

Why do the transition elements exhibit higher enthalpies of atomisation?

Example 8.2

Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

Solution

Intext Question

8.2 In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomisation of zinc is the lowest, i.e., 126 kJ mol^{-1} . Why?

8.3.3 Ionisation Enthalpies

Due to an increase in nuclear charge which accompanies the filling of the inner d orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 8.2 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. Although the first ionisation enthalpy, in general, increases, the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.

The irregular trend in the first ionisation enthalpy of the $3d$ metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of $4s$ and $3d$ orbitals. So the unipositive ions have d^n configurations with no $4s$ electrons. There is thus, a reorganisation energy accompanying ionisation with some gains in exchange energy as the number of electrons increases and from the transference of s electrons into d orbitals. There is the generally expected increasing trend in the values as the effective nuclear charge increases. However, the value of Cr is lower because of the absence of any change in the d configuration and the value for Zn higher because it represents an ionisation from the $4s$ level. 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 trend in the third ionisation enthalpies is not complicated by the $4s$ orbital factor and 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 for

copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two 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.

8.3.4 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 8.3 lists the common oxidation states of the first row transition elements.

Table 8.3: Oxidation States of the first row Transition Metals (the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

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 in which 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 ($\text{Ti}^{\text{IV}}\text{O}_2$, $\text{V}^{\text{V}}\text{O}_2^+$, $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, $\text{Mn}^{\text{VII}}\text{O}_4^-$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $\text{Fe}^{\text{II,III}}$, $\text{Co}^{\text{II,III}}$, Ni^{II} , $\text{Cu}^{\text{I,II}}$, 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.

An 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 $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, the oxidation state of nickel and iron is zero.