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d&f-block Elements

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## 01. Introduction

All transition elements belong to *d*-block. Zn, Cd, and Hg are not transition elements and are called **non-typical transition elements or pseudo transition elements**. Anhydrous  $\text{FeSO}_4$  and  $\text{CuSO}_4$  are white because of absence of crystal field splitting, though they have unpaired electrons.  $\text{Cu}^{2+}$  ( $3d^9$ ,  $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34\text{V}$ ) is more stable than  $\text{Cu}^+$  ( $3d^{10}$ ,  $E_{\text{Cu}^+/\text{Cu}}^\circ = 0.54\text{V}$ ) except for the cases of large anions, e.g.,  **$\text{CuI}$**  is more stable than  **$\text{CuI}_2$** ,  **$\text{CuCN}$**  is more stable than  **$\text{Cu}(\text{CN})_2$** . Among *d*-block elements tungsten (W, At. No. = 74) has highest m.p. ( $3410^\circ\text{C}$ ) while mercury (Hg, At. No. = 80) has lowest m.p. ( $-38.9^\circ\text{C}$ ).  ${}_{43}\text{Tc}$  was the first artificial element and was named technetium which means **artificial**. **Ionization of transition metals**. Aufbau principle cannot be used to predict electron configuration of atoms on ionization. For example, configuration of Fe based on Aufbau principle is  $4s^2 3d^6$ . Spectral and magnetic studies confirm that configuration of Fe is and not. This shows that in Fe  $3d$  has lower energy than  $4s$  which is contrary to Aufbau principle. In fact on ionization, the number of electrons decreases while nuclear charge remains constant. Thus, the  $3d$ , orbitals become stabilized relative to  $4s$ -orbital when atoms are ionized. In general, in the process of ionization, the first electrons are lost from the subshell with the highest value of  $n$  and if  $n$  is the same then from the subshell with highest value of  $l$ . The absorption of  $\text{H}_2$  by transition metals such as Pt, Pd, Ni etc. is called occlusion and is due to the interstitial hydride formation.

Many transition metal compounds have similar structures e.g.,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . This is due to almost equal ionic sizes of these metals. Such compounds are called isomorphous.

### Magnetic properties of 4d and 5d-transition elements :

We have observed earlier that magnetic properties of the first ( $3d$ ) – transition series elements can be interpreted easily to give the number of unpaired electrons by using the “**spin only**” formula. But the magnetic behavior of the heavier transition elements is more complex to interpret. The  $4d$  and  $5d$ -orbitals being larger in size can easily accommodate two electrons without much loss in stability relative to the  $3d$ -orbitals which are much smaller in size. Thus the crystal field splitting energies in  $4d$  and  $5d$ -orbitals upon complexation will be very large than in the  $3d$ -orbitals. *Therefore, in general, the first transition series ( $3d$ ) elements form mainly high spin (maximum unpaired electrons) complexes while second ( $4d$ ) and third ( $5d$ ) transition series elements always form low spin (spin paired) complexes.*

**Metal-metal bonding.** The heavier transition metals show strong tendency to form *strong M-M bonds* than their light congeners. For example, in  $\text{Re}_2\text{Cl}_8^{4-}$ , there is a strong quadruple bond between Re–Re.

The unique absorptions associated with the *f*-electrons make certain ions of the  $4f$ -series particularly useful in *light filters*. Glass which contains Nd and Pr ions absorb specifically yellow sodium light and so is used in glass **blower’s goggles**. Recently lanthanoids have attracted considerable attention because of their use in *lasers*. Thus, *neodymium oxide dissolved in selenium oxychloride* is one of the *most powerful liquid lasers known so far*. First member of each transition series, i.e., Sc, Y, La and Ac do not show variable valency. They show only +3 oxidation state.

### Colour Compound

Transition metals are coloured due to ***d-d* transition** and **charge transfer transition**.

Colour due to d-d transition is shown by transition metal compounds containing  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^4$ ,  $d^5$ ,  $d^6$ ,  $d^7$ ,  $d^8$ ,  $d^9$ , systems. The compounds containing  $d^0$  and  $d^{10}$  configurations are coloured due to charge transfer transitions as there is no possibility of  $d-d$  transitions. Charge transfer transition always produces **intense colours** since the restrictions of selection rules do not apply to transitions between atoms. MnO ion has an intense purple colour in solution due to charge transfer transition. In MnO, an electron is momentarily transferred from O to the metal, thus momentarily changing O to O and reducing the oxidation state of the metal from Mn (VII) to Mn (VI). Charge transfer transition requires that the energy levels on the two different atoms involved are fairly close. The  $s$ - and  $p$ - block elements do not have a partially filled  $d$  shell so there cannot be any  $d-d$  transitions. The energy to promote an  $s$  or  $p$  electron to a higher energy level is much greater and corresponds to U.V. light being absorbed. Thus, the compound will not be coloured.

### Magnetic moment

The magnetic moment  $\mu_{eff}$  of a transition metal can give important information about the number of unpaired electrons present in the atom and the orbitals that are occupied and sometimes indicates the structure of the molecule or complex. If the magnetic moment is due entirely to the spin of unpaired electrons, then  $\mu_{eff} = \sqrt{4S(S+1)}$  B.M.

Where  $S$  is the total spin quantum number. This equation is related to the number of unpaired electrons  $n$  by the equation  $\mu_{eff} = \sqrt{n(n+1)}$  B.M.

### General points

Lightest transition metal is Sc, heaviest and densest transition element is **Ir**, transition metal having highest melting point is W and having lowest melting point is Hg. The synthetic transition metal is **Tc** while the synthetic lanthanoid is **Pm**. Fe, Co and Ni are called ferrous metals ; Ru, Rh, Pd, Os, Ir and Pt are called platinum metals whereas Cu, Ag and Au are called **coinage metals**.

Iron pyrites is also known as **Fool's gold** ( $\text{CuFeS}_2$ ). Ni can be extracted by or food process. Chromium oxide is also known as chrome green.  $\text{Cr}_2\text{O}_3/\text{C}_3\text{H}_5\text{N}$  or solution of chromic oxide in pyridine is known as **Collin's reagent**.  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  is also known as **Guignet's green**. Zn, Cd and Hg are not expected to form covalent bond amongst themselves, hence they have relatively lower melting point. The +2 oxidation state become more stable while the +3 state become less stable from left to right in the periodic table. For the first four element of a transition series higher oxidation states are more stable than lower oxidation state. For next five-element lower oxidation state are more stable than higher oxidation state. Many transition metal compound are isomorphous e.g.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  because of almost equal ionic sizes of these metals. Lightest transition metal is Sc and heaviest and densest transition element is osmium (Os). Mercurous ion exist as dimer  $\text{Hg}_2^{2+}$  and not as  $\text{Hg}^+$  and this explains its diamagnetic nature. Pt, Pd and Ir are inert metal.  $\text{TiCl}_4$  and  $\text{TiO}_2$  are used in smoke screens. Mo is used in **X-ray tube**, Ta in **analytic weight** and instrument used in **surgery of veins**.  $\text{Fe}^{2+}$  is green and  $\text{Fe}^{3+}$  is yellow.  $\text{Fe}^{3+}$  is powerful oxidizing agent than  $\text{Fe}^{2+}$  ion. Iron carbide or cementite is  $\text{Fe}_3\text{C}$ . **Kipp's base** is  $\text{FeS} + \text{H}_2\text{SO}_4$ . Copper dissolves in an aqueous solution of  $\text{FeCl}_3$ .  $\text{CuSO}_4$  reacts only with KI does not react with KCl, KBr or KF.  $\text{CuCl}_2$  and  $\text{CuBr}_2$  are covalent and exist as polymer while  $\text{CuF}_2$  is an ionic solid. All silver halide except  $\text{AgF}$  are insoluble in water. Ag, Au and Cu are known as coinage metals. Fulminating gold is  $\text{Au}(\text{NH}_2)=\text{NH}$  or  $\text{N}_2\text{H}_3$ . Purple of cassius is a colloidal solution of gold. Mercuric salts are more stable than mercurous salts. All the elements of  $f$ -block are in group 3 of the periodic table. **Schweitzer reagent** is  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ .