TDC Part II
Paper I, Group B
Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR

B. R. A. BIHAR UNIVERSITY

Dr. Priyanka

TOPIC:-UNIT -3,Introduction &General characteristics

UNIT 3- CHEMISTRY OF THE ELEMENTS OF SECOND TRANSITION (4d) SERIES

OBJECTIVES

The course material of this unit is being written with the objective of making it easy for the learners to understand the general characteristics of the elements of second transition (or 4d) series such as their electronic configuration, variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions / compounds, catalytic activity, formation of interstitial and non-stoichiometric compounds, metallic character and alloy formation as well as other periodic properties such as atomic and ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potential and reducing properties, etc. with their variation along the series.

The comparative study of some of the above periodic properties, *viz*., ionic radii, oxidation states and the magnetic behaviour of these elements with those of their 3d analogues is also aimed at. The spectral properties ad stereochemistry of these elements and their compounds or complexes is also to be discussed to make the readers familiar with these fascinating aspects.

INTRODUCTION

The series of ten elements starting from yttrium, the element of Group 3 and ending at cadmium, the element of Group 12, constitutes the second transition series. These elements with their symbols and atomic numbers are given here:

Yttrium (Y, Z = 39), zirconium (Zr, Z = 40), niobium (Nb, Z = 41), molybdenum (Mo, Z = 42), technetium (Tc, Z = 43), ruthenium (Ru, Z = 44), rhodium (Rh, Z = 45), palladium (Pd, Z = 46), silver (Ag, Z = 47) and cadmium (Cd, Z = 48). These elements are also known as the elements of 4d transition series because the differentiating or the last electron in the atoms of these elements enters the 4d subshell progressively giving $4d^1$ to $4d^{10}$ configurations, respectively. All the characteristic properties of d-block elements are exhibited by the members of this series also. These elements are the next higher analogues of first transition series elements and are less important. This series lies between strontium (Sr, Z =38) of s-Block (Group 2) and indium (In, Z = 49) of p-Block (Group 13) so that the gradual transition of properties may occur from s- to p- Block elements in the period.

GENERAL CHARACTERISTICS OF SECOND TRANSITION (4D) SERIES ELEMENTS

All the general characteristics of the d-Block elements are applicable to the elements of second transition series though to the lesser extent. These are discussed below:

Electronic Configuration and Variable Oxidation States

In yttrium 4d-subshell begins filling, its valence shell configuration being $4d^1 5s^2$. The filling of 4d-subshell continues as we move along the series towards the last element, Cd which has $4d^{10} 5s^2$ valence shell configuration. There are observed pronounced irregularities in the valence shell configurations of these elements which have the general valence shell configuration $4d^{1-10} 5s^{1,2}$. Except for the last three elements, *viz.*, Pd, Ag and Cd which have completely filled 4d-subshell ($4d^{10}$), all have incomplete d-subshells. Y, Zr, Tc and Cd have 2 electrons in 5s-subshell ($5s^2$) but Nb, Mo, Ru, Rh and Ag have only one electron, i.e., $5s^1$, in the last shell and Pd does not have any 5s- electron ($5s^0$). The anomalous valence shell configuration of Pd (i.e. $4d^{10} 5s^0$) is due to the shifting of both 5s-electrons to 4d-subshell so that it has completely filled state (i.e., $4d^{10}$) and becomes stable, though no satisfactory explanation is available for this shifting. For the elements which have partly filled 4d-subshell but still have only one electron in 5s subshell ($5s^1$), the anomalous behaviour has not been explained with effective reasoning, only it is said for these elements that the nuclear-electron and electron-electron interactions play significant role for this behaviour. In Mo ($4d^5$) and Ag ($4d^{10}$), one electron is said to have shifted from 5s to 4d subshell to make the atoms of these elements extra stable due to exchange energy effect as has been given earlier for Cr and Cu elements of 3d- transition series.

Like the elements of first transition (3d) series, the elements of this series also exist in various oxidation states in their compounds. This is because of the availability of several electrons in 4d and 5s subshells whose energies are fairly close to each other.

Hence, under different experimental conditions different number of electrons can be used from both the subshells for bonding.

It has been found for second transition series elements that the higher oxidation states become more stable. This can be illustrated by taking Fe and its next higher analogue, Ru. Fe shows +2 and +3 stable oxidation states and +4 and +6 unstable states but Ru has +2, +3, +4 and +6 as stable oxidation states while +5, +7 and +8 are unstable states for this element. The first element Y (+3) and the last element Cd (+2) exhibit only one oxidation state (though Sc in 3d transition series has also been assigned a very uncommon oxidation state of +2) because of the stable valence shell configuration of the ions, *viz.*, Y^{3+} $[Kr]4d^0 5s^0$ and Cd^{2+} $[Kr]4d^{10} 5s^0$. All other elements show a variety of oxidation states, both stable and unstable, the variability being the maximum towards the middle of the series as happens in case of elements of 3d-transitin series. Ruthenium, lying almost in the middle of the series, exhibits maximum number of oxidation states (i.e. 7) among all the elements of the series, including the unstable ones, ranging from +2 to +8 (i.e.+2, +3, +4, +5, +6, +7,+8). Up to Ru, the next higher member of Fe group, the highest oxidation state is equal to the group number, e.g., Sc: + 3 (Group 3); Zr: +4 (Group 4); Nb: +5 (Group 5), Mo: +6 (Group 6), Tc: +7 (Group 7) and Ru: +8 (Group 8) but the latter members of the series do not follow this trend. The lowest oxidation state is +1 only for Ag, the next congener of Cu. For Ru, Pd and Cd, the lowest oxidation state is +2, and +3 is the lowest oxidation state for other members of the series. This has been shown in the table below.

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Group number	3	4	5	6	7	8	9	10	11	12
Lowest oxidation state	+3	+3	+3	+3	+4	+2	+3	+2	+1	+2
Highest oxidation state	+3	+4	+5	+6	+7	+8	+6	+6	+3	+2

Thus, it is concluded that the electronic structure of the atoms of the second transition series elements does not follow the pattern of the elements of the first transition series and also among the 4d series elements, the higher oxidation states become more pronounced and stable.