The *d*- and *f*- Block Elements - Part 2

Objectives

After going through this lesson, the learners will be able to understand the following:

- Describe the trend and variation in ionization energies for the *d*– block elements in the periodic table;
- Know the different oxidation states exhibited by the transition (*d*-block) elements and appreciate their relative stability;
- Describe trends in the standard electrode potential values of the transition series and chemical reactivity.

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Ionisation Enthalpies

There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to the increase in nuclear charge along with the filling of the inner d orbitals. Table 1 gives the values for the first three ionisation enthalpies of the first row elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Many small variations also occur. Although, the first ionization enthalpy for the successive elements, in general, increases, the magnitude of the increase in the second and third ionization enthalpies is much higher along the series (Sc to Cu).

Table 1. First Ionisation Enthalpy of Transition Elements

First Transition Series (3d- series)		**Second Transition Series (4d- series)**		**Third Transition Series (5d- series)**	
Element	Ionisation Enthalpy (kJ mol^{-1})	Element	Ionisation Enthalpy (kJ mol^{-1})	Element	Ionisation Enthalpy (kJ mol^{-1})
Sc	631	Y	616	La	541
Ti	656	Zr	674	Hf	760
V	650	Nb	664	Ta	760
Cr	653	Mo	685	W	770
Mn	717	Tc	703	Re	759
Fe	762	Ru	711	Os	840
Co	758	Rh	720	Ir	900
Ni	736	Pd	804	Pt	870
Cu	745	Ag	731	Au	889
Zn	906	Cd	876	Hg	1007

First Ionisation enthalpy of 3*d*, 4*d* and 5*d* series is tabulated in Table 1. As learnt in the module 1, when *d*-block elements form ions, n*s* electrons are lost before (n-1) *d*. The irregular trend in the first ionisation enthalpy of the 3*d* metals (Fig.1), thought of little chemical significance, can be accounted for, considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals. There is thus, a reorganisation energy accompanying ionisation with the transference of *s* electrons into *d* orbitals and from some gains in exchange energy as the number of *d*- electrons increases. So the uni-positive ions (M^+) have d^n configurations with no 4*s* electrons. There is the general expected increasing trend in the ionization enthalpy values with increase in the effective nuclear charge. However, the value of Cr is lower because of the absence of any change in the *d* configuration and the value for Zn is higher because it represents an ionisation from the 4*s* level.

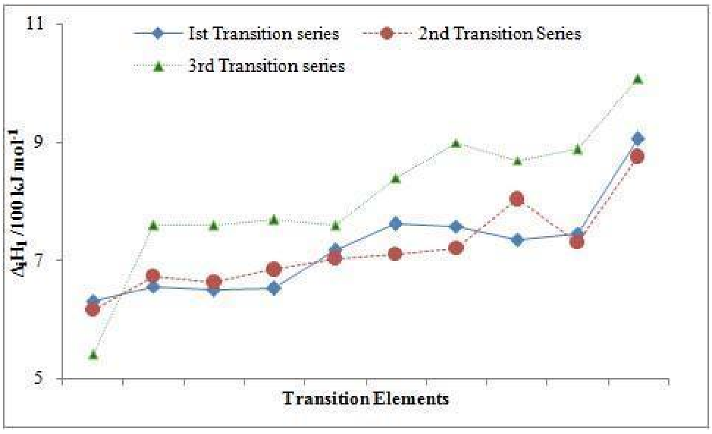

Fig. 1. Trend of first ionisation enthalpies of first, second and third transition series

The lowest common oxidation state of these metals is +2. To form the M^{2+} ions from the gaseous atoms, the sum of the first and second ionisation energies is required in addition to the enthalpy of atomisation for each element. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where the d^5 and d^{10} configurations of the M^+ ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionisation consists of the removal of an electron which allows the production of the stable d^{10} configuration. The third ionisation enthalpy is not complicated by the 4s orbital factor. The trend in third ionisation enthalpy shows the greater difficulty of removing an electron from the d^5(Mn^{2+}) and d^{10}(Zn^{2+}) ions superimposed upon the general increasing trend. In general, the third ionisation enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}. Also the high values of third ionisation enthalpy for copper, nickel and zinc indicates why it is difficult to obtain oxidation states greater than 2+ for these elements. Although ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is very complex and not amenable to ready generalisation.

Oxidation States

One of the notable features of a transition element is the great variety of oxidation states it may show in its compounds. Table 2 lists the common oxidation states of the first, second and third row of transition elements.

Table 2. Different Oxidation states of Transition elements (the most common ones are in bold types and less common /unstable are given in parentheses)

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
+3	(+2) +3 **+4**	+2 +3 +4 **+5**	+2 **+3** (+4) (+5) **+6**	**+2** (+3) +4 (+6) **+7**	**+2** **+3** +4 (+6)	**+2** **+3** (+4)	**+2** (+3) (+4)	+1 **+2**	**+2**
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
+3	(+3) **+4**	(+2) (+3) (+4) **+5**	(+2) +3 **+4** +5 **+6**	**+4** (+5) **+7**	+2 **+3** **+4** (+5) (+6) (+7) (+8)	**+3** +4 (+6)	**+2** (+3) **+4**	**+1** (+2) (+3)	**+2**
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
+3	(+3) **+4**	(+2) (+3) (+4) **+5**	+2 (+3) **+4** +5 **+6**	+3 **+4** (+5) (+6) +7	(+2) (+3) **+4** +6 +8	(+2) +3 **+4** (+6)	+2 (+3) **+4** (+5) (+6)	+1 **+3**	**+1** **+2**

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many *d* electrons (hence fewer orbitals available to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the *s* and *d* electrons upto manganese ($Ti^{IV}O_2$, $V^{V}O_2^{+}$, $Cr^{VI}O_4^{2-}$, $Mn^{VII}O_4^{-}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other by unity, e.g. V^{II}, V^{III}, V^{IV}, V^{V}. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.

Another interesting feature in the variability of oxidation states of the *d*–block elements is noticed among the groups (groups 4 through 10). Although in the *p*–block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero. The terms complex and ligands are discussed in the module 1 of unit 9; coordination chemistry.

Example 1: The first ionisation enthalpy value of zinc shows a higher increase while the second ionisation enthalpy value drops off in the otherwise increasing regular trend in 3*d* series. Explain.

Solution: Zinc has fully filled configuration; $(Ar)3d^{10}4s^2$. The first ionisation enthalpy represents the removal of 4*s* electrons while second ionisation enthalpy consists of the removal of an electron which allows the production of the stable d^{10} configuration. So the second ionisation enthalpy value drops off.

Example 2: Why the second and third ionization enthalpies of manganese and iron show anomalous dip in the values across the period?

Solution: Manganese and iron attain stable half filled configuration ($3d^5$) in +2 and +3 oxidation states respectively. So they show anomalous dip in the values across the period.

Example 3: Name a transition element which does not exhibit variable oxidation states.

Solution: Scandium (Z = 21) does not exhibit variable oxidation states.

Example 4: Which transition metal of the 3*d* series exhibits the largest number of oxidation states and why?

Solution: Manganese (Z=25) exhibits the largest number of oxidation states because it has maximum number of electrons *ns* and (n-1)*d* electrons available for the bond formation. It exhibits all oxidation states from +2 to +7.

Trends in the M^{2+} /M Standard Electrode Potentials

Table 3 contains the thermochemical parameters related to the transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials. The observed values of E° and those calculated using the data of Table 3 are compared in Fig. 2.

Table 3. Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M.

Element (M)	$\Delta_a H^{\Theta}$ (M)	$\Delta_i H_1{}^{\Theta}$	$\Delta_i H_2{}^{\Theta}$	$\Delta_{hyd} H^{\Theta}$ (M^{2+})	E^{Θ} /V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

(Source: Table 8.4, page 218, Chapter 8, Chemistry Textbook, NCERT)

The unique behaviour of Cu, having a positive E^{Θ}, accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to Cu^{2+} (aq){ $\Delta_a H^{\Theta}(M)^{+}\Delta_i H_1{}^{\Theta}+\Delta_i H_2{}^{\Theta}$} is not balanced by its hydration enthalpy{$\Delta_{hyd} H^{\Theta}$ (M^{2+})}. The general trend towards less negative E^{Θ} values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the value of E^{Θ} for Mn, Ni and Zn are more negative than expected from the trend. The stability of the half-filled *d* sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their E^{Θ} values, whereas E^{Θ} for Ni is related to the highest negative $\Delta_{hyd}H^{\Theta}$. However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2\,Cu^{+} \rightarrow Cu^{2+} + Cu$$

The stability of Cu^{2+} (*aq*) rather than Cu^{+} (*aq*) is due to the much more negative $\Delta_{hyd}H^{\Theta}$ of Cu^{2+} (*aq*) than Cu^{+}, which more than compensates for the second ionisation enthalpy of Cu.

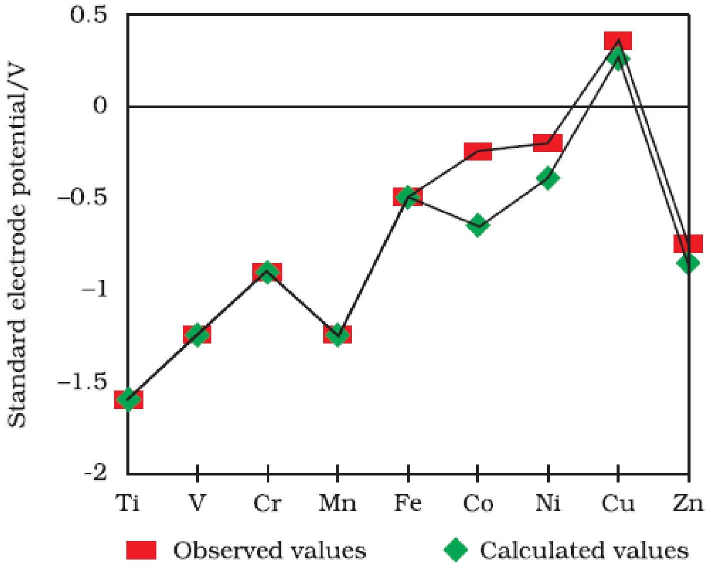

Fig. 2. Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow M$) of the elements Ti to Zn

(Source: Fig. 8.4, page 217, Chapter 8, Chemistry Textbook, NCERT)

Example 5: Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration? **Solution:** Cr^{2+} is reduced as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level (details will be discussed in modules of coordination chemistry). On the other hand, the change from Mn^{2+} to Mn^{3+} results in the half-filled (d^5) configuration which has extra stability.

E**xample 6:** The E^{Θ} (M^{2+}/M) value for copper is positive (+0.34V). What is the possible reason for this?

Solution: The $E^{\ominus}$ (M^{2+} /M) value for copper is positive (+0.34V) because the sum of first and second ionisation enthalpies for copper is very large due to exceptionally high second ionisation enthalpy which is not compensated by the hydration enthalpy ($\Delta_{hyd}H^{\ominus}$) of Cu^{2+} ion.

Example 7: Cu^+ has fully filled d^{10} configuration, but +2 is the common oxidation state for Cu (aq.). Explain.

Solution: The hydration energy of Cu^{2+} is more negative than Cu^+ and more than compensates the second ionization enthalpy of copper. So though Cu^+ has fully filled d^{10} configuration, copper exists as Cu^{2+} in aqueous solution.

Trends in the M^{3+} /M^{2+} Standard Electrode Potentials

An examination of the $E^{\ominus}$ (M^{3+} /M^{2+}) values (Table 3 of Module 1) shows the varying trends. The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+}. The comparatively high value for Mn shows that Mn^{2+} (d^5) is particularly stable, whereas comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5). The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level, modules based on the Chapter 'Coordination Compounds').

Trends in Stability of Higher Oxidation States

Table 4 shows the stable halides of the 3d series of transition metals. The highest oxidation numbers are achieved in TiX_4 (tetrahalides), VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6.

Table 4. Formulas of Halides of 3*d* Metals

Oxidation Number				
+6			CrF_6	
+5		VF_5	CrF_5	
+4	TiX_4	VX_4^I	CrX_4	MnF_4

+3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3^{I}	CoF_3			
+2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+1								CuX^{III}	

Key: X = F → I; X^{I} = F → Br; X^{II} = F, Cl; X^{III} = Cl → I

(Source: Table. 8.5, page 218, Chapter 8, Chemistry Textbook, NCERT)

Although V^{V} is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxohalides, VOX_3. Another feature of fluorides is their instability in the low oxidation states e.g., for V^{II} ; halides VX_2 (X = CI, Br or I) and the same applies to Cu^{I} halides; CuX^{III}. On the other hand, all Cu^{II} halides are known except the iodide. In this case, Cu^{2+} oxidises I^{-} to I_2:

$$2\,Cu^{2+} + 4\,I^{-} \rightarrow Cu_2I_2\,(s) + I_2$$

The ability of oxygen to stabilize the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides (Table 5) coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond Group 7, no higher oxides of Fe above Fe_2O_3, are known, although ferrates (VI) $(FeO_4)^{2-}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2. Besides the oxides, oxocations stabilize V^{V} as VO_2^{+}, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}. The ability of oxygen to stabilize these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7. The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The tetrahedral $[MO_4]^{n-}$ ions are known for V^{V}, Cr^{VI}, Mn^{V}, Mn^{VI} and Mn^{VII}.

Table 5. Oxides of Metals

Oxidation	**Groups**									
Number	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	VO_2	CrO_2	MnO_2					
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				

					Mn_3O_4 *	Fe_3O_4 *	Co_3O_4 *			
+2		TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu_2O	

* mixed oxides

(Source: Table. 8.6, page 219, Chapter 8, Chemistry Textbook, NCERT)

Example 8: How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?

Solution: This is due to the increasing stability of the lower species; $V^{5+}<Cr^{6+}<Mn^{7+}$ to which they are reduced.

Example 9: How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements?

Solution: The irregular variation of ionisation enthalpies in the first series of the transition elements is due to the stability difference of different configurations of the transition elements (for example: d^0, d^5 and d^{10} are remarkably stable). For example, first ionisation enthalpy of chromium (Cr) is low because after losing one electron chromium exhibits a stable electronic configuration i.e. $3d^5$. Zinc (Zn) has the most stable electronic configuration ($3d^{10}\ 4s^2$) due to which it is very difficult to remove an electron from a zinc atom. Therefore, zinc possesses very high ionisation enthalpy. The second ionisation enthalpy of Cr and Cu is very high because the second electron is removed from the very stable configuration of Cr^+ ($3d^5$) and Cu^+ ($3d^{10}$).

Chemical Reactivity and $E^\ominus$ Values

Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by single acids. The metals of the first series with the exception of copper are relatively more reactive and are oxidised by 1M H^+, though the actual rate at which these metals react with oxidising agents like hydrogen ion (H^+) is sometimes slow. For example, titanium and vanadium, in practice, are passive to dilute non oxidising acids at room temperature. The $E^\ominus$ values for M^{2+}/M (Table 3 of Module 1) indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative $E^\ominus$ values is related to the increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the E^{Θ} values for Mn, Ni and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled *d* subshell (d^5) in Mn^{2+} and completely filled *d* subshell (d^{10}) in zinc are related to their E^{Θ} values; for nickel, E^{Θ} value is related to the highest negative enthalpy of hydration. An examination of the E^{Θ} values for the redox couple M^{3+}/M^{2+} (Table 3 of Module 1) shows that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solutions. The ions Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.,

$$2Cr^{2+}(aq) + 2H^{+}(aq) \rightarrow 2Cr^{3+}(aq) + H_2(g)$$

Example 10: Why is the E° value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}? Explain.

Solution: Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Example 11: Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Solution: The highest oxidation state of a metal is generally exhibited in its oxides or fluoride only because the fluorine and oxygen possess very high electronegativity. They can oxidise the metal to their higher oxidation states.

Summary

In this module, we have learnt about the ionisation enthalpy, oxidation states, electrode potential and chemical reactivity of the transition elements. Successive ionisation enthalpies do not increase as steeply with increasing atomic number as in the main group elements. Hence, the loss of variable number of electrons from (n–1) *d* orbitals is not energetically unfavourable. There is the general expected increasing trend in the ionization enthalpy values with increase in the effective nuclear charge though small variations occur. The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other by unity. The general trend towards less negative E^{Θ} values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.