

CORSE :B.SC-III

PAPER :-VI

**TOPIC :Transition and innertransition
Element**

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d-and f-Block Elements

1. The transition elements may be defined as elements whose atoms or simple ions in their common oxidation state contain S partially filled d-orbitals. excluding zinc, cadmium and mercury. However, these are studied with transition elements.

The general electronic configuration of these elements is $(n - 1)d^{1 - 10} ns^{1 - 2}$. These are divided into four transition series.

- (i) **The first transition series :** (3d-series) involves the filling of 3d orbitals and has 10 elements from scandium ($Z = 21$) to zinc ($Z = 30$).

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$

- (ii) **The second transition series :** (4d series) involves the filling of 4d orbitals and has 10 elements from ytterium ($Z = 39$) to cadmium ($Z = 48$).

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4d^15s^2$	$4d^25s^2$	$4d^45s^1$	$4d^55s^1$	$4d^55s^2$	$4d^75s^1$	$4d^85s^1$	$4d^{10}5s^0$	$4d^{10}5s^1$	$4d^{10}5s^2$

- (iii) **The third transition series :** (5d series) involves the filling of 5d orbitals and has 10 elements. The first element of this series is lanthanum ($Z = 57$). It is followed by 14 elements (lanthanides, involving filling of 4f orbitals). The next nine elements are from hafnium ($Z = 72$) to mercury ($Z = 80$).

- (iv) **The fourth transition series** is incomplete and contains only three elements $_{89}\text{Ac}$, $_{104}\text{Rf}$, $_{105}\text{Ha}$.

Metallic bond And Metallic Character

Transition elements exhibit a very good mechanical properties, i.e., they are hard, malleable and ductile. They have high enthalpies of atomization, high melting and boiling points : have high thermal and electrical conductivity as well as lustre. Their mechanical properties and high melting, as well as boiling points indicate the presence of strong metallic bond. The transition elements exhibit all the three types of structures; face centred cubic (fcc), hexagonal close packed (hcp) and body centred cubic (bcc).

The strength of these metals can be traced to the presence of unpaired d-electrons. An unpaired d-electron tends to form a covalent bond. The number of such bonds will determine the overall bonds strength and thus reflect in the hardness of these metals.

Ionisation Energies

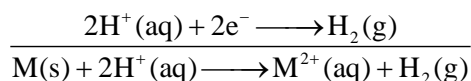
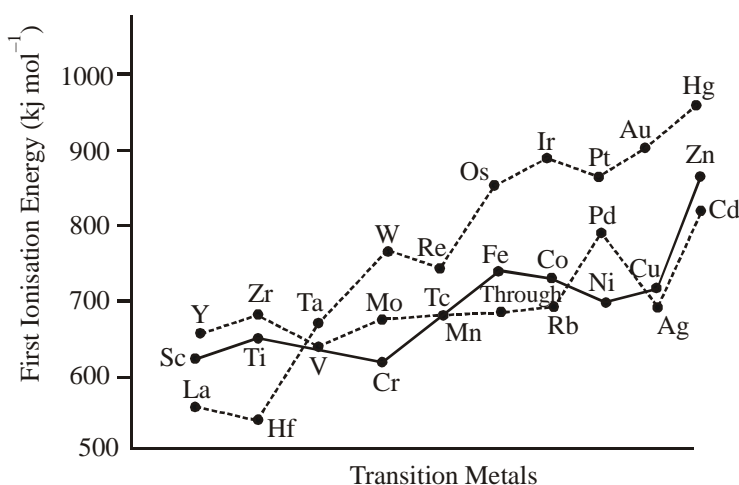
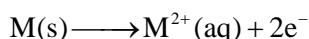
The ionisation energies of transition metals increase as we move across each series through not quite regularly.

The shrinking atomic size and increased nuclear charge results in a strong attraction between the nucleus and the electrons. Consequently, ionisation energies increase.

It is evident that first ionisation energies of most of the 5d elements are higher than those of 3d and 4d-elements. This is due to the fact that the outer valence electrons of 5d-elements experience greater effective nuclear charge due to poor shielding of the nucleus by 4f-electrons.

Electrode potential

It is possible to predict from electrode potential data, the stability of different oxidation states in aqueous solution of transition metal ions. Moreover, standard reduction potential for M^{2+}/M can be determined from

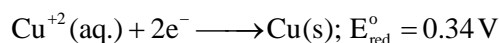
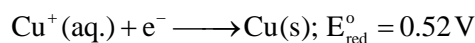


In general, transition elements have low negative values of standard reduction electrode potential values due to high ionisation energies, high heats of sublimation which are more than offset with large heats of hydration. Consequently, transition elements are **weak reducing agents** and are **less reactive**.

It must be noted that greater the reduction electrode potential more unstable the O.S and hence the metal in that O.S will be a strong oxidising agent.

- Variable oxidation states :** Transition metals exhibit a wide range of oxidation states. When ns electrons are involved, then compounds with lower oxidation states are formed. In compounds with higher oxidation states, $(n-1)d$ electrons are also involved. The highest oxidation state of an element is given by $ns + (n - 1)d$ electrons. Since the energy difference between the two sets of orbitals is not large, the transition elements exhibit variable oxidation states differing by 1 unit. The oxidation states exhibited by these elements are governed by electronic configuration of the element, the type of bonding involved, the stereochemistry, the lattice energy.

- (i) The highest oxidation state exhibited by any transition metal is +8, i.e., ruthenium tetroxide (RuO₄) and osmium tetroxide (OsO₄)
- (ii) The highest oxidation state are shown by transition metal when they combine with most electronegative elements such as fluorine or oxygen, i.e., CrO₃, Mn₂O₇ and VF₅.
- (iii) The most common oxidation state for first transition series is +2 which arises from the loss of 4s electrons.
- (iv) In lower oxidation states as +2 and +3, the bonds are mostly ionic while in higher oxidation states such as +6 or +7, the bonds are essentially covalent as in MnO₄⁻ (Mn = +7) and Cr₂O₇²⁻ (Cr = +6)
- (v) The stability of an oxidation state of a transition metal depends on the nature of the element which is in combination with it. However, clue to the relative stability of different oxidation states is provided by electrode potential data. For example, the electrode potential values for copper in +1 and +2 oxidation states in aqueous solution are as follows:



It is evident from electrode potential values that copper in +2 oxidation state is more stable in aqueous solution than copper in +1 oxidation state.

- (vi) Transition metals form complexes in zero or low oxidation state with ligands such as CO, NO or isocyanides, for example, nickel tetracarbonyl Ni(CO)₄ has nickel in zero oxidation state. The bonding in compounds such as Ni(CO)₄ is believed to occur by donation of d-electrons from nickel to carbon monoxide.

3. Formation of complexes: By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal and the ligand (or ligands) is known as a complex.

The transition metal ions form complexes because of the following reasons:

- (i) Their small cation size
- (ii) High effective nuclear charge
- (iii) Availability of vacant (n-1) d-orbitals of appropriate energy

4. Formation of coloured compounds : The transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one d-orbital to another i.e., intra d-d

transitions take place. Thus when light falls certain visible wavelengths are absorbed. The reflected light appears coloured and gives the colour of compound. The ions having no d-d transitions are colourless.

Catalytic Properties

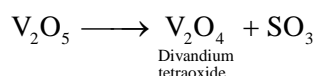
Most of the transition metals and their compounds are found to act as catalysts.

- (a) **Transition metals as catalyst :** Catalytic power of transition metals is believed to operate either by the formation of interstitial compounds to adsorb and activate the reacting substances e.g. hydrogenation of alkenes in presence of palladium or platinum is thought to take place through this mechanism.
- (b) **Transition metal compounds as catalyst:** Catalysis by metal compounds results from their ability to provide low energy pathways for reactions by either of the following two ways:
- (i) By the formation of appropriate intermediates. For example, the reaction between substance A and B in presence of transition metal X as catalyst takes place as shown below:

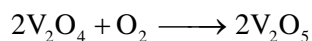


- (ii) By the change of oxidation states of transition metals. For example, V_2O_5 acts as a catalyst for the conversion of SO_2 to SO_3 because of the ability of vanadium to have several oxidation states as:

Solid V_2O_5 adsorbs a SO_2 molecule on the surface, gives it an oxygen atom to convert it to SO_3 and is itself reduced to V_2O_4 .



The divanadium tetraoxide is reconverted to V_2O_5 by reaction with oxygen



5. **Magnetic properties :** Most of the transition elements show paramagnetism. Paramagnetism arises from the presence of unpaired electrons in atoms, ions or molecules. The magnetic character is comparable in terms of magnetic moment given as $\mu = \sqrt{n(n+2)}$ Bohr magnetons. In general, more is the number of unpaired electrons greater is the magnetic character. The maximum paramagnetism is seen in d5 cases, having the maximum unpaired electrons.

$$1 \text{ BM} = eh/4\pi mc$$

Magnetic moments of some Ions of first transition series.

Ion	Outer electronic Configuration	Number of unpaired electrons	Magnetic moment, m, (BM)	
			Calculated $\mu = \sqrt{n(n+2)}$	Observed
Sc ³⁺	3d ⁰	0	0.0	0.0
Ti ³⁺	3d ¹	1	1.73	1.75
V ³⁺	3d ²	2	2.84	2.76
Cr ³⁺	3d ³	3	3.87	3.86
Mn ²⁺	3d ⁵	5	5.92	5.96
Fe ²⁺	3d ⁶	4	4.90	5.10
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	0.0

6. Formation of nonstoichiometric compounds and interstitial compounds : Transition metals can trap some of the small size atoms like hydrogen, boron, carbon, nitrogen, etc in the vacant spaces between the crystal lattice forming interstitial compounds. For example, TiC, Mn₄N, Fe₈N, TiH₂. This property differentiates these metals from the elements of other groups. Non-stoichiometric compounds like Fe_{0.94} O, Fe_{0.86} S, VH_{0.56}, TiH_{1.7} etc are often classified as interstitial compounds.

Small non-metallic atoms enter the vacant holes of the packed transition metal atoms and also forms bonds with them. The filling up of the vacant holes results in the hardness of the transition metals because the layer of their atoms cannot now easily slip past one another.

Alloy formation : Molten transition metals are miscible with one another. Therefore, on cooling a mixture solution of the transition metals results in the formation of alloys. For example, chromium dissolves in nickel to form chromium-nickel alloys; and manganese dissolves in iron to form manganese steels.

Since the atoms of transition metals have similar size, the atoms of one of the component metals can take up positions in the crystal lattice of the other. Thus solute atoms may

replace some of the atoms at the lattice points of the solvent crystal to form substitutional solid solutions known as alloys.

Transition metal oxides: In general, the transition metal oxides are:

- (i) (a) Basic, if the metal atom is in low oxidation state.
 - (b) Amphoteric if the metal atom is in intermediate oxidation state.
 - (c) Acidic if it is in high oxidation state.
 - (ii) Insoluble in water. However, basic and amphoteric oxides dissolve in non-oxidising acids like HCl to form hydrated ions, $[M(H_2O)_6]^{n+}$. Some of the oxides dissolve in acids and bases to form oxometallic salts such as CrO_4^{2-} , $Cr_2O_7^{2-}$ and MnO_4^- .
 - (iii) Highly coloured (generally black)
 - (iv) Macromolecular in structure rather than purely ionic.
7. **Inner transition elements:** The elements which in their elemental or ionic form have partly filled f-orbitals are termed as f block elements. These are known as **inner transition elements**. These are so called because electrons in these elements enter into antepenultimate shell (second outer most f-orbitals). There are two series of inner transition elements, each having 14 elements. The elements in which 4f orbitals are progressively filled are called **lanthanides**. The elements in which 5f orbitals are progressively filled are termed **actinides**.

Electronic Configuration and Some Properties of Lanthanides

Atomic number	Element	Symbol	Outer configuration	Oxidation states	M^{3+} radii (pm)
57	Lanthanum	La	$4f^0 5d^1 6s^2$	+3	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	+3, +4	103
59	Praseodymium	Pr	$4f^3 5d^0 6s^2$	+3, +4	101
60	Neodymium	Nd	$4f^4 5d^0 6s^2$	+2, +3	100
61	Promethium	Pm	$4f^5 5d^0 6s^2$	+3	98
62	Samarium	Sm	$4f^6 5d^0 6s^2$	+2, +3	96
63	Europium	Eu	$4f^7 5d^0 6s^2$	+2, +3	95

64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	+3	94
65	Terbium	Tb	$4f^9 5d^0 6s^2$	+3, +4	92
66	Dysprosium	Dy	$4f^{10} 5d^0 6s^2$	+3, +4	91
67	Holmium	Ho	$4f^{11} 5d^0 6s^2$	+3	89
68	Erbium	Er	$4f^{12} 5d^0 6s^2$	+3	88
69	Thulium	Tm	$4f^{13} 5d^0 6s^2$	+2, +3	87
70	Ytterbium	Yb	$4f^{14} 5d^0 6s^2$	+2, +3	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	+3	85

- (a) **Oxidation State :** The principal oxidation state exhibited by all the lanthanides is +3. Some of the elements exhibit +2 oxidation state, e.g. Sm^{2+} , Eu^{2+} , Tm^{2+} and Yb^{2+} exist in aqueous solutions and are good reducing agents. Some of the elements also exhibit +4 oxidation state, e.g. Pr^{4+} , Ce^{4+} , Tb^{4+} and Dy^{4+} . An aqueous solution of Ce^{4+} is good oxidising agent.

Note : The usual oxidation states such as +2 or +4 exhibited by the lanthanides can be explained on the basis extra stability associated with empty, half-filled and completely filled 4f subshell. For example Eu and Yb exhibit +2 oxidation state because they acquire the f^7 and f^{14} configuration respectively. Similarly, Ce and Tb show +4 oxidation state by acquiring f^0 and f^7 configurations respectively.

- (b) **Colour :** Most of the lanthanide metal ions are coloured because they have partly filled f-orbitals in which f-f transitions are possible.
- (c) **Melting and boiling points :** Lanthanides have fairly high melting and boiling points. However, their melting and boiling points do not show any definite trend as we move from La to Lu.
- (d) **Density :** Lanthanides have high densities which range between 6.7 and 9.74 g cm⁻³. However, densities of lanthanides do not show definite trends with rise in atomic number.
- (e) **Ionisation energies :** Lanthanides have fairly low ionization energy values due to fairly large atomic size which are quite comparable with those of alkaline earth metals particularly calcium.
- (f) **Electropositive character :** On account of low ionization energy values and fairly large size lanthanides have high electropositive character.

- (g) **Paramagnetism** : Lanthanide metal ions show para-magnetism due to the presence of unpaired electrons in their f-orbitals.
- (h) **Complex formation** : On account of large size, lanthanides have much less tendency to form complexes.
- (i) **Radioactivity** : Of all the lanthanides, only promethium is radioactive

Use of lanthanides:

- (i) A pyrophoric alloy which contains cerium (40.5%), lanthanum and neodymium (44%); iron (4.5%); calcium, carbon and silicon (10.5%) is used in cigarette lighters, toys, flame throwing tanks and tracer bullets as well as shells.
- (ii) Cerium cuts off heat and ultraviolet light and so is used in glare reducing spectacles.
- (iii) Cerium magnesium alloys are used in flash light powders
- (iv) Cerium salts are used in analysis, dyeing cotton, lead accumulators, medicines as catalysts.
- (v) Ceria and thoria are used in gas lamp mantles.

Comparison of Lanthanide and Actinide Series

Elements of lanthanide and actinides resemble in many respects but they do differ in some respects as shown below:

Similarities

Lanthanides	Actinides
1. Mainly exhibit +3 oxidation state. 2. They exhibit lanthanide contraction. 3. They show ion-exchange behavior	1. They also mainly exhibit +3 oxidation state. 2. They exhibit actinide contraction 3. They also show ion-exchange behavior

Difference

Lanthanides	Actinides
<ol style="list-style-type: none"> 1. In addition to +3 oxidation state, they exhibit +2 and +4 oxidation states only. 2. Most of their ions are colourless 3. They do not form complexes easily. 4. They do not form oxo cations. 5. Their compounds are less basic 6. Except promethium, they are non-radioactive. 7. Their magnetic properties can be easily explained. 	<ol style="list-style-type: none"> 1. In addition to +3 oxidation state, they show +4, +5, +6 and +7 oxidation states. 2. Most of their ions are coloured. 3. They have much greater tendency to form complexes. 4. They form oxocations such as UO_2^{2+}, PuO_2^{2+} and UO^+. 5. Their compounds are more basic 6. They are radioactive 7. Their magnetic properties can not be easily explained.

EXERCISES

1. The bonds present in the structure of dichromate ion are
 - (a.) Four equivalent Cr-O bonds only
 - (b.) six equivalent Cr-O bonds and one O–O bond
 - (c.) six equivalent Cr-O bonds and one CO–Cr bond
 - (d.) eight equivalent Cr-O bonds

2. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is called
- (a.) green salt (b.) Glauber's salt
(c.) Mohr's salt (d.) alum
3. Which of the following is not correct about transition metals?
- (a.) Their compounds are generally coloured
(b.) They can form ionic or covalent compounds
(c.) Their melting and boiling points are high
(d.) They do not exhibit variable valency
4. Transition metal ions show colour because
- (a.) they absorb light (b.) they emit light
(c.) they are paramagnetic (d.) they exhibit d-d transition
5. The magnetic moment of salt containing Zn^{2+} ion is
- (a.) 0 (b.) 1.87
(c.) 5.92 (d.) 2
6. The highest magnetic moment is shown by the transition metal ion with the configuration
- (a.) $3d^2$ (b.) $3d^5$
(c.) $3d^7$ (d.) $3d^9$
7. One of the following metals forms a volatile compound and this property is taken advantage of for its extraction. This metal is
- (a.) iron (b.) nickel
(c.) cobalt (d.) tungsten
8. All the metal oxides of the type MO except
- (a.) copper (b.) barium

- (c.) silver (d.) lead
9. Which of the following is philosopher's wool?
- (a.) ZnO (b.) HgO
(c.) Ag₂O (d.) CuO
10. Monel metal is an alloy of
- (a.) Cu, Ni, Fe, Mn (b.) Cu, Sn, Zn
(c.) Cu, Sn, P (d.) Cu, Zn
11. Which one of the following metals, is extracted on smelting of its ore in blast furnace ?
- (a.) Iron (b.) Sodium
(c.) Potassium (d.) Magnesium
12. Bronze is a mixture of
- (a.) Pb + Sn (b.) Cu + Sn
(c.) Cu + Sn (d.) Pb + Zn
13. Which of the following has got incompletely filled f – subshell ?
- (a.) Gadolinium (b.) Lutetium
(c.) Lawrencium (d.) Tantalum
14. The point of dissimilarity between lanthanides and actinides is
- (a.) Three outermost shells are partially filled
(b.) they show oxidation state of + 3 (common)
(c.) they are called inner transition elements
(d.) they are radioactive in nature
15. Which belongs to the actinides series?
- (a.) C_e (b.) Cf

- (c.) Ca (d.) Cs
16. In chromite ore, the oxidation number of iron and chromium are respectively
(a.) + 3, + 2 (b.) + 3, + 6
(c.) + 2, + 6 (d.) + 2, + 3
17. Anhydrous ferric chloride is prepared by
(a.) dissolving $\text{Fe}(\text{OH})_3$ in concentrated HCl
(b.) dissolving $\text{Fe}(\text{OH})_3$ in dilute HCl
(c.) passing HCl over heated iron scrap
(d.) passing Cl_2 gas over heated iron scrap
18. German silver alloy contains
(a.) zinc, silver and copper (d.) nickel, silver and copper
(c.) germanium, silver and copper (d.) zinc, nickel copper
19. The spin only magnetic moment of Mn^{4+} ion is nearly
(a.) 3 BM (b.) 6 BM
(c.) 4 BM (d.) 5 BM
20. In which metal's metallurgical process carbon is used for reduction of metal oxides ?
(a.) Na (b.) Ag
(c.) Fe (d.) Hg
21. Which of the following is correct?
(a.) Duralumin: Al + Cu + Mg + Ag (b.) German silver: Cu + Zn + C
(c.) Gun metal: Cu + Zn + C (d.) Solder: Pb + Al
22. The temperature of the slag zone in the metallurgy of iron using blast furnace is
(a.) $1200 - 1500 \text{ C}^0$ (b.) $1500 - 1600 \text{ C}^0$

- (c.) $400 - 700\text{ C}^0$ (d.) $800 - 1000\text{ C}^0$
23. What is the oxidation state of iron in Mohr's salt?
(a.) + 3 (b.) 0 (c.) +2 (d.) +1
24. Magnetic moment of manganese in $(\text{NH}_4)_2 \text{MnBr}_2$ is
(a.) 3.87 BM (b.) 5.91 BM
(c.) 4.89 BM (d.) 2.82 BM
25. KMnO_4 (acidic/alkaline) is not decolourized by
(a.) Mohr salt (b.) oxalic acid
(c.) benzene (d.) propene
26. Which of the following is not a characteristic of transition elements?
(a.) Variable oxidation states
(b.) Formation of coloured compounds
(c.) Formation of interstitial compounds
(d.) Natural radioactivity
27. Hair dyes contain
(a.) copper nitrate (b.) gold chloride
(c.) silver nitrate (d.) copper sulphate
28. The purest zinc is made by
(a.) electrolytic refining (b.) zone refining
(c.) the van-Arkel method (d.) the Mond process
29. Which of the following compound is expected to be coloured ?
(a.) Ag_2SO_4 (b.) CuF_2
(c.) MgF_2 (d.) CuCl

30. The composition of malachite is

(a.) CuFeS_2

(b.) CuCO_3

(c.) $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

(d.) Cu(OH)_2

Ans : c

ANSWERS

1. d

2. c

3. d

4. d

5. a

6. b

7. b

8. c

9. a

10. a

11. a

12. b

13. a

14. d

15. b

16. d

17. d

18. d

19. c

20. c

21. c

22. d

23. c

24. b

25. c

26. d

27. c

28. b

29. b

30. c