UNIT-IV
Transition and Inner transition elements

POINTS TO REMEMBER:

1. Atomic Radius $\alpha \frac{1}{\text{Nuclear Charge}}$

2. Ionic Radius $\alpha \frac{1}{\text{Nuclear Charge}}$

3. Ionisation Energy $\alpha \frac{1}{\text{Shielding effect}}$

4. Nuclear Charge $\alpha$ Ionisation Energy

5. Shielding Effect: Force of attraction experienced by the valence electrons is less than that experienced by inner electrons. Thus, the outermost electrons are shielded or Screened from the nucleus by inner electrons. $s>p>d>f$

6. a) On moving across a period, Atomic radius decreases
   
   b) On moving down a group, Atomic radius increases.
1. What are transition elements? Give four examples.

An element whose atom has an incomplete d subshell or which can give rise to cations with an incomplete d subshell. They occupy the central position between s and p block elements. Example: Iron, Copper, Titanium, Zinc etc.

2. Explain the oxidation states of 4d series elements.

The oxidation state of 4d metals vary from +3 for yttrium and +8 for ruthenium. The highest oxidation state of 4d elements are found in their compounds with the higher electronegative elements like O, F, Cl. For example: RuO4.

3. Explain why compounds of Cu²⁺ are coloured but those of Zn²⁺ are colourless?

i) Cu²⁺ has 3d⁹ 4s⁰ configuration and it has one unpaired electron. Hence, the compounds of Cu²⁺ are coloured.

ii) Whereas, Zn²⁺ has 3d¹⁰ 4s⁰ configuration and it has no unpaired electrons. Hence, the compounds of Zn²⁺ are colourless.

4. Which is more stable? Fe²⁺ or Fe³⁺ Explain.

Comparing Fe²⁺ and Fe³⁺ ions, Fe²⁺ ion has 3d⁶ electronic configurations with four unpaired electrons whereas, Fe³⁺ ion has 3d⁵ partially filled orbital or half filled orbital. Due to the symmetrical distribution of electrons in 3d subshell, Fe³⁺ is more stable.

5. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

Electronic configuration of Cu= [Ar] 3d¹⁰ 4s¹. When copper atom loses 1electron in 4s orbital and exhibits +1 oxidation state forms Cu⁺ ion. Hence, Copper in the 3d series tends to +1 oxidation state most frequently for achieve stable electronic configuration.

6. Why do zirconium and Hafnium exhibit similar properties?

Zirconium and Hafnium are 4d and 5d series respectively. As the electrons added to the 5d subshell, the atomic radius of 5d elements are higher than those of the 4d series. However, an atomic radius of 5d elements nearly same as that of corresponding 4d elements. This is due to lanthanide contraction.

7. Transition metals show high melting point. Why?

Most of the transition elements are hexagonal close packed, cubic close packed or body centered cubic which are the characteristics of true metals. As we move from left to right along the transition metal series, the number of unpaired electrons available for metallic bonding increases, reach high melting point.
8. Why first ionization enthalpy of chromium is lower than that of Zinc?

Chromium has 3d⁴ 4s¹ configuration and Zinc has 3d¹⁰ 4s¹ configuration. Due to most stable electronic configuration of zinc, the first electron has to remove from completely filled orbital require more energy. Hence, first ionization enthalpy of chromium is lower than that of zinc.

9. Compare the ionization energy of first series of the transition elements.

The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular. The irregular trend in 3d series due to the fact that the removal of electrons from 4s and 3d changes with relative energies. That is the number of electrons added to (n-1) d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on ns electrons with increase of dⁿ configuration and also form the transference of s-electrons into d-orbitals.

Therefore, scandium has low ionisation energy and very small difference in energies seen up to chromium. Because loss of one electron gives stable configuration 3d⁵ while Zinc has very high ionisation energy because electron has to be remove from 4s orbitals of stable 3d¹⁰ 4s² configuration.

10. Explain briefly how +2 oxidation states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

Except Scandium, all other metals show +2 oxidation state. On moving from Sc to Mn, the atomic number increases from 21 to 25. That is the number of electrons in 3d orbital also increases from Sc to Mn.

Sc²⁺ = d¹, Ti²⁺ = d², V²⁺ = d³, Cr²⁺ = d⁴, Mn²⁺ = d⁵

The oxidation state is attained by the loss of two 4s electrons. Since the number of d electrons in +2 states also increases from Ti²⁺ to Mn²⁺ and the stability increases due to d-orbital becomes more and more half filled. Hence, d⁵ configuration of Mn²⁺ is highly stable.

11. Calculate the number of unpaired electrons and spin only magnetic moment for 3d series of transition elements. (Refer text book; Page no: 110)

**NOTE:** Bohr Magneton \( \mu_B = \frac{e}{2m} \sqrt{n(n+2)} \). The orbital moment L is said to be quenched, the magnetic moment said to be \( \mu = g \sqrt{S(S+1)} \mu_B \)

12. Why do transition metals have paramagnetic properties?

Transition elements have available number of unpaired electrons can form paramagnetic compounds. The electrons are spinning around its own axis, in addition to its orbital motion around the nucleus. Due to this motion, a tiny magnetic field is generated and it is measured in terms of magnetic moment.
13. **Explain the catalytic properties of transition elements with example.**

Many industrial processes use transition metals or their compounds as catalysts. Transition metal has available number of d orbitals that can accept electrons from reactant molecule or metal can form bond with reactant molecule using its d- electrons. In the catalytic hydrogenation of alkenes, the active site of \( \pi \) electrons with an empty d-orbital of the catalyst.

For example,

i) Ni used in Hydrogenation of alkenes,

ii) \( \text{V}_2\text{O}_5 \) used to oxidize \( \text{SO}_2 \)

iii) \( \text{Co}_2(\text{CO})_8 \) used in hydroformylation of olefins

iv) Rh/Ir complex is used to prepare acetic acid from acetaldehyde.

v) \( \text{TiCl}_4 + \text{Al} (\text{C}_2\text{H}_5)_2 \) – Ziegler Natta Catalyst is used for polymerization.

14. **What are the conditions to form an alloy?**

Consider the bulk metal is named as solvent and the small portions are solute.

i) According to Hume-Rothery the difference between the atomic radii of solvent and solute is less than 15%.

ii) Both the Solvent and solute must have the same crystal structure.

iii) The valence and their electronegativity must close to zero.

15. **Why do transition elements form interstitial compounds?**

Transition metals form interstitial compounds because; there are vacant spaces or interstitial holes in the crystal lattice of transition metals which can be filled by small atoms like H, C, and N etc.

16. **Why transition metals form complex compound?**

i) Transition metal ions are small and highly positive charged.

ii) They have vacant low energy orbitals to accept an electron pair donated by other groups.

17. **Out of \( \text{Lu(OH)}_3 \) and \( \text{La(OH)}_3 \), which is more basic. Why?**

Due to lanthanide contraction, the size of lanthanide ions decreases from \( \text{La}^{3+} \) to \( \text{Lu}^{3+} \). The covalent character of the hydroxides increases and hence the basic strength decreases. \( \text{La(OH)}_3 \) is more basic and \( \text{Lu(OH)}_3 \) is less basic.

18. **Why Europium (II) is more stable than Cerium (II)?**

As we move from left to right along a period, the effective nuclear charge increases due to which lanthanide contraction takes place. The inert pair effect makes more stable and it has 4f half filled subshell makes more stable toward Europium. Most of the lanthanides are stable in +3 oxidation state.
19. Why Gd$^{3+}$ is colourless?
Gd has [Xe] 4f$^7$5d$^1$6s$^2$. Gd$^{3+}$ ion has extra stability due to the fact that has half filled 4f orbital. Hence no electron in outer 5d orbital gets excited.

**NOTE:** There will be no absorption with visible light for these electrons so the Gd$^{3+}$ is colourless.

20. Actinoid contraction is greater from element to element than the lanthanoid contraction. Why?
In lanthanoid, electrons filling in 4f subshell while in Actinoid electrons filling in 5f subshell. Thus the effective nuclear charge experienced by electrons in valence shell in Actinoid is higher than Lanthanoid. Hence, Actinoid contraction possesses greater magnitude compare to lanthanoid due to poor shielding effect of 5f orbital than 4f orbital.

21. Explain the variation in $E^\circ$ M$^{3+}$/M$^{2+}$ - 3d series.

The variation of electrode potential is due to ionisation enthalpy. All those elements with negative reduction potential act as strong reducing agent. The values of reduction potential for Ti, V, Cr are more negative indicate that the higher oxidation state. For Mn$^{3+}$/Mn$^{2+}$ the Mn$^{3+}$ is more stable than Mn$^{2+}$ due to half filled subshell and for Fe$^{3+}$/Fe$^{2+}$ the Fe$^{3+}$ is extra stability due to half filled d$^9$ configuration. But in case of Copper, the elemental copper is more stable than Cu$^{2+}$ due to stable configuration.

22. Which is stronger reducing agent? Cr$^{2+}$ or Fe$^{2+}$

On the basis of standard electrode potential, Fe$^{3+}$/Fe$^{2+}$, $E^\circ = 0.77V$. Whereas the standard electrode potential for Cr$^{3+}$/Cr$^{2+}$, $E^\circ = -0.41V$. The negative signs indicate that the higher oxidation state is preferred. That is strong reducing agent which has high negative value for reduction potential and loses electron easily.

23. Explain why Cr$^{2+}$ is strongly reducing agent while Mn$^{3+}$ is strongly oxidising agent.

$E^\circ$ value of Cr$^{3+}$/Cr$^{2+}$ is negative while that of Mn$^{3+}$/Mn$^{2+}$ is positive, this means Cr$^{3+}$ ion has 3d$^4$ can lose electrons to form Cr$^{2+}$ ion with d$^5$ half filled in $t_{2g}$ orbital makes stable and act as a reducing agent, while Mn$^{3+}$ ion with d$^5$ configuration gets converted to Mn$^{2+}$ with d$^6$ configuration giving half filled d-orbital makes stable and act as oxidising agent.

**NOTE:**

a) Both Mn$^{3+}$ and Mn$^{3+}$ have 3 $t_{2g}$ electrons and e$\bar{g}$ electrons
b) In case of Cr, neither Cr$^{3+}$ nor Cr$^{2+}$ has half filled d subshell. That is, Cr$^{3+}$ has 3 electrons while Cr$^{2+}$ has 4 electrons.

24. The $E^\circ$ M$^{2+}$/M value for copper is positive. Suggest a possible reason for this.

$E^\circ$ M$^{2+}$/M of metal depends on the energy changes involved in which molecular hydrogen under standard pressure and temperature is oxidised to solvated protons at the electrode. Copper has high energy of atomization (Enthalpy of atomization is the energy involved when separation of all atoms from its chemical composition) and low hydration energy (Energy released when one mole of ions are hydrated or solvated). Hence, the $E^\circ$ value for copper is positive. (Note: $E^\circ$Cu$^{2+}$/Cu = +0.34)
Other important Questions

1. Complete the following reaction Types. (Refer all the Reactions)
2. Lanthanide contraction and its causes.
3. Compare Lanthanides and Actinides
4. Justify the position of Lanthanides and Actinides in the periodic table

The lanthanoid include elements 58 to 71 is at Group number 3 and Period number 6 whereas Actinoid include elements 89 to 103 is at Group number 3 and Period number 7. These two rows are produced when electrons are preferentially filled in inner 4f and 5f subshell respectively. Also the properties of elements belongs to a group would be different and it would affect the proper structure of periodic table. Therefore, these elements are grouped together and placed at the bottom of the periodic table.

5. Describe the variable oxidation states of 3d series elements.

The transition metals have valence electrons in (n-1) d and ns orbitals. Since, there is very little energy difference between these orbitals, both energy levels can be used for bond formation. Thus, transition elements exhibit variable oxidation states.

At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state is stable. The number of oxidation state increases with number of unpaired electrons available, and it decreases as the number of paired electrons increases. Hence, the first and last elements show less number of oxidation states and the middle elements with high oxidation states. Example, the first element Sc has only +3, while Mn has +7 oxidation state.

The maximum oxidation state exhibited by transition metals of 4d and 5d such as Ru and Os have +8 is found in RuO₄, OsO₄.

Reference of Frost diagram, Ti, V and Cr are most thermodynamically stable oxidation state is +3. Fe has +2 and +3 oxidation states are similar. Cu has +1 oxidation state.

The relative stability of different oxidation states of 3d metals are correlated with the extra stability of half filled and fully filled electronic configuration.

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