

TDC Part II
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**TOPIC: - PROPERTIES OF
THE ELEMENTS OF FIRST
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PROPERTIES OF THE ELEMENTS OF FIRST TRANSITION SERIES

As has already been mentioned in the beginning that the first transition series is also known as 3d-series because the last or the differentiating electron in the atoms of these elements enters the 3d-subshell . This series starts at scandium, the element of Group 3 and ends at zinc, the element of Group 12, containing a total of ten elements. Thus, this series of elements lies in between calcium (Ca, $Z=20$) and gallium (Ga, $Z=31$), the elements of Group 2 and Group 13. The ten elements of the first transition series are scandium (Sc, $Z=21$), titanium (Ti, $Z=22$), vanadium (V, $Z=23$), chromium (Cr, $Z=24$), manganese (Mn, $Z=25$), iron (Fe, $Z= 26$), cobalt (Co, $Z= 27$), nickel (Ni, $Z=28$), copper (Cu, $Z= 29$) and zinc (Zn, $Z= 30$). These elements are much more important than those of second transition series. All the characteristics properties of the d-block elements are shown by the elements of first transition series which are given below:

Electronic Configuration and Variable Oxidation States.

The general valence shell electronic configuration of these elements is $3d^x4s^y$ where $x=1$ to 10 and $y= 1$ or 2 , i.e. the 3-d subshell has one to ten electrons from Sc to Zn and 4s-subshell, in general, has two electrons (i.e. $4s^2$) except in Cr and Cu which have only one 4s electron (i.e. $4s^1$). The exceptional valence shell configuration of Cr and Cu is attributed to the exchange energy effect and the extra stability of the resulting half-filled and completely-filled subshells. “The shifting of an electron from one subshell to another of similar or slightly higher energy in order to achieve the half-filled or completely-filled subshell is known as **exchange energy effect**”. The state of affairs can be shown as follows:

Cr (Z= 24): $3d^44s^2$ (expected but unstable) \longrightarrow $3d^54s^1$ (actual, more stable).

Cu (Z=29): $3d^94s^2$ (expected but unstable) \longrightarrow $3d^{10}4s^1$ (actual, more stable).

As is evident, there is exchange of electrons from 4s to 3d subshell thereby increasing the stability of the

valence shell configuration in Cr and Cu atoms. Thus, among 3d- series elements, only Cr and Cu exhibit irregular/anomalous electronic configurations. The first transition series elements generally show variable (many) oxidation states in their compounds / ionic forms. The cause of showing different oxidation states is that these elements have several 3d electrons which are quite close to 4s – electrons in energy. The minimum oxidation state shown by all the elements of this series is +2 except Cr and Cu which show +1 oxidation state as well. The number of oxidation states shown increases from Sc to Mn and then decreases till Zn which shows the +2 oxidation state only. As a result, among these elements, Cr and Mn show the maximum number of oxidation states from +1 to +6 and +2 to +7, respectively. From Sc to Mn, the highest oxidation state shown by any element is equal to the group number but the latter elements do not follow this trend. This is evident from the following table:

| Elements: | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|-------------------------|----|----|----|----|----|----|----|----|----|----|
| Group number | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Lowest oxidation state | +2 | +2 | +2 | +1 | +2 | +2 | +2 | +2 | +1 | +2 |
| Highest oxidation state | +3 | +4 | +5 | +6 | +7 | +6 | +4 | +3 | +2 | +2 |

It has been observed that the lower (+2, +3, etc.) oxidation states generally dominate the chemistry of the first transition series. For an element the relative stability of various oxidation states can be explained on the basis of the stability of d^0 , d^5 and d^{10} configurations, e.g. Ti^{4+} ion ($3d^04s^0$) is more stable than Ti^{3+} ($3d^14s^0$) because of the presence of $3d^0$ subshell. Similarly, Mn^{2+} ($3d^54d^0$) ion is more stable than Mn^{3+} ($3d^44s^0$) ion since Mn^{2+} ion has $3d^5$ subshell.

It has also been observed that first transition series elements form ionic oxides and chlorides in the lower oxidation states which are basic in nature. As the oxidation state of the elements increases, covalent character and acidic nature of these compounds also increases, e.g., MnO (+2) is basic, Mn_2O_3 (+3) and

MnO_2 (+4) are amphoteric and Mn_2O_7 (+7) is acidic. Similarly, CrO (+2) is basic, Cr_2O_3 (+3) is amphoteric and CrO_3 (+6) is acidic. Also VCl_2 (+2) is basic and VOCl_3 (+5) is acidic.