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31.

d AND f-BLOCK ELEMENTS

d-BLOCK ELEMENTS

1. INTRODUCTION

The elements in which the last electron enters (n – 1)d orbitals of the atom are called d-block elements. Also, these elements lie in between s and p block elements in the long form of the periodic table. So, they are also called transition elements.

2. ELECTRONIC CONFIGURATION AND IRREGULARITIES

The valence shell configurations of these elements can be represented by $(n-1)d^{1-10}ns^{0,1,2}$. All the d-block elements are classified into four series viz 3d, 4d, 5d and 6d orbitals of (n – 1)th main shell. Each series has 10 elements. Cr($3d^5$, $4s^1$), Cu($3d^{10}$, $4s^1$), Mo($4d^5$, $5s^1$), Pd($4d^{10}$, $5s^0$), Ag($4d^{10}$, $5s^1$) and Au($5d^{10}$, $6s^1$) clearly show irregularities in the configurations. These are explained on the basis of the concept that half-filled and completely filled d-orbitals are relatively more stable than other d-orbitals.

PLANCESS CONCEPTS

It should be noted here that when atoms of these elements form cations, electrons are removed from the outermost s-subshell instead of the penultimate d-subshell, although the former was filled earlier.

$_{25}Mn$: [Ar] $3d^5$, $4s^2$ $\quad$ Mn^{2+} : [Ar]$3d^5$

$_{26}Fe$: [Ar]$3d^6$, $4s^2$ $\quad$ Fe^{2+} : [Ar] $3d^6$

Vaibhav Krishnan (JEE 2009 AIR 22)

Illustration 1: To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example. **(JEE MAIN)**

Sol: Empty, Half-filled and completely filled orbitals have extra stability

E.g. Mn^{2+} = [Ar]$3d^5$, Sc^{3+} = [Ar]$3d^0$, Zn^{2+} = [Ar] $3d^{10}$

Illustration 2: What may be the stable oxidation state of the transition element with the following d-electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$? **(JEE ADVANCED)**

Sol: Ground state configuration	**Stable oxidation state**
$3d^3$	+5
$3d^5$	+2, + 7
$3d^8$	+2
$3d^4$	$3d^4$ does not exist

3. GENERAL PROPERTIES OF THE TRANSITION METALS

3.1 Atomic and Ionic Radii

(a) The atomic and ionic radii for transition elements are smaller than their corresponding s-block elements and are greater than their corresponding p-block elements.

(b) The atomic and ionic radii for transition elements for a given series show a decreasing trend for the first five elements and then becomes almost constant for next five elements of the series. For example, in 3d-series atomic radius decreases from $_{21}Sc$ to $_{25}Mn$ and then becomes constant for next five i.e. $_{26}Fe$ to $_{30}Zn$

Explanation: This is due to the combined effect of the increasing effective nuclear charge, (ENC) and increasing screening effect along the period. An increase in ENC favors a decrease in atomic radii, whereas increase in number of d-elements increases the screening effect and thus increases the atomic radii. Thus both ENC and screening effect act opposite to each other and therefore the atomic size is governed by the net influence of these two.

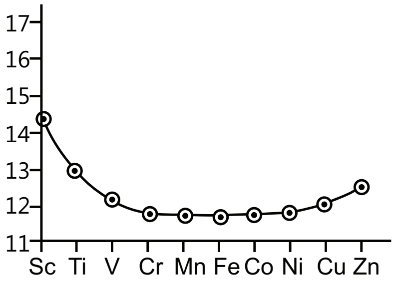


Figure 31.1: Atomic radii of element of 3d-series

(c) The atomic and ionic radii of the elements of 4d-series are higher than 3d-series as the number of shells increases down the group. However, the elements of 4d-series and 5d-series on moving down the group reveal almost constant value. For example, Zirconium and Hafnium, the members of 4d and 5d-series, respectively have the almost same size i.e. 145 pm. Similarly, Zr^{4+} and Hf^{4+} have their atomic radii as 80 pm and 81 pm respectively. This is due to the Lanthanoid contraction.

(d) The ionic radii decreases as charge on the cation increases (i.e., higher oxidation state). e.g.

$Ti^{2+} > Ti^{3+} > Ti^{4+}$

$Cr^{2+} > Cr^{3+} > Cr^{5+} > Cr^{6+}$

$Fe^{2+} > Fe^{3+}$

(e) For ions having same oxidation states, the ionic radii decreases with increase in atomic number e.g.

For 3d-series

	Sc^{2+} >	Ti^{2+} >	V^{2+} >	Cr^{2-} >	Mn^{2+} >	Fe^{2+} >	Co^{2+} >	Ni^{2+} >	Cu^{2+}
Ionic radii (in Å)	0.95	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.69

Illustration 3: In a transition series, with an increase in atomic number, the atomic radius does not change very much. Why is it so? **(JEE MAIN)**

Sol: With increase in atomic number along a transition series, the nuclear charge increases which tends to decrease the size of the atom. But, the addition of electrons in the d-subshell increases the screening effect which counterbalances the increased nuclear charge. Hence, along a transition series the atomic radius does not change very much.

3.2 Atomic Volume and Density

(a) The size decreases along the period and, therefore, atomic volume also decreases along the period.

(b) Atomic volumes are smaller than group 1 and 2 members i.e. s-block elements.

(c) The density, however, increases along the period.

3.3 Melting and Boiling Points

(a) All the transition elements have a higher melting point as compared to s-block elements due to strong metallic bonding as well as unpaired d-electrons leading to covalence.

(b) It is evident from that the melting point of transition metals or a given series increases on moving left to right in a period and attains a maximum value and after that the m.p. goes on decreasing towards the end of period. This is due to the fact that the strength of inter particle bonds in transition elements is also directly related to the number of half-filled d-orbitals. In the beginning, the number of unpaired electrons in d-orbitals increases till the middle of the period (d^1 to d^5). After this, the pairing of electrons occurs in d-orbitals (d^6 to d^{10}). An increase in inter atomic bonds due to the increase in number of unpaired electron results in higher m.p.

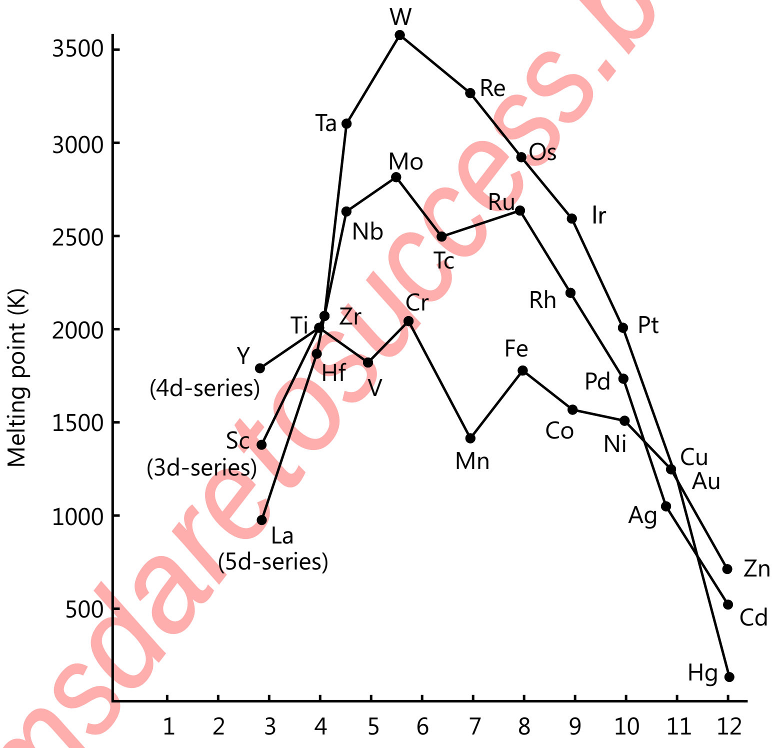


Figure 31.2: Trends in melting points of different group

3.4 Metallic Character

(a) All the transition metals possess one or two electrons in their outermost shell and thus exhibit metallic nature.

(b) All are hard, ductile and malleable solids with strong metallic bonding (except mercury which is liquid) and possess hcp, bcc or ccp crystal lattices.

(c) Transition metals show a gradual decrease in electropositive character on moving along the period.

(d) Strong metallic bonding in transition metals is due to greater effective nuclear charge and a large number of valence electrons (inner d-subshell and outermost s-subshell).

(e) Due to strong metallic bonding, transition metals are hard, possess high densities and high enthalpies for atomization.

(f) Due to metallic bonding, these are good conductors of heat and electricity.

(g) Transition metals form numerous useful alloys with other metals.

3.5 Enthalpies of Atomisation

Transition elements have a high enthalpy of atomization due to strong interatomic attraction. Greater the number of valency electrons, stronger is the resultant bonding and higher is the enthalpy of atomization. The members of 4d and 5d-series have greater enthalpy of atomization than those of 3d-series. Thus, they form metal-metal bonding frequently in their compounds.

3.6 Ionization Energy

(a) The ionization energy (IE) of d-block elements lies in between s-and p-block elements showing less electropositive character than s-block

(b) Smaller atomic size and a fairly high IE is noticed for transition metals.

(c) IE values first increases up to $_{25}$Mn and then becomes irregular or constant values due to irregular trend of atomic size after $_{25}$Mn in 3d-series. Similar trend is noticed in 5d-and 6d-series.

(d) The magnitude of ionization energies give an idea about the relative stabilities of various oxidation states of transition elements.

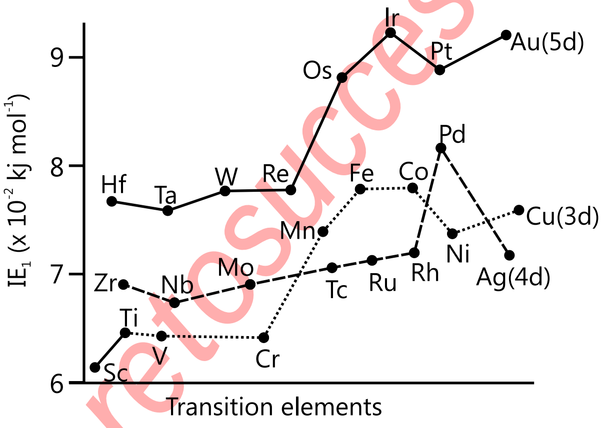


Figure 31.3: Ionization energies of transition elements

PLANCESS CONCEPTS

The ionization energy of 5-d series are higher than that of 3-d and 4-d series due to the poor shielding effect of 4-f electrons present in 3-d series

Ionization energy of Zn, Cd and Hg are abnormally higher on account of greater stability of s-subshell

Nikhil Khandelwal (JEE 2010 AIR 443)

Illustration 4: In the series Sc(Z = 21) to Zn(Z = 30), the enthalpy of atomization of zinc is the lowest, i.e. 125 kJ mol^{-1}. Why? **(JEE ADVANCED)**

Sol: In the formation of metallic bonds, no electrons from 3d-orbitals are involved in case of zinc, while in all other metals of the 3d series, electrons from the d-orbitals are always involved in the formation of metallic bond. This is why the enthalpy of atomization of zinc is the lowest in the series.

3.7 Reactivity

(a) Transition metals are less reactive than s-block elements. Their low reactivity is due to:

(i) High ionization energy.

(ii) Existence of metallic bonding among atoms which gives rise to higher heat of sublimation.

$M_{(s)} \longrightarrow M_{(g)}$ ΔH = Heat of sublimation (ΔH_s)

$M_{(g)} \longrightarrow M^+_{(g)} + e^-$ ΔH = Heat of ionization or ionization energy (IE)

$M^+_{(g)} \longrightarrow M^+_{(aq)}$ ΔH = – Heat of hydration ($-\Delta H_h$)

$M_{(s)} + H_2O \longrightarrow M^+_{(aq)} + e^-$ $\Delta H = \Delta H_s + IE - \Delta H_h$

More negative the value of ΔH for the change, lesser is the energy level for $M^+_{(aq)}$ and greater will be the stability of that oxidation state in aqueous solution.

3.8 Variable Valency and Oxidation State

(a) Most of the transition elements show variable valencies or different oxidation states because of incomplete d-subshell. The variable oxidation states of transition elements are due to the participation of ns and (n – 1) d electrons in bonding.

(b) It is thus evident that for the first five transition elements, the minimum oxidation state is given by the electrons in outermost s-subshell and the maximum oxidation state by the total number of ns and (n – 1) d-subshell electrons.

(i)	$_{21}$Sc shows +2 and +3	(due to $4s^2$ and $3d^1$ electrons)
(ii)	$_{22}$Ti shows + 2, +3 and +4	(due to $4s^2$ and $3d^2$ electrons)
(iii)	$_{23}$V shows +2, +3, +4, +5	(due to $4s^2$ and $3d^3$ electrons)
(iv)	$_{24}$Cr shows +2, +3, +4, +5, +6	(due to $4s^1$ and $3d^5$ electrons)
(v)	$_{25}$Mn shows +2 to +7	(due to $4s^2$ and $3d^5$ electrons)

PLANCESS CONCEPTS

- The transition elements in their lower oxidation states (+2 and +3) usually form ionic compounds. In higher oxidation state, compounds are normally covalent. For example, Mn in $MnCl_2$ has Mn^{2+} ion whereas in $KMnO_4$, Mn exists in +7 state of covalent nature.
- Some transition metals also exhibit zero oxidation state in their compounds such as carbonyls. Ni and Fe in $Ni(CO)_4$ and $Fe(CO)_5$ have zero oxidation state.
- The highest oxidation states of transition metals are found in their compounds with fluorine and oxygen. This is due to higher electronegativity and small atomic size of fluorine and oxygen. Eg.MnO_4^-

Neeraj Toshniwal (JEE 2009 AIR 21)

Illustration 5: Which metal in the first series of transition metal exhibits +1 oxidation state most frequently and why? **(JEE ADVANCED)**

Sol: Copper, because it will achieve a completely filled d-orbital and a stable configuration on losing an electron.

3.9 Colour

Substances appear coloured when they absorb light of a particular wavelength in the visible region of the spectrum and transmit light of other wavelengths. The colour which we see is the colour of the transmitted wavelengths. In other words, the colour of the compound observed by us is the complementary colour of the colour absorbed by the compound.

In the s-and p-block elements, there cannot be any d-d transistions and the energy needed to promote the s or p electrons to a higher level is much greater and may correspond to ultraviolet region, in which case the compound will not appear coloured to the eye.

Table 31.1: Color spectrum

Wavelength absorbed in nm	Colour absorbed	Colour observed
< 400	UV region	White/colourless
400–435	Violet	Yellow-green
435–480	Indigo	Yellow
480–490	Green-blue	Orange
490–500	Blue-green	Red
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Indigo
595–605	Orange	Green-blue
605–750	Red	Blue-green
> 750	Infra-red	White/colourless

Illustration 6: Transition metal ions like Cu^{+}, Ag^{+}, Zn^{2+}, Hg^{2+} and Cd^{2+} are colourless. Explain. **(JEE ADVANCED)**

Sol: Due to forbidden transition some metal ions are colourless. All the ions reported above have no unpaired electrons in them and the d-orbital $[(n-1)d^{10}]$ is also completely filled. Thus, due to d-d transition above mentioned metal ions are colourless.

3.10 Magnetic Properties

Magnetic Properties: When a substance is placed in a magnetic field of strength H, the intensity of the magnetic field on the substance may be greater than or less than H.

Diamagnetic: The substances which are weakly repelled by a magnetic field; absence of unpaired electrons.

Paramagnetic: The substances which are weakly attracted by the magnetic field and lose their magnetism when removed from the field; presence of unpaired electrons.

Paramagnetism is expressed by magnetic moment,

$$\mu = \sqrt{n(n+2)}\ \text{B.M.}$$

n = Number of unpaired electrons

B.M. = Bohr Magneton, unit of magnetic moment

Illustration 7: The paramagnetic character in 3d transition series increases up to Cr and then decreases. Explain **(JEE MAIN)**

Sol: As number of unpaired electron increases paramagnetic nature increases.The number of unpaired electrons increases from $_{21}Sc$: [Ar]$3d^1,4s^2$ to $_{24}Cr$: [Ar] $3d^5$, $4s^1$ and after chromium, the pairing of electrons takes place and thus number of unpaired electrons goes on decreasing continuously to $_{30}Zn$: [Ar] $3d^{10}$, $4s^2$.

PLANCESS CONCEPTS

The magnetic properties of d-block elements are due to the only spin value of the unpaired electrons present in d-orbital while in the case of f-block elements, it is due to both the orbital motion as well as spin contribution.

Magnetic moment for d-block elements: $\mu = \sqrt{n(n+2)}$ B.M. (where n is the number of unpaired electrons)

Magnetic moment of f-block elements: $\mu = \sqrt{4s(s+1)+\ell(\ell+1)}$. (where s is sum of spin quantum number and ℓ, the angular momentum quantum number)

Aman Gour (JEE 2012 AIR 230)

4. SOME IMPORTANT COMPOUNDS OF d-BLOCK ELEMENTS

4.1 Chromate and Dichromate

(a) **Preparation:** $4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{inair}]{\text{Roasting}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3. The solution is treated with calculated amount of H_2SO_4.

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

The solution is concentrated when less soluble Na_2SO_4 crystallizes out. The solution is further concentrated when crystals of $Na_2Cr_2O_7$ are obtained. Then a hot saturated solution of $Na_2Cr_2O_7$ is treated with KCl, then reddish orange crystals of $K_2Cr_2O_7$ are obtained on crystallization

(b) $K_2Cr_2O_7$ is preferred to $Na_2Cr_2O_7$ because $Na_2Cr_2O_7$ is hygroscopic but $K_2Cr_2O_7$ is not.

(c) Similarities between hexavalent Cr & S-compounds:

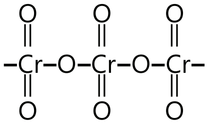
(i) SO_3 & $CrO_3 \rightarrow$ Both acidic

(ii) CrO_4^{-2} & SO_4^{2-} Isomorphous

(iii) SO_2Cl_2 & $CrO_2Cl_2 \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-} respectively

(iv) $SO_3Cl^- + CrO_3Cl^- \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-}

(v) CrO_3 & $B(SO_3)$ has same structure



$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-$

(vi) Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

(vii) It acts as a powerful oxidizing agent in an acidic medium (dilute H_2SO_4)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (E^o = 1.33V)

The oxidation state of Cr changes from +6 to +3

(d) **Uses:** As a volumetric reagent in the estimation of reducing agents such as oxalic acid, ferrous ions, iodide ions, etc.

- **(i)** For the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.
- **(ii)** In dyeing chrome tanning, calico printing, photography etc.
- **(iii)** Chromic acid as a cleansing agent for glass ware

4.2 Manganate and Permanganate

Preparation: This is the most important and well known salt of permanganic acid. It is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K_2CO_3 in the presence of atmospheric oxygen or any other oxidizing agent such as KNO_3. The mass turns green with the formation of potassium magnate, K_2MnO_4

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_3 \longrightarrow 2K_2MnO_4 + 2CO_2$$

The fused mass is extracted with water. The solution is now treated with a current of chlorine or ozone or carbon dioxide to convert magnate into permanganate.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

Another Method of Preparation:

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2KMnO_4 + MnO_2\downarrow + 2K_2SO_4 + 2H_2O$$

or $3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$

But, in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidized either by Cl_2 or by O_3,

$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$ [Unwanted MnO_2 does not form]

OR

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

Heating effect: $\underset{\text{green}}{2KMnO_4} \xrightarrow[200°C]{\Delta} \underset{\text{Black}}{K_2MnO_4} + MnO_2 + O_2$

$$2K_2MnO_4 \xrightarrow[\text{hot}]{\text{at red}} 2K_2MnO_3 + O_2$$

Oxidising Property of $KMnO_4$: (In acidic medium)

(i) $MnO_4^- + Fe^{+2} + H^+ \longrightarrow Mn^{+2} + O_2 + H_2O + Fe^{3+}$

(ii) $MnO_4^- + H_2O_2 + H^+ \longrightarrow Mn^{+2} + O_2 + H_2O$

(iii) $MnO_4^- + H_2S \longrightarrow Mn^{2+} + S\downarrow + H_2O$

In alkaline solution: $KMnO_4$ is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless. However, a brownish precipitate is formed

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O$$

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2O$$

$$2KMnO_4 + H_2O \xrightarrow{\text{alkaline}} 2MnO_2 + 2KOH + 3[O]$$

or $2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- + 3[O]$

In neutral or weakly acidic solution:

(i) $2KMnO_4 + 3MnSO_4 + 2H_2O \xrightarrow{\text{in presence } Zn^{+2} \text{or } ZnO} 5MnO_2 + K_2SO_4 + 2H_2SO_4$

Conversion of Mn^{+2} to MnO_4^-**:**

(i) PbO_2	(ii) $Pb_3O_4 + HNO_3$	(iii) $Pb_2O_3 + HNO_3$
(iv) $NaBiO_3/H^+$	(v) $(NH_4)_2S_2O_8/H^+$	(vi) KIO_4/H^+

PLANCESS CONCEPTS

In the oxidation reactions of $KMnO_4$ in acidic medium, only H_2SO_4 is used to produce an acidic medium and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as an oxidising agent.

B Rajiv Reddy (JEE 2012 AIR 11)

Illustration 8: Complete the equation of following chemical reactions: **(JEE MAIN)**

(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(\ell) \rightarrow$

(ii) $CrO_7^-(aq) + H_2S(g) + H^+(aq) \rightarrow$

Sol:

(i) In neutral or faintly alkaline solutions

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \times 8$$

$$S_2O_3^{2-} + 10OH^- \rightarrow 2SO_4^{2-} + 5H_2O + 8e^- \times 3$$

$$8MnO_3^{2-} + 10OH^- + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(ii) In acidic solutions

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$H_2S \rightarrow S + 2H^+ + 2e^- \times 3$$

$$CrO_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$$

Illustration 9: Write steps involved in the preparation of **(JEE ADVANCED)**

(i) Mn_2CrO_4 from chromite ore and

(ii) K_2MnO_4 from pyrolusite ore.

Sol: (i) Chromite ore is fused with sodium carbonate in excess of air.

$$4FeCr_2O_4 + 8Na_2CO + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Chromite ion Sod. Chromites

(ii) K_2MnO_4 from pyrolusite ore

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_3 \longrightarrow 2K_2MnO_4 + 2CO_2$$

4.3 Silver Nitrate

Properties:

(i) It is called lunar caustic because in contact with skin it produces a burning sensation that of caustic soda with the formation of finely divided silver (black colour).

(ii) Thermal decomposition

$$AgNO_3 \rightarrow AgNO_2 + \frac{1}{2}O_2$$

(iii) $6AgNO_3 + 3I_2 + 3H_2O \rightarrow 5AgI + AgIO_3 + 6HNO_3$ (excess)

(iv) $Ag_2SO_4 \xrightarrow{\Delta} 2Ag + SO_2 + O_2$

(v) A - $(AgNO_3) \xrightarrow[\text{added}]{B}$ white ppt appears quickly

B - $(Na_2S_2O_3) \xrightarrow[\text{added}]{A}$ It takes time to give white ppt.

(vi) $Ag_2S_2O_3 + H_2O \xrightarrow{\Delta} Ag_2S + H_2SO_4$

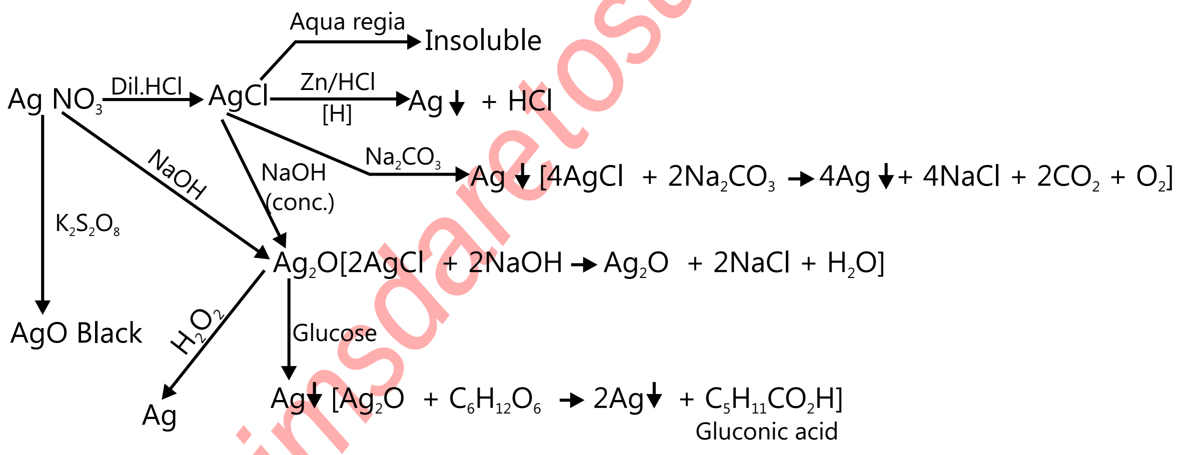
AgCl, AgBr, AgI (but not Ag_2S) are soluble in $Na_2S_2O_3$ forming $[Ag(S_2O_3)_2]^{-3}$ complexes

(vii) $AgBr + AgNO_3 \xrightarrow{KBr} \underset{\text{Pale yellow ppt.}}{AgBr} \downarrow + KNO_3$

Heating effect: $2AgNO_3 \xrightarrow{212°C} 2AgNO_2 + O_2$

$$2AgNO_3 \xrightarrow{300°C} 2Ag + 2NO + O_2$$

(viii)



$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$

$K_2S_2O_8 + 2AgNO_3 + 2H_2O \rightarrow 2AgO + 2KHSO_4 + 2HNO_3$

PLANCESS CONCEPTS

AgO is supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^{I}[Ag^{III}O_2]$

Silvering of mirror: The process of depositing a thin and uniform layer of silver on a clean glass surface is known as **silvering of mirrors.** It is employed for making looking glasses, concave mirrors and reflecting surfaces. The process is based on the reduction of ammoniacal silver nitrate solution by some reducing agent like formaldehyde, glucose, etc. The silver film deposited on the glass is first coated with a varnish and finally painted with red lead to prevent its loss due to scrap.

Rohit Kumar (JEE 2012 AIR 79)

4.4 Zinc Compounds

1. Zinc oxide, ZnO (Chinese white or philosopher's wool)

It found in nature as zincite or red zinc ore.

(a) Preparation:

(i) $2Zn + O_2 \longrightarrow 2ZnO$

(ii) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

(iii) $2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$

(iv) $Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$

(b) Physical Properties: It is a white powder, which becomes yellow on heating and again turns white on cooling, is insoluble in water, and sublimes at 400°C.

(c) Chemical Properties:

(i) $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

(ii) $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

(iii) $ZnO + H_2 \xrightarrow[400°C]{\Delta} Zn + H_2O$

(iv) $ZnO + C \longrightarrow Zn + CO$

2. $ZnCl_2$ (Zinc Chloride)

(a) Preparation:

$$\left.\begin{aligned} ZnO + 2HCl &\longrightarrow ZnCl_2 + H_2O \\ ZnCO_3 + 2HCl &\longrightarrow ZnCl_2 + H_2O + CO_2 \\ Zn(OH)_2 + 2HCl &\longrightarrow ZnCl_2 + 2H_2O \end{aligned}\right\} \text{It crystallises as } ZnCl_2 . 2H_2O$$

Anhydrous $ZnCl_2$ cannot be made by heating $ZnCl_2.2H_2O$ because

$ZnCl_2. 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$

$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$

To get anh. $ZnCl_2$:

$Zn + Cl_2 \longrightarrow ZnCl_2$

$Zn + 2HCl(dry) \longrightarrow ZnCl_2 + H_2$

Or $Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$

(b) Properties:

(i) It is deliquescent white solid (when anhydrous)

(ii) $ZnCl_2 + H_2S \longrightarrow ZnS$

(iii) $ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess}} Na_2[Zn(OH)_4]$

(iv) $ZnCl_2 + NH_4OH \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess}} [Zn(NH_3)_4]^{2+}$

(c) Uses:

(i) Used for impregnating timber to prevent destruction by insects

(ii) As a dehydrating agent when anhydrous

(iii) ZnO. $ZnCl_2$ used in dental filling

3. $ZnSO_4$ (Zinc Sulphate)

(a) Preparation:

$$Zn + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$ZnO + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnCO_3 + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$$

$$\left.\begin{array}{r} ZnS + 2O_2 \longrightarrow ZnSO_4 \\ ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2 \end{array}\right\} \text{Parallel reaction}$$

$$ZnS + 4O_3 \longrightarrow ZnSO_4 + 4O_2$$

(b) Properties

$$\begin{tikzcd} ZnSO_4.7H_2O \arrow[r, "39\text{-}70°C"] & ZnSO_4.6H_2O \arrow[r, ">70°C"] & ZnSO_4.H_2O \arrow[r, ">280°C"] \arrow[d, ">800°C"] & ZnSO_4 \\ & & \frac{1}{2}O_2 + SO_2 + ZnO & \end{tikzcd}$$

(c) Uses:

(i) In eye lotion

(ii) Lithopone making ($ZnS + BaSO_4$) as white pigment

Illustration 10: The addition of NH_4OH to $ZnSO_4$ solution produces white precipitate but no precipitate is formed if it contains NH_4Cl. Why? **(JEE ADVANCED)**

Sol: NH_4OH is a weak hydroxide. It ionizes slightly, furnishing OH^- ions. However, the OH^- ions are sufficient to cause the precipitation of $Zn(OH)_2$ as its ionic product exceeds the $K_{sp.}$

$$ZnSO_4 + 2NH_4OH \rightarrow \underset{\text{White ppt}}{Zn(OH)_2} + (NH_4)_2SO_4]$$

In the presence of NH_4Cl, the ionization of NH_4OH is further suppressed and sufficient OH^- ions are not available to cause precipitation as the ionic product does not exceed the K_{sp}.

PLANCESS CONCEPTS

Zinc oxide is white at room temperature but turns yellow on heating

Krishan Mittal (JEE 2012, AIR 199)

4.5 Copper Compounds

1. CuO:

(a) Preparation:

(i) $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$ (Commercial process)

Malachite green

(Native Cu-carbonate)

(ii) $2Cu + O_2 \longrightarrow 2CuO \;\&\; Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$

(iii) $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

(iv) $2Cu(NO_3)_2 \xrightarrow{250^\circ C} 2CuO + 4NO_2 + O_2$

(b) Properties:

(i) CuO is insoluble in water

(ii) Readily dissolves in dil. acids

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuO + HCl \longrightarrow CuCl_2$$

$$CuO + HNO_3 \longrightarrow Cu(NO_3)_2$$

(iii) It decomposes when, heated above 1100°C

$$4CuO \longrightarrow 2Cu_2O + O_2$$

(iv) CuO is reduced to Cu by H_2 or C under hot condition

$$CuO + C \longrightarrow Cu + CO\uparrow$$

$$CuO + H_2 \longrightarrow Cu + H_2O\uparrow$$

2. $CuCl_2$:

(a) Preparation:

$CuO + 2HCl(conc.) \longrightarrow CuCl_2 + H_2O$

$Cu(OH)_2.CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$

(b) Properties:

(i) It is crystallized as $CuCl_2.2H_2O$ of Emerald green colour

(ii) Dilute solution in water is blue in colour due to the formation of $[Cu(H_2O)_4]^{2+}$ complex.

(iii) conc. HCl or KCl added to dil. solution of $CuCl_2$, the colour changes into yellow, owing to the formation of $[CuCl_4]^{2-}$

(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium

$$2[Cu(H_2O)_4]Cl_2 \longrightarrow [Cu(H_2O)_4]^{2+} + [CuCl_4]^{2-} + 4H_2O$$

(v) $CuCl_2 \longrightarrow CuCl$

- $CuCl_2 + \text{Cu-turning} \xrightarrow{\Delta} 2CuCl$
- $2CuCl_2 + H_2SO_3 + H_2O \longrightarrow 2CuCl + 2HCl + 2H_2SO_4$
- $2CuCl_2 + Zn/HCl \longrightarrow 2CuCl + ZnCl_2$
- $CuCl_2 + SnCl_2 \longrightarrow CuCl + SnCl_4$

$CuF_2.2H_2O \longrightarrow$ light blue
$CuCl_2.2H_2O \longrightarrow$ green
$CuBr_2 \longrightarrow$ almost black

Anh. $CuCl_2$ is dark brown mass obtained
by heating $CuCl_2.2H_2O$ at 150°C in presence
of HCl vap.

CuI_2 does not exist

$$CuCl_2.2H_2O \xrightarrow[\text{HCl gas}]{150°C} CuCl_2 + 2H_2O$$

3. $CuSO_4$:

(a) Preparation:

$CuO + H_2SO_4(dil) \longrightarrow CuSO_4 + H_2O.$

$Cu(OH)_2 + H_2SO_4\ (dil) \longrightarrow CuSO_4 + 2H_2O.Cu(OH)_2.$

$CuCO_3 + H_2SO_4(dil) \longrightarrow CuSO_4 + 3H_2O + CO_2$

$Cu + H_2SO_4 + \frac{1}{2}O_2 \longrightarrow CuSO_4 + H_2O$ [Commercial scale]

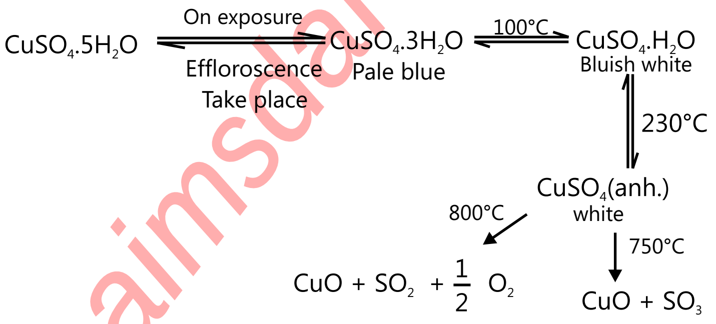
(Scrap)

$Cu + \text{dil. } H_2SO_4 \longrightarrow$ no reaction {Cu is below H in electrochemical series}

(b) Properties:

(i) It is crystallized as $CuSO_4.5H_2O$

(ii)



PLANCESS CONCEPTS

Anhydrous copper sulphate (white) regains its blue colour when moistened with a drop of water (it is a test of water).

T P Varun (JEE 2012, AIR 640)

Illustration 11: Blue copper sulphate turns white on heating. Why ? **(JEE MAIN)**

Sol: Hydrated copper sulphate ($CuSO_4.5H_2O$) is blue which on heating loses its water of crystallization to form anhydrous $CuSO_4$ a white compound. $CuSO_4.5H_2O \xrightarrow{\text{Heat}} CuSO_4 + 5H_2O$

Illustration 12: Cu^+ ion is not stable in an aqueous solution. Why ? **(JEE ADVANCED)**

Sol: $Cu^{2+}(aq)$ is much more stable than $Cu^+(aq)$. This is because although the second ionization enthalpy of copper is large but $\Delta_{hyd}H$ for $Cu^{2+}(aq)$ is much more negative than that for $Cu^+(aq)$ and therefore it more than compensates for the second ionization enthalpy of copper. Thus many copper (I) compounds are unstable in aqueous solution and undergoes disproportion as follows $2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$

4.6 Iron Compounds

1. $FeSO_4.7H_2O$:

(a) Preparation:

(i) Scrap $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2\uparrow$

(dil.)

(ii) From Kipp's waste

$$FeS + H_2SO_4(dil) \longrightarrow FeSO_4 + H_2S\uparrow$$

(iii) $FeS_2 + 2H_2O + \frac{7}{2}O_2 \longrightarrow FeSO_4 + H_2SO_4$

(b) Properties:

(i) It undergoes aerial oxidation forming basic ferric sulphate

$$4FeSO_4 + H_2O + O_2 \longrightarrow 4Fe(OH)SO_4$$

(ii) $FeSO_4.7H_2O \xrightarrow{300°C} \underset{\text{anh. white}}{FeSO_4} \xrightarrow[\text{temp.}]{\text{high}} Fe_2O_3 + SO_2 + SO_3$

(iii) Aq. Solution is acidic due to hydrolysis

$$FeSO_4 + 2H_2O \rightleftharpoons \underset{\text{Weak base}}{Fe(OH)_2} + H_2SO_4$$

(iv) It is a reducing agent

- $Fe^{2+} + MnO_4^- + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$
- $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$
- $Au^{3+} + Fe^{2+} \longrightarrow Au + Fe^{3+}$
- $Fe^{2+} + HgCl_2 \longrightarrow \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow} + Fe^{3+}$

(v) It forms double salt. Example $(NH_4)_2SO_4.FeSO_4.6H_2O$

2. FeO (Black):

(a) Preparation: $FeC_2O_4 \xrightarrow[\text{in absence of air}]{\Delta} FeO + CO + CO_2$

(b) Properties: It is stable at high temperature and on cooling slowly disintegrates into Fe_3O_4 and iron

$$4FeO \longrightarrow Fe_3O_4 + Fe$$

3. $FeCl_2$:

(a) Preparation: $Fe + 2HCl \xrightarrow{\text{heating in current of HCl}} FeCl_2 + H_2$

OR

$2FeCl_3 + H_2 \xrightarrow{\Delta} 2FeCl_2 + 2HCl$

(b) Properties:

(i) It is deliquescent in air like $FeCl_3$

(ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature

(iii) It volatilizes at about 1000°C and vapour density indicates the presence of Fe_2Cl_4. Above 1300°C density becomes normal

(iv) It oxidizes on heating in air

$12FeCl_2 + 3O_2 \longrightarrow 2Fe_2O_3 + 8FeCl_3$

(v) H_2 evolves on heating in steam $3FeCl_2 + 4H_2O \longrightarrow Fe_3O_4 + 6HCl + H_2$

(vi) It can exist as a different hydrated form

$FeCl_2.2H_2O \longrightarrow$ colorless

$FeCl_2.4H_2O \longrightarrow$ pale green

$FeCl_2.6H_2O \longrightarrow$ green

4. $FeCl_3$:

(a) Preparation: $2\,Fe(s) + 3\,Cl_2(g) \rightarrow 2\,FeCl_3(s)$

(b) Properties: Anhydrous ferric chloride is prepared by heating metallic iron in a stream of dry chlorine gas.

(i) $FeCl_3$ solid is almost black. It sublimes at about 300°C, giving a dimeric gas.

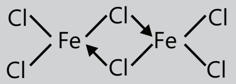
(ii) $FeCl_3$ dissolves in both ether and water, giving solvated monomeric species.

(iii) Iron (III) chloride is usually obtained as yellow-brown lumps of the hydrate $FeCl_3.6H_2O$.

(iv) This is very soluble in water and is used both as an oxidizing agent, and as a mordant in dyeing.

PLANCESS CONCEPTS

Anhydrous ferric chloride is soluble in non-polar solvents like ether, alcohol, etc as it possesses covalent bonds and has a chlorine bridge structure.



Saurabh Chaterjee (JEE Advanced 2013, AIR)

Illustration 13: $FeCl_3(aq)$ gives CO_2 with $NaHCO_3(aq)$ Explain. **(JEE ADVANCED)**

Sol: Fe^{3+} ions hydrolyse to form alkaline solution which reacts with $NaHCO_3$ to liberate CO_2.

$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3OH^-$

$OH^- + 2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$

f-BLOCK ELEMENTS

1. INTRODUCTION

1.1 Inner transition elements/f-block elements

The elements in which the additional electrons enters (n – 2)f orbitals are called inner transition elements. The valence shell electronic configuration of these elements can be represented as (n-2) $f^{0.2....14}$(n –1)$d^{0,1,2}ns^2$. These are also called as f-block elements because the extra electrons go to f-orbitals which belongs to (n–2) th main shell. 4f-block elements are also called Lanthanides or rare earths. Similarly, 5f-block elements are called actinides or actinones. The name Lanthanides and Actinide have been given due to close resemblance with Lanthanum and Actinium respectively. Lanthanides constitutes the first inner transition series while actinides constitutes second inner transition series.

General Characteristics:

1. **Electronic Configuration :** [Xe] $4f^{n+1}5d^0 6s^2$ or [Xe] $4f^n 5d^1 6s^2$
2. **Oxidation state:** They readily form M^{+3} ions. Some of them also exhibit oxidation state of +2 and +4.
3. **Colouration:** Ions of Lanthanides and Actinides are coloured in the solid state as well as in aqueous solution because of absorption of light due to f-f-transition, since they have partly filled f-orbitals.

Magnetic properties: $La^{3+}(4f^0)$ and $Lu^{3+}(4f^{14})$ having no unpaired electrons do not show paramagnetism while all other tri-positive ions of lanthanides are paramagnetic

Illustration 14: What is the basic difference between the electronic configuration of transition and inner transition elements. **(JEE MAIN)**

Sol: General electronic configuration of transition elements = [Noble gas] (n – 1) $d^{1-10}ns^{1-2}$ and for inner transition elements = (n – 2) f^{1-14}(n – 1)$d^{0-1}ns^{0-2}$. Thus, in transition elements, last electron enters d-orbitals of the penultimate shell while in inner transition elements, it enters f-orbital of the penultimate shell.

Illustration 15: What are inner transition elements ? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104. **(JEE MAIN)**

Sol: Inner transition elements are those which have incomplete 4f of 5f orbitals. Thus 59, 95 and 102 are inner transition elements.

2. LANTHANIDES AND THEIR PROPERTIES

The lanthanide series of chemical elements comprises the fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. These fifteen lanthanide elements, along with the chemically similar elements, scandium and yttrium, are often collectively known as the rare earth elements.

2.1 Lanthanide Contraction

In lanthanides, the additional electron enters the 4f-sub shell but not in the valence-shell i.e. sixth shell. The shielding effect of one electron in 4f-sub-shell by another in the same sub-shell is very little, being even smaller than that of d-electrons, because the shape of f-sub shell is very much diffused, while there is no comparable increase in the mutual shielding effect of 4f-electrons. This results in outermost shell electrons in the experience increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic radii go on decreasing as we move from La_{57} to Lu_{71}.

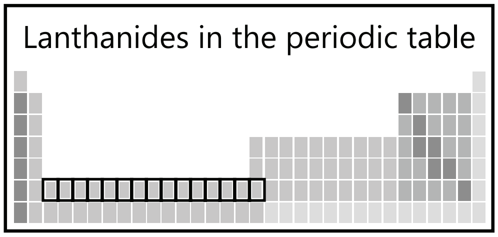


Figure 31.4: Position of lanthanides in the periodic table

Consequence of Lanthanide contraction

1. **Atomic and ionic radii of post-Lanthanide elements:** The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to lanthanide contraction.
2. **High density of post Lanthanide elements:** It is because of a very small size due to lanthanide contraction and increase in molar mass.
3. **Basic strength of oxides and hydroxides:** Due to lanthanide contraction, the decrease in size of lanthanides ions, from La^{3+} to Lu^{3+} increases the covalent character (i.e. decreases the ionic character) between Ln^{+3} and OH^- ions in Ln(III) hydroxides (Fajan's rules). Thus $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic. Similarly, there is a decrease in the basic strength of the oxides.
4. **Separation of Lanthanides:** Due to the similar size (lanthanide contraction) of the lanthanides, it is difficult to separate them. But a slight variation in their properties is utilized to separate.

PLANCESS CONCEPTS

The existence of lanthanoids in oxidation state of +2 and +4 is due to the fact that empty, half-filled or completely filled f-subshells provide lower energy levels and the ions get stabilized. For example, Ce and Tb show +4 oxidation state by attaining stable f^0 and f^7 configuration respectively whereas Eu and Yb show +2 oxidation state by attaining stable f^7 and f^{14} configuration, respectively.

Mredul Sharda (JEE Advanced 2013)

Illustration 16: Why is the separation of lanthanoids difficult? Explain. **(JEE MAIN)**

Sol: All the Lanthanoid ions are of almost the same size, so they have almost similar chemical and physical properties and thus their separation becomes difficult.

Illustration 17: Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behavior with the electronic configuration of these elements. **(JEE MAIN)**

Sol: +4 = Ce, Pr, Nd, Tb, Dy. +2 = Eu, Yb. These states are accounted by the extra stability of half-filled and completely filled f-orbitals.

2.2 Chemical Reactivity

These are very reactive metals like alkaline earth metals, however, they show very little difference in their chemical reactivity. On strong heating with H_2 and carbon, these form salt like non-stoichiometic hydrides and carbides. They burn in oxygen to give sesquioxides M_2O_3 (except Ce which gives CeO_2). Their ionic oxides react with water to form insoluble hydroxides. The oxides and hydroxides being strong base react with CO_2 to form carbonates (M_2CO_3). On burning in sulphur these form sulphides (M_2S_3).

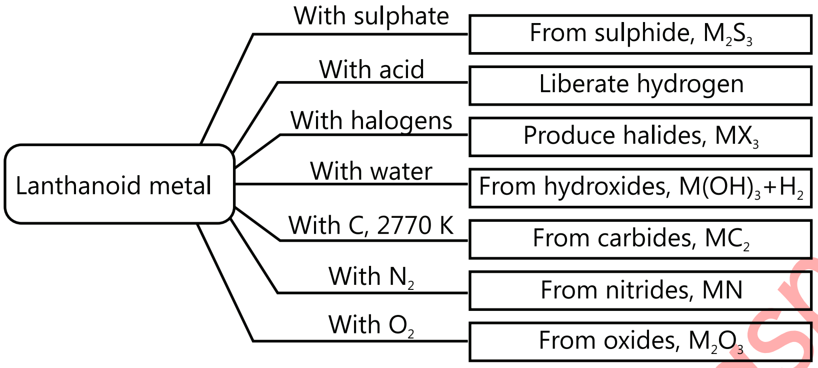


Figure 31.5: Chemical reactivity of lanthanoid metal

2.3 Uses of Lanthanoids

(i) Pyrophoric alloys, known as **Misch metals,** contain lanthanoids about 90-95% (Ce 40.5%, lanthanum and neodymium 44%), iron 4.5%, calcium, carbon and silicon about 10.5% are used in cigarette and gas lighters, flame throwing tanks, toys, tank and tracer bullets as well as in shells.

(ii) Any alloy containing 30% Misch metals and 1% Zr are used for making parts of jet engines.

(iii) Cerium salts are commonly used as catalyst in petroleum cracking (cerium phosphate), volumetric analysis and as oxidizing agent (ceric sulphate), in dying cotton, in lead accumulators etc,

(iv) Oxides of praseodymium(Pr_2O_3) and neodymium (Nd_2O_4) are used in the preparation of coloured glasses and standard filters.

(v) Oxides of cerium and thorium are used in the preparation of gas lamp mantles.

(vi) Cerium oxide is used to prepare sunglasses as cerium cuts off heat and ultraviolet light.

3. ACTINIDES AND THEIR PROPERTIES

(i) The differentiating electron occupies 5f-subshell and thus these elements also have three outermost shells not filled to their capacity . These are called actinoids or actinones.

$_{89}$Ac: ....$5f^0$, $6s^2$ $6p^6$ $6d^1$, $7s^2$

$_{90}$Th: ....$5f^1$, $6s^2$ $6p^6$ $6d^1$, $7s^2$

$_{103}$Lw: ....$5f^0$, $6s^2$ $6p^6$ $6d^1$, $7s^2$

(ii) The electronic configuration of actinoids is [Rn] $5f^{0-14}$, $6d^{0-2}$, $7s^2$ where [Rn] stands for radon core. Like lanthanoids, they are placed together because of similar chemical nature.

(iii) Like lanthanoids contraction, these too show actinoid contraction due to poor shielding effect of 5f-subshells. Thus, atomic size of actinoids too decreases gradually from Ac to Lw.

(iv) Actinoids show a range of oxidation states, which is due to comparable energies of 5f, 6d and 7s-orbitals. Tl general oxidation state of actinoids is +3; the elements in the first half of the series show higher oxidation states.

(v) All these elements are strong reducing agents and are very reactive metals. Actinoids are radioactive and, therefore, it is difficult to study their chemical nature. However, relatively more stable isotopes of these elements beyond uranium have been discovered and the chemistry of these elements has been studied to an extent by using radiotracer techniques.

Like lanthanoids, they react with oxygen, halogens, hydrogens, sulphur and acids.

Uses of Actinoids: Only U, Th have found applications in nuclear reactions undergoing nuclear fission to produce nuclear power and nuclear bombs.

PLANCESS CONCEPTS

The 5f orbitals extend in space beyond 6s and 6p orbitals and participate in bonding.

Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 18: The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. **(JEE MAIN)**

Sol: This difference is due to occurrence of a wide range of oxidation states in actinoids. Also, their radioactivity causes a hindrance in their study.

POINTS TO REMEMBER

- General electronic configuration of d-block elements is (n – 1)$d^{1-10}ns^{0,1,2}$ and that of f-block element is (n-2) $f^{0.2....14}$(n –1)$d^{0,1,2}ns^2$
- Their melting and boiling points are high which are attributed to the involvement of (n–1)d electrons resulting in strong metallic bonds.
- Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from (n –1) d orbitals is not energetically unfavourable.
- Ionisation energies where the electron is removed from half-filled or completely filled orbiatls are especially large. Hence, Zn^{3+} is not formed.
- The metals, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.
- Reactivity of these elements is calculated as a sum of heat of sublimation, ionization enthalpy as well as heat of hydration.
- The transition elements are sufficiently electropositive to dissolve in mineral acids. Of the first series, with the exception of copper, all the metals are relatively reactive.
- The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures.
- These oxides dissolve in acids and bases to form oxometallic salts.
- The two series of inner transition elements, lanthanoids and actinoids constitute the f-block of the periodic table. With the successive filling of the inner orbitals, 4f, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (lanthanoid contraction). This has far reaching consequences in the chemistry of the elements succeeding them.
- Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally.

Solved Examples

JEE Main/Boards

Example 1: On what basis can you say that scandium (Z = 21) is a transition elements since Zinc (Z = 30) is not?

Sol: On the basis of incompletely filled 3d-orbitals. In case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled d-orbitals ($3d^{10}$) in its ground state as well as in its oxidized state, hence it is not regarded as transition element.

Example 2: Explain briefly how +2 becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

Sol: Elements of 1st half 3d-series are: Sc, Ti, V, Cr, Mn. Their electronic configuration are Sc = $[Ar]4s^2,3d^1$; Ti = $[Ar]4s^2, 3d^2$; V = $[Ar]4s^2, 3d^2$; Cr = $[Ar]\ 4s^1, 3d^5$ and Mn = $[Ar]4s^2, 3d^5$. As we move from Sc to Mn, the number of empty d-orbitals reduced in +2 ion thereby imparting more stability.

Example 3: Give reasons for the following. Transition metals have high enthalpies of atomization.

Sol: Due to strong interatomic interaction between valence electrons.

Example 4: What are interstitial compounds? Why are such compounds well known for transition metals?

Sol: Interstitial compounds are formed when small non-metallic atoms like H and C are trapped inside the crystal lattice of metals.

Example 5: Why is E° value for the M^{3+}/M^{2+} couple much more positive than that of Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}? Explain.

Sol: Much larger third ionization energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Example 6: Why is $AgNO_3$ kept in brown coloured bottles ?

Sol: Due to decomposition of $AgNO_3$ in presence of light. $AgNO_3$ decomposes on exposure to light and is thus stored in brown bottles to prevent the action of light.

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

Example 7: The species $[CuCl_4]^{2-}$ exist but $[CuI_4]^{2-}$ does not.

Sol: This can be explain by considering the reducing properties of the two ion. I^- ion is a stronger reducing agent than Cl^- ion. It reduces Cu^{2+} ion into Cu^+ ion. Hence, cupric iodide is converted into cuprous iodide. Thus, the species $[CuI_4]^{2-}$ does not exist.

Example 8: Which of the two compounds $Lu(OH)_3$ and $La(OH)_3$ is more basic and why?

Sol: Large is cation more is covalent character–Fajan's rule. More the ionic character more is the basicity. Due to lanthanoid contraction, the size of Lu^{3+} is increased and therefore $Lu(OH)_3$ shows more covalent character. Thus, $La(OH)_3$ is more ionic and thus more basic.

Example 9: Why is europium (II) more stable than cerium (II)?

Sol: In Eu^{2+}, f-subshell is half-filled and d-subshell is completely filled and thus more stable.

Example 10: In d-block metal ions, the colour of the complex changes with the ligand used while in f-block metal ion complexes, the colour remains almost constant and does not depend upon the nature of ligand, why?

Sol: Colour of a metal ion depends upon energy difference of two energy levels involved in transition. Splitting of degenerate d-orbitals into t_{2g} and e_g orbitals is greatly affected by nature of ligand. i.e., why $[Ni(NH_3)_6]^{2+}$ is blue, $[Ni(H_2O)_6]^{2+}$ is green and $[Ni(NO_2)_6]^{4-}$ is brown. Color of f block metal is due to f-f transition. 4f-orbitals in lanthanoids are deeply embedded in the atom and are deeply shielded bu 5s and 5p orbitals. Thus they remain almost unaffected by complex formation. Because of this color does not depend upon nature of ligand.

JEE Advanced/Boards

Example 1: What is the effect of increasing pH of $K_2Cr_2O_7$ solution?

Sol: In aqueous solution, we have

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

When pH < 4 (acidic medium), it exists as $Cr_2O_7^{2-}$ and the colour is orange. When pH > 7 (basic medium), it exists as CrO_4^- and the colour is yellow.

Example 2: Why does Mn(II) ion show the maximum paramagnetic behavior among bivalent ions of the first transition series ?

Sol: The electronic configurations of Mn and Mn (II) ion are

${}_{25}Mn : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

$Mn^{+2}: 1s^2, 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$

The Mn^{+2} ion has five unpaired electrons in its 3d subshell which is the maximum value for a transition metal ion. Hence, Mn(II) shows the maximum paramagnetic behavior (due to unpaired electrons) among bivalent ions of the first transition series.

Example 3: How can $AgNO_3$ be determined volumetrically?

Sol: $AgNO_3$ is titrated using NH_4SCN as an intermediate solution with ferric alum as indicator. When precipitation is completed, an additional drop of NH_4SCN produces red colour with the indicator of ferric alum.

$$AgNO_3 + NH_4SCN \longrightarrow \underset{\text{White ppt}}{AgSCN} + NH_4NO_3$$

$$Fe^{3+} + 3SCN^- \longrightarrow \underset{\text{Red colour}}{Fe(SCN)_3}$$

Example 4: For M^{2+}/M and M^{3+}/M^{2+} systems the E° values for some metals are as follows:

Cr^{2+}/Cr – 0.9V/Cr^{3+}/Cr^{2+} –0.4V

Mn^{2+}/Mn – 1.2V/Mn^{3+}/Mn^{2+} +1.5V

Fe^{2+}/Fe – 0.4V/Fe^{3+}/Fe^{2+} +0.8V

Use this data to comment upon:

The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+}.

Sol: Fe^{3+} converts more easily to Fe^{2+} and Mn^{3+} do not as indicated by E° value. The E^o_{OP} for H/H^+, Mn^{2+}/Mn^{3+}, Cr^{2+}/Cr^{3+} and Fe^{2+}/Fe^{3+} are 0, – 1.5, + 0.4 and – 0.8 V. Thus, stability of Fe^{3+} ion in acid medium is less than Cr^{3+} but more than Mn^{3+}.

Example 5: The yellow colour aqueous solution of Na_2CrO_4 changes to orange red on passing CO_2 gas. Explain.

Sol: CO_2 on dissolution in water produces acidic medium.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

Na_2CrO_4 changes to $Na_2Cr_2O_7$ (orange-red) in acidic medium.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

Example 6: An aqueous solution of inorganic compound (X) gives following reactions:

(i) With an aqueous solution of barium chloride a precipitate insoluble in dil. HCl is obtained.

(ii) Addition of excess of KI gives a brown ppt. which turns white on addition of excess of hypo.

(iii) With an aqueous solution of $K_4Fe(CN)_6$ a chocolate coloured precipitate is obtained. Identify (X) and give equations for the reaction for (i), (ii) and (iii) observations.

Sol: (i) Step (i) suggests that compound (X) contains SO_4^{2-} radical.

(ii) Step (iii) suggests that the compound (X) contains Cu^{2+} radical.

(iii) Hence, the salt is $CuSO_4$

Reactions:

(i) $$\underset{(X)}{CuSO_4} + BaCl_2 \rightarrow \underset{\substack{\text{White ppt.} \\ \text{(Insoluble in HCl)}}}{BaSO_4} + CuCl_2$$

(ii) $$\underset{(X)}{2CuSO_4} + 4KI \rightarrow 2Cu\,I_2 + 2K_2SO_4$$

$$\underset{\text{Unstable}}{2CuI_2} \rightarrow Cu_2I_2 + I_2$$

$$I_2 + 2Na_2S_2O_3 \rightarrow \underset{\text{Colourless}}{Na_2S_4O_6} + 2NaI$$

(iii)

$$\underset{(X)}{2CuSO_4} + K_4\left[Fe(CN)_6\right] \rightarrow \underset{\text{Chocolate coloured ppt.}}{Cu_2\left[Fe(CN)_6\right]} + 2K_2SO_4$$

Example 7: Give complete and balanced chemical equations for the following:

(i) Mercurous nitrate reacts with excess of KI solution.

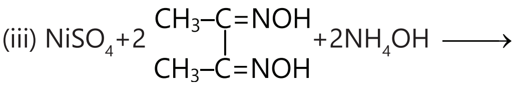
(ii) Sodium chromite solution reacts with H_2O_2 in presence of NaOH.

(iii) Nickel sulphate reacts with dimethyl glyoxime reagent in ammoniacal solution.

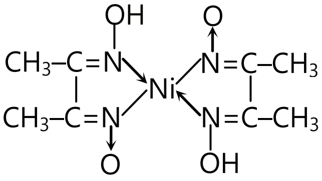
Sol: (i) $Hg_2(NO_3)_2 + 2KI(\text{excess}) \rightarrow Hg_2I_2 + 2KNO_3$

$Hg_2I_2 + 2KI \rightarrow K_2HgI_4 + Hg$

(ii) $Na_2CrO_3 + H_2O_2 \rightarrow Na_2CrO_4 + H_2O$



(iii) $NiSO_4 + 2\begin{array}{l}CH_3-C=NOH\\ \quad\;\;|\\ CH_3-C=NOH\end{array} + 2NH_4OH \longrightarrow$



$+(NH_4)_2SO_4 + 2H_2O$

Example 8: Out of cobalt and zinc salts, which is attracted in a magnetic field?

Sol: Out of cobalt and zinc salts, the cobalt salts are attracted in a magnetic field, because the cobalt ion containing unpaired electron is characterized by a permanent magnetic moment. Zn^{2+} ion contains $3d^{10}$ configuration, i.e, no unpaired electrons, so zinc salts are not attracted in magnetic field.

Example 9: A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine gives a precipitate (D) which is soluble in NH_4OH. On adding aqueous solution of (B) to hypo solution a white precipitate (E) is obtained. (E) turns black on standing. Identify (A) to (E).

Sol: (i) The compound (B) reacts with NaCl (brine) to give white precipitate (D) soluble in NH_4OH, so (D) is AgCl.

(ii) Thus, (B) must contain Ag^+ ion.

(iii) (B) is obtained from (A) and dil. HNO_3, so (B) is $AgNO_3$ and (A) is Ag.

Reactions:

$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$
(A) (B) (C)

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
(B) (D)

$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2Cl + 2H_2O$
(D) Soluble

$Ag_2NO_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$
(B) (E) White

$Ag_2S_2O_3 \rightarrow Ag_2S + SO_3$
(E) Black

Example 10: Pyrolusite on heating with KOH in the presence of air gives a dark green compound (A). The solution of (A) on treatment with H_2SO_4 gives a purple coloured compound (B), which gives following reactions:

(i) KI on reaction with alkaline solution of (B) changes into a compound (C).

(ii) The colour of the compound (B) disappears on treatment with the acidic solution of $FeSO_4$.

(iii) With conc. H_2SO_4, compound (B) gives (D) which can decompose to yield (E) and oxygen. Identify (A) to (E) and write balanced chemical equations for the formation of (A) and (B) and for the steps (i) to (iii).

Sol: $MnO_2 + 2KOH \xrightarrow{[O]} K_2MnO_4 + H_2O$
Pyrolusite Dark green (A)

$3K_2MnO_4 + 2H_2O \xrightarrow{\text{Dil. } H_2SO_4} 2KMnO_4 + MnO_2 + 4KOH$
Purple (B)

(i) $2KMnO_4 + KI + H_2O \rightarrow KIO_3 + 2MnO_2 + 2KOH$
(C)

(ii) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4$
$\rightarrow 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(iii) $2KMnO_4 + H_2SO_{4(conc)} \rightarrow K_2SO_4 + Mn_2O_7 + H_2O$
(D)

$2Mn_2O_7 \rightarrow 4MnO_2 + 3O_2$
(D) (E)

JEE Main/Boards

Exercise 1

Q.1 Why are Mn^{2+} compound more stable than Fe^{2+} towards oxidation in their + 3 state?

Q.2 Write complete equation for oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium.

Q.3 Answer the following equations:

(i) Which element in the first series of transition elements does not exhibit variable oxidation state and why ?

(ii) Why do actinides, in general exhibit a greater range of oxidation states than the lanthanides ?

Q.4 Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number ?

Q.5 Write chemical equations for the reactions involved in the manufacture of potassium permanganate from pyrolusite ore.

Q.6 What is misch metal ? Mention its two important uses.

Q.7 To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

Q.8 (a) Name two properties of the central metal ion which enable it to form stable complex entities.

(b) Account for the following: Zinc salts are white, Cu^{2+} salts are coloured.

Q.9 How do you account for the following ?

(a) All scandium salts are white ?

(b) The first ionization energies of the 5d transition elements are higher than those of the 3d and 4d transition elements in respective groups ?

Q.10 What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

Q.11 Explain the following observations:

(a) The elements of the d-series exhibit a larger number of oxidation states than the elements of f-series.

(b) The Cu^{+} salts are colorless while Cu^{2+} salts are coloured.

Q.12 Mention the direct consequence of the following factors on the chemical behavior of the transition elements:

(i) They have incomplete d-orbitals in the ground state or in one of the oxidized states of their atoms.

(ii) They contribute more valence electrons per atom in the formation of metallic bonds.

Q.13 What are the characteristics of the transition elements and why are they called transition elements? Which of the d-block elements may not be regarded as the transition elements?

Q.14 How would you account for the following situations ?

(i) The transition metals generally form coloured compounds.

(ii) With $3d^4$ configuration, Cu^{2+} acts as a reducing agent but Mn^{3+} acts as oxidizing agent

(iii) The actinides exhibit a larger number of oxidation states than the corresponding lanthanides.

Q.15 How would you account for the following

(i) The transition elements have high enthalpies of atomization.

(ii) The transition metals and their compounds are found to be good catalysts in many processes.

Q.16 Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behavior.

(ii) The enthalpies of atomization of the transition metals are high.

(iii) The transition metals generally form coloured compounds.

(iv) Transition metals and their many compounds act as good catalyst

Q.17 Give reason for each of the following:

(i) Size of trivalent lanthanide cations decreases with increase in the atomic number

(ii) Transition metal fluorides are ionic in nature, whereas bromides and chlorides are usually covalent in nature.

(iii) Chemistry of all the lanthanides is quite similar

Q.18 Discuss the general characteristics of the 3d series of the transition elements with special reference to their.

(i) Atomic sizes

(ii) Enthalpies of atomization

(iii) Tendency for complex formation

Q.19 Predict which of the following will be coloured in aqueous solution. Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+}. Give reasons for each.

Q.20 Write down electronic configuration of the following:

(i) La^{3+} (ii) Gd^{3+} (iii) Eu^{2+}

(iv) Zn^{4+} (v) Ru^{2+} (vi) Ce^{4+}

Q.21 What are alloys ? Name an important alloy which contains some of the lanthanide metals. Mention its uses.

Q.22 (a) Give one example each of amphoteric and acidic oxides of transition metals

(b) Describe the trends in the following cases:

(i) Melting points of elements in the 3d transition series.

(ii) Atomic sizes of elements in the 4f transition series.

Q.23 How would you account for the following ?

(i) Sc, the first member of first transition series does not exhibit variable oxidation state.

(ii) K_2PtCl_6 is well-known compound whereas corresponding compound of nickel is not known.

(iii) Only transition metals form complex compounds with ligands such as CO.

Q.24 Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

Q.25 Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate ?

Q.26 Assign reason for the following:

(i) From element to element, the actinides contraction is greater than lanthanide contraction.

(ii) The E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(iii) Scandium (Z = 21) does not exhibit variable oxidation states and yet it is regarded as transition element.

Q.27 Describe the oxidizing action of potassium dichromate and write the ionic equations for its reaction with:

(i) Iodide (ii) iron (iii) H_2S

Q.28 (a) Describe the general trends in the following properties of the first series of the transition elements:

(i) Stability of +2 oxidation state

(ii) Formation of oxometal ions.

(b) Assign reason for each of the following:

(i) Transition elements exhibit variable oxidation states.

(ii) Transition metal ions are usually coloured

Q.29 (a) Write the steps involved in the preparation of:

(i) $K_2Cr_2O_7$ from Na_2CrO_4

(ii) $KMnO_4$ from K_2MnO_4

(b) What is meant by lanthanide contraction?

What effect does it have on the chemistry of the elements which follow lanthanides?

Exercise 2

Single Correct Choice Type

Q.1 The number of moles of acidified $KMnO_4$ required to convert one mole of sulphite ion into sulphate ion is

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

Q.2 $N_2(g) + 3H_2(g) \xrightleftharpoons{Fe + Mo} 2NH_3(g)$; Haber's process, Mo is used as

(A) A catalyst (B) A catalytic promoter

(C) An oxidizing agent (D) None of these

Q.3 An ornament of gold is made up of 75% of gold, it is of..........carat.

(A) 18 (B) 16 (C) 24 (D) 20

Q.4 Solution of MnO_4^- is purple-coloured due to

(A) d-d transition

(B) Charge transfer from O to Mn

(C) Due to both d-d-transition and charge transfer

(D) None of these

Q.5 Transition elements having more tendency to form complex than representative elements (s and p-block elements) due to

(A) Availability of d-orbitals for bonding

(B) Variable oxidation states are not shown by transiton elements

(C) All electrons are paired in d-orbitals

(D) f-orbitals are available for bonding

Q.6 During estimation of oxalic acid Vs $KMnO_4$ self-indicator is

(A) $KMnO_4$ (B) Oxalic acid

(C) K_2SO_4 (D) $MnSO_4$

Q.7 A compound of mercury used in cosmetics, in ayurvedic and yunani medicines and known as Vermilon is

(A) $HgCl_2$ (B) HgS (C) Hg_2Cl_2 (D) HgI

Q.8 Acidified chromic acid + H_2O_2

$\xrightarrow{\text{Org. solvent}}$ X + Y, X and Y are

(A) CrO_5 and H_2O (B) Cr_2O_3 and H_2O

(C) CrO_2 and H_2O (D) CrO and H_2O

Q.9 Transition element are usually characterised by variable oxidation states by Zn does not show this property because of

(A) Completion of np-orbitals

(B) Completion of (n – 1)d orbitals

(C) Completion of nd orbitals

(D) None of these

Q.10 Coinage metals show the properties of

(A) Typical elements

(B) Normal elements

(C) Inner-transition elements

(D) None of these

Q.11 Bayer's reagent used to detect olefinic double bond is

(A) Acidified $KMnO_4$

(B) Aqueous $KMnO_4$

(C) 1% alkaline $KMnO_4$ solution

(D) $KMnO_4$ in benzene

Q.12 The transition metal used in X-rays tube is

(A) Mo (B) Ta (C) Pb (D) Tc

Q.13 The higher oxidation states of transition elements are found to be in the combination with A and B, which are

(A) F, O (B) O, N (C) Cl,O (D) S, F

Q.14 1 mole of Fe^{2+} ions are oxidised to Fe^{3+} ions with help of (in acidic medium)

(A) 1/5 moles of $KMnO_4$ (B) 5/3 moles of $KMnO_4$

(C) 2/5 moles of $KMnO_4$ (D) 5/2 moles of $KMnO_4$

Q.15 The metals present in insulin and haemoglobin are respectively

(A) Zn Hg (B) Zn Fe (C) Cu, Hg (D) Cu, Fe

Q.16 Solid $CuSO_4.5H_2O$ having covalent, ionic as well as co-ordinate bonds. Copper atom/ion forms..........co-ordinate bonds with water.

(A) 1 (B) 2 (C) 3 (D) 5

Q.17 Purple of cassius is:

(A) Pure gold (B) Colloidal solution of gold

(C) Gold (I) hydroxide (D) Gold (III) chloride

Q.18 Number of moles of $SnCl_2$ required for the reduction of 1 mole of $K_2Cr_2O_7$ into Cr_2O_3 is (in acidic medium)

(A) 3 (B) 2 (C) 1 (D) 1/3

Q.19 The aqueous solution of $CuCrO_4$ is green because it contains.

(A) Green Cu^{2+} ions

(B) Green CrO_4^{2-} ions

(C) Blue Cu^{2+} ions and green CrO_4^{2-} ions

(D) Blue Cu^{2+} ions and yellow CrO_4^{2-} ions

Q.20 Manganese steel is used for making railway tracks because

(A) It is hard with high percentage of Mn

(B) It is soft with high percentage of Mn

(C) It is hard with small concentration of manganese with impurities

(D) It is soft with small concentration of manganese with impurities

Q.21 Transition elements in lower oxidation states act as Lewis acid because

(A) They form complexes

(B) They are oxidizing agents

(C) They donate electrons

(D) They do not show catalytic properties

Q.22 The Ziegler-Natta catalyst used for polymerization of ethane and styrene is $TiCl_4 + (C_2H_5)_3Al$, the catalyzing species (active species) involved in the polymerization is

(A) $TiCl_4$ (B) $TiCl_3$ (C) $TiCl_2$ (D) TiCl

Previous Years' Questions

Q.1 In nitroprusside ion, Iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by ***(1998)***

(A) Estimating the concentration of iron

(B) Measuring the concentration of CN^-

(C) Measuring the solid state magnetic moment

(D) Thermally decomposing the compound

Q.2 Among the following the compound that is both paramagnetic and coloured is ***(1997)***

(A) $K_2Cr_2O_7$ (B) $(NH_4)_2(TiCl_6)$

(C) $VOSO_4$ (D) $K_3[Cu(CN_4)]$

Q.3 Potassium manganate (K_2MnO_4) is formed when ***(1988)***

(A) Chlorine is passed into aqueous $KMnO_4$ solution

(B) Manganese dioxide is fused with potassium hydroxide in air

(C) Formaldehyde reacts with potassium permanganate in presence of a strong alkali

(D) Potassium permanganate reacts with conc. sulphuric acid

Q.4 The aqueous solution of the following salts will be coloured in the case of ***(1990)***

(A) $Zn(NO_3)_2$ (B) $LiNO_3$

(C) $Co(NO_3)_2$ (D) $CrCl_3$ (E) Potash alum

Q.5 Which of the following alloys contains Cu and Sn ***(1993)***

(A) Bronze (B) Brass (C) Gun metal (D) Type metal

Q.6 Which of the following statement(s) is (are) correct. When a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ***(1998)***

(A) A deep red vapours is evolved

(B) The vapours when passed into NaOH solution gives yellow solution of Na_2CrO_4

(C) Chlorine gas is evolved

(D) Chromyl chloride is formed

Q.7 Addition of high proportions of manganese makes steel useful in making rails or railroads, because manganese ***(1998)***

(A) Gives hardness to steel

(B) Helps the formation of oxide of iron

(C) Can remove oxygen and sulphur

(D) Can show highest oxidation state of +7

Q.8 **Assertion:** Rusting of an iron is an example of corrosion. ***(2008)***

Reason: Rusting of iron is decreased by acids and electrolytes

Q.9 **Assertion:** AgBr is used in photography ***(1996)***

Reason : AgBr undergoes photochemical reaction.

Q.10 **Assertion:** Tungsten filament is used in electric bulbs. ***(1994)***

Reason : Tungsten is a metal of high melting point.

Q.11 Assertion: In transition elements ns orbital is filled up first and (n – 1)d afterwards, during ionization ns electrons are lost prior to (n – 1)d electrons. ***(1995)***

Reason: The effective nuclear charge felt by (n – 1)d electrons is higher as compared to that of ns electrons.

Q.12 Assertion: The degree of complex formation in actinides decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$ ***(1997)***

Reason: Acitnides form complex with π-bonding ligands such as alkyl phosphines and thioethers.

Q.13 Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being ***(2008)***

(A) 4f orbitals more diffused than the 5f orbitals

(B) Lesser energy difference between 5f and 6d than between 4f and 5d orbitals

(C) More energy difference between 5f and 6d than between 4f and 5d orbitals

(D) More reactive nature of the actinoids than the lanthanoids

Q.14 Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements in incorrect? ***(2009)***

(A) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.

(B) The ionic sizes of Ln (III) decrease in general with increasing atomic number.

(C) Ln (III) compounds are generally colourless.

(D) Ln (III) hydroxides are mainly basic in character.

Q.15 The correct order of $E^{\circ}_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is ***(2010)***

(A) Mn > Cr > Fe > Co (B) Cr > Fe > Mn > Co

(C) Fe > Mn > Cr > Co (D) Cr > Mn > Fe > Co

Q.16 The magnetic moment (spin only) of $\left[NiCl_4\right]^{2-}$ is ***(2011)***

(A) 5.46 BM (B) 2.83 BM

(C) 1.41 BM (D) 1.82 BM

Q.17 In context of the lanthanoids, which of the following statements is not correct? ***(2012)***

(A) All the members exhibit +3 oxidation state

(B) Because of similar properties the separation of lanthanoids is not easy.

(C) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

(D) There is a gradual decrease in the radii of the members with increasing atomic number in the series.

Q.18 Which of the following arrangements does not represent the correct order of the property stated against it? ***(2013)***

(A) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: Paramagnetic behaviour

(B) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: Ionic size

(C) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: Stability in aqueous solution

(D) Sc < Ti < Cr < Mn: Number of oxidation states

Q.19 The pair having the same magnetic moment is: ***(2016)***

[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]

(A) $\left[Cr(H_2O)_6\right]^{2+}$ and $\left[Fe(H_2O)_6\right]^{2+}$

(B) $\left[Mn(H_2O)_6\right]^{2+}$ and $\left[Cr(H_2O)_6\right]^{2+}$

(C) $\left[CoCl_4\right]^{2-}$ and $\left[Fe(H_2O)_6\right]^{2+}$

(D) $\left[Cr(H_2O)_6\right]^{2+}$ and $\left[CoCl_4\right]^{2-}$

JEE Advanced/Boards

Exercise 1

Q.1 Explain why the greenish solution of potassium manganate turns purple when CO_2 is bubbled in the solution.

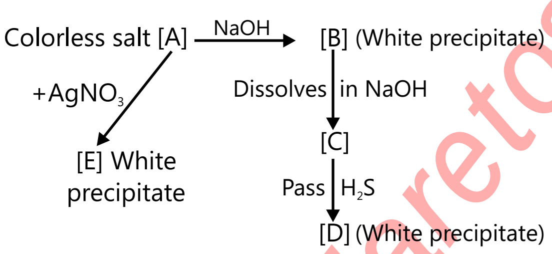
Q.2 Explain why mercurous compounds are formed when mercury is oxidized in a limited amount of an oxidizing agent whereas with an excess of oxidizing agent mercuric compounds are formed.

Q.3 Explain why $[Co(NH_3)_6]^{3+}$ is diamagnetic and $[CoF_6]^{3-}$ is strongly paramagnetic.

Q.4 What happens when NaOH or NH_4OH are added in excess to $AlCl_3$ and $ZnCl_2$?

Q.5 Why is zinc oxide used in paints instead of lead salts?

Q.6 Identify from [A] to [E].



Q.7 Why are melting and boiling points of zinc, cadmium, and mercury is lower than those of other transition metals?

Q.8 Why is HCl not used to acidify $KMnO_4$ for volumetric estimations?

Q.9 Colourless salt (A) $\xrightarrow{?}$ (B) + (C) gas.

(B) Dissolves both in acid and alkali solution.

(C) Turns lime water milky and acidified $K_2Cr_2O_7$ solution green.

(A) Gives white precipitate (D) with H_2S when the solution is alkaline. Identify [A] to [D].

Q.10 (i) K_2MnO_4 in acidic medium changes to MnO_2 and $KMnO_4$. What would be the equivalent weight of K_2MnO_4.

(ii) Draw the structures of MnO_4^- and CrO_4^{2-}

Q.11 A complex has the formula $PtCl_4.2KCl$. The electrical conductance of the compound shows that each formula unit had 3 ions. $AgNO_3$ on treatment with the complex does not give a precipitate of AgCl. What should be the correct formula of the complex?

Q.12 $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ both are tetrahedral in shape but $[NiCl_4]^{2-}$ is paramagnetic whereas $[Ni(CO)_4]$ is diamagnetic. Explain in the difference in magnetic behavior both the complexes.

Q.13 $FeSO_4$ solution is mixed with $(NH_4)_2SO_4$ in the molar ratio 1 : 1. It gives test of Fe^{2+}. When $CuSO_4$ is mixed with liquid ammonia (in the ratio 1 : 4) the mixture does not give test of Cu^{2+}. Explain the difference.

Q.14 (A), (B) and (C) are three complexes of Cr(III). Its formula is $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ions as ligands. (A) does not react with conc. H_2SO_4 whereas (B) and (C) loss 6.75% and 13.5% of their original weight respectively on treatment with conc. H_2SO_4. Find [A], [B] and [C]

Q.15 A metal complex having composition $Cr(NH_3)_4Cl_2.Br$ has been isolated in two forms (A) and (B). (A) reacts with $AgNO_3$ to give a white precipitate soluble in dilute ammonia while (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formulae of (A) and (B) and hybridization state of Cr in the compounds.

Q.16 A monomeric compound of cobalt gives the following data on quantitative analysis: Co^{3+}: 21.24%; NH_3: 24.77%; Cl^-: 12.81%; SO_4^{3-} : 34.65%; H_2O: 6.53% Deduce the empirical formula of the complex and the possible isomers.

Exercise 2

Single Correct Choice Type

Q.1 $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$, X and Y are respectively

(A) X = OH^-, Y = H^+ (B) X = H^+, Y = OH^-

(C) X = OH^-, Y = H_2O_2 (D) X = H_2O_2, Y = OH^-

Q.2 CrO_3 dissolves in aqueous NaOH to give

(A) $Cr_2O_7^{2-}$ (B) CrO_4^{2-}

(C) $Cr(OH)_3$ (D) $Cr(OH)_2$

Q.3 $(NH_4)_2Cr_2O_7$ (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is

(A) Cr_2O_3 (B) CrO_2 (C) Cr_2O_4 (D) CrO_3

Q.4 The d-block elements which is liquid at room temperature, having high specific heat, less reactivity than hydrogen and its chloride (MX_2) is volatile on heating is

(A) Cu (B) Hg (C) Ce (D) Pm

Q.5 Iron becomes passive by.................due to formation of..............

(A) Dil. HCl, Fe_2O_3

(B) 80% conc. HNO_3, Fe_3O_4

(C) Conc. H_2SO_4, Fe_3O_4

(D) Conc. HCl, Fe_3O_4

Q.6 Cu + conc. $HNO_3 \rightarrow Cu(NO_3)_2$ + X (oxide of nitrogen); then X is-

(A) N_2O (B) NO_2 (C) NO (D) N_2O_3

Q.7 When $KMnO_4$ solution is added to hot oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time. This is because

(A) Mn^{2+} acts as auto catalyst

(B) CO_2 is formed

(C) Reaction is exothermic

(D) MnO_4^- catalyses the reaction

Q.8 $CuSO_4$ solution reacts with excess KCN to give

(A) $Cu(CN)_2$ (B) CuCN

(C) $K_2[Cu(CN)_2]$ (D) $K_3[Cu(CN)_2]$

Q.9 Pick out the incorrect statements:

(A) MnO_2 dissolves in conc. HCl, but does not form Mn^{4+} ions

(B) MnO_2 oxidizes hot concentrated H_2SO_4 liberating oxygen

(C) K_2MnO_4 is formed when MnO_2 in fused KOH is oxidized by air, KNO_3, PbO_2 or $NaBiO_3$

(D) Decomposition of acidic $KMnO_4$ is not catalysed by sunlight

Q.10 The rusting of iron is formulated as $Fe_2O_3.xH_2O$ which involves the formation of

(A) Fe_2O_3 (B) $Fe(OH)_3$

(C) $Fe(OH)_2$ (D) Fe_2O_3 + $Fe(OH)_3$

Q.11 Metre scales are made-up of alloy

(A) Invar (B) Stainless steel

(C) Electron (D) Magnalium

Q.12 A metal M which is not affected by strong acids like conc. HNO_3, conc. H_2SO_4 and conc. solution of alkalies like NaOH, KOH forms MCl_3 which finds use for toning in photography. The metal M is-

(A) Ag (B) Hg (C) Au (D) Cu

Q.13 $KMnO_4$ + HCl $\rightarrow H_2O$ + X(g), X is a (acidified)

(A) Red liquid (B) Violet gas

(C) Greenish yellow (D) Yellow-brown gas

Q.14 In nitroprusside ion, the iron exists as Fe^{2+} and NO as NO^+ rather than Fe^{3+} and NO respectively. These forms of ions are established with the help of

(A) Magnetic moment in solid state

(B) Thermal decomposition method

(C) By reaction with KCN

(D) By action with K_2SO_4

Multiple Correct Choice Type

Q.15 The metal(s) which does/do not form amalgam is/are

(A) Fe (B) Pt (C) Zn (D) Ag

Q.16 The highest oxidation state among transition element is

(A) + 7 by Mn (B) + 8 by Os

(C) +8 by Ru (D) + 7 by Fe

Q.17 Amphoteric oxide(s) is/are

(A) Al_2O_3 (B) SnO (C) ZnO (D) Fe_2O_3

Q.18 Interstitial compounds are formed by-

(A) Co (B) Ni (C) Fe (D) Ca

Q.19 To an acidified dichromate solution, a pinch of Na_2O_2 is added as shaken. What is observed:

(A) Blue colour

(B) Orange colour changing to green

(C) Copious evolution of oxygen

(D) Bluish-green precipitate

Q.20 Amongst CuF_2, $CuCl_2$ and $CuBr_2$

(A) Only CuF_2 is ionic

(B) Both $CuCl_2$ and $CuBr_2$ are covalent

(C) CuF_2 and $CuCl_2$ are ionic but $CuBr_2$ is covalent

(D) CuF_2, $CuCl_2$as well as $CuBr_2$ are ionic

Q.21 $CuSO_4(aq) + 4NH_3 \rightarrow X$, then X

(A) $[Cu(NH_3)_4]^{2+}$

(B) Paramagnetic

(C) Coloured

(D) Has magnetic moment 1.73 BM

Q.22 Amphoteric oxide(s) of Mn is/are

(A) MnO_2 (B) Mn_3O_4

(C) Mn_2O_7 (D) MnO

Q.23 The lanthanide contraction is responsible for the fact that

(A) Zr and Hf have same atomic sizes

(B) Zr and Hf have same properties

(C) Zr and Hf have different atomic sizes

(D) Zr and Hf have different properties

Q.24 Potash alum is a double salt, its aqueous solution shows the characteristic of-

(A) Al^{3+} ions (B) K^+ ions

(C) SO_4^{2-} ions (D) Al^{3+}, ions but not K^+ ions

Q.25 Addition of non-metals like B and C to the interstitial sites of a transition metal results the metal-

(A) Of more ductability (B) Of less ductability

(C) Less malleable (D) Of more hardness

Q.26 Mercury is a liquid at 0ºC because of-

(A) Very high ionization energy

(B) Weak metallic bonds

(C) High heat of hydration

(D) High heat of sublimation

Q.27 The ionization energies of transition elements are-

(A) Less than p-block elements

(B) More than s-block elements

(C) Less than s-block elements

(D) More than p-block elements

Q.28 The catalytic activity of transition elements is related to their-

(A) Variable oxidation states

(B) Surface area

(C) Complex formation ability

(D) Magnetic moment

Q.29 In the equation: $M + 8CN^- + 2H_2O + O_2 \rightarrow 4[M(CN)_2]^- + 4OH^-$, metal M is-

(A) Ag (B) Au (C) Cu (D) Hg

Q.30 An elements of 3d-transtion series shows two oxidation states x and y, differ by two units then-

(A) Compounds in oxidation state x and ionic if x > y

(B) Compounds in oxidation state x are ionic if x < y

(C) Compound in oxidation state y are covalent if x < y

(D) Compounds in oxidation state y are covalent if x > y

Q.31 Ion(s) having non zero magnetic moment (spin only) is/are

(A) Sc^{3+} (B) Ti^{3+} (C) Cu^{2+} (D) Zn^{2+}

Assertion Reasoning Type

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both assertion and reason are true and reason is the correct explanation of assertion

(B) if both assertion and reason are true but reason is not correct explanation of assertion

(C) if assertion is true but reason is false

(D) if assertion is false and reason is true

Q.32 Statement-I: Equivalent mass of $KMnO_4$ is equal to one-third of its molecular mass when it acts as a oxidizing agent in an alkaline medium.

Statement-II: Oxidation number of Mn is + 7 in $KMnO_4$.

Q.33 Statement-I: K_2CrO_4 has yellow colour due to charge transfer.

Statement-II: CrO_4^{2-} ion is tetrahedral in shape.

Q.34 Statement-I: The highest oxidation state of chromium in its compounds is +6.

Statement-II: Chromium atom has only six electrons in ns and (n – 1) d orbitals.

Q.35 Statement-I: Tungsten has a very high melting point.

Statement-II: Tungsten is a covalent

Q.36 Statement-I: Cu^+ ion is colourless.

Statement-II: Four water molecules are coordinated to Cu^+ ion.

Previous Years' Questions

Q.1 The pair of compounds having metals in their highest oxidation state is ***(2004)***

(A) MnO_2, $FeCl_3$ (B) $[MnO_4]^-$,CrO_2Cl_2

(C) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$ (D) $[NiCl_4]^{2-}$, $[CoCl_4]^-$

Q.2 When I^- is oxidized by MnO_4^- in alkaline medium, I^- converts into- ***(2004)***

(A) IO_3^- (B) I_2 (C) IO_4^- (D) IO^-

Q.3 Which of the following pair is expected to exhibit same colour in solution? ***(2005)***

(A) $VOCl_2$; $FeCl_2$ (B) $CuCl_2$; $VOCl_2$

(C) $MnCl_2$; $FeCl_2$ (D) $FeCl_2$; $CuCl_2$

Q.4 Which of the following will not be oxidized by O_3? ***(2005)***

(A) KI (B) $FeSO_4$ (C) $KMnO_4$ (D) K_2MnO_4

Q.5 Which of the following alloys contains Cu and Zn ? ***(1993)***

(A) Bronze (B) Brass (C) Gun metal (D) Type metal

Q.6 Which of the following statement(s) is/are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4? ***(1998)***

(A) A deep red vapours is formed

(B) Vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4

(C) Chlorine gas is evolved

(D) Chromyl chloride is formed

Q.7 Which of the following statement(s) is/are correct? ***(1998)***

(A)The electronic configuration of Cr is [Ar] $3d^5 4s^1$ (Atomic number of Cr = 24)

(B) The magnetic quantum number may have a negative value

(C) In silver atom 23 electrons have a spin of one type and 24 of the opposite type (Atomic number of Ag = 47)

(D) The oxidation state of nitrogen in HN_3 is – 3

Q.8 Reduction of the metal centre in aqueous permanganate ion involves ***(2011)***

(A) Three electrons in neutral medium

(B) Five electrons in neutral medium

(C) Three electrons in alkaline medium

(D) Five electrons in acidic medium

Q.9 A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion of the compound. ***(1997)***

Q.10 Give reasons: CrO_3 is an acid anhydride. ***(1999)***

Q.11

$$\underset{\text{White fumes with pungent smell}}{B} \xleftarrow{\text{Moist air}} \underbrace{(MCl_4)}_{\text{(M=Transition element-colorless)}} \xrightarrow{Zn} \underset{\text{Purple color}}{A}$$

Identify the metal M and hence MCl_4. Explain the difference in colours of MCl_4 and M. ***(2005)***

Q.12 Among the following metal carbonyls, the $C-O$ bond order is lowest in ***(2007)***

(A) $\left[Mn(CO)_6\right]^+$ (B) $\left[Fe(CO)_5\right]$

(C) $\left[Cr(CO)_6\right]$ (D) $\left[V(CO)_6\right]$

Q.13 Among the following the coloured compound is ***(2008)***

(A) CuCI (B) $K_3\left[Cu(CN)_4\right]$

(C) CuF_2 (D) $\left[Cu(CH_3CN)_4\right]BF_4$

Q.14 The spin only magnetic moment value (in Bohr magnetron units) of $Cr(CO)_6$ s ***(2009)***

(A) 0 (B) 2.84 (C) 4.90 (D) 5.92

Q.15 Match each of the reactions given in column I with the corresponding product(s) given in column II. ***(2009)***

Column I	**Column II**
(A) Cu + dilHNO_3	(p) NO
(B) Cu + concHNO_3	(q) NO_2
(C) Zn + dil HNO_3	(r) N_2O
(D) Zn + conc HNO_3	(s) $Cu(NO_3)_2$
	(t) $Zn(NO_3)_2$

Q.16 The complex showing a spin-only magnetic moment of 2.82 B.M. is ***(2010)***

(A) $Ni(CO)_4$ (B) $\left[NiCl_4\right]^{2-}$

(C) $Ni(PPh_3)_4$ (D) $\left[Ni(CN)_4\right]^{2-}$

Q.17 Among the following complexes $(K-P)$ ***(2011)***

$K_3\left[Fe(CN)_6\right](K), \left[Co(KNH_3)_6\right]Cl_3, (L),$

$Na_3\left[Co(oxalate)_3\right](M), \left[Ni(H_2O)_6\right]Cl_2\,(N),$

$K_2\left[Pt(CN)_4\right](O)$ and $\left[Zn(H_2O)_6\right](NO_3)_2\,(P)$

(A) K, L, M N (B) K, M, O, P

(C) L, M, O, P (D) L, M, N, O

Q.18 The colour of light absorbed by an aqueous solution of $CuSO_4$ is ***(2012)***

(A) Orange-red (B) Blue-green

(C) Yellow (D) Violet

Q.19 Consider the following complex ions, P, Q and R

$P = \left[FeF_6\right]^{3-}, Q = \left[V(H_2O)_6\right]^{2+}$ and $R = \left[Fe(H_2O)_6\right]^{3+}$

The correct order of the complex ions, according to their spin–only magnetic moment values (in B.M.) is ***(2013)***

(A) $R < Q < P$ (B) $Q < P < Q$

(C) $R < P < Q$ (D) $Q < P < R$

Q.20 For the octahedral complexes Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetrons (When approximated to the nearest integer) is [Atomic number of Fe = 26] ***(2015)***

Q.21 Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$ $[Co(NH_3)_4\ Cl_2]$, Cl, $Na_3\ [CoFe_6]$, Na_2O_2 the total number of paramagnetic compounds is ***(2016)***

(A) 2 (B) 3 (C) 4 (D) 5

Q.22 The geometries of the ammonia complexes Ni^{2+}, Pt^{2+} and Zn^{2+} respectively, are ***(2016)***

(A) Octahedral, square planar and tetrahedral

(B) Square planar, octahedral and tetrahedral

(C) Tetrahedral, square planar and octahedral

(D) Octahedral, tetrahedral and square planar

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.3 Q.5 Q.6
Q.9 Q.12 Q.14 (ii)
Q.17 Q.19 Q.22 (a)
Q.23 (ii) Q.29

Exercise 2

Q.3 Q.4 Q.8
Q.11 Q.19 Q.21

Previous Years' Questions

Q.1 Q.2 Q.6
Q.9

JEE Advanced/Boards

Exercise 1

Q.5 Q.7 Q.9
Q.11 Q.13

Exercise 2

Q.4 Q.8 Q.11
Q.14 Q.19 Q.20
Q.24 Q.26 Q.29

Previous Years' Questions

Q.8 Q.11

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 A **Q.2** B **Q.3.**A **Q.4** B **Q.5** A **Q.6** A
Q.7 B **Q.8** A **Q.9** B **Q.10** D **Q.11** C **Q.12** A
Q.13 A **Q.14** A **Q.15** B **Q.16** D **Q.17** B **Q.18** A
Q.19 D **Q.20** A **Q.21** A **Q.22** B

Previous Years' Questions

Q.1 C **Q.2** C **Q.3** B, C **Q.4** C, D **Q.5** A, B **Q.6** A, B, D **Q.7** A, C
Q.8 C **Q.9** B **Q.10** A **Q.11** A **Q.12** B **Q.13** B **Q.14** C
Q.15 A **Q.16** B **Q.17** C **Q.18** A **Q.19** A

JEE Advanced/Boards

Exercise 1

Q.1 Formation of MnO_4^-

Q.2 Due to disproportionation of Hg_2^{2+}

Q.3 NH_3-strong ligand causes pairing of electrons. So complex is diamagnetic. F^- is a weak ligand and pairing is not possible.

Q.4 $[Al(OH)_3]$ and $NaAlO_2$; $Zn(OH)_2$ and Na_2ZnO_2 also $[Zn(NH_3)_4]^{2+}$

Q.5 [ZnS is white but PbS is black]

Q.6 [A] = $ZnCl_2$; [B] = $Zn(OH)_2$; [C] = Na_2ZnO_2; [D] = ZnS; [E] = AgCl

Q.7 All the three elements have d^{10}

Q.8 See text for the reaction of HCl and $KMnO_4$.

Q.9 [(A) = $ZnSO_3$; (B) = ZnO; (C) = SO_2; (D) = ZnS]

Q.10 3/2 M **Q.11** $K_2[PtCl_6]$

Q.12 Cl^- is a weak ligand, so no pairing of electrons. CO is a strong field ligand and, therefore, causes pairing of electrons.

Q.13 In the first case, a double salt is formed. In the second case, a complex is formed. So, no test.

Q.14 (A) = $[Cr(H_2O)_6]Cl_3$; (B) = $[Cr(H_2O)_5]Cl_2H_2O$
(C) = $[CrCl_2(H_2O)_4]Cl_2.2H_2O$

Q.15 (A) = $[Cr(NH_3)_4ClBr]+Cl^-$ and (B) = $[Cr(NH_3)_4Cl_2]+Br^-$.

Q.16 $[Co(NH_3)_4Cl(H_2O)]SO_4$; $[Co(NH_3)_4(SO_4)(H_2O)]$
$Cl[Co(NH_3)_4(SO_4)(Cl)]H_2O$

Exercise 2

Single Correct Choice Type

Q.1 A **Q.2** B **Q.3** A **Q.4** B **Q.5** B **Q.6** B
Q.7 A **Q.8** D **Q.9** D **Q.10** D **Q.11** A **Q.12** C
Q.13 C **Q.14** A

Multiple Correct Choice Type

Q.15 A, B **Q.16** B, C **Q.17** A, B, C **Q.18** A, B, C **Q.19** A, C **Q.20** A, B
Q.21 A, B, C, D **Q.22** A, B **Q.23** A, B **Q.24** A, B, C **Q.25** B, C, D **Q.26** A, B
Q.27 A, B **Q.28** A, B, C **Q.29** A, B **Q.30** B, C **Q.31** B, C

Assertion Reasoning Type

Q.32 A **Q.33** B **Q.34** A **Q.35** C **Q.36** C

Previous Years' Questions

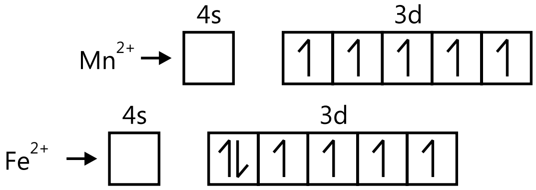
Q.1 B **Q.2** A **Q.3** B **Q.4** C **Q.5** A, B, C **Q.6** A, B, C, D
Q.7 A, B, C **Q.8** A **Q.12** B **Q.13** C **Q.14** A
Q.15 A → p, s; B → q, s; C → r, t; D → q, t **Q.16** B **Q.17** C **Q 18** A
Q.19 B **Q.20** 4 **Q.21** B **Q.22** A

Solutions

JEE Main/Boards

Exercise 1

Sol 1:



Mn^{2+} has half-filled 3d orbitals.

So, its stable.

Sol 2: $Fe^{+2} \rightarrow Fe^{+3} + e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$

Sol 3: (i) Zn doesn't show variable O. S. because of stable pseudo inert gas configuration of Zn^{+2}

$Zn^{2+} \rightarrow [Ar]\ 3d^{10}$

(ii) Actinides show greater range of O. S. because of comparable energies of 5f, 6d, 7s-orbitals.

Sol 4: In the first half of 3d elements, Mn^{2+} implies that there are unpaired e^- in 3d shell as we go from Sc to Mn, the exchange pairs increases as Mn^{2+} is nearly symmetrical.

Sol 5: Pyrolusite → MnO_2 (impure)

$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{fusion}} 2K_2MnO_4 + 2H_2O$

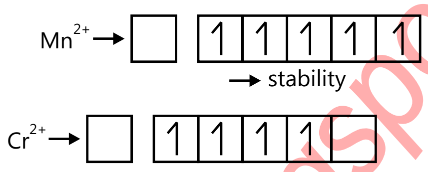
$3MnO_2 + 6KOH + KClO_3 \xrightarrow{\text{fusion}} 3K_2MnO_4 + KCl + 3H_2O$

$K_2MnO_4 \xrightarrow{\text{electrolysis}} KMnO_4$

$$\left(\begin{array}{l} H_2O \rightleftharpoons H^+ + OH^- \\ MnO_4^{2-} \rightarrow MnO_4^- + e^- \\ 2H^+ + 2e^- \rightarrow H_2 \end{array}\right)$$

Sol 6: Misch metal is an alloy of rare-earth elements in various naturally occurring proportion. Generally it contains 50% cerium, 25% lanthanum & small amounts of other. It is used preparation of most of the rare earth elements. When alloyed with iron, its was is lighters.

Sol 7: Electronic configurations play an important role in deciding the stability of an ion. Generally half-filled & full filled states are more stable. It also depends on no. of unpaired e^-, symmetry, exchange pairs, etc.

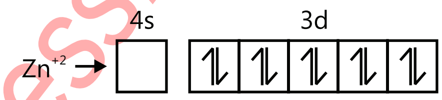


→ Not so stable.

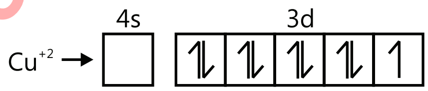
Sol 8: (a) To form stable complexes, the metal most have

(i) Electronic configuration (ii) Hybridisation

(b)



→ no unpaired e^-.



→ 1 unpaired e^-.

So, Cu^{+2} shows colour but not Zn^{2+}.

Sol 9: (a) All scandium salts have Sc^{+3}

$Sc^{+3} \rightarrow [Be]\ 3s^2\ 3p^6$

There are no unpaired e^- to show colour.

(b) Due to lanthanide contraction, the sizes of 5d elements are smaller compared to expected size. But nuclear charge will be high.

Sol 10: $3d^3 \rightarrow V \rightarrow +3$

$3s^5 \rightarrow Mn \rightarrow +7, +2$

$3d^8 \rightarrow Ni\ ; \rightarrow +2$

$3d^4 \rightarrow Cr \rightarrow +6, +3$

Sol 11: (a) Most of the f-block elements show +3 oxidation state (few have +2, +4). It is because of the fact that its outer shell has 2s electron & penultimate shell has 1d e^-. So, stability of there O. S has less dependence on f e^-.

(b) $Cu^+ \rightarrow 3d^{10} \rightarrow$ No. unpaired $e^- \rightarrow$ White

$Cu^{2+} \rightarrow 3d^9 \rightarrow$ 1 unpaired $e^- \rightarrow$ Colour

Sol 12: (i) They can exhibit multiple oxidation sates. They can accept e$^-$ pairs from ligands to form complexes.

(ii) Metallic bond strength is very high. So, they are strong metals.

Sol 13: They are called transition elements because their position in the periodic table is between s & p blocks their properties are transitional between highly reactive s-metals & constant bond forming p elements. Zn, Cd, Hg has ns^2 $(n-1)d^{10}$ configuration, so, they are not included in transition elements.

Sol 14: (i) Most of the transition metals form coloured compounds due to the presence of unpaired e$^-$ or complex formation.

(ii) Mn^{+2} has half-filled orbitals, So Mn^{+3} acts as oxidizing agent. Cr^+ has full-filled d-orbitals, So Cr^{2+} acts as reducing agent.

(iii) The energy difference between 7s, 7d, 5f is very less. So, they can show multiple oxidation states.

Sol 15: (i) They have high enthalpies of atomisation because of the strong metallic bonds. Each element in d-block provides more electrons for metallic bonding compared to s-block metals.

(ii) They are good catalysts, because of the presence of more than 1 stable O. S So, they can be used for oxidation & reductions.

Sol 16: (i) Paramagnetic is due to the presence of unpaired e$^-$ many transition metals have unpaired e$^-$ in d-orbitals.

Sol 17: (i) d-orbitals have poor shielding effect. As atomic number increases, there is increase in nuclear charge also. So, the size decreases.

(ii) The electronegativity difference between transition metals & F is high but not so for Cl, Br.

(iii) Most of them have similar sizes, they show a common stable oxidation state (+3).

Sol 18: (i) The size of atoms decrease as we go from left to right in the series because poor screening effect of d-electrons.

(ii) There is not a good trend for enthalpies of atomisation for 3d-elements. As we go from left to right, if first increases and then decreases with a sudden dip at the centre.

(iii) Tendency of complex formation increases as the size decreases.

Sol 19: Ti^{+3}, V^{+3}, Mn^{3+}, Fe^{3+}, Co^{3+} have unpaired e$^-$. So, they are colored. Cu^+, Sc^{3+} have no unpaired e$^-$. So, they are not colored.

Sol 20:

(a) $La^{3+} \rightarrow [Xe]$

(b) $Cd^{3+} \rightarrow [Xe]\ 4f^7$

(c) $Eu^{2+} \rightarrow [Xe]\ 4f^7$

(d) $Zn^{4+} \rightarrow [Ar]\ 3d^{10}$

(e) $Ru^{2+} \rightarrow [Kr]\ 5s^2\ 4d^4$

(f) $Ce^{4+} \rightarrow [Xe]$

Sol 21: Alloy is a mixture a solid solution compared of a metal and another element. Misch metal contains Lanthanoids. It is used in preparation of f-block elements. When mixed with iron, its used in lighters.

Sol 22: (a) ZnO → Amphoteric.

Chromium oxide → Acidic

(b) (i) M. P's first increases to the right till chromium group, then decreases.

(ii) The size decreases as we go right in the series. It decreases due to poor-shielding effect of e$^-$.

Sol 23: (i) Configuration of Sc $\rightarrow 4s^2\ 3d^1$

It has only 1 stable O. S. i. e. +3 because Sc^+, Sc^{+2} have no stabilising factors & Sc^{+3} is inert gas configuration.

(ii) K_2NiCl_6 doesn't exist because of the small size of Ni compared to Pt. It cannot hold 6 Cl^- ions around it.

(iii) Co is a strong ligand and metals need vacant d-orbitals for forming bonds.

Sol 24: $Ce \rightarrow [Xe]\ 4f^1\ 5d^1\ 4f^1$

$Ce^{+3} \rightarrow [Xe]\ 4f^1$

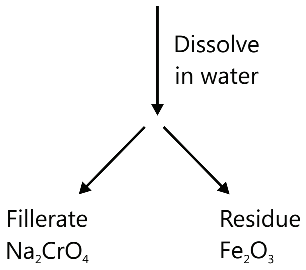
Magnetic moment = $\sqrt{n(n+2)}$ BM

and n = 1 i. e. no of unpaired e$^-$

$\therefore$ MM = $\sqrt{3}$ = 1. 73 BM

Sol 25: $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{air}]{\text{red hot}}$

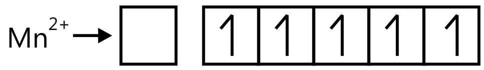
$$\underbrace{8\,Na_2CrO_4 + 2Fe_2O_3 + 8CO_2}$$



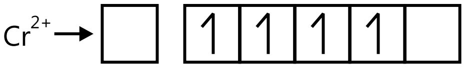
$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O$

$Cr_2O_7^{2-} \xrightarrow{H^+} CrO_3^{2-}$

Sol 26: (i) The actinoid contraction is high because of poor shielding effect of earlier 4f e^- and nearly coming 5f e^-.

(ii) 

$\rightarrow$ Stability



$\rightarrow$ Not so stable

So E for Mn^{3+}/Mn^{2+} is much positive than Cr^{+3}/Cr^{+2}

(iii) It is regarded as transition metal because if has incomplete d-orbitals and its last electron enters into 3d orbitals.

Sol 27: In all the reaction

$K_2Cr_2O_7 \rightarrow Cr^{+3}$

(i) $I^- \rightarrow I_2$

(ii) $Fe^{2+} \rightarrow Fe^{3+}$

(iii) $H_2S \rightarrow S$

Sol 28: (a) (i) Mn, Zn have stable +2 O. S. because of presence of half or full filled orbitals. Fe, Ni, Co also have stable +2 O. S. whereas others don't show +2 in most of the compounds.

(ii) Most of the transition metals don't form oxometal ions (Cr, Mn are exceptions.) They form MO. Acidity increases, ionic nature decreases.

(b) (i) They exhibits variable O. S. because of the presence of unpaired e^- in d-orbitals. (ii) Same is the reason for paramagnetism & colour of compounds.

Sol 29: (a) (i) $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O$

$Na_2Cr_2O_7 + KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$

(ii) $3K_2MnO_4 + 2H_2O \rightleftharpoons \underset{\text{Purple}}{2KMnO_4} + \underset{\text{dark brown}}{MnO_2} \downarrow + 4KOH$

(b) Lanthanide contraction is used to describe the greater than expected decrease in ionic radii of the elements in the lanthanide series. It is due to the poor shielding-effect of 4f electrons. The atomic radius of Hf (6th period) is less than that of Zr(5th period).

Exercise 2

Single Correct Choice Type

Sol 1: (A) $KMnO_4 \rightarrow Mn^{+2}$, Z = 5

$SO_3^{2-} \rightarrow SO_4^{2-}$, Z = 2

$\therefore\ n = \frac{2}{5}$

Sol 2: (B) Fe is catalyst

Mo is promoter

Sol 3: (A) Carats $= 24 \times \frac{M_g}{M_m} = 24 \times \frac{3}{4} = 18$

Sol 4: (B) MnO_4^-, $Cr_2O_7^{2-}$ show colour due to charge transfer from O to metal.

Sol 5: (A) It is due to availability of vacant d-orbitals for bonding.

Sol 6: (A) $KMnO_4$ is the self indicator as it's colour changes from purple (+7) during it's reduction.

Sol 7: (B) Vermilon is from the ore cinnabar (HgS).

Sol 8: (A) Chromic acid + $H_2O_2 \xrightarrow[\text{Org Solvent}]{H^+} \underset{\text{Chromium peroxide (Blue)}}{CrO_5} + H_2O$

Sol 9: (B) Zn has completed (n – 1) d orbitals. So, it's not included in transition elements.

Sol 10: (D) Coinage metals → Cu, Au, Ag i. e. transition metal.

Sol 11: (C) Bayer's reagent is alkaline $KMnO_4$

Sol 12: (A) Molybdenum (MO) is used in X-rays tube.

Sol 13: (A) F, O because of high electro-negativity.

Sol 14: (A) $Fe^{+2} \rightarrow Fe^{+3}$, Z = 1

$KMnO_4 \rightarrow Mn^{2+}$, Z = 5

$\therefore$ 1/5 moles of $KMnO_4$

Sol 15: (B) Haemoglobin → Fe

Insulin → Zn

Sol 16: (D) Cu → $5H_2O$ as ligands

H_2O will form H-bonding with SO_4^{2-} ion.

Sol 17: (B) It's colloidal solution of gold.

It's formed by the reaction of gold salts with Tin(II) chloride.

Sol 18: (A) $SnCl_2 \rightarrow Sn^{4+}$, Z = 2

$K_2Cr_2O_7 \rightarrow Cr_2O_3$, Z = 6

$n = \frac{6}{2} = 3.$

Sol 19: (D) Cu^{2+} → blue

CrO_4^{2-} → yellow.

Sol 20: (A) It is very hard. It has high proportions of manganese.

Sol 21: (A) They can form complexes by taking e^- pairs from ligands.

Sol 22: (B) $TiCl_3$ is an intermediate during catalysis.

$TiCl_4 \rightarrow TiCl_3 + Cl.$

Previous Years' Questions

Sol 1: (C) The existence of Fe^{2+} and NO^+ in nitroprusside ion $[Fe(CN)_5NO]^{2-}$ can be established by measuring the magnetic momentum of the solid compound which should correspond to ($Fe^{2+} = 3d^6$) four unpaired electrons.

Sol 2: (C) $V^{+4} \rightarrow 3d^1 4s^0$ 1 unpaired electrons. Hence it is paramagnetic and coloured compound.

Sol 3: (B, C) $2KOH + \underset{\text{Manganese dioxide}}{MnO_2} + O \rightarrow \underset{\text{Potassium manganate}}{K_2MnO_4} + H_2O$

$HCHO + 2KMnO_4 + 2KOH \rightarrow K_2MnO_4 + H_2O + HCOOH$

Sol 4: (C, D) $Co(NO_3)_2$ and $CrCl_3$ has unpaired electron, hence they are coloured; while $Zn(NO_3)_2$, $LiNO_3$ and potash alum have no unpaired electron hence they are colourless.

Sol 5: (A, B) Gun metal contain Cu and Sn while type metal contains Pb, Sn and Sb.

Sol 6: (A, B, D) $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$

$CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$

Chromyl chloride Yellow solution

Sol 7: (A, C) Manganese (Mn) imparts hardness to steel as well as removes oxygen and sulphur from steel by forming slag as $MnSiO_3$

$Fe_2O_3 + 3Mn \rightarrow 3MnO + 2Fe$

$MnO + SiO_2 \rightarrow MnSiO_3$

(Slag)

Sol 8: (C) Rusting involves reduction of absorbed oxygen to OH^- ions and oxidation of iron to Fe^{2+} ions. The two ions combine to yield $Fe(OH)_2$ which gets oxidized to give $Fe_2O_3.nH_2O$ (rust). The presence of acid helps dissolution of pure iron to ferrous ions while electrolytes increases the conductivity and assist the cell action.

Sol 9: (B) AgBr is the most sensitive silver halide to photo reduction. Hence it is used as the light sensitive material in photographic films. The unchanged AgBr is dissolved in hypo solution to cast an image on photographic plate.

$2AgBr \xrightarrow{hv} 2Ag + Br_2$

Sol 10: (A) Tungsten is a metal of high melting point and its filament gives brilliant light on passing electric current.

Sol 11: (A) In transition elements ns orbital is filled up first and (n – 1)d afterwards, during ionization ns electrons are lost prior to (n – 1)d electrons because the effective nuclear charge felt by (n – 1)d electrons is higher as compared to that of ns electrons.

Sol 12: (B) The higher the charge on metal ion, smaller is the ionic size and more is the complex forming decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$. The higher tendency of complex formation of MO_2^{2+} of charge on metal atom M in MO_2^{2+}

Sol 13: (B): Being lesser energy difference between 5f and 6d than 4f and 5d orbitals.

Sol 14: (C) Ln^{+3} compounds are mostly coloured.

Sol 15: (A) The correct order of $E^{\circ}_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is Mn > Cr > Fe > Co

Sol 16: (B) In $\left[NiCl_4\right]^{2-}$, n = 2

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

$$= \sqrt{2(2+2)} = 2.82\ \text{BM}$$

Sol 17: (C) The general O.S of lanthanides is +3, only few elements exhibit +4 O.S.

Sol 18: (A)

(A) V^{2+} = 3 unpaired electrons

Cr^{2+} = 4 unpaired electrons

Mn^{2+} = 5 unpaired electrons

Fe^{2+} = 4 unpaired electrons

Hence the order of paramagnetic behaviour should be

$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(B) Ionic size decrease from left to right in same period

(C) As per data from NCERT.

$Co^{3+}/Co^{2+} = 1.97$; $Fe^{3+}/Fe^{2+} = 0.77$; $Cr^{3+}/Cr^{2+} = -0.41$

Sc^{3+} is highly stable (it does not show + 2)

(D) The oxidation states increases as we go from group 3 to group 7 in same period.

Sol 19 : (A) Each $\left[Cr(H_2O)_6\right]^{2+}$ and $\left[Fe(H_2O)_6\right]^{2+}$ Contain 4 unpaired electron.

JEE Advanced/Boards

Exercise 1

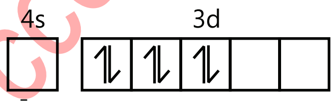
Sol 1:

$$K_2MnO_4 + CO_2 + H_2O \rightarrow \underset{\text{Purple}}{KMnO_4} + MnO_2 + KHCO_3$$

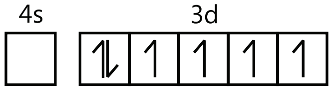
Sol 2: $Hg_2^{2+} \rightarrow Hg + Hg^{2+}$

Sol 3: No. of e^- in $Co^{3+} \rightarrow$ 24

NH_3 is a strong ligand



F^- is a weak ligand



there are unpaired e^-

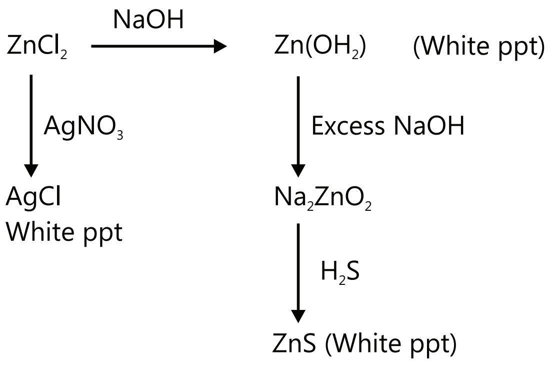
Sol 4: For NaOH we get $MaAlO_2$, Na_2ZnO_2.

For NH_4OH, we get $[Zn(NH_3)_4]^{2+}$.

But it doesn't form complexes.

Sol 5: PbS is black solid where as ZnS is white.

Sol 6: A → $ZnCl_2$ because $Zn(OH)_2$ & $Al(OH)_3$ dissolve in excess NaOH but Al_2S_3 is gray solid.



Sol 7: They are not transition metals. They have (x – 1) d^{10} configuration.

Sol 8: $KMnO_4$ will oxidize Cl^- to Cl_2

Sol 9: Colourless salt (A) $\xrightarrow{?}$ (B) + (C) gas.

B must be Zn or Al salt.

ZnS is white

$\Rightarrow$ B = ZnO

C is a reducing agent & turns lime water milky

$\Rightarrow$ C = SO_2

$\Rightarrow$ A = $ZnSO_4$ & D = ZnS

Sol 10: $MnO_4^{2-} \to MnO_4^- + 1e^-$ ......(i)

$MnO_4^{2-} \to 4H^+ + 2e^- \to MnO_2 + 2H_2O$ ......(ii)

2 × (i)

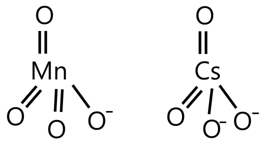
$3MnO_4^{2-} + 4H^+ \to 2MnO_4^- + MnO_2 + 2H_2O$

So 3 moles of MnO_4^{2-} need

$2e^- \Rightarrow Z = \frac{2}{3}$

$\therefore E = \frac{M}{2} = \frac{3M}{2}$

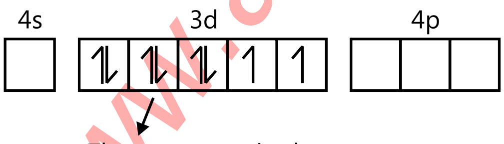
(b) MnO_4^- CrO_4^{2-}



Sol 11: $K_2[PtCl_6] \to$ It has 3 ions.

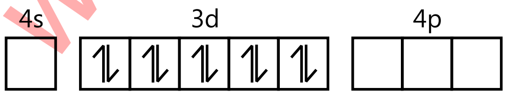
We don't get : AgCl precipitate because there are no. Cl^- ions in the solution. There are only K^+ and $[PtCl_6]^{2-}$ ions.

Sol 12: Ni^{2+} with weak ligands is paramagnetic



There are unpaired e^-

Ni with strong ligands diamagnetic



In $[NiCl_4]^{2-}$, there is magnetic moment but not in $[Ni(CO)_4]$.

Sol 13: Fe^{+2} doesn't form complex with NH_3 so, there are Fe^{2+}, NH_4^+, SO_4^{2-} ions in the solution.

In 2nd case, $[Cu(NH_3)_4]^{2+}$ will be formed & there will no Cu^{2+} Ions.

Sol 14: In A, all H_2O are ligands to Cr.

In B, some H_2O is evaporated So, that is water of crystalisation.

$W_{H_2O} = \frac{6.75}{100} M_{complex} = 18$ g.

So, there is 1 water of crystallisation.

In (C)

$W_{H_2O} = \frac{13.5}{100} M = 36$ gm.

A $\to$ $[Cr(H_2O)_6]\,Cl_3$

B $\to$ $[Cr(H_2O)_5Cl]Cl_2\,H_2O$

C $\to$ $[Cr(H_2O)_4Cl_2]Cl.\ 2H_2O$

Sol 15: AgBr is not soluble in dilute NH_3

So, there is Cl^- in A Cr^{3+} & strong

AgBr is pale yellow

So, there is Br^- in B

A $\to$ $[Cr(NH_3)_4Cl\ Br]Cl \to d^2sp^3$

B $\to$ $[Cr(NH_3)_4Cl_2]Br \to d^2sp^3$

Sol 16: Ratio of moles of Co^{3+} :

$NH_3 : Cl^- : SO_4^{2-} : H_2O$

$\frac{21.24}{57} : \frac{24.77}{17} : \frac{12.81}{35} : \frac{34.65}{96} : \frac{6.53}{18}$

i. e. 1 : 3 : 1 : 1 : 1

So, complex can be

$\to$ $[Co(NH_3)_3\,ClSO_4]\,.\,H_2O$

$[Co(NH_3)_3\,SO_4(H_2O)]Cl$

$[Co(NH_3)_3\,(H_2O)Cl]\ SO_4$

Exercise 2

Single Correct Choice Type

Sol 1: (A) $Cr_2O_7^{2-} \underset{Y}{\overset{X}{\rightleftharpoons}} 2CrO_7^{2-}$

y is H^+, $Cr_2O_7^{2-}$ is stable in acidic medium.

x is OH^-

Sol 2: (B) $CrO_3 \xrightarrow{NaOH} CrO_4^{2-}$

Sol 3: (A) $(NH_4)_2\, Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$\downarrow$

Green

Sol 4: (B) Mercury is ligand in room temperature (Hg).

Sol 5: (B) 80% conc HNO_3 is an oxidising agent

So $Fe \rightarrow Fe_3O_4$

Sol 6: (B) $Cu + \text{Conc } HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

Sol 7: (A) $Mn^{+7} \xrightarrow[\text{reduction}]{} Mn^{+2}$

Acts as catalyst and increases further rate of reaction.

Sol 8: (D) $CuSO_4 + \underset{\text{(Excess)}}{KCN} \rightarrow Cu(CN)_2$

$$CuSO_4 + \underset{\text{(Excess)}}{KCN} \quad Cu(CN)_2$$

$$\downarrow$$

$$Cu(CN) + \frac{1}{2}\ (CN)_2$$

$$\downarrow \text{KCN}$$

$$K_3[Cu(CN)_4]$$

Sol 9: (D) $MnO_4 + 4HCl \rightarrow Cl_2 + MnCl_2 + xH_2O$

Acidic $KMnO_4$ decomposition can be catalysed by sunlight.

Sol 10: (D) $Fe_2O_3.xH_2O$ & $FeO(OH).Fe(OH)_3$ constitute the rust.

Sol 11: (A) Invar is used to make meter scales. Invar consists of Nickel, Iron & small quantities of other metals.

Sol 12: (C) Ag, Pt, etc, are inert to conc. acids & alkalis.

$AuCl_3$ is used for toning in photography.

Sol 13: (C) Cl^- will be oxidised to Cl_2 (greenish-yellow gas).

Sol 14: (A) NO has unpaired e^-. NO^+ is stable taking magnetic moment into consideration.

Multiple Correct Choice Type

Sol 15: (A,B) Pt doesn't form any alloys. Fe doesn't form amalgam.

Sol 16: (B, C) Os, Ru show +8 O. S.

There are in same group as Iron (Fe)

Sol 17: (A, B, C) Al_2O_3, SnO, ZnO are amphoteric

$Fe_2O_3 \rightarrow$ Basic.

Sol 18: (A, B, C) Transition metals from interstitial compounds. So, Co, Ni, Fe.

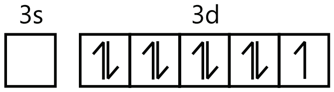
Sol 19: (A, C)

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + \underset{\text{Blue colour}}{3O_2} \uparrow + 2H_2O$$

Sol 20: (A, B) CuF_2 is ionic $CuCl_2$, $CuBr_2$ are covalent (exist as polymers).

Sol 21: (A, B, C, D) $CuSO_4(aq) + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} SO_4^{2-}$

Cu^{2+} & NH_3 is a strong ligand



It's paramagnetic, so coloured

$MM = \sqrt{n(n+2)}$ BM & n = 1 = $\sqrt{3}$ BM.

Sol 22: (A, B) MnO_2, $Mn_3O_4 \rightarrow$ Amphoteric

$MnO \rightarrow$ Basic

$Mn_2O_7 \rightarrow$ Acidic

Sol 23: (A,B) Zr, Hf have similar sizes & properties due to lanthanide contraction.

Sol 24: (A, B, C) Potash alum → $KAl(SO_4)_2$

SO, we get K^+, Al^{3+}, SO_4^{2-}.

Sol 25: (B, C, D) They will get harder due to the filling of interval spaces. So, they will be less ductile & malleable.

Sol 26: (A, B) Metallic bonding is very weak in Hg.

Sol 27: (A, B) Transition elements have high IP than s-block & lower IP than p-block. They are like connecting blocks between s & p-blocks. So, they are called transition elements.

Sol 28: (A, B, C) Catalytic activity depends on

Variable OS

Surface area

Reactivity (Complex forming ability)

It doesn't depend on magnetic moment.

Sol 29: (A, B) Ag, Au form such complexes

Cu generally forms $[Cu(CN)_4]^{3-}$.

Sol 30: (B, C) If x > y then x will be covalent

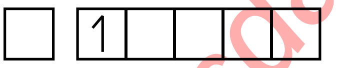
Y will be Ionic

Ex. $KMnO_4 \rightarrow MnO_4^-$ is covalent

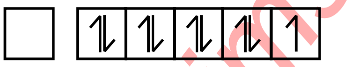
$MnCl_2 \rightarrow$ Ionic.

Sol 31: (B, C) $Sc^{3+} \rightarrow$ no unpaired e^-

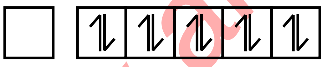
$Ti^{3+} \longrightarrow$ 1 unpaired e-



$Cu^{2+} \longrightarrow$ 1 unpaired e-



$Zn^{2+} \longrightarrow$ 0 unpaired e-



So, Ti^{3+}, Cu^{2+}

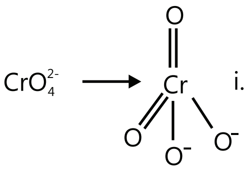
Assertion Reasoning Type

Sol 32: (A) In alkaline medium

$Mn^{+7} \rightarrow Mn^{+4}$, $Z = 3 = \frac{\text{mol. wt}}{2} = \frac{\text{mol. wt}}{3}$

Z is different for different conditions

Sol 33: (B) The yellow colour of CrO_4^{2-} is due to charge transfer from O to metal.



i.e. tetrahedral

Sol 34: (A) Maximum O. S. of Cr is +6. Because it has only $6e^-$ in 4s & 3d orbitals.

Sol 35: (C) Tungsten has very high MP due to strong metals bondings. It's a metal, not a covalent compound.

Sol 36: (C) Cu^+ is colourless because of no unpaired e^-. All of Cu^+ salts need not have 4 H_2O molecules statement-2 is false.

Previous Years' Questions

Sol 1: (B) In MnO_4^-, Mn^{7+} is in highest oxidation state possible for Mn. In CrO_2Cl_2, Cr^{6+} is in highest oxidation state possible for Cr.

Sol 2: (A) $MnO_4^- + I^- + OH^- \rightarrow MnO_4^{2-} + IO_3^-$

Sol 3: (B) In $CuCl_2$, Cu^{2+} had d^9 configuration, exhibit d-d- transition and show colour. Similarly in $VOCl_2$, V^{4+} had d^1 configuration, can exhibit d-d transition and show colour.

Sol 4: (C) $KMnO_4$ is itself a very strong oxidising agent, O_3 cannot oxidise it.

Sol 5: (A,B,C) Brass = Cu and Zn

Gun metal = Cu, Sn, Zn

Bronze = Cu, Zn and Sn

Type metal = Pb, Sn, Sb

Sol 6: (A,B,C,D) $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2$

Chromyl chloride
(Red vapour)

$+ 4NaHSO_3 + 2KHSO_4 + 3H_2O$

Sol 7: (A,B,C) Cr : $[Ar]3d^5 4s^1$

Magnetic quantum number: $-\ell$ ....0.......$+\ell$

$Ag(4d^{10}5s^1)$: All paired electrons have opposite spin. The last one has unpaired spin.

Sol 8: (A) In neutral medium:

$MnO_4^- \rightarrow MnO_2 (Mn^{7+} + 3e^- \rightarrow Mn^{4+})$

In alkaline medium:

$MnO_4^- \rightarrow MnO_2 (Mn^{7+} + 3e^- \rightarrow Mn^{4+})$

In acidic medium:

$MnO_4^- \rightarrow Mn^{2+} (Mn^{7+} + 5e^- \rightarrow Mn^{2+})$

Sol 9: $\mu = \sqrt{n(n+2)}$ BM where 'n' is number of unpaired electrons.

$1.73 = \sqrt{n(n+2)}$

$n = 1$; V^{4+} $3d^1$

Sol 10: CrO_3 is anhydride of chromic acid:

$CrO_3 + H_2O \rightarrow H_2CrO_4$

Chromic acid

Sol 11: $A = [Ti(H_2O)_6]^{3+}$ and M = Ti, B = TiO_2, Ti(IV) has no electron in 3d orbital, no d-d transition is possible, therefore MCl_4 is colourless. In A, there is one electron in 3d orbital and its d-d transition is responsible for colour.

Sol 12: (B)

(A) $Mn^+ = 3d^5\ 4s^1$ in presence of CO effective configuration = $3d^6\ 4s^0$. Three lone pair for back bonding with vacant orbital of C in CO

(B) $Fe^0 = 3d^6\ 4s^2$ in presence of CO effective configuration = $3d^8$ four lone pair for back bonding with CO.

(C) $Cr^0 = 3d^5\ 45s^1$ Effective configuration = $3d^6$ three lone pair for back bonding with CO.

(D) $V^- = 3d^4\ 4s^2$ Effective configuration = $3d^6$ three pair for back bonding with co. Maximum back bonding is present in $Fe(CO)_s$ there for CO bond order is lowest here.

Sol 13: (C) In the crystalline form CuF_2 is blue coloured.

Sol 14: (A) $[Cr(CO)_6]$

$Cr(24) = [Ar]3d^5 4s^1$

Since (CO) is strong ligand, in $Cr(CO)_6$ no unpaired electron is present. So 'spin only' magnetic moment is zero.

Sol 15: A → p, s; B → q, s; C → r, t; D → q, t

$$3Cu + \text{dil } 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$Cu + \text{conc. } 4HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$4Zn + \text{dil. } 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$Zn + \text{conc.}4HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

Sol 16: (B) $[Ni(CN)_4]^{2-}$, O.S. of Ni = +2

$Ni(28) = 3d^8 4s^2$

$Ni^{+2} = 3d^8$

No. of unpaired electrons = 2

Magnetic moment $\mu = 2.82$ BM

Sol 17: (C) Following compounds are diamagnetic.

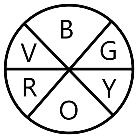
$L : [Co(NH_3)_6]CI_3$

$M : Na_3[Co(Ox)_3]$

$O : K_2[Pt(CN)_4]$

$P : [Zn(H_2O)_6](NO_3)_2$

Sol 18: (A) Aqueous solution of copper sulphate absorbs orange red light and appears blue (complementary colour).



Sol 19: (B)

P = Fe^{+3} (no. of unpaired e^- = 5)

Q = V^{+2} (no. of unpaired e^- = 3)

R = Fe^{+2} (no. of unpaired e^- = 4)

As all ligands are weak field, hence the no. of unpaired electrons remains same in the complex ion.

$\mu = \sqrt{n(n+2)}$B.M

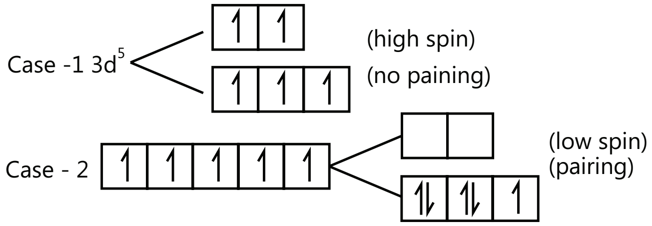
Hence (B) is correct.

Sol 20: $[Fe(SCN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$

In both the cases the electronic configuration of Fe^{3+} will be $1s^2, 2s^2, 2p^6, 3s^2, 3p^6 3d^5$

Since SCN^- is a weak field ligand and CN^- is a strong field ligand, the pairing will occur only in case of

$\left[Fe(CN)_6\right]^{3-}$



Case-1 $\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.91$ BM

Case-2 $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM

Difference in spin only magnetic moment

$= 5.91 - 1.73 = 4.18$

≈ 4

Sol 21: (B) $\left[Ni(CO)_4\right] - sp^{3-}$ - Diamagnetic

$\left[NiCI_4\right]^{-2}$ sp^3 – Paramagnetic

$\left[Co(NH_3)_4 CI_2\right]CI - d^2sp^3$ – Diamagnetic

$Na_3\left[CoF_6\right] - sp^3d^2$ – Paramagnetic

Na_2O_2 i.e. O_1^{2-} – Diamagnetic

CsO_2 i.e $O^-{}_2$ – Paramagnetic

Sol 22: (A) $\left[Ni(NH_3)_6\right]^{2+}$ = Octahedral

$\left[Pt(NH_3)_4\right]^{+2}$ = Square planar

$\left[Zn(NH_3)_4\right]^{+2}$ = Tetrahedral

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