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UNIT NO.4 TRANSITION ELEMENTS AND INNER TRANSITION ELEMENTS

- * TRANSITION ELEMENTS:

- (i) Introduction:
- (ii) Position of d – block elements in the periodic table.
- (iii) Electronic configuration

- * GENERAL TRENDS IN PROPERTIES:

- (a) Metallic behaviour
- (b) Variation of atomic and ionic size
- (c) Ionization enthalpy
- (d) Standard electrode Potential of Transition metals
- (e) Magnetic properties
- (f) Catalytic Properties

GENERAL TRENDS IN PROPERTIES

* METALLIC BEHAVIOUR:

- (i) All the Transition elements are Metals.
- (ii) Most of the Transition elements are HCP, CCP or BCC which are the characteristics of TRUE metals. The Figure 4.2, shows lattice Structures of 3d, 4d and 5d transition metals.
- (iii) Variation in melting point of 3d series elements. Graph shows (K) Vs 3d series elements.
- (iv) The maximum melting point at about the middle of Transition metal series indicates that d⁵ configuration is favourable for strong interatomic attraction.

VARIATION OF ATOMIC AND IONIC SIZE

* In Fig.4.4(a) ATOMIC RADIUS OF 3d ELEMENTS

(i) As we move from Sc to Zn in 3d series the extra electrons are added to the 3d orbitals, the added 3d electrons only partially shielded the increased nuclear charge and effective nuclear charge increases slightly.

(ii) However, the extra electrons enter added to 3d subshell strongly repel the 4s electrons and these two forces are operated in opposite direction and they tend to balance each other, it leads to constancy in atomic radii.

(iii) Figure 4.4(a) graph shows Atomic number in x-axis, and Atomic radius in y – axis.

VARIATION OF ATOMIC AND IONIC SIZE

- * In Figure 4.4(b), Graph Atomic number in x – axis, and Atomic radius in y – axis
- * The graph shows radius of 4d elements
- * At the end of the series, d – orbitals of Zn contain 10 electrons in which repulsive interaction between the electrons is more than the effective nuclear charge .
- * Hence the orbitals slightly expand and atomic radius slightly increases.

VARIATION OF ATOMIC AND IONIC SIZE

- * In Figure 4.4© Atomic radius of 5d elements Atomic number taken as x-axis, and Atomic radius taken as y – axis.
- * As we move down the group atomic radius increases the same trend is expected in d-block elements.
- * As the electrons are added to the 4d subshell, the atomic radii of the 4d elements are higher than the corresponding elements of the 3d series
- * There is an unexpected observation in the atomic radius of 5d elements which have nearly same atomic radius of corresponding 4d elements. This is due to Lanthanide contraction.

IONIZATION ENTHALPY

- * As we move from left to right in a transition metal series, the ionization enthalpy increases as expected.
- * This is due to increase in nuclear charge corresponding to the filling of d-electrons. The following Graph shows Figure 4.5 Variation of ionization energy of 3d series elements. The graph shows x-axis variation in I.E. and y-axis kJ.mol^{-1} .
- * The Ionization enthalpy values can be used to predict thermodynamically stability of their compounds.
- * For an example Nickel, and Platinum.

OXIDATION STATE

- * The first transition metal Scandium exhibits only +3 oxid. state but all other transition elements exhibit variable oxidation state by losing electrons from (n-1) d – orbital and ns orbital as the energy difference between them is very small.
- * No. of. Oxid. state increases with no. of. electrons available and it decreases as no. of paired electrons increases.
- * Generally going down a group a stability of the higher oxid. state increases while the lower oxid. state decreases. It is evident from the Frost diagram [ΔG is shown below]
- * For Titanium, Chromium, and Vanadium the most thermodynamically stable is +3. For Iron, the stabilities of +3 and +2 oxidation states are similar.
- * For Copper is unique in 3d series having a stable +1 oxidation state,
- * It is prone to disproportionate to the +2 and 0 oxidation states.

STANDARD ELECTRODE POTENTIALS OF TRANSITION METALS

- * The substance which is oxidised is reducing agent and the one which is reduced is an oxidising agent. The oxidizing and reducing power of an element measured in terms of Standard electrode potentials.
- * E° [Std. electrode potential] of metals large and negative the metal is a "POWERFUL REDUCING AGENT" BECAUSE IT LOSES ELECTRONS easily.
- * In the general trends the figure shows that $[E^\circ M^{2+}/M]$ Figure 4.7(a) Metal negative value Vs Std. red. Potential-3d-series.
- * Value for manganese and Zinc are more negative than the regular trend.
- * It is due to extra stability which arises due to the half-filled d^5 configuration in Mn^{2+} and completely filled d^{10} configuration in Zn^{2+} . The std. electrode potential for the M^{3+}/M^{2+} half cell gives the relative stability between M^{3+} and M^{2+} .
- * It is shown in the figure 4.7(b) the high reduction potential of Mn^{3+}/Mn^{2+} , Indicates Mn^{2+} is more stable than Mn^{3+} .
- * Mn^{3+} has $3d^4$ configuration while, that of Mn^{2+} is $3d^5$ configuration.
- * The extra stability associated with a half-filled d-subshell makes the reduction Mn^{3+} very feasible. $[E^\circ = + 1.51V]$.

MAGNETIC PROPERTIES

- * Magnetic ,Paramagnetic, and Ferromagnetic.
- * The Magnetic moment formula:
- * $\mu = g \sqrt{S(S+1)} \mu_B$
- * S = Spin quantum number of unpaired electron.
- * μ_B = Bohr Magneton.
- * g = electron. Here $S = n/2$; $g = 2$
- * $\mu = 2\sqrt{(n/2).(n/2 + 1)} \mu_B$
- * $\mu = 2\sqrt{[n(n+2)/4]} \mu_B$
- * $\mu = \sqrt{n(n+2)} \mu_B$

CATALYTIC PROPERTIES

- * Catalyst based Manufacturing process are advantageous. It enhance the conversion of reactants and products.
- * In certain Catalytic process the variable oxidation state of transition metals and find applications.
- * Hydroformylation of Olefins,
- * Prep. Of Acetic acid from acetaldehyde.
- * Ziegler-Natta catalyst.

ALLOY FORMATION

- * ALLOY – Definition

- * HUME ROTHERY RULE :

To form a substitute Alloy the difference between the atomic radii of solvent and solute is less than 15%.

Both the solvent and solute must have same crystal structure and valence and their electronegativity difference must be close to zero.

- * TRANSITION METALS: Satisfying these mentioned conditions form a number of alloys among themselves , since their atomic size are similar and one metal atom can be easily replaced by another metal from its crystal lattice to form an alloy.

- * The alloy so formed are hard and often have high melting points.

- * Examples : Ferrous alloys, gold – copper alloy, chrome alloys etc.

FORMATION OF INTERSTITIAL COMPOUNDS & COMPLEXES

- * FORMATION OF INTERSTITIAL COMPOUNDS:
 - * An interstitial compounds or alloy is a compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes in a metal lattice.
 - * They are usually non-stoichiometric compounds.
 - * Examples : TiC, ZrH, Mn₄N etc.
 - * PROPERTIES OF INTERSTITIAL COMPOUNDS:
 - (i) They are hard and show electrical and Thermal conductivity.
 - (ii) They have high melting point higher than those of pure metals.
 - (iii) Transition metal hydrides are used as powerful reducing agents.
 - (iv) Metallic carbides are metallic inert.
 - * FORMATION OF COMPLEX:
 - (i) Transition metals are small and highly charged and they have vacant lower energy orbitals to accept an electron pair donated by other groups.
- Eg: [Fe(CN)₆]⁴⁻, [Co(NH₃)₆]³⁺ etc.

IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

- * OXIDES & OXOANIONS OF METALS:

(i) The oxidation number of metal in metal oxides ranges from +2 to +7. As the oxidation number of metal increases, ionic character decreases.

Mn_2O_7 - Covalent ; HMnO_4 – permanganic acid;

CrO_3 gives H_2CrO_4 – Chromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$ – dichromic acid.

- * Generally lower oxides may be amphoteric or basic.

- * For eg: Cr_2O_3 – amphoteric; CrO – basic in nature.

POTASSIUM DICHROMATE

- * PREPARATION:
- * PHYSICAL PROPERTIES:
- * STRUCTURE OF DICHROMATE ION:
- * CHEMICAL PROPERTIES: Oxidation, Chromyl Chloride test.
- * USES:

POTASSIUM PERMANGANATE

- * PREPARATION:
- * CHEMICAL OXIDATION:
- * ELECTROLYTIC OXIDATION:
- * PHYSICAL PROPERTIES:
- * STRUCTURE OF PERMANGANATE ION:
- * CHEMICAL PROPERTIES:
- * BAYER'S REAGENT:
- * USES:

F-BLOCK ELEMENTS – INNER TRANSITION ELEMENTS

- * INTRODUCTION: Lanthanoids & Actinoids
- * POSITION OF LANTHANIDES IN PERIODIC TABLE:
- * ELECTRONIC CONFIGURATION OF LANTHANOIDS:
- * OXIDATION STATE OF LANTHANOIDS
- * CAUSES OF LANTHANOID CONTRACTION
- * CONSEQUENCES OF LANTHANOID CONTRACTION
- * ACTINOIDS
- * ELECTRONIC CONFIGURATION
- * OXIDATION STATE OF ACTINOIDS
- * DIFFERENCES BETWEEN LANTHANOIDS AND ACTINOIDS

NOTE

- * HCl cannot be used for making the medium acidic since it reacts with KMnO_4 as follows.
- * $2\text{MnO}_4^- + 10\text{HCl}^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$
- * HNO_3 also cannot be used since it is good oxidising agent and reacts with reducing agent in the reaction.
- * However, H_2SO_4 is found to be most suitable since it does not react with potassium permanganate.

NOTE

- | * Content | Medium | Value |
|----------------------------|--|-----------------|
| * Eq.Wt.of KMnO_4 | Acid
(no.of.moles of electrons transferred) | $158/5 = 31.6$ |
| * Eq.Wt.of KMnO_4 | Basic
(no.of moles of electron transferred) | $158/1 = 158$ |
| * Eq.Wt.of KMnO_4 | Neutral
(no. of. Moles of electron transferred) | $158/3 = 52.67$ |



THANK YOU