

CHAPTER
21

THE d- AND f-BLOCK ELEMENTS

LEARNING OBJECTIVES

- (i) Know the electronic configurations of the transition (d-block) and the inner transition (f-block) elements.
- (ii) Appreciate the relative stability of various oxidation states in terms of electrode potential values.
- (iii) Describe the preparation, properties, structures and uses of some important compounds such as $K_2Cr_2O_7$ and $KMnO_4$.
- (iv) Understand the general characteristics of the d- and f-block elements and the general horizontal and group trends in them.
- (v) Describe the properties of the f-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.

INTRODUCTION

Many of the most important elements of modern society are transition and inner transition elements. Iron, copper, silver and gold are among the transition elements that have played important roles in the development of human civilisation. The inner transition elements such as Th, Pa and U are proving excellent sources of nuclear energy in modern times. The transition elements are those which as elements or as ions have partly filled $(n - 1)$ d-orbitals. Since in these the differentiating electron enters the $(n - 1)$ d-orbitals, these are also called d-block elements. The d-block of the periodic table contains the elements of the groups 3-12 in which the d orbitals are progressively filled in each of the four long periods.

The elements which as free elements or as ions have partly filled $(n - 2)$ f-orbitals are called f-block or inner-transition elements. Since in these elements the differentiating electron enters the f-orbitals [viz. $(n - 2)$ orbitals], these are also called f-block elements. Elements of f-blocks are formal members of group 3 from which they have been taken out to form a separate f-block of the periodic table.

THE TRANSITION ELEMENTS (d-BLOCK) :

In the long form of periodic table elements are classified based on electronic configuration. The elements which are classified between 's' and 'p' block are 'd' block elements or Transition elements. In these elements the differentiating electron enters in the 'd' orbitals of penultimate shell. General configuration for 'd' block elements is $ns^{1-2}(n-1)d^{1-10}$. i.e., in 'd' block elements the valence shell has constant number of electrons whereas the number of electron in penultimate shell go on increasing. Elements which have atleast one unpaired electron in their 'd' orbital in atomic or any oxidation state are called as Transition elements. Thus all transition elements are 'd' block elements but all 'd' block elements may not be transition elements. Transition elements are classified between 's' and 'p' blocks from fourth period onwards.

Series of transition elements are four –

1st Series - They are classified in fourth period and are called as '3d' series of elements. Their atomic numbers are 21(Sc) to 30(Zn).

2nd Series- They are classified in fifth period and are called as '4d' series of elements. Their atomic numbers are 39(Y) to 48(Cd).

3rd series- They are classified in sixth period and are called as '5d' series of elements. Their atomic numbers are 57(La), 72(Hf) to 80(Hg)

4th Series - They are classified in the seventh period and are called as '6d' series of elements. This is an incomplete series. Their atomic numbers are 89(Ac), 104(Ku) to 112 (Uub).

Electronic configuration of first series of transition elements.

Atomic number	Element	Symbol	Electronic configuration
21.	Scandium	Sc	[Ar] 4s ² 3d ¹
22.	Titanium	Ti	[Ar] 4s ² 3d ²
23.	Vanadium	V	[Ar] 4s ² 3d ³
24.	Chromium	Cr	[Ar] 4s ¹ 3d ⁵
25.	Manganese	Mn	[Ar] 4s ² 3d ⁵
26.	Iron	Fe	[Ar] 4s ² 3d ⁶
27.	Cobalt	Co	[Ar] 4s ² 3d ⁷

The d- and f-block elements

28.	Nickel	Ni	[Ar] 4s ² 3d ⁸
29.	Copper	Cu	[Ar] 4s ¹ 3d ¹⁰
30.	Zinc	Zn	[Ar] 4s ² 3d ¹⁰

Chromium and copper are elements having exceptional electronic configurations of [Ar] 4s¹3d⁵ and [Ar] 4s¹3d¹⁰ instead of [Ar] 4s²3d⁴ and [Ar] 4s²3d⁹.

Zn (30) is [Ar] 4s²3d¹⁰, Cd (48) is [Kr] 5s²4d¹⁰, Hg (80) is [Xe] 6s² 4f¹⁴ 5d¹⁰

These three elements do not have any unpaired electrons in their 'd' orbitals in atomic as well as in ionic states. Therefore they are only classified as 'd' block elements and not as transition elements. Copper, Silver and Gold, the elements of IB group i.e., coinage metals, have ns¹ (n-1)d¹⁰ configuration. They are transition elements as in their higher oxidation state they have an unpaired electron in their 'd' orbitals.

GENERAL PROPERTIES OF d-BLOCK ELEMENTS

All the elements of '3d' series are good reducing agents except copper. In general the reactivity of transition elements is less. Their reactivity decreases with increase in atomic number. The atomic radii of transition elements decrease by negligible amounts due to the shielding of valence shell electrons, provided by electrons of 'd' orbitals of penultimate shell. The ionisation potential of transition elements increases by negligible amounts due to shielding effect.

Metallic character : All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two. These elements occur in three types face centered cubic (fcc), hexagonal closed packed (hcp) and body-centred cubic (bcc). They are hard malleable and ductile. IB (11) group elements Cu, Ag and Au are most ductile and soft. These are good conductor of heat and electricity (due to free e⁻). They are most conductive in nature. Their order of conductivity is Ag > Cu > Au > Al.

Atomic size : Atomic and ionic radii of d-block elements is smaller than s-block elements. Atomic radii depends on effective nuclear charge (Z_{eff}) and screening effect (SE).

In 3d series :

Sc → Cr ($Z_{\text{eff}} > \text{SE}$) ∴ radius decreases

Mn → Ni ($Z_{\text{eff}} = \text{SE}$) ∴ radius remains constant

Cu → Zn ($Z_{\text{eff}} < \text{SE}$) ∴ radius increases

Decrease in the radii with increase in atomic number is not regular. Atomic radii tend to reach minimum near at the middle of the series and increase slightly towards the end of the series.

In dipositive ions of 3d series Cu⁺² is the smallest in size. The elements of 4d and 5d series belongs to a particular group have almost same atomic radii. This is due to Lanthanide contraction, e.g. Zr □ Hf, Tc □ Re, Nb □ Ta, Ru □ Os etc.

In d-block elements : Largest atomic radii - La, Smallest atomic radii - Ni

In IIIB (13) group order of atomic radii is : Sc < Y < La (No lanthanide contraction)

Density : The atomic volume of the transition elements are low compared with s-block, so their density is comparatively high. Except Sc, Y and Ti, all the d-block elements have density greater than 5 gm cm⁻³. Os (22.57 gm cm⁻³) and Ir (22.61 gm cm⁻³) have highest density. In all the groups there is normal increase in density from 3d to 4d series, and from 4d to 5d it increases just double it is due to lanthanide contraction. Ti < Zr << Hf

In 3d series : Sc → Cr density increases, Mn, Fe, Co, Ni → almost constant, Cu → Zn decreases

In 3d series highest density – Cu, lowest density – Sc

Some important orders of density : Fe < Ni < Cu ; Fe < Cu < Au ; Fe < Hg < Au

Melting and boiling points : M.P. and B.P. of d-block is greater than s-block (the reason is stronger metallic bond and presence of covalent bond formed by unpaired d-electrons.) In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond, their m.p. and b.p. are very low. (Volatile metals Zn, Cd, Hg). In 3d series: Sc → Cr; m.p. b.p increases,

Mn → Zn m.p. b.p decreases. Mn and Tc possess comparatively low m.p., it due to stable configuration (Half filled). Lowest mp Hg - 38°C, Highest mp. W □ 3400°C.

Ionisation potentials : The ionisation potential values of most of the d-block elements lie in between those of s- and p-block elements. This indicates elements lie in between those of s- and p-block elements. This indicates that the d-block elements are less electropositive than those of the elements of groups IA and IIA (s-block elements). Thus d-block elements do not form ionic compounds so readily as the alkali and alkaline earth metals do.

The ionisation potentials of d-block elements increase as we move across each series from left to right, although the increase is not quite regular, e.g., in the first series, the values for Sc, Ti, V and Cr differ very slightly. Similarly the values Fo, Co, Ni and Cu are fairly close to one another. The value for Zn is appreciably higher due to the additional stability associated with completely filled 3d-level in Zn (Zn → 3d¹⁰4s²).

Slight variations that occur in ionisation potentials across the series are mainly due to the slight changes in atomic radii which

are an account of the fact that the screening effect caused by the addition of extra electrons to 3d-level almost compensates the effect in increase in nuclear charge, as we move from left to right in the series.

- (a) **Variable valency or variable oxidation states :** They exhibit variable valency due to involvement of (ns) and (n-1)d electrons in bonding. This is due to less energy difference between these electrons.

The oxidation states of all transition elements of '3d' series are :

Sc	[Ar]	4s ² 3d ¹	+3					
Ti	[Ar]	4s ² 3d ²	+2	+3	(+4)			
V	[Ar]	4s ² 3d ³	+2	+3	+4	(+5)		
Cr	[Ar]	4s ¹ 3d ⁵	+1	+2	(+3)	+4	+5	(+6)
Mn	[Ar]	4s ² 3d ⁵	(+2)	+3	+4	+5	+6	(+7)
Fe	[Ar]	4s ² 3d ⁶	(+2)	(+3)	+4	+5	+6	
Co	[Ar]	4s ² 3d ⁷	(+2)	(+3)	+4			
Ni	[Ar]	4s ² 3d ⁸	(+2)	+3	+4			
Cu	[Ar]	4s ¹ 3d ¹⁰	+1	(+2)				

The most common oxidation states are in bracket ().

Most common oxidation state among the transition elements is +2. Highest oxidation state shown by transition elements of '4d' and '5d' series is +8. The elements showing this oxidation state are Ruthenium (44) and Osmium (76). The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable. In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.

For example, In chromate ion CrO_4^{-2} , the bonds between Cr and O are covalent.

Generally higher oxidation states are exhibited in the compounds which are formed with highly electronegative elements like O and F. They also shows zero oxidation state in their carbonyl compounds like $\text{Ni}(\text{CO})_4$. Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.

Highest oxidation state of transition elements can be calculated by = n + 2 (n = no. of unpaired e-) (It is not applied for Cr and Cu)

The transition metal ions having stable configuration are stable. Metal ions of '3d' series having 3d⁰ configuration Sc^{+3} , Ti^{+4} and V^{+5} etc. are stable. Transition metal ions having 3d⁵ configuration are stable like Mn^{+2} , Fe^{+3} . In aqueous medium Cr^{+3} is stable. Co^{+2} and Ni^{+2} are stable. Transition metal ion with 3d¹⁰ configuration which is stable is Cu^{+1} . In aqueous medium Cu^{+2} is more stable than Cu^{+1} .

Ex. – Ti^{+2} , V^{+2} , Fe^{+2} , Co^{+2} etc are reducing agents

Cr^{+6} , Mn^{+7} , Mn^{+4} , Mn^{+5} , Mn^{+6} etc are oxidising agents.

Standard oxidation potentials and reducing properties :

The oxidation potential value of the member of first transition series are as follows :

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation potential value (v) for M → $\text{M}^{2+} + 2\text{e}^-$	–	1.63	1.18	0.90	1.18	0.44	0.28	0.25	0.34	0.76
$\text{M} \rightarrow \text{M}^{3+} + 3\text{e}^-$	–	–	–	0.74	–	–	–	–	–	–
	2.10	–	–	–	–	–	–	–	–	–

The irregular trend is due to the variation in ionization energies, sublimation energies and the hydration energies of the divalent ion of the member of the transition series. The value of standard oxidation potential reveal that the value for any element except Cu is higher than that of standard hydrogen electrode (taken as zero). It is therefore expected that these metals, except Cu, would evolve H₂ gas from acid solution. In actual practice the rate at which most of the metal react with acid is very slow. Some of the metals get protected from further attack of the acid due to the formation of a thin protective layer of their oxide, which prevent the acid to come in further contact with metals.

Ex. Although E_{ox}^0 of Cr is high, it get coated with its non-reactive oxide (Cr_2O_3) which make the Cr metal so unreactive that it can be used as a protective non-oxidizing metals.

Inspite of the fact that metals of first transition series, except Cu, have high value of E_{ox}^0 , these are not good reducing agent as the metal of IA, IIA and IIIA groups. The poor reducing capacity of the transition metal is due to high heats of vapourization, high ionization potential and low heat of hydration of their ions.

Magnetic properties : Matter, in general is associated with magnetic properties. Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. Diamagnetic substance is one which is slightly repelled by a magnetic field. $\text{Ti}^{+2} [\text{Ar}]3\text{d}^2$, $\text{Ti}^{+3} [\text{Ar}]3\text{d}^1$, $\text{V}^{+2} [\text{Ar}]3\text{d}^3$, $\text{Cr}^{+3} [\text{Ar}]3\text{d}^3$

The d- and f-block elements

As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having $3d^0$ and $3d^{10}$ configuration exhibit diamagnetic nature. An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning. Each electron may, in fact, be considered as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. Thus substances containing unpaired electrons get attracted towards the magnets exhibiting paramagnetic nature. The magnetic moment (μ) created due to spinning of unpaired electrons can be

calculated by using $\mu = \sqrt{n(n+2)}$, where 'n' is the number of unpaired electrons in the metal ion, μ = Magnetic moment in Bohr Magnetons (B.M.)

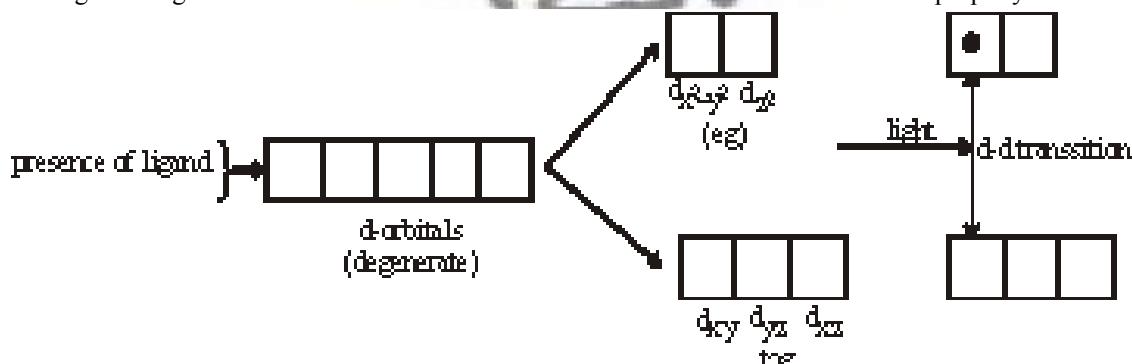
The magnetic moment of diamagnetic substances will be zero. As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases. Transition metal ions having d^5 configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

Colour Property: Most of the transition metal ions exhibit colour property. This is due to the presence of unpaired electrons in their 'd' orbitals. They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour. $Ti^{+2}[Ar]3d^2$, $V^{+2}[Ar]3d^3$ etc.

These are having unpaired electrons in their 'd' orbitals therefore they are coloured. Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like $3d^0$ and $3d^{10}$ configurations, do not exhibit any colour property.

Ex., $Sc^{+3}[Ar]3d^0$, $Cu^{+1}[Ar]3d^{10}$, $Ti^{+4}[Ar]3d^0$ etc are colourless ions.

A transition metal ion absorbs a part of visible region of light and emits rest of the six colours, the combination of which is the colour of emitted light. The colour of metal ion is the colour of the emitted light. In transition metal ion the 'd' orbitals split into lower energy set t_{2g} orbitals and higher energy set e_g orbitals. The electrons from t_{2g} set get excited to higher energy set i.e., e_g set. This excitation of electrons is called as 'd-d' transition. As d-d transition requires less amount of energy they absorb visible region of light. Due to this 'd -d' transition the transition metal ions exhibit colour property.



$KMnO_4$ (dark pink), $K_2Cr_2O_7$ (orange) having d^0 configuration are coloured due to charge transfer spectrum.

Some of the coloured metal ions are as follows :

Ti^{+3} -	Purple	Cr^{+3}	Green
Mn^{+2} -	Light pink	Fe^{+2} -	Pale green
Fe^{+3} -	yellow	Co^{+2} -	Blue
Ni^{+2}	green	Cu^{+2} -	Blue

Complex formation : Transition metal ions have maximum tendency to form complexes. In the formation of complexes they form coordinate covalent bonds and act as electron pair acceptors. Transition metal ions have smaller size and have high positive charge, i.e., high valence density up to this they have maximum tendency to accept electrons. They have vacant 'd' orbitals available on them hence they can accept lone pairs of electrons forming coordinate covalent bond. The greater the charge density on the transition metal ion, the greater they have tendency to form complexes. Thus Ti^{+2} to Ni^{+2} the stability of complexes formed goes on increasing. Compounds like $NaCl$, $Al_2(SO_4)_3$ and K_2SO_4 provide only two types of ions in aqueous solution i.e., cation and anions, called as simple salt. When two or more simple salt solutions are mixed and then subjected to crystallisation, the crystals which are obtained are addition compounds. The addition compound formed may behave in one of the following ways

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The addition compound which undergoes complete ionisation to form three types of ions i.e., two types of cations and one type of anion respectively is called as double salt. These double salts loose their identity in aqueous solution.

