What is a Transition Metal?

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block). Properties of transition elements include:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form compounds which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and compounds;
- form compounds with profound catalytic activity;
- form stable complexes.

Table 23.1.1 : Summary of select physical properties of transition elements:

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Sc	3	2.99	1541	2831	164	[Ar] $3d^14s^2$	631	
Ti	4	4.50	1660	3287	147	[Ar]$3d^24s^2$	658	- engines/aircraft industry- density is 60% of iron
V	5	5.96	1890	3380	135	[Ar]$3d^34s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr	6	7.20	1857	2670	129	[Ar]$3d^54s^1$	653	-alloys eg with C steel, the most significant use
Mn	7	7.20	1244	1962	137	[Ar]$3d^54s^2$	717	-alloys eg with Cu
Fe	8	7.86	1535	2750	126	[Ar]$3d^64s^2$	759	-alloys eg with C steel, the most significant use
Co	9	8.90	1495	2870	125	[Ar]$3d^74s^2$	758	-alloys eg with Cr and W for hardened drill bits
Ni	10	8.90	1455	2730	125	[Ar]$3d^84s^2$	737	-alloys Fe/Ni armor plating, resists corrosion
Cu	11	8.92	1083	2567	128	[Ar]$3d^{10}4s^1$	746	-high electrical conductivity (2nd to Ag), wiring
Zn	12	7.14	420	907	137	[Ar]$3d^{10}4s^2$	906	

Densities and Metallic Radii

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Atomic radii:

The atomic radii of the d-block elements of a particular series decreases gradually upto midway element and then these values remain almost same upto the element of group IB (Cu, Ag, Au). The last element of eash series (Zn, Cd, Hg) shows an increase in its atomic radius.

Explanation: For the elements from Sc to Mn the atomic radii decreases. This decrease is because of the gradual increase in nuclear charge with the increase in atomic number. The increase nuclear charge makes the atom to shrink in size & hence the size of the atom decreases. Upto Mn ($3d^5 4s^2$) electron-electron repulsion do not occur because there is no pairing of electrons in 3d orbitals. But in case of the elements from Fe to Zn, the pairing of electrons in 3d orbitals take place & electron-electron repulsions are produced. Now the increase in electron-electron repulsion makes the atom to expand in size while the nuclear charge makes the atom to shrink in size. Thus, these opposing effects almost counterbalance each others & there is no major change in size on going from Fe to Cu, from Ru to Ag and Os to Au.

In the last element of each period viz. Zn, Cd & Hg, the electron-electron repulsion becomes greater than the attraction between the nucleus & outermost s electrons & therefore there is an increase in size.

The d-block elements have a valence shell electronic configuration of $(n\text{-}1)d^{1\text{-}10}ns^{0\text{-}2}$ where (n-1) stands for inner shell whose d-orbitals may have one to ten electrons and the s-orbitals of the outermost shell (n) may have no electron or one or two electrons. The filling of d-orbitals takes place after the s-orbital of next higher shell has already filled as has been discussed in Aufbau principle in Unit 1 (BCH-101). This is because ns orbitals have lower energy than (n-1)d orbitals. But during ionization of the elements (oxidation), the electrons are first lost from ns level followed by the expulsion from (n-1)d subshell (deviation from the expected behaviour) because (n-1)d subshell becomes of the lower energy than ns subshell once the filling of electrons commences in (n-1)d subshell.

Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises of the two subshells, *viz.*, (n-1)d and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left → middle ← right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state. As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

1.3.2 Complex Formation Tendency:

The cations of d-block elements are unique in their tendency to form complexes with several molecules such as ammonia, water, etc. or different ions such as cyanide, NO^-_2, halide ions, etc. These molecules or ions are called ligands. The complex forming tendency of these elements is attributed to the following factors:

(a) Small size and high positive charge density,
(b) Availability of vacant d-orbitals of right energy to accept the lone pairs of electrons from the approaching ligands,
(c) Exhibition of variable oxidation states.

The detailed account of this tendency will be given in the respective sections mentioned ahead.

1.3.3 Magnetic Properties:

Many compounds of d-block elements exhibit magnetic properties. Qualitatively speaking, there are several kinds of magnetism. The substances which are weakly repelled by the strong magnetic field are termed as **diamagnetic** while those which are weakly attracted by the strong magnetic field are called **paramagnetic.** These substances lose their magnetism on removing the magnetic field. Diamagnetism is the property of the completely filled electronic subshells and is shown by all substances to more or less extent. Paramagnetism is produced by the presence of unpaired electrons and because most of the d-block metal atoms and ions have unpaired electrons, they are paramagnetic in behaviour.

In some transition metals (e.g. Fe, Co, Ni) unpaired electron spins are more pronounced and show much more paramagnetism than the other d-block metals. Such metals are called **ferromagnetic** metals and magnetic property shown by them is known as ferromagnetism. Such metals can be permanently magnetized. The detailed account will be given in the section 1.4 of this unit and in subsequent units.

1.3.4 Formation of Coloured Ions/ Compounds:

The majority of compounds of d-block elements, whether ionic or covalent, are coloured in solid or solution state. This property of d-block elements is in marked difference from those of s or p-block elements which are white or light coloured.

The colour of a substance arises from the property of the substance to absorb light of certain wavelength in the region of visible light (white light) when the latter interacts with the substance. The coloure of the substance is the colour of the transmitted light component and is complementary to the colour of light component absorbed. The colour of d-block metal ions is associated with

(a) an incomplete d-subshell in the metal ion,

(b) the nature of surrounding groups around the metal ion.

The whole act of exhibition of colour by d-block ions/compounds can be explained as follows. In a free gaseous or isolated ion the five d-orbitals are degenerate, i.e. of same energy. Since five d-orbitals are oriented differently in space, the surrounding groups affect the energy of some orbitals more than others in the compounds. This destroys their degeneracy. For example, in the simplest case of an octahedral complex, they form two groups of orbitals of different energy:

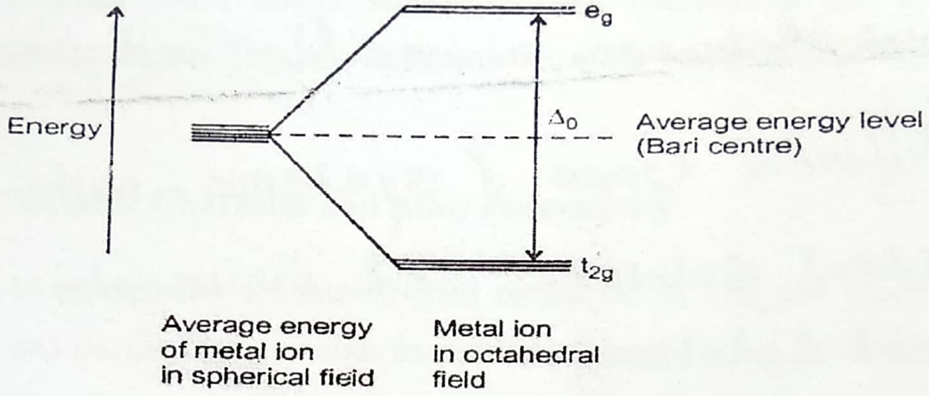

***Fig. 1.1** Bary centre*

Thus, in d-block metal ions with partially filled d-subshell, it is possible to promote electron(s) from one set of d-orbitals to another set (group) of higher energy by fairly small energy absorbed from the visible light. The colour of the compounds depends on the energy difference (gap) between the two groups (sets) of d-orbitals. This in turn depends on the nature of ligands and their arrangement around the metal ion in the compound / complex.

1.3.5 Catalytic Activity:

The catalytic activity of d-block elements and their compounds is associated with their variable oxidation states and their capability of forming interstitial compounds. A number of d-block metals and their compounds are known to catalyse various reactions of industrial importance, e.g., vanadium (V) oxide in the manufacture of sulphuric acid by contact process, etc. An important view of the mechanism of catalysis is that at solid surface of the catalyst, bonds would be formed between the molecules of the reactants and atoms of the catalysts thereby increasing the concentration of the reactants at the surface. This weakens the bonds of the reactant molecules due to lowering of the activation energy.

1.3.6 Formation of Interstitial and Non-stoichiometric Compounds:

The d-block elements form interstitial compounds with small non-metal atoms such as H, C, N, B, Si, etc. due to the ability of metal lattice to accommodate these non–metal atoms between the metal atoms without distortion of structure.

One of the striking properties of these metals is the formation of non-stoichiometric compounds which often exhibit semiconductivity, fluorescence and behave as heterogeneous catalysts. This non-stoichiometry is due to the defects in the solid structures.

1.3.7 Metallic Character and Alloy Formation:

All the d-block elements are metals, good conductors of heat and electricity, are malleable and ductile. All are solids except Hg (mercury) which exists as liquid at ordinary temperature.

These metals form alloys with each other due to almost similar sizes of the atoms. Thus the atoms of one metal can easily take up positions in the crystal lattice of the other. The alloys are usually harder and have higher melting points than the parent metals, are more resistant to corrosion than their constituents.

1.3.8 Periodic Properties and Their Variation along the Series:

The atomic radii, atomic volumes, ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potential and reducing properties, etc. are the important periodic properties of the d–block elements which vary and have a definite trend, in general, along each series. These will be discussed below:

a) Atomic Radii, Atomic Volumes and Ionic Radii.

The atomic radii generally decrease, with a few exceptions, on moving from left to right in each series of the transition elements due to increased nuclear charge at each step and constant value of the azimuthal quantum number (i.e. l) receiving the last electron.

The d-block elements have low atomic volumes as compared to those of the neighbouring s- and p-block elements. This is due to the fact that in these elements

Oxid

Sc →	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	3,4	2-5,	2,3,6 (4,5)	2,4,7 (3,5,6)	2,3 (4,5,6)	2,3 (4,5)	2 (3,4)	1,2	2

( ) → indicates disproportionate

$$Sc(III) < Ti(IV) < V(V) < Cr(VI) < Mn(VII)$$

Reducing Properties:

Except Cu, the E°_{red} value of negetive & there is no regular trend, since the I.E. ($I_1 + I_2$) & sublimati energies of these metals donot show any regular tren These values have been used to explain the reducing Property & reactivity of these metals.

	V	Cr	Mn	Fe	Co	Ni	Cu
E°_{red}:	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

$$M^{+2} + 2e \rightleftharpoons M$$

I.E: The value of I.E. increases as we move from left to right although increase is not regular. The increase Nuclear charge would attract the ns^2 elect cloud would greater force.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
658	650	653	718	759	758	736	745	906
	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	664	685	702	711	720	805	731	867
	Ta	W	Re	Os	Ir	Pt	Au	Hg
	761	770	760	840	880	870	890	1007

Q. what are isopoly and heteropoly acids?

Ans: The MO_4^{-2} ions of Mo(VI) and W(VI) show a tendency to condense in strongly basic medicum forming Polyoxoanion in solution as well as solid state. This tendency is shown to same extent by V(V) in VO_4^{-3}, P(V) in PO_4^{-3} and also present in Nb(V), Ta(V). These Polyoxometallates and their corresponding Protonated specis are called isopolyacids and their salts. In isopolyacids the condensed moiety contain only one kind of oxometal ion.

Example: $Mo_7O_{24}^{-6}$ (pH = 6) $Mo_8O_{26}^{4-}$ (pH < 6)

$H_2W_6O_{12}^{-6}$, $W_7O_{24}^{-6}$ and $W_{12}O_{42}^{-10}$

The $Mo_7O_{24}^{-6}$ moiety contain of MoO_6 octahedral units. In the solid state $Mo_2O_7^{-2}$ ion is also known - $(NH_4)_2Mo_2O_7$ has an infinite chain of MoO_6 octahedral and MoO_4 tetrahedral units.

The specis formed by condensation of isopolyoxometal ions with another type of oxoanions (PO_4^{-3}, SiO_4^{-4}) are known as heteropolyacids & their salts.

Example: $(NH_4)_3[PO_4Mo_{12}O_{36}]$ Ammonium phosphomolybdate

$Na_3[\overset{V}{P}Mo_{12}O_{40}]$, $H_3[\overset{V}{P}Mo_{12}O_{40}]$

Sodium dodecamolybdophosphate

) The colour of the absorbed light also depends on the nature of the ligands. Strong field ligand absorbed higher energy and weak field ligand absorbed lower energy.

$[Ni(H_2O)_6]^{2+}$ absorbed red radiation and gives blue green colour. On the other hand $[Ni(NH_3)_6]^{2+}$ ion absorbs yellow colour and gives blue in colour.

(iv) The transition metal ions absorb only incident light whose wavelength lies in between 4000 A° – 8000 A° (visible region). The energy associated with the wavelength of the radiation absorbed by a complex ion can be calculated.

$$\text{Frequency in wave number} = \frac{1}{\text{wave length } (A^\circ)}$$

$$= \frac{1}{\lambda \times 10^{-8}\ cm} = \frac{10^8}{\lambda}\ cm^{-1}$$

350 cm^{-1} = 1 kcal mole^{-1}

837 cm^{-1} = 1 KJ mole^{-1}

$$\therefore \frac{10^8}{\lambda}\ cm^{-1} = \frac{10^8}{350 \times \lambda (A^\circ)}\ Kcal\ mol^{-1}$$

$$\therefore \frac{10^8}{\lambda}\ cm^{-1} = \frac{10^8}{837 \times \lambda (A^\circ)}\ KJ\ mole^{-1}$$

Colour of absorb light	Range of wavelength (A°)	Colour of transmitted light
1. violet	1. 4000 – 4500	1. yellow green
2. Blue	2. 4500 – 4800	2. yellow
3. Green blue	3. 4800 – 4900	3. orange
4. Blue green	4. 4900 – 5000	4. Red
5. Green	5. 5000 – 5600	5. violet (Purple)
6. yellow green	6. 5600 – 5750	6. violet
7. yellow	7. 5750 – 5900	7. Blue
8. orange	8. 5900 – 6250	8. Green blue
9. Red	9. 6250 – 7500	9. Blue green

Energy (Δo) decreases ↓

Frequency decreases ↓

Wavelength increases ↓