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**B.Sc. 2nd Year**

**Inorganic Chemistry Paper-I**

**UNIT-I**

**Chapter 2**

**PART-I**

**CHEMISTRY OF THE ELEMENTS OF SECOND ANDTHIRD TRANSITION SERIES**

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**CHEMISTRY OF THE ELEMENTS OF SECOND ANDTHIRD TRANSITION SERIES**

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 **Introduction**

The second and third transition series contains ten elements in each. These elements have not been extensively studied as those of the first transition series elements. The elements of this series showed quite similar chemical properties but due to variation in electronic configurations some differences observed in chemistry of these elements.

 **Occurrence**

Most of these elements are rare and found in minor constituents in the ore of another elements. They are extracted from the sludges of other ores.

 **General characteristics of second and third transition series**

 **Electronic configuration:**

Similar to first transition series in atoms of these elements 4d and 5d sub-shell of penultimate shell are regularly filled. **The general valence shell electronic configuration of the elements can be written as** **(n-1) d1-10 nso.-2**  and **(n-1) d1-10 ns1.-2** which are given below for second and third transition series. It is remarkable to mention here that much more irregular electronic configuration shown by second transition series elements than third series. In the 2nd series nearly six elements has irregular electronic configuration. **The electronic configuration of Mo, Ag and Au can be explained on the basis of half field and completely filled.** But it is not easy to explain other elements on the basis of this fact .It is probably due to higher atomic number, force of attraction, repulsive forces, exchange energy forces, etc. There is no exact and clear explanation for irregular configuration of 4d and 5d series elements. **Electronic configuration of tungsten(W) is not easy to explain why it have 5d4  not 5d5  configuration.** Table -1 Electronic configuration of second (4d) series

|  |  |  |  |
| --- | --- | --- | --- |
| Elements  | At. No | symbol | Electronic configuration |
| **Yttrium****Zirconium****Niobium****Molybdenum****Technetium****Ruthenium****Rhodium****Palladium****Silver** **Cadmium** | 39404142434445464748 | **Y****Zr****Nb****Mo****Tc****Ru****Rh****Pd****Ag****Cd** | 1s2, 2s2, 2p6, 3s2, 3p6,3d10 4s2, 4p6, 4d1, 5s21s2, 2s2, 2p6, 3s2, 3p6, 3d10 4s2, 4p6, 4d2, 5s21s2, 2s2, 2p6, 3s2, 3p6, 3d10 4s2, 4p6, 4d4, 5s11s2, 2s2, 2p6, 3s2, 3p6, 3d10 4s2, 4p6, 4d5, 5s11s2, 2s2, 2p6, 3s2, 3p6, 3d10 4s2, 4p6, 4d5, 5s21s2, 2s2, 2p6, 3s2, 3p6, 3d10 4s2, 4p6, 4d7, 5s11s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6, 4d8, 5s11s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6, 4d10, 5s01s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6, 4d10, 5s11s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6, 4d10, 5s2 |

**Table- 2 Electronic configuration of third (5d) series**

|  |  |  |  |
| --- | --- | --- | --- |
| **Elements** | At. No | **symbol** | Electronic configuration |
| **Lanthanum****Hafnium****Tantalum****Tungsten****Rhenium****Osmium****Iridium****Platinum****Gold** **Mercury** | 57727374757677787980 | **La****Hf****Ta****W****Re****Os****Ir****Pt****Au****Hg** | 1s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,4d10, 5s2, 5p6,5d1,6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d2, 6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d3, 6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d4, 6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d5, 6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d6, 6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d7, 6s21s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d9, 6s11s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4d10, 5p6, 4f14, 5d10, 6s11s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2, 4p6,5s2, 4 d10, 5p6, 4f14, 5d10, 6s2 |

 **Metallic character:** The elements of these two series are metals due to presence of one or two electrons in their valence shell. Likewise, other metallic elements, they can lose these electrons easily because of low ionization energy values. They are good conductor of heat and electricity, ductile and malleable and forms alloys with other metals due to metallic bonding. Gold and silver are exceptionally high electrical and thermal conductivities Covalent and metallic bonding exist between the atoms of these elements. Covalent bonding makes harden and increase on the number of d-electrons increase. Three types of structures i.e. face centred cubic (fcc), hexagonal close packed (hcp) and body centred cubic (bcc) exhibited by these elements. Cadmium and mercury have no unpaired electrons and they are soft and exist in liquid state. Their softness is due to their crystal structure (fcc) in which large number of vacant places are present. This leads to deformation in crystal lattice.

 **Atomic and Ionic Radii**

**A regular decrease in atomic and ionic radii observed with increase in atomic numbers in the period from left to right.** But the size increases from the second to third transition series is almost very less. **This is due to the inclusion f-subshell and lanthanide contraction in 5d series.** Whereas, in general for a given series a regular decrease in atomic radii is seen as the atomic number increases and very little after middle due to screening effect and then increases towards ends of series is due to repulsion in between electron because presence of d10 full field orbital. The following table 2.3 show the atomic and ionic radii values ( in +2and+4 oxidation states) for compression.

 **Table -3 Atomic Radii and Ionic Radii in +2 and +4 (A0):**

 **First Transition Series(3d)**

Elements: **Sc**  **Ti** **V**   **Cr**   **Mn** **Fe**  **Co**  **Ni**  **Cu** **Zn**

Atomic Radii : 1.44 1.32 1.22 1.18 1.17 1.17 1.16 1.15 1.17 1.25

Ionic Radii (+2): 0.95 0.90 0.88 0.74 0.80 0.76 0.74 0.72 0.69 0.77

 **Second Transition Series(4d)**

Elements: **Y**   **Zr** **Nb**  **Mo**  **Tc** **Ru**  **Rh**  **Pd**  **Ag**  Cd

Atomic Radii: 1.62 1.45 1.34 1.29 - 1.25 1.25 1.28 1.34 1.48 Ionic Radii (+4) : - 0.79 0.74 0.69 - 0.67 - 0.69 - -

 **Third Transition series(5d)**

Elements:  **La** **Hf**   **Ta**  **W** **Re**  **Os**  **Ir** **Pt**  **Au** **Hg**

Atomic Radii: 1.69 1.44 1.34 1.34 1.30 1.28 1.26 1.29 1.34 1.47

Ionic Radii (+4): - 0.78 - 0.70 0.72 0.69 0.68 0.65 - -

**Reactivity:** The elements of these series are less reactive due to their high ionization energy and high heat of sublimation and low hydration energy. Gold and platinum are least reactive among the two series elements.

 **Stability of complexes**

The elements form complex salt owing to presence of small highly charged ions i.e. high positive charge density with vacant d-orbitals that accommodate lone pair electrons. The elements of first transition series are labile towards N, O and F atoms containing donor groups, whereas second and third series elements form stable complexes with P, S and heavier chalcogen donors.

 **Formation of complex with coordination number**

Complex with coordination number more than six are common for second and third transition series as compared with maximum coordination number i.e. six for first transition series. This is observed only for smaller ligands due to less repulsion and allows highest coordination number. Thus, there is mono capped octahedron, pentagonal bipyramidal, trigonal prism geometry in this case is observed. The pentagonal biprism geometry is adopted in [ZrF7], [VF7] and [UO2F5]5-. However, coordination number greater than seven are also known in Na3[Mo(CN)8] and [Mo(CN)8] ( given in 1st chapter).

 **Magnetic properties**

Magnetic properties arise due to presence of unpaired electrons while those having no unpaired electrons or vacant d-orbital i.e. d0, are diamagnetic. All the transition metals are found to be paramagnetic except those which have no unpaired electrons i.e. in paramagnetic substance presence of unpaired electron in d-orbital is compulsory. For example, in II and III series Cd and Hg are diamagnetic due to presence of paired electrons i.e. d10 configuration. Paramagnetic behaviour arises due to interaction of unpaired electrons to the applied magnetic field, which is aligned with external magnetic field. Thus, samples to be attracted into the magnetic field further and the interaction of the spin and orbital angular momentum results the magnetic moments of the one atom or ion related to the total spin quantum number (S) and total orbital angular quantum numbers (L). This can be represented as:

 **µS+L =g** $√$ **4S(S+1) + L (L+1)**

where g is the gyromagnetic ratio having a value 2.00023. Thus, now above expression may be written as:

 **µS+L =** $√$ **4S(S+1) + L (L+1)**

Now, if the orbital angular momentum is quantized so that 4S(S+1)>>>L(L+1) then

 **S= 4S(S+1) or µ =** $√$ **n(n+2) BM** , here µ is magnetic moment and n is the no.of unpaired electron. **BM=Bohr Magneton.**

 This represent the spin only value of magnetic moment for total number of unpaired electron present in any species and this value is found to be a good agreement with observed value. This value is generally found less than or equal to observed value.

 In transition metal complex having octahedral geometry, the number of unpaired electron result either in a low spin or high spin depends upon the strength of ligands. If ligand possesses a strong field, they create a large energy difference between t2g and eg orbitals. If the energy difference is high the electron remained occupy in t2g energy level and complexes are case of low spin. Whereas on the other hand if the ligand possesses weak field, then create a small energy difference between t2g and eg orbitals. Such complexes are called high-spin complexes. Thus, it is generally found that with elements of first transition series depending on the strength of ligands, form both high or low spin complexes. Whereas elements of second and third transition series prefer to form low-spin complexes irrespective of the ligand field strength.

 **Catalytic properties**: Many transition metal complexes among second and third transition series possess good catalytic activity; palladium platinum, molybdenum, silver, tungsten etc. are used as catalyst in different chemical reactions. On the basis of their variable valency they can form unstable intermediate compound and regenerated. They also provide a surface area for the reactants to be absorbed so that products are readily formed.

 **Oxidation state**

The elements of 4d and 5d transition series show variable oxidation state along with increasing atomic number for the left side of the elements than the for the right half of the members. As compared to first series elements they exhibit higher common oxidation number. Stability of oxidation state depends upon the combining elements of these metals. Fluorine and oxygen stabilises the highest oxidation number for these elements due to small size and high electronegativity.

**Table- 4 Various most common oxidation states of second transition series**

|  |  |
| --- | --- |
| **Elements** | **Most common Oxidation state** |
| YttriumZirconiumNiobiumMolybdenumTechnetiumRutheniumRhodiumPalladiumSilverCadmium | +3 +3, +4 +2, +3, +4, +5 +2, +3, +4, +5, +6 +4, +5, +7 +2, +3, +4, +5, +6, +7, +8 +2, +3, +4, +5, +6 +2, +3, +4, +5, +6 +1, +2, +3 +2  |

**Table-5 Various most common oxidation states of third transition series**

|  |  |
| --- | --- |
| **Elements** | **Most common Oxidation state** |
| LanthanumHafniumTantalumTungstenRheniumOsmiumIridiumPlatinumGoldMercury | +3+3, +4+2, +3, +4, +5 +2,+3, +4, +5, +6, +2, +3, +4, +6, +7+2, +3,+4 +6, +8+2, +3, +4, +6+1, +2, +4,+5,+6+1, +3+1, +2 |

**From the observation of the above table following point may be noted:**

(**a)** Oxidation state number +2 and +3 are most common and stable state in first transition series. But the oxidation states +5 and +3 are more common and stable oxidation number in second and third transition series.

(**b)** Tungsten, rhenium and platinum show high oxidation state in their compounds; WCl6, ReF7 and PtF6 but there is no such compound in first transition series.

**(c)** Cr, Mo, and W all form the oxides with (VI) oxidation state in their compound; CrO3 is highly oxidizing nature but MoO3 and WO3 does not show such oxidizing properties.

**(d)** Lower oxidation number (+2 and +3) forms generally ionic compounds whereas the high oxidation number; the bonds are generally covalent in nature.

 **Ionization Energy**: The ionization energy is the amount of energy required to remove loosely bonded electron from outer most (lowest energy) orbital of the gaseous atom. It is observed that the ionization energy of d-block elements is higher than the s-block elements and lesser than p-block elements. These elements showed a rapid increase in third ionization energy than first and second ionization energy. There is a general increase of second and the third series of transition element in their third ionization energy. But it was observed that a discontinuation in the value after manganese, because of doubly occupied d- orbital. For example; Fe (Z=26) is 3d6 4s2. On the other hands from iron to zinc element the ionization energy is found lower because of increasing inter electron repulsion in the same orbital.

 The ionization energy of the third transition series is rather more than the first and second series element due to lanthanide contraction. The atomic radii of these two series are almost same but their atomic number differs by 32.

 Thus, the ionization energy increases from left to right across the first, second and third transition series.

 **Spectral properties:** The elements of second and third transition series show transition of electrons from t2g to eg energy set. This is called d-d transition or ligand field transition. Thus, absorption of energy by the complex compounds or ions gives specific spectrum due to d-d electron transition. The colour of the transition elements depends on number of unpaired electrons in the d-orbital. The elements that have completely vacant or filled d-orbitals i.e. d0 and d10 configuration are colourless. There is no possibility of d-d transition in such cases. Further the appearance of colours of these elements may arise due to charge transfer spectra beside d-d transition. The colour of the second and third transition series elements is due to the two major reasons. Firstly, splitting of 4d and 5d orbitals is larger as compared to 3d orbitals and in order of 5d>4d>3d. Secondly, the colour of the complexes is developed by the crystal defect also in addition to d-d transition and charge transfer.

 In transition elements the spectra arise due to the excitement of electron from one energy level to another energy level. When light falls on a complex, they absorb the visible region of electromagnetic radiation of wave length 4000 A0to 7000 A0. By measuring this absorption by spectrum, colour of the complex can be predicted we can understand by the spectrum of [Ti(H2O)6]3+ complex. This compound absorbs in 3100 cm-1 and 5000 cm-1gives two spectral bands at this frequency. Consequently, it shows violet colour of this complex and it can be shown as:

 

 **Fig. d-d transition in [Ti (H2O)6] 3+ complex.**