E-Content

B.Sc. 2nd Year

Inorganic Chemistry Paper-I

Unit-I

Transition Elements

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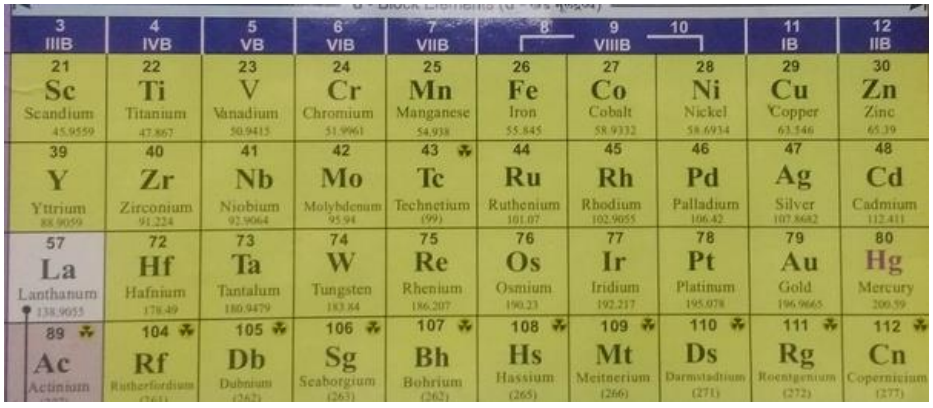
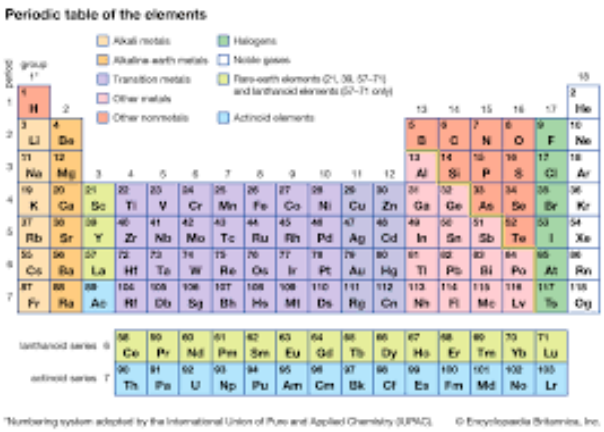
What are Transition elements?

The elements lying between s and p-block of periodic table that constitute a large block of elements are called transition elements. These elements have partly field (n-1)d orbital. Since last electron fill into d-orbital, so they are called transition elements or d-block elements. They show transitional behavior.

Transition elements or d-block elements

They are classified into four series 3d, 4d, 5d and 6d series or I, II, III and IV series. Each series has ten (10) elements while 6d series has at present only one element namely Actinium (Z=89). The elements of IB group, Cu, Ag and Au should not be included in d-block because of their filled d-orbital and Zn, Cd, Hg are also have filled d-orbitals except their formation of complex .These elements are much differ from the properties of next of the elements due to the periodic classification. These elements show a wide application such as in heavy industries paint industries, catalytic use, building materials, jewellery items and coins. Biologically active compounds such as hemoglobin, myoglobin, blue proteins, synthetic, oxygen carriers, vitamin B_{12} contain different transition elements. The elements of group IIIB, IVB, VB, VIB,VIIB,VIII, IB, IIB(3-12) belong to this block.





Position of elements in periodic table

These d-block elements are placed into four series of ten elements in each, which are kept in 4^{th} period (3d series); 5^{th} period (4d series) 6^{th} period (5d series) and 7^{th} period (6d series incomplete series).

4^{th}	Period	–	first transition series	(Sc-Zn, Z= 21-30)
5^{th}	Period	–	second transition series	(Y-Cd , Z= 39-47)
6^{th}	period	–	third transition series	(La-Hg, Z= 57-80)
7^{th}	period	_	forth transition series	(Ac- Lr, Z=89-112)

General characteristic of d- block elements:

(i) All transition metals are hard except for group 11 (copper family) and have high melting and boiling point. Nearly ten transition elements have melting point above 2000˚C and three elements Ta, W and Re have melting points above 3000˚C.(ii) They are hard, strong refractory and electropositive.(iii) The transition elements all have high densities. Os and Ir have densities of the order of 23g/cm^3. (iv) Most of the transition elements are malleable and ductile.(v) Most of the

transition metals are good electrical conductors.(vi) Most of elements form coloured compounds of every colour of the rainbow.(vii) They form alloy with other metals.(viii) These elements form well known coordination complexes.(ix) Transition metals exhibit several oxidation states.(x) Most of the transition metals and compounds are used as catalyst.

The general properties of d-block elements of all the series (3d, 4d, 5d ,6d are not so different because of their electronic configuration. Which includes the number of electrons in d-orbital are generally same only vary in number in s-orbital it is invariably 0, 1 or 2. important physical properties of the elements are discussed below and the data are given in table -A.

Important physical properties of first transition (3d) series elements

Property/ Element	**SC**	**TI**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Atomic number	21	22	23	24	25	26	27	28	29	30
Outer electronic configuration	**$3d^1\ 4s^2$**	**$3d^2 4s^2$**	**$3d^3\ 4s^2$**	**$3d^4\ 4s^2$**	**$3d^5\ 4s^2$**	**$3d^6\ 4s^2$**	**$3d^7\ 4s^2$**	**$3d^8\ 4s^2$**	**$3d^{10}\ 4s^1$**	**$3d^{10}4s^2$**
Atomic size (A^0)	1.60	1.46	1.1.31	1.25	1.29	1.26	1.25	1.25	1.28	1.33
Ionic radius ((A^0)M^{2+} M^{3+}		0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.69	0.79
Stable oxidation state	+3	+4	+3, +4, +5	+2, +3 +6	+2, +3, +6,+7	+2, +3, +7	+2, +3	+1, +2	+1 +2	+2

Red.Pot.E^0 M^{2+}/M (V)	-	-1.63	-1.20	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
Density (gm/ml)	3.1	4.5	6.1	7.2	7.6	7.9	8.7	8.9	8.9	7.1
Melting Point (^{0}C)	1539	1725	1900	1875	1245	1536	1495	1453	1083	420
Boiling Point (^{0}C)	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
I^{st}Ionization Energy/mol)	632	659	650	652	717	762	758	736	746	906
Electronegativity	1.3	1.5	1.05	1.6	1.05	1.8	1.8	1.8	1.8	1.6
Heat of Fusion (Kj /mol)	15.9	15.5	17.6	13.8	14.6	15.3	15.2	17.6	13.0	7.4
Heat of vaporization	338.8	405.4	443.5	305.3	224.6	333.7	389.7	380.7	338.9	114.6
Crystal structure	Fcc	Hcp	Bcc	Bcc	Bcc	Bcc	fcc	hcp	Fcc	hcp

Properties

1, Electronic configuration of Transition Series Elements:

The electronic configuration of 4d and 5d series are given for comparison with 3d series. The outermost electronic configuration (valence shell) of the series can be represented by $3d^{1-10}4s^{1-2}$ (table-1.1). First two electrons go into 4s-orbital due to their low energy state compared to 3d-orbital. The rest electron enters into 3d- orbital. Since the filling of electron takes places from 1 to 10 in d-orbitals, these are called 3d series, 4d series, 5d series and 6d series. There are certain exception in configuration of Cr (Z=24) and Mo (Z=42). The expected configuration of Cr (Z=24) atom is $[Ar]^{18}$ $3d^4$ $4s^2$ but

actual configuration as Cr (Z=24) $[Ar]^{18}$ $3d^5$ $4s^1$. This can be explained on fact that these two orbitals have close energy separation thus giving rise to six nearly same energy state and extra stable configuration is observed for both Cr and Mo as given above .In table 1.1,1.2 and 1.3 two type electronic distribution are given one is predicated and another is observed. Observed is actual electronic configuration found by experiments. The irregularities found in observed configuration from predicated i.e. Cr, Cu, Mo, Pd, Ag, and Au are explained on the basis of half field completely field d-orbitals are relatively more stable than other d-orbital. On the basis of this concept it is however not easy to explain the irregularities found in other elements. Since one has to consider net effect of so many other factors such as (i) nuclear-electronic attraction

(ii) shielding of one electron by several other electrons, (iii) interelectronic repulsive forces, (iv) exchange energy forces, etc. All these forces play an important part together in determining the final stability of an electronic distribution of an atom. It is not easy to explain configuration of Nb, Ru, Rh and tungsten unlike chromium ($3d^5$ $4s^1$) and molybdenum ($4d^5$ $5s^1$) should have idealised the configuration $4f^{14}$ $5d^4$ $6s^2$.

Table -1.1 Electronic distribution of first transition series elements:

Elements	**Symbol**	**Atomic number**	**Electronic distribution**	
			Predicted	**Observed**
Scandium	Sc	21	[Ar] $3d^1$ $4s^2$	[Ar] $3d^1$ $4s^2$
Titanium	Ti	22	[Ar] $3d^2$ $4s^2$	[Ar] $3d^2$ $4s^2$
Vanadium	V	23	[Ar] $3d^2$ $4s^2$	[Ar] $3d^2$ $4s^2$

Chromium	Cr	24	[Ar] $3d^4\ 4s^2$	[Ar] $3d^5\ 4s^1$
Manganese	Mn	25	[Ar] $3d^5\ 4s^2$	[Ar] $3d^5\ 4s^2$
Iron	Fe	26	[Ar] $3d^6\ 4s^2$	[Ar] $3d^6\ 4s^2$
Cobalt	Co	27	[Ar] $3d^7\ 4s^2$	[Ar] $3d^7\ 4s^2$
Nickel	Ni	28	[Ar] $3d^8\ 4s^2$	[Ar] $3d^8\ 4s^2$
Copper	Cu	29	[Ar] $3d^9\ 4s^2$	[Ar] $3d^{10}\ 4s^1$
Zinc	Zn	30	[Ar] $3d^{10}\ 4s^2$	[Ar] $3d^{10}\ 4s^2$

Here, [Ar] means electronic distribution of atomic no. 18. The general electronic configuration of the 3d series elements may be given as $(n-1)d^{1-10}\ ns^{1-2}$; n=4.

Table1.2 Electronic distribution of second transition series elements:

Elements	**Symbol**	**Atomic number**	**Electronic distribution**	
			Predicted	**Observed**
Yttrium	Y	39	[Kr] $4d^1\ 5s^2$	[Kr] $4d^1\ 5s^2$
Zirconium	Zr	40	[Kr] $4d^2\ 5s^2$	[Kr] $4d^2\ 5s^2$
Niobium	Nb	41	[Kr] $4d^3\ 5s^2$	[Kr] $4d^4\ 5s^1$
Molybdenum	Mo	42	[Kr] $4d^4\ 5s^2$	[Kr] $4d^5\ 5s^1$
Technetium	Tc	43	[Kr] $4d^5\ 5s^2$	[Kr] $4d^5\ 5s^2$
Ruthenium	Ru	44	[Kr] $4d^6\ 5s^2$	[Kr] $4d^7\ 5s^1$
Rhodium	Rh	45	[Kr] $4d^7\ 5s^2$	[Kr] $4d^8\ 5s^1$
Palladium	Pd	46	[Kr] $4d^8\ 5s^2$	[Kr] $4d^{10}\ 5s^0$
Silver	Ag	47	[Kr] $4d^9\ 4s^2$	[Kr] $4d^{10}\ 4s^1$

Cadmium	Cd	48	[Kr] $4d^{10}$ $5s^2$	[Kr] $4d^{10}$ $5s^2$

Here, [Kr] means electronic distribution of atomic no. 36. The general electronic configuration of the 4d series elements may be given as $(n-1)d^{1-10}$ ns^{0-2}; n=5.

Table. 1.3 Electronic distribution of third transition series

Elements	Symbol	Atomic number	Electronic distribution	
			Predicted	Observed
Lanthanum	La	57	[Xe] $5d^1$ $6s^2$	[Xe] $5d^1$ $6s^2$
Hafnium	Hf	72	[Xe] $4f^{14}$ $5d^2$ $6s^2$	[Xe] $4f^{14}$ $5d^2$ $6s^2$
Tantalum	Ta	73	[Xe] $4f^{14}$ $5d^3$ $6s^2$	[Xe] $4f^{14}$ $5d^3$ $6s^2$
Tungsten	W	74	[Xe] $4f^{14}$ $5d^4$ $6s^2$	[Xe] $4f^{14}$ $5d^4$ $6s^2$
Rhenium	Re	75	[Xe] $4f^{14}$ $5d^5$ $6s^2$	[Xe] $4f^{14}$ $5d^5$ $6s^2$
Osmium	O s	76	[Xe] $4f^{14}$ $5d^6$ $6s^2$	[Xe] $4f^{14}$ $5d^6$ $6s^2$
Iridium	Ir	77	[Xe] $4f^{14}$ $5d^7$ $6s^2$	[Xe] $4f^{14}$ $5d^7$ $6s^2$
Platinum	Pt	78	[Xe] $4f^{14}$ $5d^8$ $6s^2$	[Xe] $4f^{14}$ $5d^9$ $6s^1$
Gold	Au	79	[Xe] $4f^{14}$ $5d^9$ $6s^2$	[Xe] $4f^{14}$ $5d^{10}$ $6s^1$
Mercury	Hg	80	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$

Here, [Xe] means electronic distribution of atomic no. 54. The general electronic configuration of the 5d series elements may be given as $(n-1)d^{1-10}$ ns^{1-2}; n=6

2.Melting and Boiling points: The d-block elements have very high melting and boiling points and melts above 900 c. Due to completely filled d-orbital elements like Zn, Cd, and Hg do not form covalent compound. The formation of covalent

bond present in rest elements as it also accounts of the having incomplete d-orbital.

3. Atomic and ionic radii:

These points may be noted from the data of table. (i) As it is clear from the table-A that the atomic and ionic radii show a gradual decrease in their values in any period. This is due to increase in nuclear charges try to pull the electron clouds toward itself that is attraction of electrons towards nucleus increases. This increase in attraction leads to decrease in radii values across each period. There are however few exceptions, the atomic radii of the elements from chromium to copper are very close to one another. This is explained as further the addition of extra electrons screen the outer electron very effectively from the nuclear charge thus screening effect increase considerably due to increase in atomic number and hence there is a marginable increase in effective nuclear charge .Thus results a small change in atomic radii of the middle elements in any period .

(ii) In any particular series, the atomic radius attains the minimum value for elements of 8^{th} group (that is 8,9 and 10) and increases again towards the end of the series. This is explained in terms of increase force of repulsion among the added electrons which dominate to the attractive forces due to increased nuclear charge and results in expansion of electron cloud.

(iii) On descending in the group, principal quantum number ‘n’ increases and atomic size is therefore is expected to increase from top to bottom but the increase are not same for all the members. The difference in radius of second and third series elements is very small as compared to first and second series

members. This is due to lanthanide contraction here the inclusion of 14 lanthanide elements between La and Hf.

4. Density: The transition elements show a high density compared to alkali and alkaline earth metals. Due to smaller size and increased nuclear charge and poor screening effect by the orbitals the electron are attached more strongly towards the nucleus this results a decrease in atomic volume of transition metals and there is an increase in density .It can be also seen a trend of table that densities increases from period 4 to 6 elements the osmium and iridium with highest values ($23g/cm^3$) and then decreases in a group there is also an increase in density of elements. Thus, increase in densities is due to small radii and closed packed structure of the elements .The densities of the second series is nearly two times those of the second series elements due to the atomic masses because twice those of the first series elements .

5.Ionization Energy: There is a considerable increase ionization energy value from left to right in first series (table) due to effective attraction of nuclear charge on the outer electrons. A perusal of table 3 and 4 showed higher value of ionization energies of third series than first and second series. It can be explained on the basis of poor shielding of outer most electron due to presence of 4f orbital in the third series elements. The outermost electrons are more exposed nuclear charge and therefore it in enhance the ionization energy of third series elements

6. Oxidation states

This is one of the peculiar properties of transition element that the element exists in different stable oxidation state. Change in oxidation state usually shown a unit change of Fe^{3+} and Fe^{2+} as compared to non–metals usually changed by two units. After calcium (atomic no. 20 the electronic configuration $1s^2$, 2s2, 2p6, 3s2, 3p6, 4s2) the next ten elements will have the electronic configuration started with filling of 3d orbital from one to ten. This prevails exception in the case of Cr and Cu, due to extra stability of their half filed or completely filled configuration, these two electrons prefer to shift their one 4s electron to 3d orbital. Therefore, the first element of 1st transition series have an oxidation number (+II) when two 4s electron are engaged in bonding and (+III) when addition of one 3d electron is involved in bonding .Thus, from titanium to chromium a regular change in oxidation state takes place with a correlation between electronic structure and minimum and maximum oxidation states. Further the highest oxidation state of these elements, all of the s and d electrons are used in bonding. After the $3d^5$ configuration the tendency to show higher oxidation state decreases among the rest elements. Fe has a maximum (+VI) oxidation state and ruthenium and rhodium the often two elements of their group contain oxidation state (+VIII) due to their larger size. The oxidation states of these elements are shown in Table 1.6

Table- 1.4 Different oxidation states of first transition elements

Element	**SC**	**TI**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Electronic structure	$3d^14s^2$	$3d^24s^2$	$3d^3\,4s^2$	$3d^54s^1$	$3d54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
Oxidationstate	II	II	I						I	

	III	III	II	II	II	II	II	II	II	II
		IV	III	III	III	III	III	III		
			IV	IIV	IV	IV	IV	IV		
			V	V	V	V	V	V		
				VI	VI	VI				

Copper has a stable completely filled configuration (table1.3) shows +1 by losing one electron from 4s orbital whereas Zn show only one oxidation state (+II) reveals that 3d shell is completely filled. Folloing point may be noted from data of table (i) There is an increase in number of oxidation state in going from left to right in a period, however the elements towards middle of the series have more oxidation states than those towards the end of the series. The increase in number of oxidation states in proceeding left to right in a period is due to readily availability of s and d electrons for binding maximum number of oxidation state is reached somewhere in the middle of the series.(ii) The relative stabilities of various oxidation state shown by given oxidation state can be explained on the basis of stability of d^0, d^5 and d^{10} electronic configuration. For example (a) Ti^{4+} ($3d^0$ $4s^0$) is more stable than Ti^{3+} ($3d^0$ $4s^0$) because of presence of d^0 orbital in Ti^{4+} ion. (b) Mn^{2+} ($3d^5$ $4s^0$) is more stable than Mn^{3+} ($3d^4$ $4s^0$) because of presence of $3d^5$ orbital in Mn^{2+}. (c) Ag^+ ($4d^{10}$ $5s^0$) is more stable than Ag^{2+}($4d^9$ $5s^0$) due to presence of d^{10} orbital. (iii)Transition element can form ionic bond in their lower oxidation state and covalent bond in higher oxidation state. The acidic nature of metal-oxygen and metal-chloride bond increases with increasing oxidation state.

7. Magnetic properties: The substances when placed in a magnetic field show a decrease or increase in in magnetic field of strength. If the external magnetic field is larger than applied field the substance is called paramagnetic. Diamagnetic substance repelled by magnetic filled of strength.

The transition metal compounds are generally paramagnetic in nature due to having unpaired electrons in their d- orbitals. Fe, Co and Ni are ferromagnetic in nature due to large number of unpaired electrons. In these element alignments occur when these materials are magnetised and behave as a permanent magnet.

The magnetic propertied shown by majority of compounds of transition metals. This arises due to spin of electrons and orbital motion, which produce a spin moment and orbital moment respectively. Therefore, an interaction of spin magnetic moment and orbital magnetic moment continues to produce magnetic properties in an atom ion or molecules.

The unit of magnetic moment expressed is called Bohr magneton (BM). For an electron it is given by:

$$\mu_B = eh/4\pi mc$$

where e=charge on electron , h=planks constant, c=velocity of light and

m=mass of the electron

Magnetic moment of a single electron is given by:

$$\mu_s = \sqrt{4S+1}$$

Where, S=total spin quantum number of unpaired electrons.

thus, for a single electron μ_s is given by:

$$\mu_s = = \sqrt{4x1/2 + 1} = \sqrt{3} = 1.73 \text{ BM}$$

Magnetic moment for an atom or ion or molecules containing more than one unpaired electron (n) can be calculated as:

$$\mu_s = \sqrt{n(n+2)}$$

for n=1 $\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM

for n=2 $\mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ BM

It is observed that the experimental value for magnetic moment is found to be more than the spin only value due to orbital motion contribution of the electron. This is given by the expression:

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

where L=total orbital angular momentum.

The observed and calculated values of magnetic moments for first transition series elements are given in the following table 1.7

Table 1.4 Magnetic moments of first transition series metal ions

Metal ion	S	L	μ_{SL}	μ_{obs}	μ_S
V^{4+}	1/2	2	3.00	1.7 – 1.8	1.73
V^{3+}	2/2	3	4.47	2.6 – 2.8	2.83
Cr^{3+}	3/2	3	5.20	~3.8	3.87
Co^{3+}	4/2	2	5.48	~5.4	4.90
Fe^{3+}	5/2	0	5.92	~5.9	5.92

8. Colour: Transition metal compound are coloured in contrast to s and p block elements. Properties of these and differentiate to main group element due to absorption of radiations in visible region of the spectrum, the transmitted light is coloured with the complementary colour, the light absorbed. Absorption of radiation takes place due to electronic transition caused by changes in electronic energy. This is also called electronic spectra. The transition elements compounds show various colour depend upon the oxidation states and nature of ligand surround the metal ion. Thus, an aqueous solution of titanium (III) compound is blue green colour. This compound absorbs light at 493 nm corresponds to blue green with complementary colour of reddish violet colour. The copper compounds appear reddish blue as it absorbs red region. The various colours are given in table of first transition series elements.

Table1.5 Colour of different metal ion of first transition series

Ion	**Outer electronic configuration**	**Number of unpaired electrons**	**Color of the ion**
Sc^{3+}	$3d^0$	0	colorless

Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^{10}$	0	colorless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	violet
Mn^{2+}	$3d^5$	5	Light pink
Mn^{3+}	$3d^4$	4	violet
Fe^{2+}	$3d^6$	5	yellow
Fe^{3+}	$3d^5$	3	pink
Co^{3+}	$3d^7$	2	green
Ni^{2+}	$3d^8$	1	colorless
Cu^{2+}	$3d^9$	0	colorless
Cu^{+}	$3d^{10}$	0	Colorless
Zn^{2+}	$3d^{10}$	0	Colorless

Metal ions which contain completely filled d- orbital like $m^{2+,}$ $Hg^{2+,}$ Cu^{+} etc are normally white for example $ZnCl_2$ is white.

9. Catalytic properties of transition metal: Transition metals play an important role in catalytic activities for the several commercial syntheses of various organic as well as inorganic compounds, hydrogenation of unsaturated compounds, nickel

is used as catalyst. In Haber process of synthesis of ammonia, iron and molybdenum are used as catalyst. Manganese dioxide and vanadium pentoxide are used to catalyse the decomposition of H_2O_2 and SO_2 to get O_2 and SO_3 respectively. Other metals like chromium, platinum etc. are also used in different chemical reaction.

10. Formation of complex Compounds:

The transition elements have unique property to form complex salts due to presence of vacant d-orbital to accept electron from Lewis bases, groups which are capable to donate a pair of electrons. These groups are called ligands. The number of ligands coordinated to metal is called the coordination number of metal ion. The ligand may be neutral groups as NH_3 and ion as Cl^- or CN^- etc. $(Fe(CN)_6)^{4-}$and $(Fe(CN)_6)^{3-}$complex compounds are formed by donation of six pairs of electrons from CN^- to Fe^{2+} and Fe^{+3} respectively .

$[Ni(CN)_4]^{2-}$and $[Ni(Cl)_4)^{2-}$ complex compounds are formed by the gain of four pairs of electrons from CN^- and Cl^- ions. Various other transition metals also form complex compounds with N,O,F and S atoms as donor .

11. Reactivity: The reactivity towards other groups is found less for the transition metal's high ionization potential and smaller size. Thus, they have tendency to remain un reactive. Elements like platinum and gold do not react with air and are called noble metals.

Binary compounds of the first transition series:

The element with only one other element combines to form binary compound. These are the simplest type of compound formed by transition element with a variety of non-metals like oxygen nitrogen phosphorous halogens and carbon to form binary compounds. In lower oxidation state metals form simple salts and show electropositive character whereas in higher oxidation state oxides are formed and metal show more electropositive character.

Oxides: Oxides of the elements of first transition series shown by general formula as MO, M_2O_3, MO_2, M_2O_5 and MO_3.Their stability increases from scandium to zinc. It indicates that the elements from starting in the 3d series attain stable state to reduce electrons and this show their strong reducing nature. In these elements Cr(II) and V(II) oxides are strong reducing agent, copper and zinc do not show +3 oxidation state.

The oxides are basic in the low oxidation state and basic in high oxidation state of the metal involved. Therefore, basicity decreases from left to right in the first series of elements. Amphoteric oxides are formed by the intermediate oxidation state of metal the basic and amphoteric oxides when dissolved in acid forming hexaaquo complex ions $[(M(H_2O]_6^{n+}$.

MO type oxides in which each M^{2+} metal ions and each O^{2-} ion is surrounded by six M^{2+} ion have a NaCl type crystal structure.

Iron form non-stochiometric oxides in which ratio of metal to oxygen is not a whole number.

All oxides are very stable and are insoluble in water or aqueous acid except NO_2 dissolves in acid to give NO^{2+} ions. Chromium trioxide is soluble in water converting dichromate ion.

$$2CrO_3+H_2O= H_2CrO_7.$$

It is a strong oxidizing agent and oxidizes many organic compounds the acid base character of the first transition series oxides in different oxidation state are given in the following table.

Hydrides: Almost all the hydrides of first transition series forms hydrides by the accumulation of hydrogen atoms in their interstitial space. Such hydrides are called interstitial hydrides and show variable composition e.g. $TiH_{1.8}$, $PdH_{0.6}$ and $NbH_{0.7}$ etc. The M-H bond cannot categorise as ionic o covalent. These are solid metal like appearance, brittle with magnetic and conducting properties.

Carbides: The metals interact with carbon at high temperature forming carbides. Apart from carbon, atom like boron and nitrogen can occupy empty spaces between the atoms of these metals. Such compounds are called interstitial compounds and called as carbides, borides and nitrides respectively. The carbon atoms cause a distortion in space of metals like Cr, Mn, Fe, Co and Ni due to less space in crystal lattice to occupy. This is the reason that is why they are highly reactive. These interstitial compounds are high melting and hard. These are used for making heat resistant material and cutting tools as well as kiln and gas turbine and jet engines.

Table 1.6 Binary compounds of the first transition series elements

Elements	Oxidation state						
	+1	+2	+3	+4	+5	+6	+7
Sc	-----	-------	ScO_3	--------	--------	------	-------
Ti	------	TiO	Ti_2O_3	TiO_2			
V		VO	V_2O_3	VO_2	V_2O_5		
Cr		CrO	Cr_2O_3	CrO_2	$Cr2O_5$	CrO_3	
Mn		MnO	Mn_2O_3	MnO_2	$Mn2O_5$	MnO_3	Mn_2O_7
Fe		FeO	Fe_2O_3	FeO_2			
Co		CoO	Co_2O_3	CoO_2			
Ni		NiO	Ni_2O_3	NiO_2			
Cu	Cu_2O	CuO	Cu_2O_3				
Zn		ZnO					

1.5. Complexes with Relative stability of oxidation state: Tendency of the elements to form complex compounds is directly related to their oxidation reduction potential. Further the oxidation state of the elements is stabilised in accordance with its electronic configuration. Such configuration, d^0, d^5, and d^{10} possess more stable oxidation state.

From left to right in 3d series stability of +2 oxidation state will increase from Sc to Zn. Thus, lower elements in +2 oxidation state e. g. V and Cr show powerful reducing nature while Cu and Zn do not behave as reducing agents.

It is observed that from Sc to Cu, the stability of +3 oxidation state decreases. That is why +3 oxidation state of Sc is very stable, Ti is also oxidised to Ti^{3+} and is also oxidised toTi^{4+}.Mn^{2+} is also unstable, whereas Fe^{3+} is a state of stable oxidation state. Following point may be noted-

(i) stability of complex compounds decreases with increasesing atomic number of central transition metal atom.

(ii)Transition metal in high oxidation state form stable complexes with the small highly electronegative and basic ligands like F^-, Cl^-, NH_3, IO_6^{5-}, TeO_6^{6-}, etc. While these metal in low oxidation state (e.g. +1, 0, -1) give stable complexes with pi acid ligand like CO, CN^-, PCl_3, C_6H_6 etc. The complex compound formed by transition metal atoms in low oxidation states contain L $\rightleftharpoons$ M coordination bond.

(iii) When transition metal form complexes with same ligand in different oxidation states, the complex compound having the metal in higher oxidation state is more stable e,g, $[Co^{3+}(NH_3)_6]^{3+}$ is more stable than $[Co^{2+}(NH_3)_6]^{2}$. Greater stability is due to the fact the metal cations having higher charge has greater power to attract the lone pair of electron on the ligand. In other words we can say that since the metal cation with high charge is smaller in size, it can attract the lone pair of electrons of the ligend more strongly and hance can give more stable complex ion.

1.6.Coordination number (C.N.) and geometry of complexes formed by the transition series elements-

First transition elements show 0 to 12 coordination number but greater than 8 is not isolated and very rare. These compounds are formed by reaction of their respective metal salts and species like NH_3, H_2O etc, containing the lone pair

electrons, called ligands are Lewis bases. The bonding between metal and ligands are explained by Werner's coordination theory suggesting two types valency, primary and secondary valency. Now the term primary valency is called oxidation state of metal ion and secondary valency termed as coordination number.

Thus, the coordination number is the number of ligands which surround the metal in a specific arrangement in space this specific arrangement of ligands around metal ion adopt a definite shape to have a minimum electrostatic repulsion and maximum stability. This definite shape is termed as geometry of complex compound. For example, in the compound $[Co(NH_3)_6]\ Cl_2$, metal ion Co^{2+} is surrounded by six ammonia molecules, formed the coordination compound and of coordination number six and octahedral geometry. Metals Cu, Ag and Au form complexes with coordination two and adopt a linear geometry. The examples of such coordination compounds are $[CuCl_2]$,$[Ag(NH_3)_2]^+$,$[Ag(CN)2]^-$ and $[Au(CN)_2]^-$. In such cases all the complexes are linear and involved completely filled d-orbital(d^{10}) metal atom. Complexes with coordination number three are not very common. Examples are:$[Hg\ I_3]^-$,adopt a planar geometry having coordination three. Other complexes which show coordination three are $K_2[(CN)_3].H_2O$,$Sc[N(Si\ Me_3)_2]_3$

Complex compound with coordination number four can isolated for number of metals, these are usually adopted tetrahedral and square planar geometry . Although both the complexes have same coordination number four, but adopt different geometry because of steric and electronic factor. A tetrahedral geometry is more favoured due to steric effect makes maximum distance between ligands and minimum repulsion. This can be also explained on the basis

of strength of ligand and formation of hybrid orbitals of central metal atoms , Ni involves 4s and 4p orbital in $Ni(Cl_4)_4$ whereas 3d and 4s in $[Ni(CN)_4]^{2-}$ complexes adopt a tetrahedral and square planar geometry respectively Other complexes of square planar geometry are $[Cu(NH_4)]^{2+}$ and $[Ni(Py)_4]$;Py=pyridine , $[Ni(NH)_4]^{2+}$ etc.

Complexes with coordination number one relatively rare. Examples of five coordinated complexes are $[Cu(Cl)_5]^{3-}$, $[Cu(Br)_5]^{3-}$,$[FeCO)_5]$ and $[Cd (Cl)_5]$. Five coordinated complexes adopt a trigonal bipyramidal or square pyramidal geometry. These complexes are not very stable. This can be prepared on the basis of the formation of a dimer of $MoCl_5$ of coordination number six bridging by chlorine atom between two Mo metals.

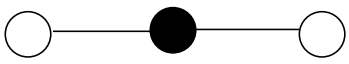
The most common coordination of transition metal complexes is six, which adopt a regular or distorted octahedral geometry. Tetragonally distorted structure is obtained for ligands surround metal atom results of elongating or contraction of the octahedral geometry. Examples of octahedral complexes formed by transition metals are;

$[Fe(F_6)]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{3+}$, $K_3[Fe(CN_6)]$, $[Cr(NH)_6]^{3+}$,

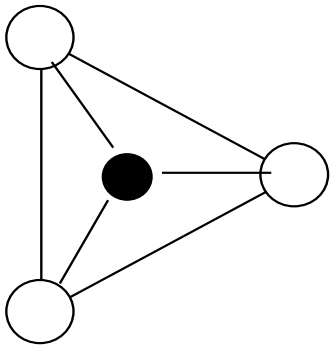
$[Mn(CN)_6]^{3-}$, and $[Sc(F)_6]^{3-}$ etc. The geometry of various complexes in several CN numbers are shown below.

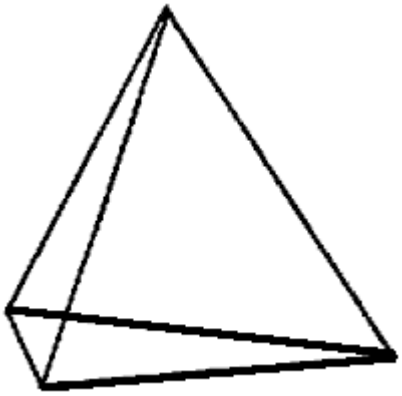
For example-

(i) CN=2 linear geometry, example- $CuCl_2^-$, $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$

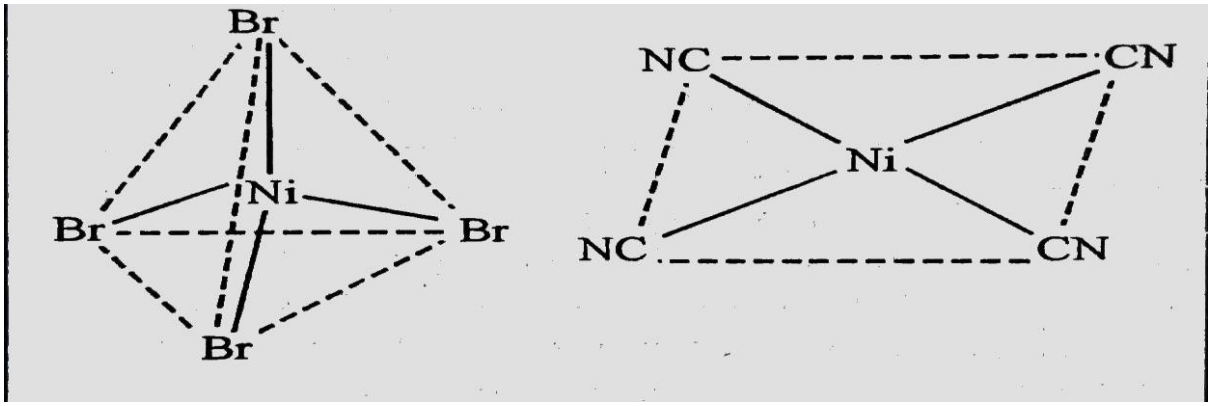


(iii) CN=3 geometry planar and pyramidal, example- $K_2[Cu(CN)_3]H_2O$ and HgI_3^-

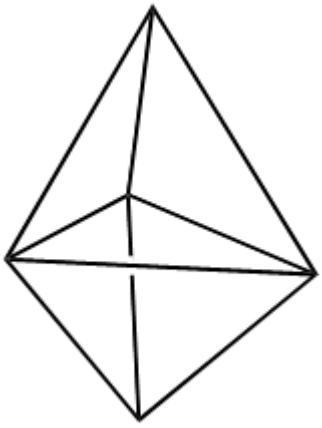


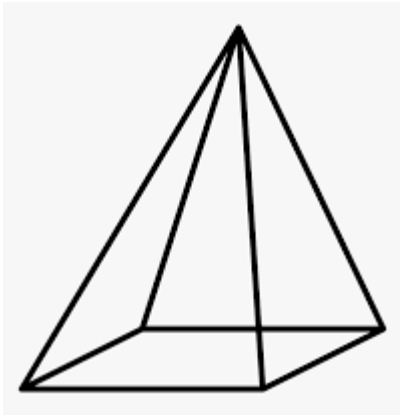


(iv) CN=4 geometry square planar and tetrahedral, given in above figure 1.0 example- $Ni(CN)_4^{2-}$ and $NiCl_4^{2-}$ and $NiBr_4^{2-}$

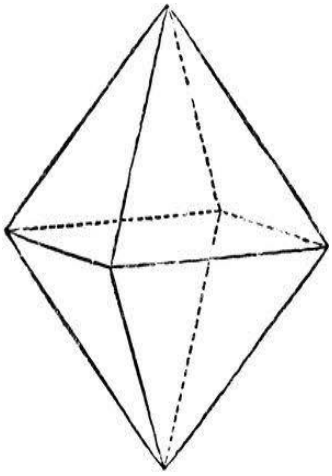


(v) CN=5 trigonal bipyramidal and square pyramidal, example- $[CuCl_5]^{3-}$, $Fe(CO)_5$ and $Ni(Et_3P)_2Br_3$

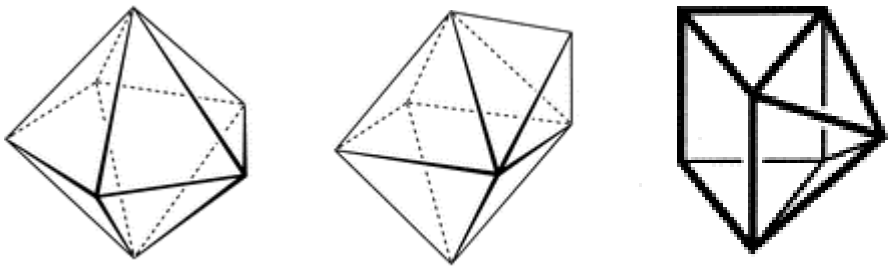




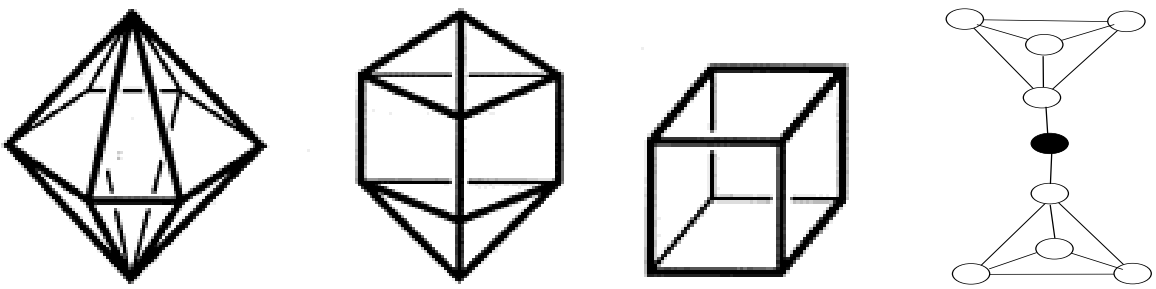
(vi) CN=6 octahedral geometry given in above figure 1.1 example- $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]^{3+}$



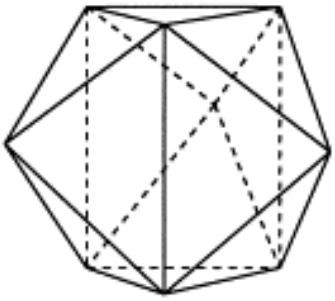
(vii) CN=7 pentagonal bipyramidal, capped octahedron and capped trigonal prism, example- $[Zr(F)_7]^{3-}$, $[MoF_7]^{-}$ $[M(F)_7]^{2-}$, M=Nb or Ta

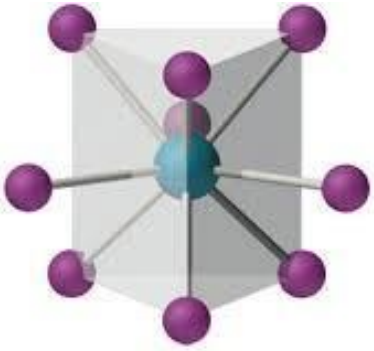


(viii) CN=8 cube, hexagonal bipyarmidal, bicapped trigonal prism, bicapped trigonal antiprism, example- $[Mo(CN)_8]^{3-}$, $[Ta(F)_8]^{3-}$, $[Zr(C_2O_4)_4]^{4-}$, $[Zr(acac)_4]$



(ix) CN=9 tricapped trigonal prism, example- ReH_9^{2-}





Exercise-

Long Answer Type Questions:

1. Discuss the following general characteristics of transition elements with special reference to

3d-series:

(a) Electronic Configuration (b) Atomic and Ionic radii (c) Ionization Potential (d) Variable

valency (e) Magnetic behaviour and (f) Complex formation (BHU (Hons) 1986)

2. What are transition elements? Briefly discuss the general characteristics of transition

elements with respect to following:

(a) Electronic configuration (b) variable oxidation (c) complex formation tendency (Gorakhpur 1990)

3. Discuss the general characteristics of the d-block elements with respect to the following:

(a) Electronic configuration (b) Magnetic properties (c) colour (d) complex formation (Lucknow 1988)

4. What are transition elements? Discuss the characteristics in which they differ from non- transition elements. Is Zinc a member of the first transition series? (Lucknow 1990)

5. The elements of second and third transition series resemble each other more closely they resemble the elements of first transition series. Explain this fact with reference to their atomic radii, oxidation states, magnetic behaviour and complex formation tendency. (VBSPU Jaunpur, 2006)

6. What are transition elements? How are they classified? Discuss the electronic configuration and tendency to form complexes in different oxidation states of the elements of transition series. (VBSPU Jaunpur, 2007).

7. Discuss the following properties of transition metals:

(a) Oxidation state (b) Colour (c) Magnetic properties. (MGKV Varanasi 2009)

8. What are d-block elements? How do d-block elements differ from f-block elements? Comment on their (a)size (b) oxidation state (c) Magnetic properties. (MGKV Varanasi 2010)

9. Define first series transition metal elements. Comment on their:

(a) size (b) colour of salt (c) magnetic properties (d) complex formation properties. (MGKV Varanasi 2012)

10. What are transition elements. Discuss the electronic configuration and colour of the first Transition series. (MGKV Varanasi 2014)

11. Discuss binary compounds of first transition series elements with respect to oxides and carbides.

12. Discuss binary compounds of first transition series elements with respect to oxides and hydrides.

13. Discuss binary compounds of first transition series elements with following respect: (i) oxides (ii) hydride (iii) carbide

14. Discuss binary compounds of first transition series elements with following respect:

(i) interstitial hydrides (ii) interstitial carbides

15. Discuss the coordination number and geometry found in 3d series transition elements.

Short Answer type Questions:

1. Why the common oxidation of the first transition series elements increases up to manganese and then decreases?

2. Why Ti^{3+} complex compounds are coloured but Ti^{4+} complex compounds are colourless?

3. Cu^{2+} complexes are coloured but Zn^{2+} complexes are colourless. Give reason.

4. $[Fe(CN)_6]^{3-}$ is paramagnetic but $[Fe(CN)_6]^{4-}$ is diamagnetic. Why?

5. Give the colours of the following aquatic ions.Ti^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+} (MGKV 2017)

6. Write a note on variable oxidation states in transition metal ions. (Allahabad 2012)

7. Give with reason the more common oxidation state shown by first transition series (3d) Elements. (Kanpur 2008)

8. Find the Number of unpaired electrons in Mn4+ and Cr^{3+}. (Kanpur 2011)

9. Why transition metal ions are coloured? (Agra 2008)

10. Transition elements show variable valency state. Why? (Agra 2009)

11. Transition metal ions act as Lewis acids. Explain. (VBSPU Jaunpur)

12. What do you understand by magnetic moment? (Lucknow 2011)

13. Why Mn(II) show maximum paramagnetic character among the bivalent ions of first Transition series. (Garhwal 2011)

14. Mn^{2+} is more stable than Mn^{3+}. Explain. (Lucknow 2011)

15. Write the following oxide with their increasing order of acidity, VO, VO_2, V_2O_5 and V_2O_3. (Garhwal 2011)

16. Why Mn shows a large variety of oxidation states?

17. Calculate the magnetic moment of Mn^{2+}, Cr^{6+} ions.

18. Discuss binary compounds of 3d series as oxides.

19. Describe reducing properties of oxides of 3d series elements.

20. Discuss the stability of complex compounds of first transition series elements.

21. Why $[Co(NH_3)_6]^{3+}$ is more stable than $[Co(NH_3)_6]^{2+}$?

Multiple Choice Questions

1. The first element of transition series is

(a) Sc (b) W (c) Mo (d) Pt

2. General electronic configuration of 1st transition series elements:

(a) (n-1) $d^{10}ns^0$ (b) (n-1) $d^{1-10}ns^{1-2}$ (c) (n-1) $d^{1-10}ns^0$ (d) (n-1) $d^{0-10}ns^2$

3. Ti3+ is coloured due to having unpaired electron

(a) 2 (b) 3 (c) 1 (d) 0

4. Manganese has highest oxidation number

(a) +3 (b) +5 (c) +6 (d) +7

5. Which ion has highest paramagnetic character?

(a) Mn^{2+} (b) Cr^{3+} (c) Sc^{3+} (d) Cu^{2+}

6. Which ion has maximum paired electrons in following?

(a) Fe^{2+} (b) Ni^{2+} (c) Cu^{2+} (d) Mn^{2+}

7. Among the Sc^{3+},Ti^{4+}, Zn^{2+}, Cu^{+} ions

(a) all diamagnetic

(b) all paramagnetic

(c) Sc^{3+}, Ti^{4+} paramagnetic and Zn^{2+}, Cu^{+} diamagnetic

(d) none of these

8. Cr^{3+} has magnetic moment

(a) 2.84 (b) 4.80 (c) 3.87 (d) 1.73

9. Why transition elements are coloured?

(a) due to metallic nature

(b) due to small size

(c) due to higher oxidation state

(d) due to unpaired electrons

10. Monel metal is an alloy of

(a) Cu and Ni (b) Cu, Ni and Zn (c) Cu, Ni and Cr (d) Ni and Cr

11. What is the coordination number of Nickel and shape of complex in $[Ni(CN)_4]^{2-}$

.

(a) 4 and square planar (b) 4 and tetrahedral

(c) 4 and trigonal bipyramidal (d) none of these

12. What is the coordination number of Nickel and shape of complex in $[NiCl_4]^{2-}$.

(a) 4 and planar (b) 4 and square planar

(c) 4 and tetrahedral (d) 5 and pyramidal

13. What is the coordination number of Iron and shape of complex in K4[$Fe(CN)_6$].

(a) 6 and pentagonal (b) 4 and tetrahedral (c) 4 and square planar (d) 6 and octahedral14. What is the coordination number of Rhenium and shape of complex in $[ReH_9]^-$?.

(a) 9 and tricapped trigonal prism (b) 8 and hexagonal bipyramid

(c) 6 and octahedral (d) none of these

15. What is the coordination number of Molybdenum and shape of complex in $[Mo\ (CN)_8]^{3-}$.

(a) 8 and Hexagonal bipyramid (b) 8 and cube

(c) 8 and pentagonal bipyramid (d) none of these

Answers 1- (a), 2-(b), 3-(c), 4-(d), 5-(a), 6-(c), 7-(a), 8-(c), 9-(d), 10-(a), 11-(a), 12-(c), 13-(d), 14-(a), 15-(b)