TDC Part II
Paper I, Group B
Inorganic Chemistry

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TOPIC: - CHEMISTRY OF THE ELEMENTS OF FIRST TRANSITION (3-d) SERIES

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OBJECTIVES

The objective of writing the text material of this unit is to acquaint the readers to the characteristic properties of the d-block elements, in general, such as their general electronic configuration and variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions/compounds, catalytic activity, etc. and periodic properties, *viz.*, atomic radii, atomic volume, ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potentials and reducing properties, etc. along with their periodic variation along the series. It is also aimed at throwing light on the above properties of the first transition series, in particular, to illustrate the relative stability of the oxidation states of these elements along with to discuss the coordination number and geometry of their complexes and the binary compounds of these elements.

INTRODUCTION

The d-block elements have been defined as “the elements whose atoms receive the last electron in the

d-subshell belonging to the penultimate or (n-1)th shell”. The d-block elements are also called the transition elements or metals. This is because they exhibit gradual transitional behavior between highly reactive s-block

(Electropositive) and p-block (electronegative) elements, i.e. their properties have been found to be intermediate between those of the s-block and p-block elements. Thus these elements are located in the middle of the periodic table and are the members of the Groups 3 to 12 (IIIB to VIII to II B) in the modern periodic table. According to IUPAC definition, “a transition element is an element which has an incomplete d-subshell in either neutral atom or in ions in chemically significant (or common) oxidation state”. According to this definition zinc (Zn), cadmium (Cd) and mercury (Hg) are excluded from the list of transition elements as they neither have partly filled d-subshell in their atoms or ions nor they show the usual properties of transition elements to an appreciable extent. Still in order to rationalize the classification of elements, they are studied along with other d-block elements.

There are four series of elements which constitute the *d*-block elements. Each series comprises ten elements as given below:

1. **Elements of the First Transition series or 3d-Transition series:** The elements from scandium (Sc, Z = 21) to Zinc (Zn, Z = 30) form the 3d-series.

2. **Elements of the Second Transition series or 4d-Transition series:** This series consists of the elements from yttrium (Y, Z = 39) to cadmium (Cd, Z = 48).

3. **Elements of the Third Transition series or 5d-Transition series:** The elements lanthanum (La, Z= 57) and hafnium (Hf, Z= 72) to mercury (Hg, Z = 80) constitute the 5d-Transition series.

4. **Elements of the Fourth Transition series or 6d-Transition series:** The elements actinium (Ac, Z = 89)

and rutherfordium (Rf, Z = 104) to copernicum (Cn, Z = 112) are the members of this series. All these elements are radipoactive and do not occur in nature. These have been artificially made in the laboratory.

CHARACTERISTIC PROPERTIES OF D-BLOCK ELEMENTS

Some of the important characteristics of the d-block elements are summarized as follows:

Electronic Configuration and Variable Oxidation States

The d-block elements have a valence shell electronic configuration of $(n-1)d^{1-10}ns^{0-2}$ where (n-1) stands for inner shell whose d-orbital's may have one to ten electrons and the s-orbital's of the outermost shell (n) may have no electron or one or two electrons. The filling of d-orbital's takes place after the s-orbital of next higher shell has already filled as has been discussed in Aufbau principle in Unit 1 (BCH-101). This is because ns orbital's have lower energy than (n-1)d orbital's. But during ionization of the elements (oxidation), the electrons are first lost from ns level followed by the expulsion from (n-1)d subshell (deviation from the expected behavior) because (n- 1)d subshell becomes of the lower energy than ns subshell once the filling of electrons commences in (n-1)d subshell.

Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises of the two subshells, *viz*., (n-1)d and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left → middle ← right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state. As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

Complex Formation Tendency:

The cations of d-block elements are unique in their tendency to form complexes with several molecules such as ammonia, water, etc. or different ions such as cyanide, NO^{-} 2, halide ions, etc. These molecules or ions are called ligands. The complex forming tendency of these elements is attributed to the following factors:

(a) Small size and high positive charge density,
(b) Availability of vacant d-orbitals of right energy to accept the lone pairs of electrons from the approaching ligands,
(c) Exhibition of variable oxidation states.

The detailed account of this tendency will be given in the respective sections mentioned ahead.

Magnetic Properties:

Many compounds of d-block elements exhibit magnetic properties. Qualitatively speaking, there are several kinds of magnetism. The substances which are weakly repelled by the strong magnetic field are termed as **diamagnetic** while those which are weakly attracted by the strong magnetic field are called **paramagnetic.** These substances lose their magnetism on removing the magnetic field. Diamagnetism is the property of the completely filled electronic subshells and is shown by all substances to more or less extent. Paramagnetism is produced by the presence of unpaired electrons and because most of the d-block metal atoms and ions have unpaired electrons, they are paramagnetic in behavior.

In some transition metals (e.g. Fe, Co, Ni) unpaired electron spins are more pronounced and show much more paramagnetism than the other d-block metals. Such metals are called **ferromagnetic** metals and magnetic property shown by them is known as ferromagnetism. Such metals can be permanently magnetized. The detailed account will be given in the section 1.4 of this unit and in subsequent units.

Formation of Coloured Ions/ Compounds:

The majority of compounds of d-block elements, whether ionic or covalent, are coloured in solid or solution state. This property of d-block elements is in marked difference from those of s or p-block elements which are white or light coloured.

The colour of a substance arises from the property of the substance to absorb light of certain wavelength in the region of visible light (white light) when the latter interacts with the substance. The coloure of the substance is the colour of the transmitted light component and is complementary to the colour of light component absorbed. The colour of d-block metal ions is associated with

(a) an incomplete d-subshell in the metal ion,
(b) The nature of surrounding groups around the metal ion.

The whole act of exhibition of colour by d-block ions/compounds can be explained as follows. In a free gaseous or isolated ion the five d-orbitals are degenerate, i.e. of same energy. Since five d-orbitals are oriented differently in space, the surrounding groups affect the energy of some orbitals more than others in the compounds. This destroys their degeneracy. For example, in the simplest case of an octahedral complex, they form two groups of orbitals of different energy:

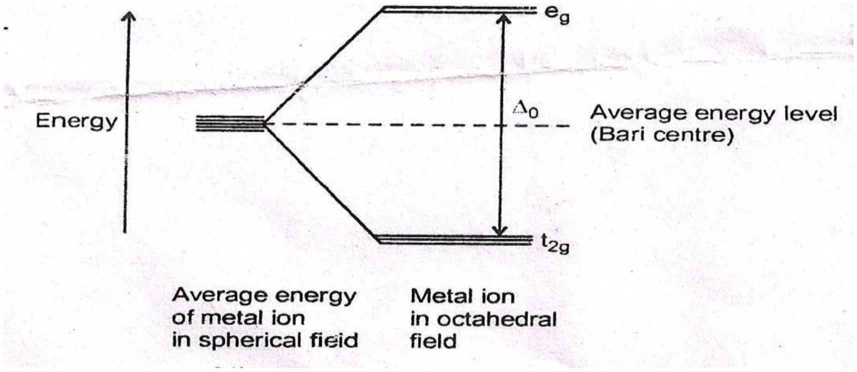

Fig. 1.1 *Bary centre*

Thus, in d-block metal ions with partially filled d-subshell, it is possible to promote electron(s) from one set of d-orbitals to another set (group) of higher energy by fairly small energy absorbed from the visible light. The colour of the compounds depends on the energy difference (gap) between the two groups (sets) of d-orbitals. This in turn depends on the nature of ligands and their arrangement around the metal ion in the compound / complex.