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CLASS 12th

d&f-block Elements

misostudy



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 FeSO_4 and 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., **CuI** is more stable than **CuI_2** , **CuCN** is more stable than **$\text{Cu}(\text{CN})_2$** . Among *d*-block elements tungsten (W, At. No. = 74) has highest m.p. (3410°C) while mercury (Hg, At. No. = 80) has lowest m.p. (-38.9°C). ^{43}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 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 μ_{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** ($CuFeS_2$). Ni can be extracted by or food process. Chromium oxide is also known as chrome green. Cr_2O_3/C_5H_5N or solution of chromic oxide in pyridine is known as **Collin's reagent**. $Cr_2O_3.2H_2O$ 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. $FeSO_4.7H_2O$ and $ZnSO_4.7H_2O$ 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 Hg_2^{2+} and not as Hg^+ and this explains its diamagnetic nature. Pt, Pd and Ir are inert metal. $TiCl_4$ and 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**. Fe^{2+} is green and Fe^{3+} is yellow. Fe^{3+} is powerful oxidizing agent than Fe^{2+} ion. Iron carbide or cementite is Fe_3C . **Kipp's base** is $FeS + H_2SO_4$. Copper dissolves in an aqueous solution of $FeCl_3$. $CuSO_4$ reacts only with KI does not react with KCl, KBr or KF. $CuCl_2$ and $CuBr_2$ are covalent and exist as polymer while CuF_2 is an ionic solid. All silver halide except AgF are insoluble in water. Ag, Au and Cu are known as coinage metals. Fulminating gold is $Au(NH_2)=NH$ or N_2H_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 $[Cu(NH_3)_4]SO_4$.

Etard reagent is CrO_2Cl_2 . **Barfoed's reagent** is $\text{Cu}(\text{CH}_3\text{COO})_2 + \text{CH}_3\text{COOH}$. **Milon's reagent** is the solution of mercuric and mercurous nitrate. **Zeigler natta catalyst** is $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$.

Lindlar's catalyst is Pd/BaSO_4 . **Wilkinson's catalyst** is $[\text{Ph}_3\text{P}]_3\text{RhCl}$. **Adam catalyst** is Pt/PtO .

Brown's catalyst is Nickel boride (P-2 catalyst).

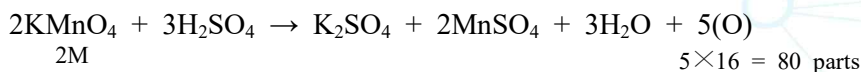
Both Au and Pt are inert and noble metals but they dissolve in aqua regia (3 parts conc. $\text{HCl} + 1$ part conc. HNO_3) due to the formation of H_2PtCl_6 and HAuCl_4 respectively. Finely reduced form of Pt in the form of velvety black powder is called **platinum black**. A mixture of TiO_2 and BaSO_4 is called **titanox** while a mixture of ZnS and BaSO_4 is called **lithopone**. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ are **isomorphous**. Basic copper acetate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2]$ is called **Verdigris** which is used as a green pigment in paints. Copper acetate, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ is **dimeric** in vapour state. Silver is not attacked by **aqua regia** but it reacts with conc. H_2SO_4 and HNO_3 . Mercury does not react with steam or water and hence cannot form any hydroxide. **Rinman's green** is green pigment containing $\text{ZnO} \cdot \text{CoO}$. Zinc sulphate containing trace of radium salt (1 part in 10 million parts) is used as luminous paint for watch dials. Due to high ionic potential (charge/radius ratio), transition metal cations generally undergo hydrolysis in aqueous solution. Most stable oxidation state for Cu is +2, Ag is +1 and for Au is +3. The monovalent Cu^+ , Ag^+ and Au^+ salts are insoluble in water and colourless except Cu_2O which is red. The red colour is due to charge transfer transitions. Most abundant transition metal is iron. Copper is second most useful metal (the first being iron). Mercury is the only transition metal which is liquid at room temperature. This is due to the very high ionization enthalpy making it difficult for electrons to participate in metallic bonding. $\text{K}_2\text{Cr}_2\text{O}_7$ is preferred to $\text{Na}_2\text{Cr}_2\text{O}_7$ for use in volumetric analysis (titrations) because the Na-compound is **hygroscopic** whilst the K-compound is not. Thus, $\text{K}_2\text{Cr}_2\text{O}_7$ can be used as a primary standard. In KMnO_4 titrations, only sulphuric acid is found to be suitable for making the solution acidic because it does not react with KMnO_4 or the reducing agent used. Hydrochloric acid cannot be used in KMnO_4 titrations for acidifying the solution as it reacts with KMnO_4 and introduces an error into the results. $2\text{MnO}_4^- + 10\text{Cl}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$

Nitric acid cannot be used in KMnO_4 titrations as it itself is an oxidizing agent and reacts with reducing agents.

Equivalent mass of KMnO_4 :

Equivalent mass of an oxidizing agent is the number of parts by mass of it which give 8 parts by mass of oxygen or it is the molecular mass divided by the number of electrons gained by one molecule of the substance in a redox reaction. If M is the molecular mass of KMnO_4 ($M = 39 + 55 + 64 = 158$), then we have

(i) In acidic medium



$$\therefore \text{Equivalent mass of } \text{KMnO}_4 = \frac{M}{5} = \frac{158}{5} = 31.6$$