**TDC Part II**

**Paper I, Group B**

**Inorganic Chemistry**



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**TOPIC:-UNIT -3,Introduction &Periodic properties and their variation**

### Atomic Radii, Atomic Volumes and Ionic Radii

### Melting and Boiling Points

### Ionization Energies and Reactivity

## Periodic Properties and Their Variation along the Series

The periodic properties of second transition series elements such as the atomic radii, ionic radii, atomic volumes, ionization energies, melting and boiling points, standard electrode potentials, reactivity and reducing properties also vary along the series from the first element Y to the last element Cd. These have been discussed below along with their variation in the series.

### Atomic Radii, Atomic Volumes and Ionic Radii

It has been observed that the atomic radii of the elements of second transition series, though not known with certainty, decrease from the first element, Y to Rh, the next congener of Co and increase thereafter up to the last element, Cd. The values are very close from Mo to Pd because of the increased screening effect of the 4d electrons which more or less counter balance the nuclear pull exerted on the 5s electrons. Then the screening effect becomes more and more pronounced thereby decreasing the attractive force between the nucleus and the outer electrons. As a result, atomic radii of Ag and Cd are increased. Cd has next highest atomic radius which is only lower than that for Y. These values have been given below:

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Elements | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Atomic radii  (pm) | 162 | 145 | 134 | 130 | 127 | 125 | 125 | 128 | 13  4 | 148 |

The atomic volumes of these elements which are dependent on the atomic radii show the same trend in their variation. The atomic volumes are being listed below:

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Elements | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Atomic  volume (Cm3) | 19.8 | 14.0 | 10.8 | 9.4 | - | 8.3 | 8.3 | 8.9 | 10.3 | 13.0 |

For Tc its value has artibrarily been calculated but is not known with certainty. The values decrease from the first element, Y, upto Rh and then increase due to the obvious reason, i.e. increasing atomic radii values.

The ionic radii follow almost the same trend as the atomic radii at least for the few elements. These elements form ions of variety of oxidation states but only those ions may be considered which bear the same charge. This analogy does not apply to the ions of these elements. For various ions, the ionic radii are listed here:

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Ions | Y3+ | Zr4+ | Nb5+ | Mo4+ | Tc4+ | Ru3+ | Rh3+ | Pd2+ | Ag+ | Cd2+ |
| Ionic radii  (pm) | 104 | 86 | 70 | 79 | - | 81 | 80 | 80 | 123 | 97 |

As is evident from this table, ionic radii values are showing an irregular trend particularly for the later elements.

### Melting and Boiling Points

The melting and boiling points of these elements are generally very high, almost similar to those of the elements of first transition series except for a few elements which have very high values, e.g., Nb to Ru (see the table given below). The last element Cd, has exceptionally low value of melting point even lower than that of Zn. This may be attributed to its high atomic volume, almost one and half times to that of Zn. This results in weaker metallic bonding in the metal lattice of Cd. Melting point values of these elements are as follows:

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Melting point  (0C) | 1490 | 1860 | 2415 | 2620 | 2200 | 2450 | 1970 | 1550 | 960 | 321 |

The highest melting point is for Mo followed by Ru and other elements have comparable values of melting point. Cd has the lowest value. These elements have very high boiling points, greater than 22000C except for Cd (7650C).

### Ionization Energies and Reactivity

The first ionization energies of these elements generally increase from the first element to the last one with a marked drop in the value for Ag. The values are listed below:

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | Y | Zr | Nb | Mo | Tc | Ru | Ph | Pd | Ag | Cd |
| First ionization  energy (kJ/mol) | 636 | 669 | 664 | 694 | 698 | 724 | 745 | 803 | 732 | 866 |

These high values of first ionization energies can be correlated with the values of atomic radii which generally decrease along the series and the screening effect increases; therefore, the elements accordingly have higher values. For Ag low value is attributed to slightly higher atomic radius and availability of a single 5s electron. Appreciably higher value of ionization energy for Cd is due to the stability associated with filled 4d and 5s subshells (4d105s2).

As discussed in section 1.3 above, various factors are responsible for low reactivity of the elements of second transition series. They are even less reactive than those of the first transition series.

### Standard Electrode Potentials and Reducing Properties

As is well known that the standard electrode potential (reduction) is related with the reducing properties of the elements, in general. Metals with negative values of standard electrode potential as compared to standard hydrogen electrode for which E0 value is taken as zero, act as reducing agents. Such metals can displace hydrogen gas from dilute acids. For the metals with negative E0 values but not reacting with acids, some other factors also play an import role such as formation of protective coating on the metal surface and making it unreactive. Strong reducing properties of metals make them displace other metal ions from their solutions. Though standard electrode potential values are available only for a few elements of this series, these are given below:

Cd2+ + 2e → Cd, E0 = - 0.40 V (can displace H2 from dilute acids) Ag+ + e → Ag, E0 = + 0.80 V (does not react with dilute acids)

From the above, it can be concluded that Cd2+ ions can give up the electrons and act as reducing agents while Ag+ ions do not give the electrons, rather take up the electrons easily. Hence, act as oxidizing agents when react with reducing ions, e.g.,

Zn + 2Ag+ → Zn2+ + 2Ag.