

## 1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	The <i>d</i> - and <i>f</i> - Block Elements: Part 1
Module Id	lech_10801
Pre-requisites	Writing Electronic Configuration, Periodic table, Periodic properties, Types of bonds.
Objectives	After going through this module, the learner will be able to: <ul style="list-style-type: none"><li>• Identify the <i>d</i>- and <i>f</i>-block elements in the periodic table;</li><li>• Write the electronic configurations of the transition (<i>d</i>-block) elements and their ions;</li><li>• Explain the general physical properties of the <i>d</i>-block;</li><li>• Explain the trend and cause of variation of the atomic and ionic sizes of the transition elements.</li></ul>
Keywords	<i>d</i> -block elements, transition elements, lanthanoids, actinoids electronic configuration, melting point, enthalpy of atomisation, atomic radii, ionic radii. lanthanoid contraction

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**1. General Introduction:** 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 of the periodic table. The *f*- block consists of elements in which the *4f* and *5f* orbitals are progressively filled and is placed in separate panels at the bottom of the periodic table. The names transition metals and inner transition metals are often used to refer to the elements of *d*- and *f*- blocks respectively.

There are four series of *d*- block, *3d* series (Sc to Zn), *4d* series (Y to Cd), *5d* series (La, Hf to Hg) and *6d* series (Ac, Rf to Cn). The two series of the inner transition metals; *4f* (Ce to Lu) and *5f* (Th to Lr) are known as lanthanoids and actinoids respectively. The first formal member of group 3 of *5d* and *6d* series has been discussed with the elements of the *f*-block due to its resemblance in properties with the *f*-block elements. Most of the elements of *6d* (transuranium) are short-lived and synthetic.

Strictly speaking, a transition element has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states. Zinc, cadmium and mercury of group 12 have complete  $d^{10}$  configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the *d*-series, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled *d* or *f*-orbitals in their atoms sets the study of the transition elements and their compounds which makes them different from that of the main group elements. However, the usual theory of valence as applicable to the main group elements can also be applied successfully to the transition elements.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium form part of the transition metals.

In this module, we shall deal with the electronic configuration, occurrence and general characteristics of the transition elements with special emphasis on the trends in the properties of the first row (*3d*) transition metals and the preparation and properties of some important

compounds. This will be followed by general electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

## 2. The Transition Elements (*d*-Block)

**Position in the Periodic Table:** The *d*-block occupies the large middle section in the periodic table flanked by *s*- and *p*- blocks. The name ‘transition elements’ is given to the *d*-block as they exhibit properties intermediate between the *s*- and *p*- block elements. The *d*-orbitals of the penultimate energy level of atoms receive electrons which give rise to the four rows of the transition metals, i.e., 3*d*, 4*d*, 5*d* and 6*d*. These series of the transition elements are shown in Table 1.

**Table 1:** Outer electronic configuration of the Transition Elements (ground state)

1 <sup>st</sup> series										
Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
2 <sup>nd</sup> series										
Z	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10
3 <sup>rd</sup> series										
Z	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
4 <sup>th</sup> series										
Z	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

(Source: Table 8.1, page 211, Chapter 8, NCERT Chemistry Textbook)

**3. Electronic Configurations of the *d*-Block Elements:** In general the electronic configuration of these elements is  $(n-1) d^{1-10} ns^{0-2}$ . The  $(n-1)$  stands for the inner *d*- orbitals which may have one to ten electrons and the outermost *ns* orbital may have none, one or two electrons. This generalisation is because of very little energy difference between  $(n-1) d$  and *ns* orbitals. Furthermore, half and completely filled sets of orbitals are relatively more stable. A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3*d* series. Consider the case of Cr, for example, which has  $3d^5 4s^1$  instead of  $3d^4 4s^2$ ; the energy gap between the two sets (3*d* and 4*s*) of orbitals is small enough to prevent electron

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entering the 3d orbitals. Similarly in case of Cu, the configuration is  $3d^{10}4s^1$  and not  $3d^94s^2$ . The outer electronic configurations of the transition elements are given in Table 1.

The electronic configurations of Zn, Cd, Hg and Cn are represented by the general formula  $(n - 1)d^{10} ns^2$ . The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, these are not regarded as transition elements.

**Electronic Configurations of the ions of the d-Block Elements:** In d-block elements, ns electrons are removed before  $(n - 1)d$ . This is in contrast to the ions of main group elements where last added valence electrons are lost first.

*Example 1:* On what ground can you say that scandium ( $Z = 21$ ) is a transition element but zinc ( $Z = 30$ ) is not?

*Solution:* Scandium atom in its ground state ( $3d^1$ ) has incompletely filled 3d orbitals, so, it is regarded as a transition element. On the other hand, zinc atom has completely filled d orbitals ( $3d^{10}$ ) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.

*Example 2:* Silver atom has completely filled d orbitals ( $4d^{10}$ ) in its ground state. How can you say that it is a transition element?

*Solution:* For an element to be termed as a transition element, it should have partially filled d-orbitals in its atom or in commonly found oxidation states. Silver can exhibit +2 oxidation state ( $3d^9$ ) in which it has partially filled d-orbitals. Due to this reason, we can say that silver is a transition element.

*Example 3:* Name the transition elements which do not have partially filled d- orbitals in their atoms or in commonly found oxidation states.

*Solution:* The last member of each of the transition series i.e. Zinc (Zn), Cadmium (Cd) and Mercury (Hg) are the transition elements which do not have partially filled d- orbitals in their atom as well as simple ions (having oxidation state of +2). Therefore, these elements do not possess characteristic properties of transition elements and hence, generally not regarded as transition elements.

*Example 4:* Write down the electronic configuration of:

(i)  $\text{Cr}^{3+}$       (ii)  $\text{Ni}^{2+}$       (iii)  $\text{Mn}^{2+}$       (iv)  $\text{Fe}^{3+}$       (v)  $\text{Cu}^+$       (vi)  $\text{Zn}^{2+}$

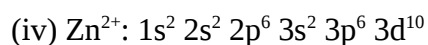
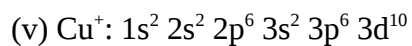
*Solution:*

(i)  $\text{Cr}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

(ii)  $\text{Ni}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

(iii)  $\text{Mn}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

(iv)  $\text{Fe}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$



#### 4. General Properties of the Transition Elements (*d*-Block)

The *d* orbitals of the transition elements project to the periphery of an atom more than the *s* and *p* orbitals. So, they are more influenced by the surroundings and also affect the atoms or molecules surrounding them. With partly filled *d* orbitals, these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions, paramagnetic behaviour, catalytic properties, and entering into complex formation with a variety of ligands. All these characteristics have been discussed in detail in the next modules.

The horizontal row similarities in the properties are more significant among the transition elements in contrast to the main group elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3*d* row) and then consider some group similarities.

**Physical Properties:** Nearly all the transition elements are metallic in nature and have simple hcp, ccp or bcc lattices (Table 2). With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

**Table 2.** Lattice Structures of Transition Metals

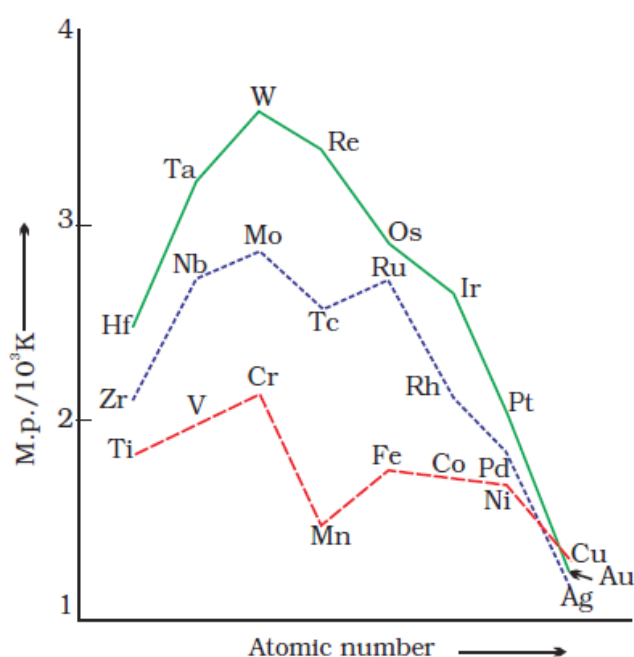
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	bcc	bcc (ccp)	bcc (hcp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	Hcp	ccp	ccp	ccp	X (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp (ccp, bcc)	hcp (bcc)	bcc	bcc	hcp	Hcp	ccp	ccp	ccp	X

(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed;

X = a typical metal structure)

Transition elements exhibit typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. These metallic

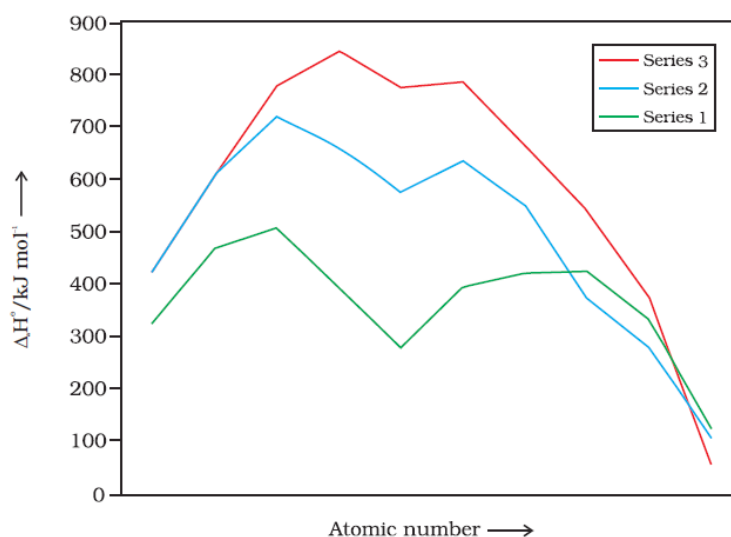
properties are attributed to the involvement of greater number of unpaired electrons from  $(n-1)d$  in addition to the  $ns$  electrons in the interatomic metallic bonding. In general, greater is the number of unpaired  $d$  electrons, stronger is the resultant metallic bonding. The transition metals (with the exception of Zn, Cd and Hg) are very much hard and have low volatility. Their melting and boiling points are high. The exceptions like Zn, Cd and Hg do not show typical metallic properties due to fully filled  $d$ - orbitals. Fig. 1 depicts the melting points of the  $3d$ ,  $4d$  and  $5d$  transition metals. In any row the melting points of these metals rise to a maximum at  $d^5$  except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.



**Fig. 1.** Trends in melting points of transition elements

(Source: Fig. 1, page 212, Chapter 8, NCERT Chemistry Textbook)

They have high enthalpies of atomisation which are shown in Fig. 2. The maxima at about the middle of each series indicates that one unpaired electron per  $d$  orbital is particularly favourable for strong interatomic interaction. Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, so the metals with very high enthalpy of atomisation tend to be noble in their reactions (see later for electrode potentials).



**Fig. 2.** Trends in enthalpies of atomisation of transition elements

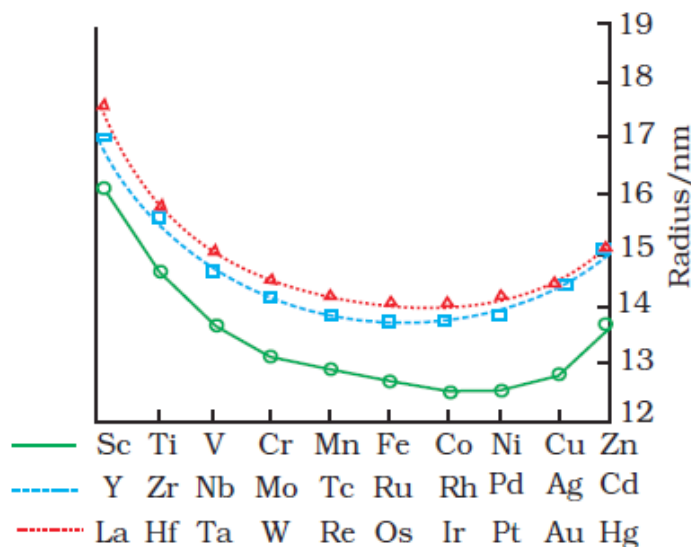
(Source: Fig. 8.2, page no. 213, Chapter 8, NCERT Chemistry Textbook)

Another generalisation that may be drawn from Fig. 2 is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series; this is an important factor in accounting for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition metals.

**5. Variation in Atomic and Ionic Sizes of Transition Metals:** In general, atoms and ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because, as the new electron enters in *d*-orbital, each time, the nuclear charge increases by unity. It may be recalled that the shielding effect of a *d*-electron is not effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small. The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium ( $Z = 22$ ) to copper ( $Z = 29$ ) the significant increase in the density may be noted (Table 3).

An interesting point emerges when atomic sizes of one transition series are compared with those of the corresponding elements in the other series. The curves in Fig. 3 show an increase in atomic radii from the first (*3d*) to the second (*4d*) series of the elements but the radii of the third (*5d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the *4f* orbitals which must be filled before the *5d* series of elements begin. The filling of *4f* before *5d* orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates

for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the elements of second and the third *d*-series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties, much more than the two congeners of *p*-block elements.



**Fig. 3.** Trends in atomic radii of transition elements

(Source: Fig. 8.3, page no. 214, Chapter 8, NCERT Chemistry Textbook)

The factor responsible for the lanthanoid contraction is somewhat similar to that observed in an ordinary transition series and is attributed to similar cause, i.e., the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one *4f* electron by another is less than that of one *d* electron by another, and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire *4f<sup>n</sup>* orbitals.

**Table 3:** Electronic Configurations and some other Properties of the First Series of Transition Elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
<b>Z</b>	21	22	23	24	25	26	27	28	29	30
<b>Electronic Configuration</b>										
M	3d <sup>1</sup> 4s <sup>2</sup>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>8</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s <sup>1</sup>	3d <sup>10</sup> 4s <sup>2</sup>
M <sup>+</sup>	3d <sup>1</sup> 4s <sup>1</sup>	3d <sup>2</sup> 4s <sup>1</sup>	3d <sup>3</sup> 4s <sup>1</sup>	3d <sup>5</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>6</sup> 4s <sup>1</sup>	3d <sup>7</sup> 4s <sup>1</sup>	3d <sup>8</sup> 4s <sup>1</sup>	3d <sup>10</sup>	3d <sup>10</sup> 4s <sup>1</sup>
M <sup>2+</sup>	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>4</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	3d <sup>8</sup>	3d <sup>9</sup>	3d <sup>10</sup>
M <sup>3+</sup>	[Ar]	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>4</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	-	-
<b>Enthalpy of atomisation, ΔaH° /kJ mol<sup>-1</sup></b>										
	326	473	515	397	281	416	425	430	339	126
<b>Ionisation enthalpy/ ΔiH° /kJ mol<sup>-1</sup></b>										
I	631	656	650	653	717	762	758	736	745	906
II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734



III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
<b>Metallic /ionic radii /pm</b>										
M	164	147	135	129	137	126	125	125	128	137
M <sup>2+</sup>	-	-	79	82	82	77	74	70	73	75
M <sup>3+</sup>	73	67	64	62	65	65	61	60	-	-
<b>Standard Electrode Potential, E° /V</b>										
M <sup>2+</sup> /M	-	- 1.63	- 1.18	- 0.90	- 1.18	- 0.44	- 0.28	- 0.25	+ 0.34	- 0.76
M <sup>3+</sup> /M <sup>2+</sup>	-	- 0.37	- 0.26	- 0.41	+ 1.57	+ 0.77	+ 1.97	-	-	-
<b>Density /g cm<sup>-3</sup></b>										
	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

(Source: Table 8.2, page no. 214, Chapter 8, Chemistry Textbook, NCERT)

*Example 5:* Why do the transition elements exhibit higher enthalpies of atomisation?

*Solution:* Because of large number of unpaired electrons per atom, transition metals have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

*Example 6:* In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is 126 kJ mol<sup>-1</sup> i.e., the lowest. Why?

*Solution:* The last element of the first transition series i.e. Zinc (Z = 30) has completely filled 3d- orbitals. Therefore, these paired electrons are not involved in the formation of metallic bonds. On the other hand, other elements of the transition series (from Sc to Cu) have unpaired electrons and these valence electrons present are involved in the metallic bonding. Hence, interatomic metallic bonding is the weakest in zinc and it has the lowest enthalpy of atomisation.

*Example 7:* Why transition metals are hard metals?

*Solution:* The transition metals possess large number of (n-1)d and ns valence electrons per metal atom, which participate in interatomic metallic bond formation. Because of large number of metallic bonds, these are hard metals.

**6. Summary:** In this module, we have introduced d- block elements in which the d- orbitals are progressively filled. The d- block occupies the large middle section of the periodic table and consists of Groups 3-12. The elements of the d- block are also known as transition elements except the last members of the series i.e., group 12. The transition elements have partially filled d- orbitals in their atom or commonly found ions. As Zinc, Cadmium and Mercury have fully filled d- orbitals in their atoms and stable oxidation state, so these elements do not show the characteristic properties of the transition elements.

In general, the electronic configuration of d- block elements is (n-1) d<sup>1-10</sup> ns<sup>0-2</sup>. When d-block elements form ions, they lose electrons from ns before (n-1) d orbital.

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The series of transition metals show large horizontal similarities in properties though some group similarities are also there.

All the transition elements exhibit typical metallic properties such as high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character. Their melting and boiling points are high which are attributed to the involvement of  $(n-1)$   $d$  electrons resulting into strong interatomic bonding. In many of these properties, the maxima occur at about the middle of each series which indicates that one unpaired electron per  $d$  orbital favours strong interatomic interaction.

In general, atoms and ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. However, the variation within a series is quite small. The atomic radii from the first ( $3d$ ) to the second ( $4d$ ) series of the elements increases, but the radii of the third ( $5d$ ) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with Lanthanoid contraction.