

TRANSITION & INNER TRANSITION ELEMENTS



Lecture 3.

Q. 1 – In 3d series, which metal is showing the highest oxidation state?

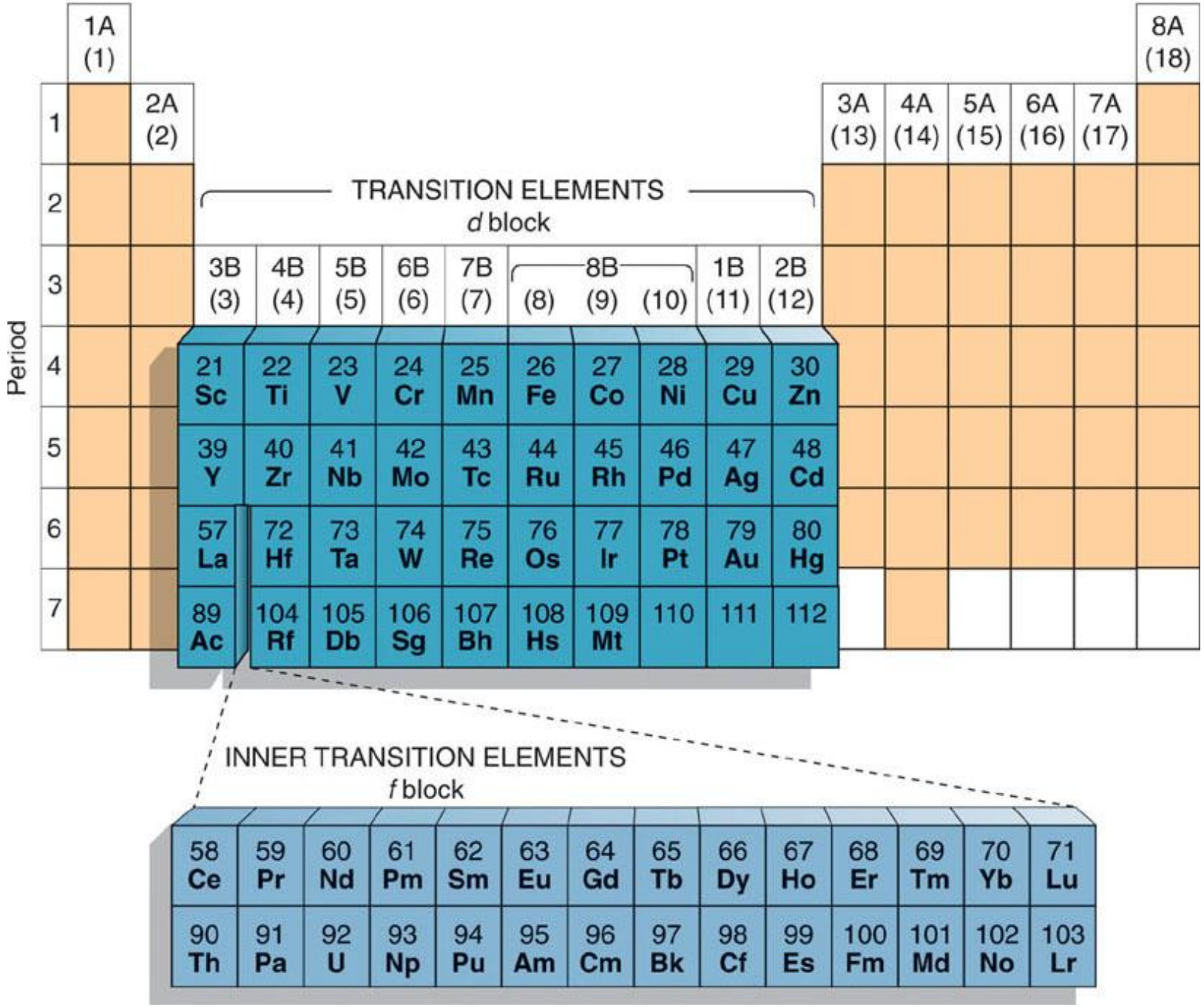
Q.2 - In 3d series, which metal does not exhibit multiple oxidation states?



Answer:

1. Mn – +7.
2. Zn – only +2




1A (1)
8A (18)
2A (2)
3A (13)
4A (14)
5A (15)
6A (16)
7A (17)
TRANSITION ELEMENTS
d block
3B (3)
4B (4)
5B (5)
6B (6)
7B (7)
8B
(8) (9) (10)
1B (11)
2B (12)
Period
1 2 3 4 5 6 7
21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn
39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd
57 La 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg
89 Ac 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 111 112
INNER TRANSITION ELEMENTS
f block
58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu
90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr

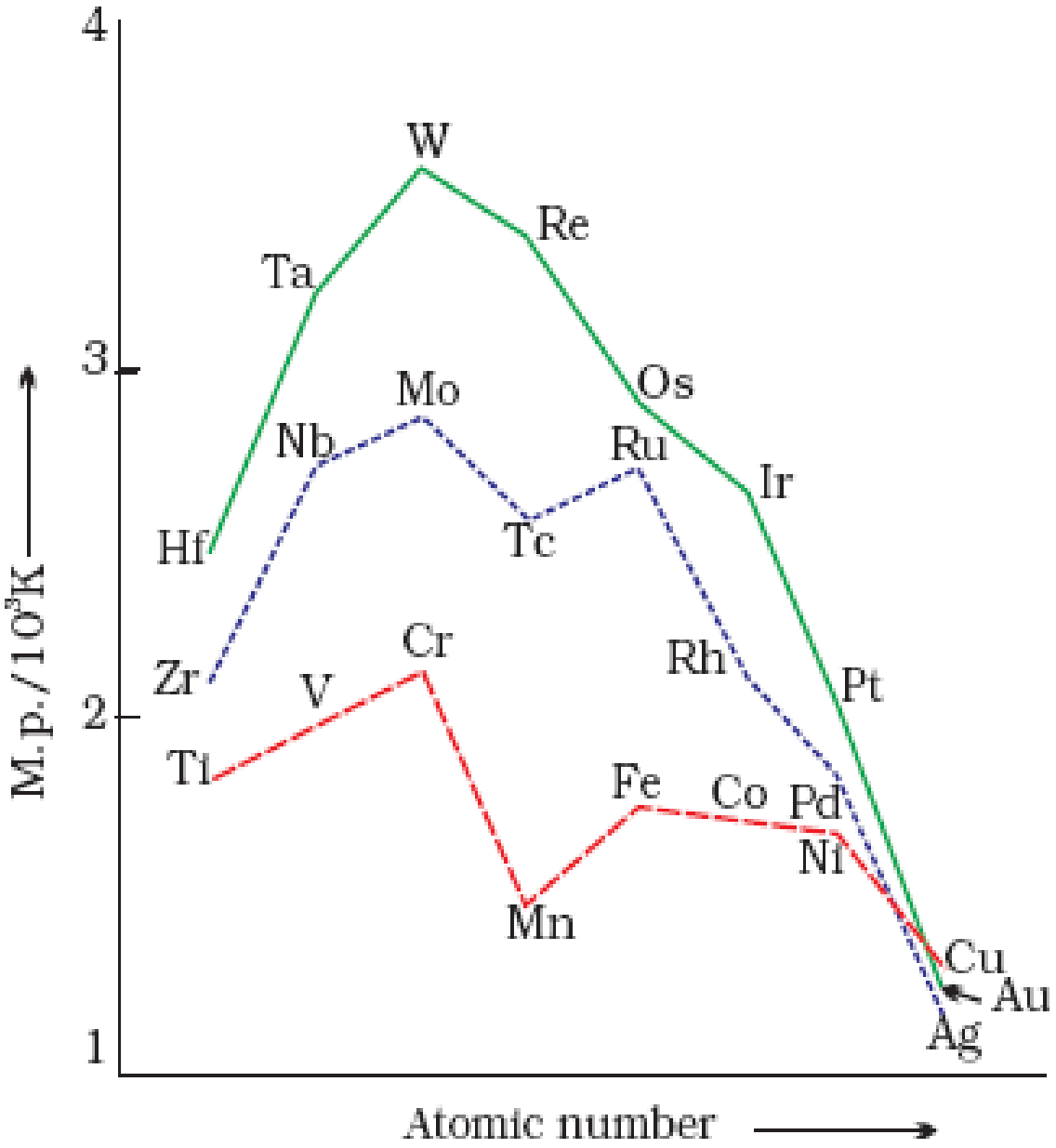
Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_a H^\ominus$/kJ mol^{-1}		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy/$\Delta_i H^\ominus$/kJ mol^{-1}											
$\Delta_i H^\ominus$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\ominus$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\ominus$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic	M	164	147	135	129	137	126	125	125	128	137
radii/pm	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard											
electrode	M^{2+}/M	–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	-0.76
potential $E^\ominus$/V	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–
Density/g cm^{-3}		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

OXIDATION STATES

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

Elements	Outer elecronic configuration	Oxidation states	Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1\ 4s^2$	+2, +3	Fe	$3d^6\ 4s^2$	+2, +3, +4, +5, +6
Ti	$3d^2\ 4s^2$	+2, +3, +4	Co	$3d^7\ 4s^2$	+2, +3, +4, +5
V	$3d^3\ 4s^2$	+2, +3, +4, +5	Ni	$3d^{10}\ 4s^2$	+2, +3, +4
Cr	$3d^5\ 4s^1$	+2, +3, +4, +5, +6	Cu	$3d^{10}\ 4s^1$	+1, +2
Mn	$3d^5\ 4s^2$	+2, +3, +4, +5, +6, +7	Zn	$3d^{10}\ 4s^2$	+2

MELTING POINT

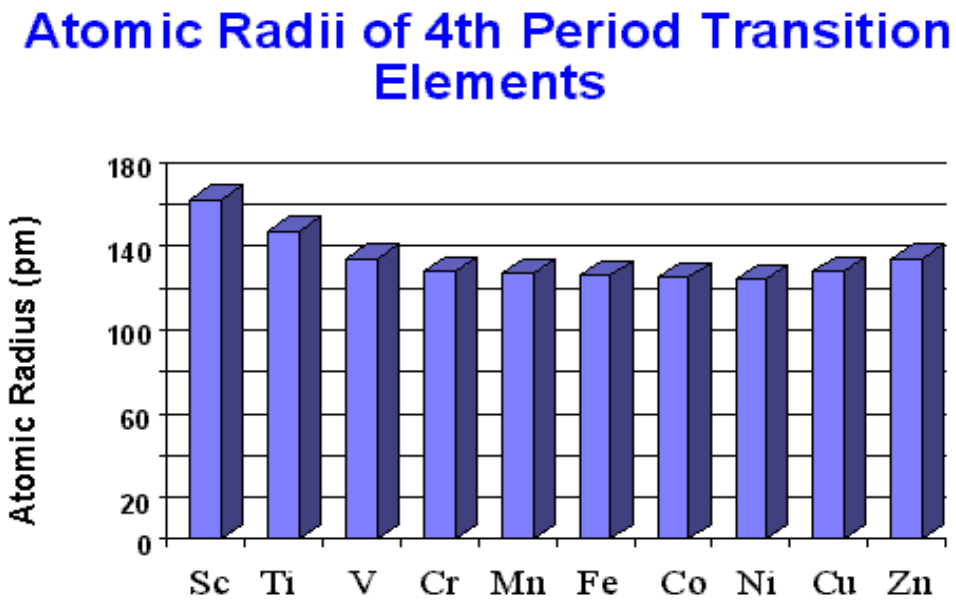


Trends in melting points of transition elements

- Involvement of greater number of electrons from (n-1)*d* in addition to the n*s* electrons in the inter atomic metallic bonding.
- Melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.
- Melting and Boiling points are high.
- A large number of unpaired electrons take part in bonding so they have very strong metallic bonds and hence high melting & boiling points.

ATOMIC & IONIC RADIUS

- Across a period, nuclear charge increases but the penultimate d-sub shell has poor shielding effect so atomic and ionic size remain almost same .
- New electron enters a d orbital each time the nuclear charge increases by unity.
- Shielding effect of a d electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases



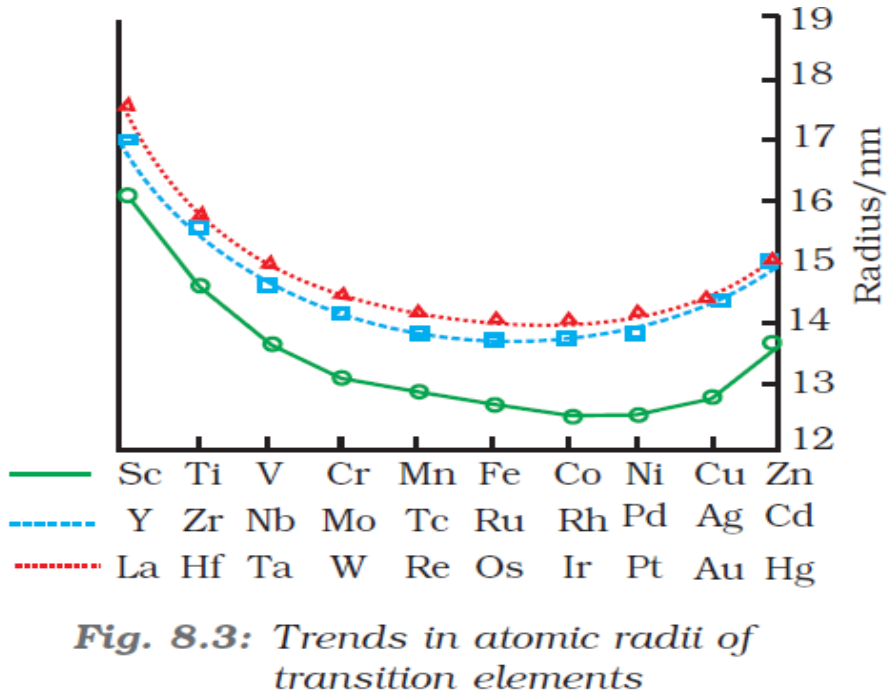
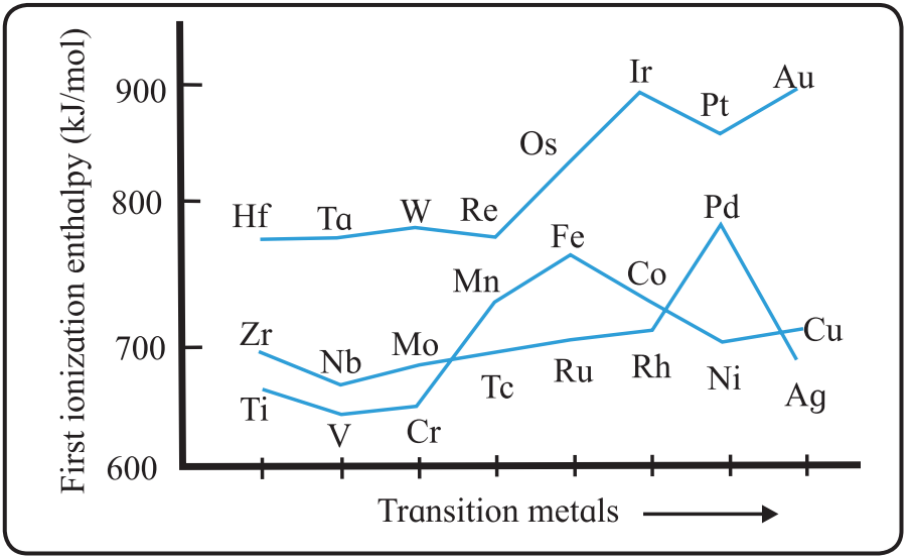


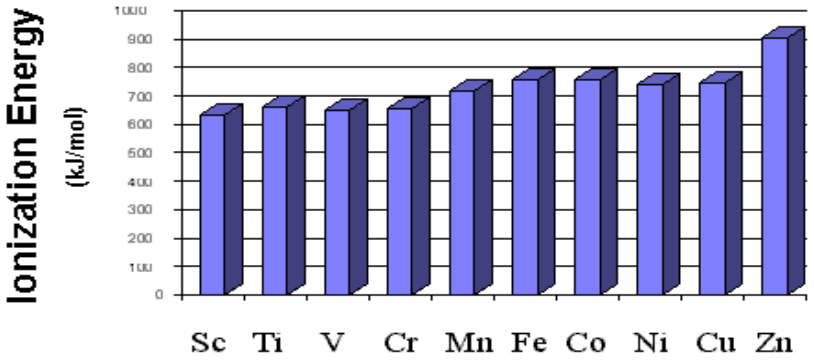
Fig. 8.3: Trends in atomic radii of transition elements

3d< 4d= 5d

IONIZATION ENTHALPY



First Ionization Energies of 4th Period Transition Elements



- 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.
- I.E. values are intermediate to those of s-block & p-block elements.
- Ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states.
- Although the first ionisation enthalpy, in general, increases, the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.
- IE1<IE2 <IE3.

Element / IE	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE_1	632	659	650	652	717	762	756	736	744	906
IE_2	1245	1320	1376	1635	1513	1563	1647	1756	1961	1736
IE_3	2450	2721	2873	2994	3258	2963	3237	3400	3560	3838

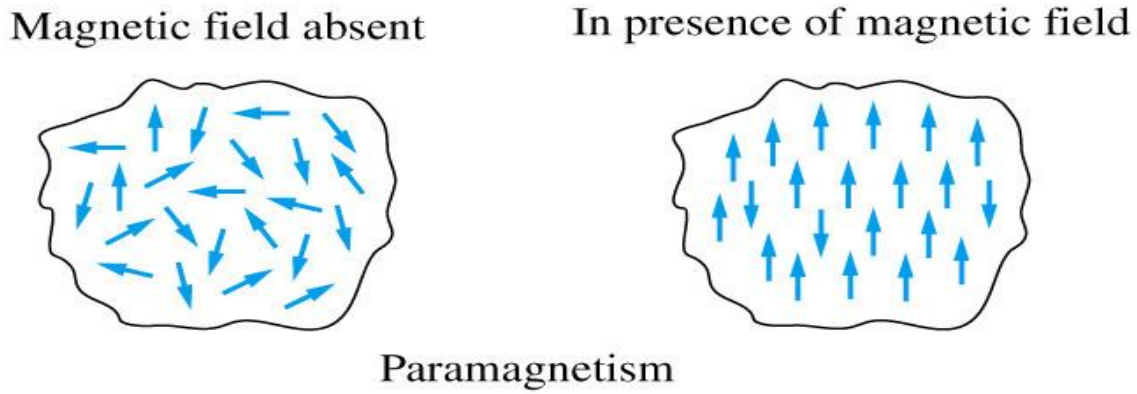
(IE = Ionisation Enthalpy in kJ/mol)

I.E. values: 3d< 4d<< 5d

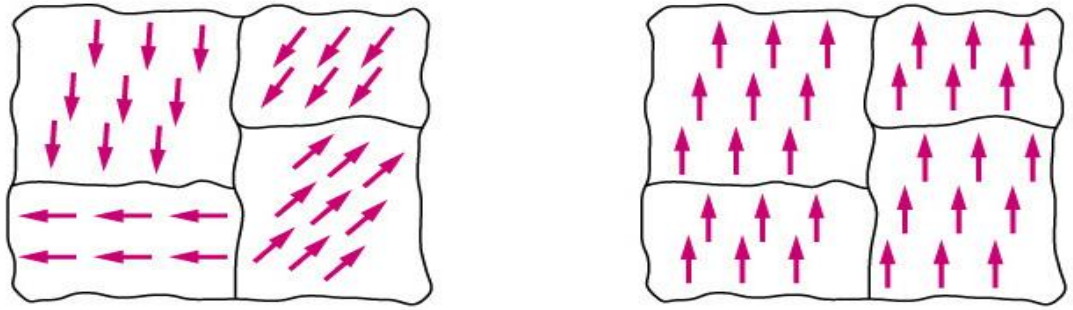
MAGNETIC BEHAVIOUR

- 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


Ferromagnetism

- 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).
- $\mu = \sqrt{n(n+2)}$ BM

  where, μ = magnetic moment; BM = Bohr magneton (unit).
- A single unpaired electron has a magnetic moment of 1.73BM.

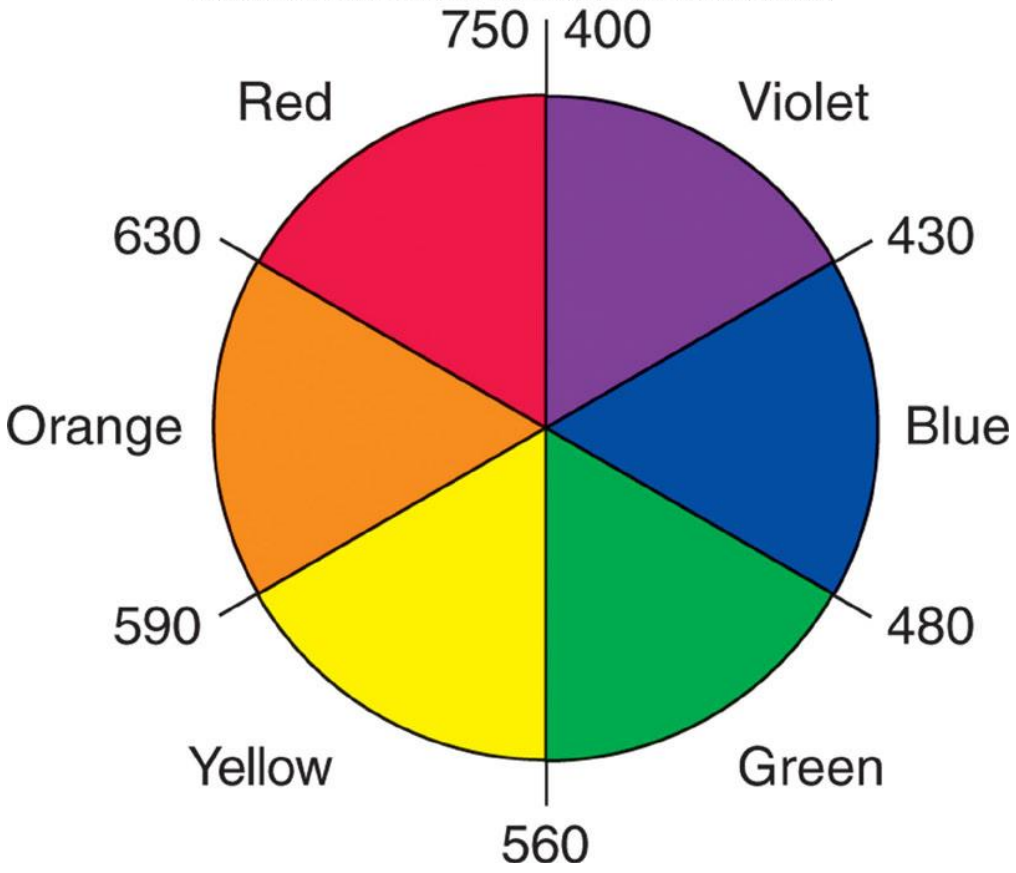
- More the no. of unpaired electrons ,more the magnetic moment.
- The paramagnetism first increases in any transition element series, and then decreases.
- The maximum paramagnetism is seen around the middle of the series.

Ion	Outer electronic configuration	Number of unpaired electrons	Calculated value of magnetic moment	Experimental value
$Sc^{3\oplus}$	$3d^0$	0	0	0
$Ti^{3\oplus}$	$3d^1$	1	1.73	1.75
$V^{3\oplus}$	$3d^2$	2	2.84	2.76
$Cr^{3\oplus}$	$3d^3$	3	3.87	3.86
$Cr^{2\oplus}$	$3d^4$	4	4.90	4.80
$Mn^{2\oplus}$	$3d^5$	5	5.92	5.96
$Fe^{2\oplus}$	$3d^6$	4	4.90	5.3-5.5
$Co^{2\oplus}$	$3d^7$	3	3.87	4.4-5.2
$Ni^{2\oplus}$	$3d^8$	2	2.84	2.9-3.0, 4.0
$Cu^{2\oplus}$	$3d^9$	1	1.73	1.8-2.2
$Zn^{2\oplus}$	$3d^{10}$	0	0	0

COLOUR

- Generally the elements/ions having unpaired electrons produce coloured compound.
- Most of the transition metal compounds (ionic as well as covalent) are coloured both in solid state & in aqueous state.

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Table 23.11 Relation Between Absorbed and Observed Colors

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

- Colour of a transition metal ion depends on:
  - i. presence of unpaired d-electrons
  - ii. d-d transition.
  - iii. Nature of ligands attached to the central metal ion.
  - iv. Geometry of the complex formed by the metal ion.

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

Ion	Outer electronic configuration	Number of unpairedelectrons	Colour
$Sc^{3\oplus}$	$3d^0$	0	Colourless
$Ti^{3\oplus}$	$3d^1$	1	Purple
$Ti^{4\oplus}$	$3d^0$	0	Colourless
$V^{3\oplus}$	$3d^2$	2	Green
$Cr^{3\oplus}$	$3d^3$	3	violet
$Mn^{2\oplus}$	$3d^5$	5	Light pink
$Mn^{3\oplus}$	$3d^4$	4	Violet
$Fe^{2\oplus}$	$3d^6$	4	Pale green
$Fe^{3\oplus}$	$3d^5$	5	Yellow
$Co^{2\oplus}$	$3d^7$	3	Pink
$Ni^{2\oplus}$	$3d^8$	2	Green
$Cu^{2\oplus}$	$3d^9$	1	Blue
$Cu^{\oplus}$	$3d^{10}$	0	Colourless
$Zn^{2\oplus}$	$3d^{10}$	0	Colourless

CATALYTIC PROPERTIES

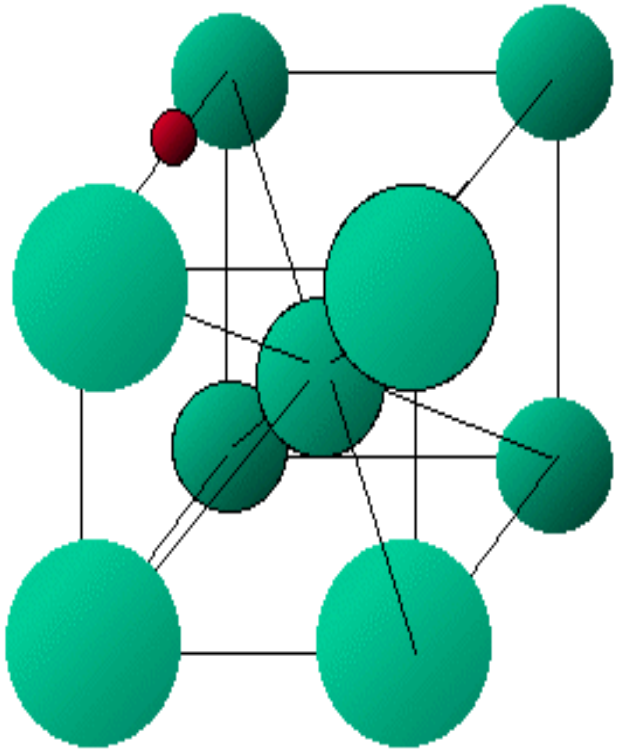
- ✓Vanadium(V) oxide,V_2O_5 (in Contact Process)
- ✓Finely divided Iron (in Haber's Process)
- ✓Molybdenum (in Haber's Process)
- ✓Nickel (in Catalytic Hydrogenation)
- ✓Cobalt (Synthesis of gasoline)
- ✓MnO_2 (in decomposition of $KClO_3$)

This property is due to:

- Presence of unpaired electrons in their incomplete d orbitals.
- Variable oxidation state of transition metals.
- Provision of large surface area with free valencies.

INTERSTITIAL COMPOUNDS

- The transition elements form a large number of interstitial compounds in which small atoms such as hydrogen, carbon, boron and nitrogen occupy the empty spaces in their lattices.
- They are usually non stoichiometric and are neither typically ionic nor covalent.
- Example: TiC, Mn_4N, Fe_3H, $VH_{0.56}$, $TiH_{1.7}$ etc.



PROPERTIES OF INTERSTITIAL COMPOUNDS

1. They are hard.
2. They are good conductors of heat & electricity.
3. Their chemical properties are similar to the parent metal.
4. Their melting points are higher than the pure metals.
5. Their densities are less than the parent metal.
6. Their metal carbides are chemically inert and are extremely hard as diamond.
7. Hydrides of transition metals are used as powerful reducing agents.

Next Lecture:

1. Trends in the properties of D-block elements.

Any Question



“It is not the answer that enlightens, but the question.”

- Eugene Ionesco