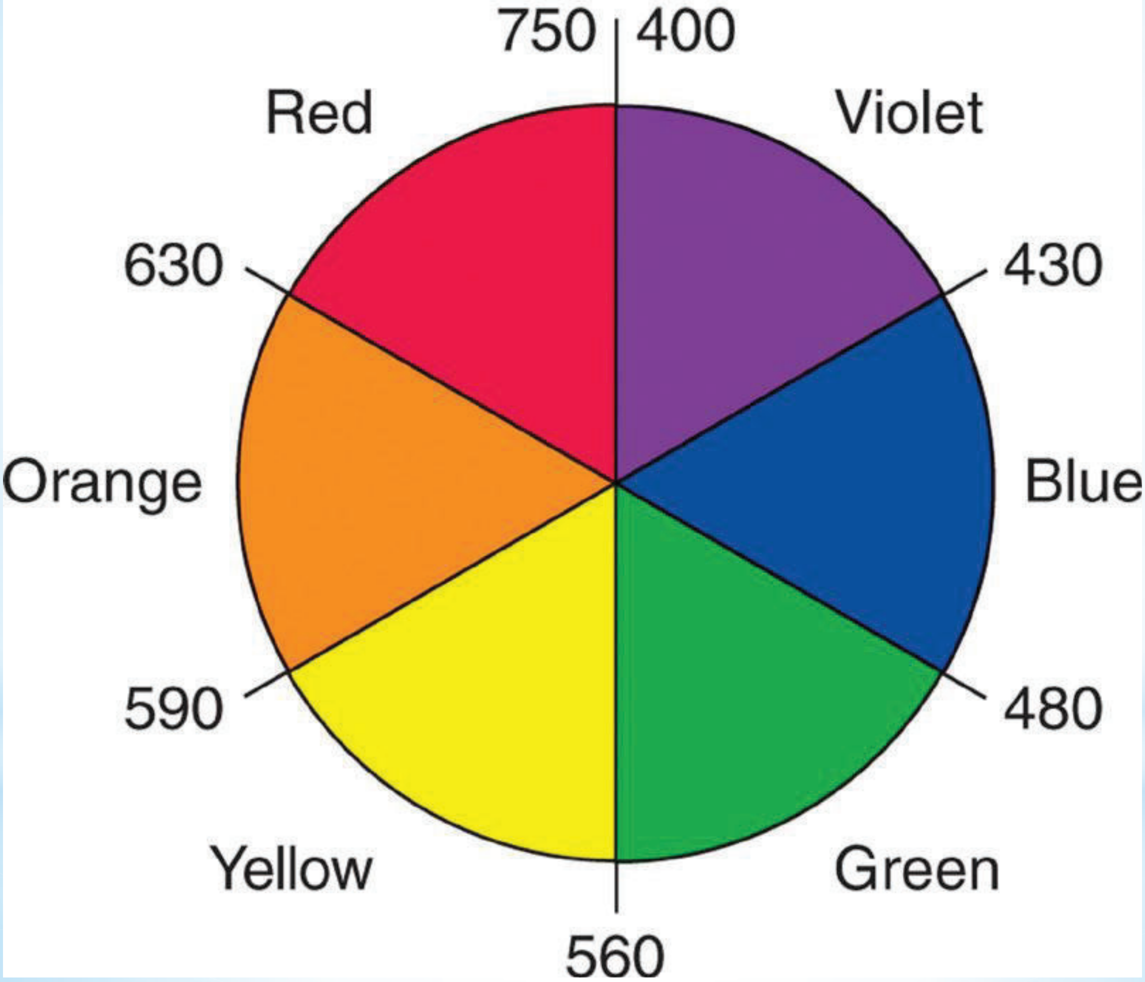
Splitting of d-orbital energies by an octahedral field of ligands





complex in electronic Ground State (GS) → d-d transition → complex in electronic excited state (ES)

An artist's wheel



CATALYTIC PROPERTIES

- ✓Vanadium(V) oxide, V_2O_5 (in Contact Process)
- ✓Finely divided iron (in Haber's Process)
- ✓Nickel (in Catalytic Hydrogenation)
- ✓Cobalt (Synthesis of gasoline)

- ➢ This property is due to-
- ➢ Presence of unpaired electrons in their incomplete d orbitals.
- ➢ Variable oxidation state of transition metals.
- ➢ In most cases , provide large surface area with free valencies.

For example

iron(III) catalyses the reaction between iodide and per sulphate ions

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

Explanation

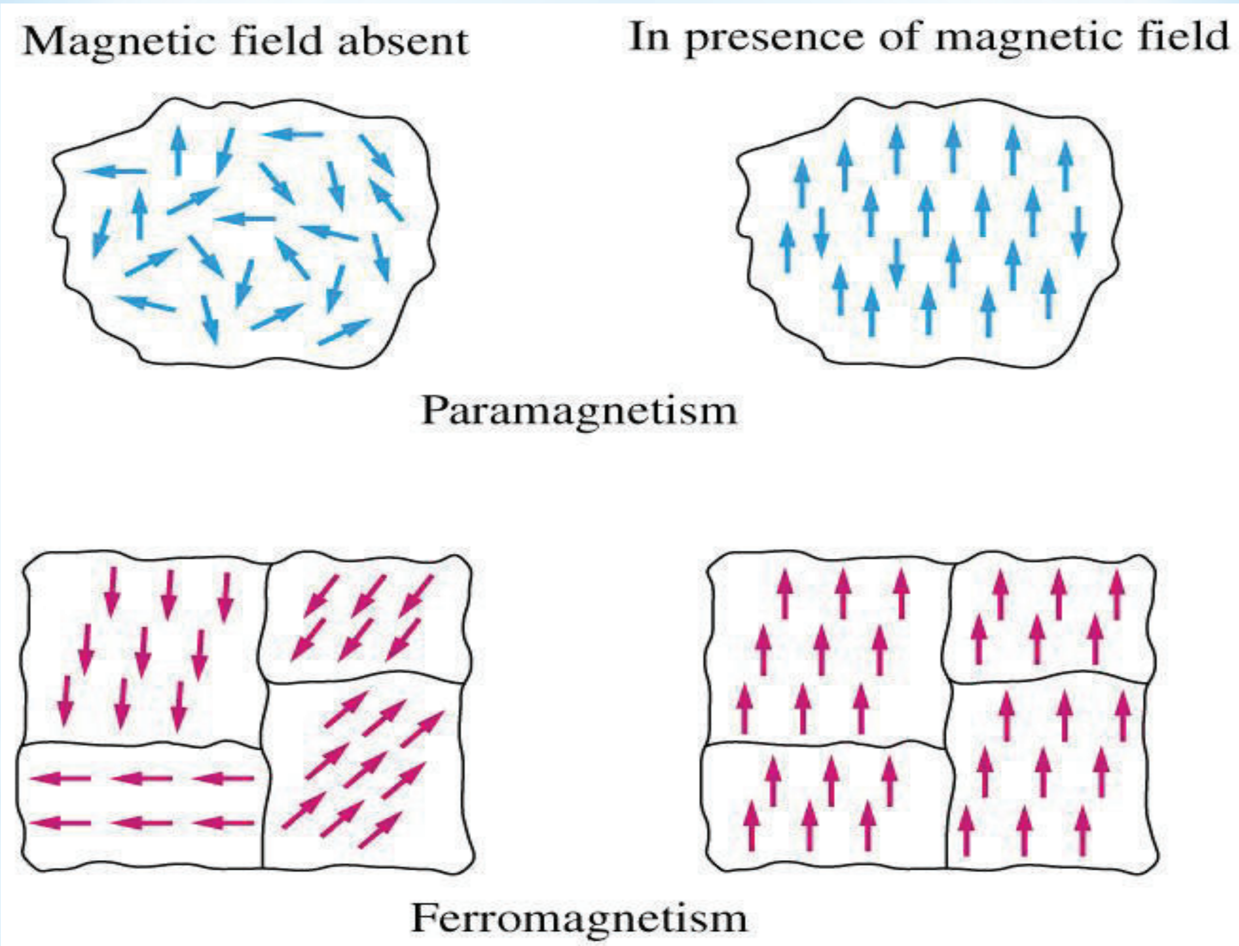
$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2SO_4^{2-}$$

MAGNETIC PROPERTIES

- When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism and paramagnetism.*
- Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted.
- Substances which are attracted very strongly are said to be *ferromagnetic*.
- In fact, ferromagnetism is an extreme form of paramagnetism.

- Most of the transition elements and their compounds show paramagnetism.
- Paramagnetism arises from the presence of unpaired electrons, each such electron have a magnetic moment.
- The magnetic moment of any transition element or its compound/ion is given by (assuming no contribution from the orbital magnetic moment).
- $\mu_s = \sqrt{n(n+2)}$ BM
- Here n is the number of unpaired electrons


Magnetic field absent
In presence of magnetic field
Paramagnetism
Ferromagnetism

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Tl^{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	

- The paramagnetism first increases in any transition element series, and then decreases. The maximum paramagnetism is seen around the middle of the series.

QUESTIONS-

- Q. 1: Which ion has maximum magnetic moment

  (a) V^{3+} (b) Mn^{3+}

  (c) Fe^{3+} (d) Cu^{2+}

- Ans: c
- Q.2. What is the magnetic moment of Mn^{2+} ion (Z= 25) in aqueous solution ?
- Ans.- With atomic number 25, the divalent Mn^{2+} ion in aqueous solution will have d^5 *configuration (five unpaired electrons).Hence, The magnetic moment, μ is*
- $\mu = \sqrt{5(5 + 2)} = 5.92BM$

Formation of Complex Compounds

- Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties.
- The transition metals form a large number of complex compounds.
- A few examples are: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$.

This property is due to the-

- comparatively smaller sizes of the metal ions
- their high ionic charges and the
- availability *of d orbitals for bond formation*.

Questionnaire:

1. What are D-Block elements?
2.Differentiate between D-Block elements and Transition elements?
3.Explain Electronic configuration of D-block elements?
4.How are the oxidation states of these elements given and what are they?
5.What are complex compounds? How are they formed in transition elements? Explain with examples?
6.What are complex compounds? Explain how transition elements can form complex compounds?
7. How can we get magnetic momentum of D-Block elements? Explain?

Assignment:

1.Differentiate between D-Block elements and Transition elements?
2.Explain Electronic configuration of D-block elements?
3.How are the oxidation states of these elements given and what are they?
4.Explain the splitting of d-orbital energies by an octahedral field of ligands?
5.Explain the catalytic properties of D-block elements?
6.What are complex compounds? How are they formed in transition elements? Explain with examples?

THANK YOU