

d-Block Elements

There are six sections, Section 1 discusses general properties of d-Block Elements, Section 2 discusses chromium, Section 3 discusses Manganese, Section 4 discusses Iron, Cobalt Nickel groups, Section 5 discusses Copper and Section 6 is on Zinc group.

GENERAL PROPERTIES OF TRANSITION ELEMENTS

Section - 1

Three series of elements are formed by filling the $3d$, $4d$ and $5d$ shells of elements, together called the d-block elements (Group 3-12). They are often called '*transition elements*' because their position is between the s -block and p -block. Strictly speaking, a transition element is the one which has incompletely filled d -orbitals in its ground state or in any one of its oxidation states. Thus Zn, Cd, Hg of group 12 having full d^{10} configuration are not regarded as transition metals. Compounds of these elements are thus not typical and show some differences from the others. In general the electronic configuration of these elements is $(n-1) d^{1-10} ns^{1-2}$. In the case of Cr and Cu, the configuration is $d^5 s^1$ and $d^{10} s^1$ instead of $d^4 s^2$ and $d^9 s^2$ respectively. This is because of the additional stability when the d -orbitals are exactly half filled or completely filled.

Oxidation states and their stability

Transition elements show a great variety of oxidation state. The prominent oxidation states are shown in the following table:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic structure	$d^1 s^2$	$d^2 s^2$	$d^3 s^2$	~~$d^4 s^2$~~ $d^5 s^1$	$d^5 s^2$	$d^6 s^2$	$d^7 s^2$	$d^8 s^2$	~~$d^9 s^2$~~ $d^{10} s^1$	$d^{10} s^2$
Oxidation states	II III	II III IV	II III IV IV	I II III IV V VI	II III IV V VI VII	II III IV V VI	II III IV V	II III IV	I II III	II

The various oxidation states show a difference in stability. In general the second and third row elements exhibit higher coordination numbers and their higher oxidation states are more stable than the corresponding first row elements. This is interesting because in p -block elements the lower oxidation states are favoured by the heavier elements (due to inert pair effect).

Atomic and Ionic Sizes

The covalent radii decreases from left to right across the period in d-block until near the end when the size increases slightly.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
1.62	1.45	1.34	1.29	-	1.24	1.25	1.28
La *	Hf	Ta	W	Re	Os	Ir	Pt
1.69	1.45	1.34	1.30	1.28	1.26	1.26	1.29

14 Lanthanide elements

On going down the group the size increases as expected. But it is noticed that the increase in radius between the second and third member of a group is virtually negligible. This is due to the intervention of the $4f$ orbitals which must be filled before the $5d$ series begins. The f -shells shield the nuclear charge poorly as compared to s , p , d shells and thus lead to a decrease in radii called **Lanthanoid contraction** or **f -block contraction** which compensates for the expected increase in atomic size with increasing atomic number.

Melting and boiling points

The transition metals (except Zn, Cd and Hg) are very much hard and have high m.p. and b.p.. They typically melt over 1000°C . Zn, Cd and Hg behave abnormally (Hg is in fact a liquid with m.p. -38°C) because they have a complete d shell and d electrons do not participate in metallic bonding.

Density

Due to low atomic volumes as compared with Group 1 and 2 metals, they have high densities (almost all have greater than 5gcm^{-3}). To get a feel of high densities of Os (22.57g/cc) and Ir (22.61g/cc), a football of Os or of diameter 30cm would weight 320kg !

Colour

Many ionic and covalent compounds of transition elements are coloured (In contrast those of s and p block are generally white). Colour arises when a compound is able to absorb some wavelength in the visible region of the spectrum. The colour of the compound is then that of the transmitted light i.e. the complementary colour to the colour of the light absorbed. Ions having d^{10} or d^0 configuration are usually uncoloured. Thus ZnSO_4 and TiO_2 are colourless because in $\text{Zn}^{2+}(d^{10})$ and $\text{Ti}^{4+}(d^0)$ it is not possible to promote electrons within the d -level.

Another reason for colour can be charge transfer from one atom to another as occurs in MnO_4^- (intense purple).

Magnetic Properties

When an external magnetic field H is applied on a substance, the intensity of field inside it may be greater than or less than H . If the field is greater than H , the substance is paramagnetic and if the field is less than H it is diamagnetic. Ferromagnetic materials are a special case of paramagnetism in which the moments on individual atoms become aligned and all point in the same direction increasing the magnetic susceptibility drastically. Fe, Co and Ni are ferromagnetic. Antiferromagnetism is just opposite to ferromagnetism when the moments on individual atoms are aligned in the opposite direction to that of H . It occurs in several simple salts of Fe^{3+} , Mn^{2+} and Gd^{3+} . Since ferromagnetism and antiferromagnetism depend on orientation they disappear in solution.

Paramagnetism arises from the presence of unpaired electrons each having a magnetic moment due to its spin and due to its orbitals angular momentum. The 'spin only' formula is :

$\mu_s = \sqrt{n(n+2)}$, where n is the number of unpaired electrons. The unit is Bohr Magnetron (BM). For the 3- d series effect of orbitals angular momentum is effectively negligible.

Catalytic Properties

Transition elements and their compounds are important catalysts. In some cases they form variable valency unstable intermediates and in other cases they provide a suitable reaction surface. For example, TiCl_3 is used as 'Ziegler-Natta catalyst' in the production of polythene, MnO_2 is used as a catalyst to decompose KClO_3 to give O_2 , Pd is used for hydrogenation and V_2O_5 converts SO_2 to SO_3 in the Contact Process for which Fe was formerly used.

Complexes

The transition elements have an unparalleled tendency to form coordination compounds with lewis bases called *ligands*. Some example are $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$. The reason for this is that transition elements have small, highly charged ions and vacant low energy orbitals to accept lone pairs of electrons donated by other groups.

IN-CHAPTER EXERCISE - A

1. Why do second and third rows of transition elements resemble each other more closely than the first row?
2. Give reasons :
 - (i) Most transition metals show paramagnetic behaviours.
 - (ii) Transition metal and their many compounds are coloured.