Chapter

22

The *d*- and *f*-Block Elements

THE TRANSITION ELEMENTS (*d*-BLOCK)

Position in the Periodic Table

The elements which lie in between s and p - block elements are called transition elements. They are called d - block elements since in them, 3d, 4d, 5d and 6d sub - shells are incomplete and the last electrons enters the (n – 1) d subshell. A transition element is defined as an element whose atoms in ground state or ions in one of the common oxidation states, has incomplete d - subshell.

Classification of d-Block Elements

Transition elements consist of the following four series

(i) 3d series $_{21}$Sc to $_{30}$Zn $3d^{1-10}4s^{1-2}$
(ii) 4d series $_{39}$Y to $_{48}$Cd $4d^{1-10}5s^{0-2}$
(iii) 5d series $_{57}$La $_{72}$Hf to $_{80}$Hg $5d^{1-10}6s^{1-2}$
(iv) 6d series $_{89}$Ac $_{104}$Rf to $_{111}$Rg

Electronic Configuration of *d*-Block Elements

General electronic configuration of these elements is $(n-1)\,d^{1-10}\,ns^{1-2}$.

The last shell electronic configuration of Cr and Cu are $3d^5 4s^1$ (instead of $3d^4\,4s^2$) and $3d^{10}\,4s^1$ (instead of $3d^9\,4s^2$). This is because of extra stability associated with half and completely filled orbitals.

The electronic configurations of Zn, Cd and Hg are represented by general formula $(n-1)\,d^{10}\,ns^2$. The orbitals in these elements, in ground as well as in common oxidation state, are completely filled and hence, they are not regarded as transition elements but they show properties of transition elements to appreciable extent.

General Properties of Transition Elements

Since only penultimate shell i.e., (n – 1) is expanding, they have resemblance in their physical and chemical properties.

(i) All the *d*-block elements behave as metals.

They are hard, malleable and ductile. i.e., Cu, Ag and Au are most ductile. They are good conductors of heat and electricity (due to free electrons).

Explanation :

The electronic configuration of these elements reveals that they have one or more unpaired electrons present in either ns or (n – 1) d-orbitals which are available for bond formation. In general, greater the number of such electrons available, more will be the chances of their mutual combination and more will be strength of the metallic bond.

(ii) Melting and boiling points :

Strong metallic bonds between the atoms of these elements are responsible for the high melting and boiling points. This is clear from their high **enthalpies of atomization.** (i.e., *heat required to break the metal lattice to get free atoms*)

Metals of 4d and 5d series have greater enthalpies of atomisation than 3d series due to much more frequent metal-metal bonding in their compounds. Greater is the number of unpaired d-electrons stronger will be metallic bonding. Thus in a particular series metallic strength increased up to middle and then decreases.

Note : In Zn, Cd, and Hg there is no unpaired electron present in *d*-orbital, so the metallic bond is weak and their m.pt. and b.pt. are very low. (Volatile metals Zn, Cd, Hg)

(iii) Density

The atomic volume of the transition elements are low compared with *s*-block, so their density is comparatively high.

There is a normal increase in density from 3*d* to 4*d* series. However from 4*d* to 5*d*, it becomes almost double due to lanthanoid contraction.

In 3*d* series
Sc → Cr density increases
Cu → Zn decreases

(iv) Atomic and ionic sizes

They lie between those of *s* - and *p* - block elements. Atomic radii in a series decreases with increase in atomic number but the decrease is small after mid-way. This is because in the begining, the nuclear charge increases but screening effect of d-electron is less. After mid-way screening effect of d-electrons increases which counter balances increased nuclear charge and hence increase in size is not much.

At the end of period, there is a slight increase in atomic radii. This is because near the end of series, the increased $e^- - e^-$ repulsions between added electrons in same orbital are greater than attractive forces due to increased nuclear charge.

Amongst the dipositive ions of 3*d* series, Cu^{2+} is the smallest in size.

The elements of 4*d* and 5*d* series have almost similar atomic radii. This is due to Lanthanoid contraction. E.g. atomic radii of Zr ≃ Hf; Tc ≃ Re; Nb ≃ Ta; Ru ≃ Os etc.

(v) Ionisation enthalpies

The IE increases with increase in atomic number due to increased nuclear charge. However, some irregularities are observed. This is because removal of an electron alters the relative energies of 4s and 3d orbitals. Thus, there is a **reorganisation energy** accompanying ionisation. This results into the release of exchange energy which increases as the number of electrons increases in the d^n configuration and also from the transference of s-electrons into d-orbitals.

Difference between IE of any two successive d-block elements is very less as compared to s or p-block elements. It is because addition of d electrons in last but one [(n – 1) or penultimate] shell with increase in atomic number provides a screening effect and thus shields the outer s electrons from inward nuclear pull.

The 1st IE of Zn, Cd and Hg are very high due to fully filled $(n-1)\,d^{10}\,ns^2$ configuration.

The order for IE_2 for 1st series is:

$_{23}V < _{24}Cr > _{25}Mn$ and $_{28}Ni < _{29}Cu > _{30}Zn$

This is because after removal of one e^-, Cr and Cu acquire stable configuration (d^5 and d^{10}), so removal of 2nd e^- becomes difficult.

Third IE of Mn (25, $3d^5\,4s^2$) is very high as the third e^- has to be removed from stable half - filled 3d – orbital.

Third IE for change from Fe^{2+} to Fe^{3+} ($_{26}Fe$, $3d^6\,4s^2$) is small because loss of third e^- gives stable configuration of $3d^5$.

The high values of third IE for Cu, Zn and Ni explain why they have a maximum O.S. of +2.

The first IE's of 5d elements are higher as compared to those of 3d and 4d elements. This is because of the weak shielding effect of electrons present in 4f-orbitals which results in greater effective nuclear charge. Thus in 5d elements outer valence electrons are more tightly held.

(vi) Oxidation states

Transition metals exhibit a large no. of O.S. This is because there is little difference in energies of (n – 1) d and ns orbitals and hence, both the levels can be used for bond formation.

Most common O.S. of first row transition metals is +2 due to loss of two ns^2 electrons (exception: Sc, it has + 3). In +2 and +3 O.S, ionic bonds are formed. In higher O.S., bonds formed are covalent as they are formed by sharing of d-electrons. The elements which show maximum no. of O.S. occur in or near middle of series. For ex: Mn → + 2 to + 7. Highest O.S. is + 8 (shown by osmium). In a group, higher O.S. are more stable for heavier elements. For ex: in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). This is why Cr (VI) in $Cr_2O_7^{2-}$ is a stronger oxidizing agent in acidic medium whereas MoO_3 and WO_3 are not.

Low O.S. are found when a complex compound has ligands capable of π - acceptor character in addition to σ – bonding. The compounds of metals with F and O exhibit highest O.S. as F and O are small in size and highly electronegative. O stabilizes the highest O.S. even more than F. This is due to the ability of O to form multiple bonds with metal atoms. Usually transition metal ions in their lower oxidation state behave as reducing agents and in higher oxidation state, they behave as oxidising agents.

E.g. : Ti^{+2}, V^{+2}, Fe^{+2}, Co^{+2} etc are reducing agents

Cr^{+6}, Mn^{+7}, Mn^{+4} Mn^{+5}, Mn^{+6} etc are oxidising agents.

(vii) Standard electrode potentials (E°) and chemical reactivity

Thermodynamic stability of compound of transition metals can be evaluated in terms of its IE. Smaller the IE of metal, stabler is its compound. In solution, the stability of the compounds depends upon electrode potentials which depends on $\Delta_{sub}H$, IE and $\Delta_{hyd}H$.

The lower the electrode potential, i.e., more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal ion in aqueous medium.

Element →	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E°(M^{2+}/M)$ in volts (V)	−1.63	−1.18	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34	−0.76
$E°(M^{3+}/M^{2+})$ in volts (V)	−0.37	−0.26	−0.41	+1.57	+0.77	+1.97	–	–	–

The irregular trend is due to variation in ionization energies and sublimation energies. E° values along the series becomes less negative generally it is due to increase in sum of IE_1 and IE_2.

Cu has a +ve value of E° (M^{2+} / M). As a result, it does not liberate H_2 gas from acids.

The E° (M^{2+} / M) values for Mn, Ni and Zn are more –ve than expected. This is due to greater stability of half-filled 3d-orbital in Mn^{2+} (d^5) completely filled 3d-orbital in Zn^{2+} (d^{10}) and exceptional behaviour of Ni is due to high –ve enthalpy of hydration for Ni^{2+}.

A very low E° (Sc^{3+} / Sc^{2+}) value reflects the stability of Sc^{3+} which has noble gas configuration. The highest E° (M^{3+} / M^{2+}) for Zn is due to high stability of Zn^{2+} with d^{10} configuration. Comparitively high value of E° (Mn^{3+} / Mn^{2+}) is due to stable d^5 configuration of Mn^{2+}. Low value of E°(Fe^{3+} / Fe^{2+}) is due to extra stability of Fe^{3+} (d^5). Low value for V is due to stability of V^{2+} due to its half filled t_{2g}^3 configuration. E° values for the redox couple M^{3+} / M^{2+} indicate that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solution whereas Ti^{2+}, V^{2+} and Cr^{2+} are the strongest reducing agents and can liberate hydrogen from a dilute acid, Ex :

$$2Cr^{2+}(aq) + 2H^{+}(aq) \longrightarrow 2Cr^{3+}(aq) + H_2(g)$$

(viii) Magnetic properties

Transition metals contain unpaired electrons in (n – 1) d orbitals and hence most of transition metal ions and their compounds are paramagnetic.

Transition metals which have paired electrons are diamagnetic. Magnetic moment of transition metal ions is calculated by using 'spin - only' formula given as: $\mu = \sqrt{n(n+2)}$ B. M. where 'n' is the no. of unpaired electrons. As the number of unpaired electrons increases the magnetic moment also increases. Ions with d^5 configuration have maximum magnetic moment.

(ix) Coloured ions

Most transition metal compounds are coloured both in solid and in aqueous solution. Colour is due to presence of incomplete d - subshell. The d - orbitals split into two sets, one with lower energy and other with higher energy. The e^- absorbs energy and gets excited to higher energy level. When this excited e^- falls back to the ground state, it emits radiation which falls in the visible range of spectrum.

Thus, colour of transition metals is due to d-d transitions. Sc^{3+} and Ti^{4+} have empty d - orbitals and are colourless. Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+} have completely filled d-orbitals, there are no vacant d - orbitals for promotion of electrons, hence they are also colourless.

(x) Complex formation

Transition metal ions form a large no. of complex compounds because:

(a) of comparatively smaller size of their metal ions.
(b) of their high positive charge.
(c) of availability of vacant d - orbitals so that they can accept lone pair of e^{-1} s donated by ligands.

(xi) Catalytic properties

Transition metals act as catalysts due to following reasons:

(a) presence of unpaired electrons in their incomplete d-orbitals and posses the capacity to absorb and re-emit wide range of energies.
(b) Transition metals exhibit variable oxidation states and may form intermediate compounds with one of reactants providing a new path with lower activation energy.
(c) Transition metals provides a suitable large surface are with free valencies on which reactants are adsorbed.

Note : When transition elements and their compounds are in powdered state, their catalytic behaviour increases. This is due to greater surface area available in the powdered state.

(xii) Interstitial compounds

Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc. The smaller sized atoms get entrapped in between the interstitial spaces of the metal lattices. These interstitial compounds are non stoichiometric in nature and hence cannot be given any definite formula.

Some important characteristics of these compounds are:

(a) they have high m. pts. higher than those of pure metals.
(b) they are very hard and rigid.
(c) they show conductivity like that of pure metal.
(d) they are chemically inert.

(xiii) Alloy formation

Alloys are homogeneous solid solutions of two or more metals obtained by melting the components and then cooling the melt.

Transition metals have similar atomic radii and other characteristics, hence they form alloys readily. Alloys are generally harder, have higher m. pts. and more resistant to corrosion than individual metals.

Some important alloy :

1. Bronze – Cu (75 - 90 %) + Sn (10 - 25 %)
2. Brass – Cu (60 - 80 %) + Zn (20 - 40 %)
3. Gun metal – (Cu + Zn + Sn) (87 : 3 : 10)
4. German Silver – Cu + Zn + Ni (2 : 1 : 1)
5. Bell metal – Cu (80%) + Sn (20%)
6. Nichrome – (Ni + Cr + Fe)

Some Important Compounds of Transition Metals

Oxides and oxoanions

Oxides are formed by reaction of O_2 with metals at high temperatures. They are formed in O.S. from +1 to +7 As oxidation number of metal increases, ionic character decreases.

e.g.,
$$\begin{array}{ccccc} MnO, & Mn_3O_4, & Mn_2O_3, & MnO_2, & Mn_2O_7 \\ +2 & +8/3 & +3 & +4 & +7 \end{array}$$

Ionic character decreases

The oxides in lower OS of metals are basic and in higher OS they are acidic whereas in intermediate OS, they are amphoteric.

For ex:

(i)

MnO	Mn_3O_4	Mn_2O_3	MnO_2	Mn_2O_7
Basic	Amphoteric	Amphoteric	Amphoteric	Acidic

$(\therefore\ Mn_2O_7 + H_2O)$
$HMnO_4$

(ii)

V_2O_3	V_2O_4	V_2O_5
basic	less basic	amphoteric (mainly acidic)

($\therefore$ V_2O_5 reacts with alkalies and acids to give VO_4^{3-} and VO_4^+)

(iii)

CrO	Cr_2O_3	CrO_3
basic	amphoteric	acidic

(CrO_3 dissolves in water to give the acids H_2CrO_4 and $H_2Cr_2O_7$)

Potassium dichromate ($K_2Cr_2O_7$)

Preparation : It is prepared from ore called chromite or ferrochrome or chrome iron, FeO. Cr_2O_3. The various steps involved are:

(i) $$4FeCr_2O_4 + 8\,Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

(ii) $$\underset{\text{Sodium chromate}}{2Na_2CrO_4} + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(iii) $$\underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\text{Potassium chromate}}{K_2Cr_2O_7} + 2NaCl$$

Properties:

(i) It forms orange crystals which melt at 669 K.
(ii) It is moderately soluble in cold water and freely soluble in hot water.
(iii) When heated, it decomposes with the evolution of oxygen.

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2\,Cr_2O_3 + 3O_2$$

(iv) The chromates and dichromates are interconvertible in aqueous solution depending on pH of the solution.

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

$$CrO_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

$$\underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O \xrightleftharpoons{\text{At pH = 4}} \underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+$$

(v) $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are strong oxidising agents. In acidic medium, it furnishes 3 atoms of available oxygen as shown by the equation :

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

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

It oxidises

$$2I^- \longrightarrow I_2 + 2e^-$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$3H_2S \longrightarrow 6H^+ + 3S + 6e^-$$

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2e^- + 2H^+$$

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

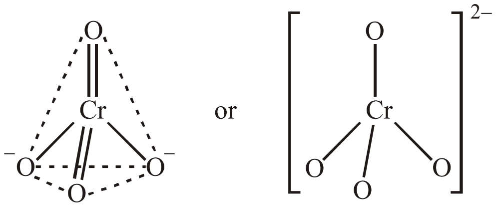
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

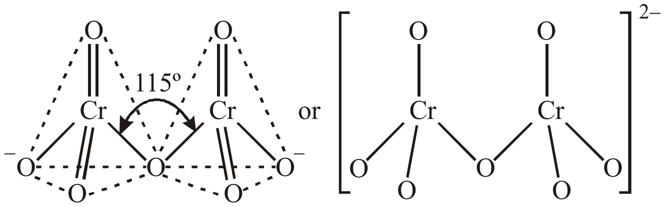
Uses -

(i) In chrome tanning,
(ii) In dyeing-calico printing,
(iii) In photography
(iv) Chromic acid (mixture of $K_2Cr_2O_7 + H_2SO_4$) used as cleaning agent,
(v) In preparation of compounds such as $K_2SO_4.Cr_2(SO_4)_2.24H_2O, CrO_2Cl_2$ etc.

Structures of chromate and dichromate ions :



Chromate ion – Tetrahedral structure



Dichromate ion – Two tetrahedra showing one oxygen atom at one corner

Note :

(i) OS of Cr in chromate and dichromate is same, i.e., +6.
(ii) It is used in the detection of Cl^- in qualitative analysis in the chromyl chloride test.
(iii) $Na_2Cr_2O_7$ is more soluble in water than $K_2Cr_2O_7$.
(iv) $Na_2Cr_2O_7$ is not used in volumetric analysis as it is deliquescent

Potassium permanganate ($KMnO_4$)

Preparation

(i) **Conversion of MnO_2 into potassium manganate :**
Pyrolusite is fused with KOH or K_2CO_3 in presence of air or oxidising agent (i.e., KNO_3 or $KClO_3$)

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

$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$

Oxidation of K_2MnO_4 to $KMnO_4$:

(a) **Chemical oxidation :**

$$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 \downarrow + 2K_2CO_3$$

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

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

(b) **Electrolytic oxidation :** The alkaline manganate solution is electrolysed between iron electrodes :

$$K_2MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At anode : $MnO_4^{2-} \longrightarrow MnO_4^- + e^-$

At cathode : $H^+ + e^- \longrightarrow H$

$2H \longrightarrow H_2$

(ii) **Laboratory method :**

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Properties

(i) It exists as deep purple black prisms with greenish lustre which become dull in air due to superficial reduction.
(ii) It is moderately soluble in H_2O at room temperature.
(iii) When heated, it decomposes at 513 K

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

At red heat.

$$2K_2MnO_4 \xrightarrow[\text{heat}]{\text{red}} 2K_2MnO_3 + O_3$$

(iv) It is a powerful oxidising agent (in neutral, alkaline and acidic medium)

In **neutral** medium, the reaction is

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

In **alkaline** medium:

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

$$I^- + 6OH^- \rightarrow IO_3^- + 3H_2O + 6e^-$$

$$C_6H_4\left\langle\begin{matrix}NO_2\\CH_3\end{matrix}\right. + 7OH^- \rightarrow C_6H_4\left\langle\begin{matrix}NO_2\\COO^-\end{matrix}\right. + 5H_2O + 6e^-$$

In **acidic** medium :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}\ 4H_2O$$

$$S^{2-} \longrightarrow S + 2e^-$$

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

Note : Volumetric titrations involving $KMnO_4$ are carried out only in presence of H_2SO_4 not HCl or HNO_3. This is because oxygen produced from $KMnO_4$ + dil. H_2SO_4 is used only for oxidising the reducing agent. Moreover, H_2SO_4 does not give any oxygen of its own to oxidize the reducing. In case HCl is used, the oxygen produced from $KMnO_4$ + HCl is partly used up to oxidise HCl to chlorine and in case HNO_3 is used, it itself acts as oxidising agent and partly oxidizes the reducing agent.

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last e^- enters the anti - penultimate energy level, i.e., (n – 2) f-orbitals are called f - block elements. They are also called inner transition elements.

Their general electronic configuration is :

$$(n-2)\, f^{1-14}\, (n-1)\, d^{0-1}\, ns^2.$$

The f - block consists of two series, lanthanoids and actinoids.

The Lanthanoids (Ln)

Electronic configurations

They have electronic configuration with $6s^2$ common but with variable occupancy of 4 f-level. The electronic configuration of their tripositive ions are of the form $4f^n$.

Atomic and ionic sizes

In lanthanoids with increasing atomic number, there is a progressive decrease in the atomic as well as ionic radii. This regular decrease in size with increasing atomic number is called **lanthanoid contraction**. It arises due to imperfect shielding of the electrons by the f - subshell.

In the lanthanoid series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from La^{+3} to Lu^{+3}. This contraction in size is known as lanthanoid contraction.

Cause of lanthanoid contraction :

As we move along lanthanoid series, the nuclear charge increases by one unit at each element and is added into same sub-shell (4*f*). Due to shape of *f*-orbitals, there is imperfect shielding of one electron by another. This imperfect shielding is unable to counterbalance the effect of increased nuclear charge, thus resulting in contraction in size.

Consequences of lanthanoid contraction

(i) Difficulty in the separation of lanthanoids due to very small change in their atomic radii

(ii) Similarity in size of elements belonging to same group of second and third transition series.

(iii) As the size decreases from La^{3+} to Lu^{3+}, covalent character of hydroxides increases and hence, the basic strength decreases. Thus $La(OH)_3$ is most basic while $Lu(OH)_3$ is least basic..

Oxidiation states

The typical OS of Ln is +3. Oxidation states + 2 and +4 occur particularly when they lead to :

(i) A noble gas configuration e.g. Ce^{4+} (f^0)

(ii) A half filled '*f*' orbital e.g. Eu^{2+}, Tb^{4+}, (f^7)

(iii) A completely filled '*f*' orbital e.g. Yb^{2+} (f^{14})

They show limited OS due to large energy gap between 4f and 5d subshells.

General characteristics

(i) They are silvery white soft metals and tarnish rapidly in air.

(ii) They have high densities and melting points.

(iii) They have typical metallic structure and are good conductors of heat and electricity.

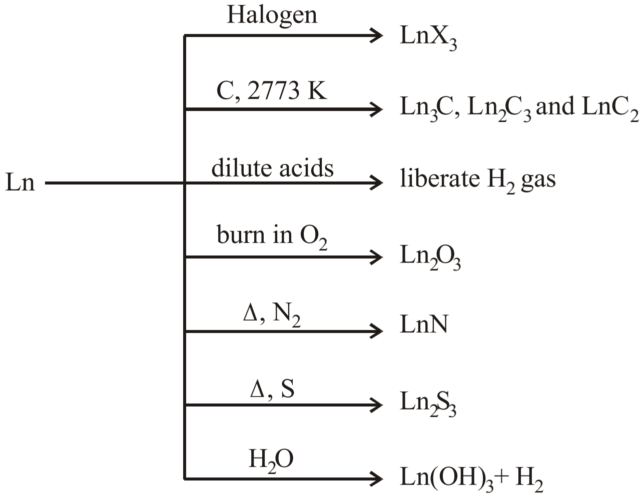
(iv) The lanthanoid ions have unpaired electrons in their incomplete 4*f* orbitals. Thus these electrons absorbs energy in visible region of light and undergo *f*-*f* transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. Lanthanoid ions having $4f^0$, $4f^7$ and $4f^{14}$ are colourless.

(v) Their ions [except La^{3+} (f^0) and Lu^{3+} (f^{14})] show paramagnetism due to unpaired electrons in 4f - subshell.

(vi) They have low IE and are highly electropositive. They readily loose e^{-1} s and are thus good reducing agents.

(vii) Because of their large size and low charge density they do not have much tendency to form complexes.

(viii) *Chemical behaviour*



Uses of lanthanoids

(i) Lanthanoids are used in production of alloy steels for plates and pipes. Ex: misch metal (Ln metal (95%), iron (5%) and traces of S, C, Ca and Al. Misch metal is used in making magnesium based alloys, bullets, shells and lighter flints.

(ii) Their oxides are used in glass industry, for polishing glass and for making coloured glasses for goggles as they give protection against UV light.

(iii) Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.

(iv) Lanthanoid compounds like cerium molybdate, cerium tungstate are used as paints and dyes.

The Actinoids (Ac)

Electronic configurations

The general configuration of actinoides may be given as [Rn] $5f^{1-14}\, 6d^{0-1}\, 7s^2$. They have common $7s^2$ configuration and variable occupancy of 5f and 6d subshells. Though 4f and 5f orbitals have similar shapes but 5f is less deeply buried than 4f. Hence, 5f electrons can participate in bonding to a far greater extent

Ionic sizes

They show a general trend of decrease in size like lanthanoids. This is referred to as actinoid contraction. The contraction is greater from element to element resulting from poor shielding by 5f - electrons.

This is on account of the reason that the 5f orbitals are more diffused than the orbitals present in 4f sub-shell. Consequently, the shielding by 5f electrons is much less than by 4f electrons in lanthanoids. The magnitude of actinoid contraction is more than that of lanthanoid contraction.

Oxidation states

They show larger no. of OS due to small energy gap between 5f, 6d and 7s subshells. General OS is +3. They also show OS of +4. Compounds with +3 and +4 oxidation state tend to hydrolyse.

General characteristics

(i) Actinoid metals have silvery appearance.

(ii) Actinoid cations are coloured due to f - f transitions. Cations with f^0, f^7 and f^{14} configurations are colourless.

(iii) They have high m.pt and b.pt., high densities, low IE and are highly electropositive.

(iv) They are strongly paramagnetic, strong reducing agents and are radioactive.

Note : The actinoids have lower ionization enthalpies than lanthanoids because 5f is less penetrating than 4f.

Comparison of lanthanoids and actinoids

Similarities:

(i) Both show an OS of +3

(ii) Both are electropositive and highly reactive.

(iii) Both exhibit magnetic and spectral properties.

Differences:

	Lanthanoids		Actinoids
1	Besides +3 OS, they show +2 and +4 OS in few cases.	1	Besides +3 OS, they show higher OS of +4, +5, +6, +7 also.
2	Most of their ions are colourless.	2	Most of their ions are coloured.
3	They have less tendency to form complexes.	3	They have greater tendency to form complexes.
4	Lanthanoid compounds are less basic.	4	Actinoid compounds are more basic
5	Non-radioactive, except promethium	5	Radioactive
6	Their magnetic properties can be explained easily.	6	Their magnetic properties cannot be explained easily.

CONCEPT MAP

THE d- & f-BLOCK ELEMENTS

The d-Block Elements

- **Four transition series:**
  (a) 3d series : From Sc(21) to Zn (30)
  (b) 4d series : From Y (39) to Cd (48)
  (c) 5d series : 57 (La), 72 (Hf) to Hg 80
  (d) 6d series : 89 (Ac), 104 (Ku) to (Uub) 112
- **Electronic configuration:** (n – d) d^{10} n-s^2
- **Oxidation state:** Shows variable oxidation states
- **Magnetic property:** Transition elements and many of their compounds are paramagnetic.
- **Coloured compounds:** Forms coloured compounds due to *d-d* transition.
- **Forms complexes:** Due to small highly charged ions and vacant d-orbitals
- **Forms interstitial compounds:** As they are able to entrap atoms of elements having small atomic size like H, C, N, B etc.
- **Oxides:** Oxides in lower oxidation states are basic, whereas those with higher. oxidation state are acidic or amphoteric

Some important d-block elements compound

$K_2Cr_2O_7$

- Prepared from chromite ore
- Oxidising properties

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$2I^- \longrightarrow I_2 + 2e^-$

$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

$KMnO_4$

- Prepared from the mineral pyrolusite
- Oxidising properties

In neutral medium :

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

In alkaline medium:

$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$

In acidic medium :

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$S^{2-} \longrightarrow S + 2e^-$

$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$

$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$

$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$C_2O_4{}^{2-} \longrightarrow 2CO_2 + 2e^-$

$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

The f-Block Elements

Lanthanoids

- 14 elements from Ce to Lu
- General E.C:
  $6s^2\, 5d^{0-1}\, 4f^{1-14}$
- Shows lanthanoid contraction due to poor shielding effect of 4f electrons.
- Most stable O.S. is +3

Actinoids

- General E.C:
  [Rn] $5f^{1-14}\, 6d^{0-1}\, 7s^2$
- Most stable O.S. is + 3. Also shows O.S like +4, + 5, +6 and +7
- These are mostly radioactive
- Have much greater tendency to form complexes than lanthanides.

Chemical properties

Lanthanoids

$\xrightarrow{\text{Burn in } O_2} Ln_2O_3$

$\xrightarrow{\text{with S}} Ln_2S_3$

$\xrightarrow{\text{with } N_2} LnN$

$\xrightarrow[\text{277 3K}]{\text{with C}} LnC_2$

$\xrightarrow{H_2O} Ln(OH)_3$

$\xrightarrow{\text{with halogens}} LnX_3$

$\xrightarrow{\text{with acids}}$ H_2 is liberated

EXERCISE - 1

Conceptual Questions

1. The oxides, CrO_3, MoO_3, and WO_3 are strongly
(a) neutral (b) acidic
(c) basic (d) none of these

2. $4K_2Cr_2O_7 \xrightarrow{\text{heat}} 4K_2CrO_4 + 3O_2 + X$. In the above reaction X is:
(a) CrO_3 (b) Cr_2O_7
(c) Cr_2O_3 (d) CrO_5

3. Which one of the following ionic species will impart colour to an aqueous solution?
(a) Ti^{4+} (b) Cu^+
(c) Zn^{2+} (d) Cr^{3+}

4. The aqueous solution containing which one of the following ions will be colourless? (Atomic number: Sc = 21, Fe = 26, Ti = 22, Mn = 25)
(a) Sc^{3+} (b) Fe^{2+}
(c) Ti^{3+} (d) Mn^{2+}

5. When tin is treated with concentrated nitric acid:
(a) it is converted into stannous nitrate
(b) it is converted into stannic nitrate
(c) it is converted into metastannic acid
(d) it becomes passive

6. In which of the following pairs both the ions are coloured in aqueous solutions ?
(a) Sc^{3+}, Ti^{3+} (b) Sc^{3+}, Co^{2+}
(c) Ni^{2+}, Cu^+ (d) Ni^{2+}, Ti^{3+}
(At. no. : Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)

7. Which of the following ions has the maximum magnetic moment?
(a) Mn^{+2} (b) Fe^{+2}
(c) Ti^{3+} (d) Cr^{+2}.

8. For the ions Zn^{2+}, Ni^{2+} and Cr^{3+} which among the following statements is correct?
(atomic number of Zn = 30, Ni = 28 and Cr = 24)
(a) All these are colourless
(b) All these are coloured
(c) Only Ni^{2+} is coloured and Zn^{2+} and Cr^{3+} are colourless
(d) Only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured

9. Copper and con. H_2SO_4 react to produce
(a) Cu (b) SO_2
(c) H_2 (d) O_2

10. The volatile metal is :
(a) Fe (b) Zn
(c) Cu (d) Ag

11. Which of the following metal ions is not coloured?
(a) Ti^{3+} (b) Fe^{3+}
(c) V^{2+} (d) Cu^+

12. The transition metal with least atomic number is :
(a) Os (b) Zr
(c) Pt (d) Ru

13. Which of the following element is not a member of transition elements ?
(a) Zn (b) Pt
(c) Ce (d) Mo

14. Which of the following configuration is correct for iron ?
(a) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4$
(b) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6 4s^2$
(c) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2$
(d) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2 4s^2$

15. Percentage of silver in German silver is :
(a) 0% (b) 1%
(c) 5% (d) none of these

16. In first transition series, the melting point of Mn is low because
(a) due to d^{10} configuration, metallic bonds are strong
(b) due to d^7 configuration, metallic bonds are weak
(c) due to d^5 configuration, metallic bonds are weak
(d) None of these

17. The number of unpaired electrons in gaseous species of Mn^{3+}, Cr^{3+} and V^{3+} respectively are.
(a) 4, 3 and 2 (b) 3, 3 and 2
(c) 4, 3 and 2 (d) 3, 3 and 3

18. The liquified metal expanding on solidification is
(a) Ga (b) Al
(c) Zn (d) Cu

19. In which of the following metallic bond is strongest ?
(a) Fe (b) Sc
(c) V (d) Cr

20. Stainless steel contains iron and
(a) Cr + Ni (b) Cr + Zn
(c) Zn + Pb (d) C +Cr + Ni

21. Among the following, the compound that is both paramagnetic and coloured, is
(a) $KMnO_4$ (b) CuF_2
(c) $K_2Cr_2O_7$ (d) All are coloured

22. Which of the following elements shows maximum number of different oxidation states in its compounds?
(a) Eu (b) La
(c) Gd (d) Am

23. $K_2Cr_2O_7$ on heating with aqueous NaOH gives
(a) CrO_4^{2-} (b) $Cr(OH)_3$
(c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

24. CrO_3 dissolves in aqueous NaOH to give
(a) $Cr_2O_7^{\ 2-}$ (b) $CrO_4^{\ 2-}$
(c) $Cr(OH)_3$ (d) $Cr(OH)_2$

25. To prevent corrosion, iron pipes carrying drinking water are covered with zinc. The process involved is
(a) alloy formation (b) electroplating
(c) galvanising (d) soldering

26. When $KMnO_4$ acts as an oxidising agent and ultimately forms $[MnO_4]^{-2}$, MnO_2, Mn_2O_3, Mn^{+2} then the number of electrons transferred in each case respectively is
(a) 4, 3, 1, 5 (b) 1, 5, 3, 7
(c) 1, 3, 4, 5 (d) 3, 5, 7, 1.

27. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is:
(a) +3 (b) +2
(c) +6 (d) +4

28. When the same amount of zinc is treated separately with excess of H_2SO_4 and excess of NaOH, the ratio of volumes of H_2 evolved is
(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) 9 : 4

29. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives
(a) HgO (b) Hg_2O
(c) $NH_2-Hg-Hg-Cl$ (d) Hg_2NH_2Cl

30. Copper becomes green when exposed to moist air for longer period –
(a) because of the formation of a layer of cupric oxide on the surface of copper
(b) because of the formation of a layer of basic carbonate of copper on the surface of copper
(c) because of the formation of a layer of cupric hydroxide on the surface of copper
(d) because of the formation of a layer of cupric acetate on the surface of copper

31. Copper displaces which of the metal from their salt solutions ?
(a) $AgNO_3$ (b) $ZnSO_4$
(c) $FeSO_4$ (d) All of the above

32. Gun metal is an alloy of :
(a) Cu and Al (b) Cu and Sn
(c) Cu, Zn and Sn (d) Cu, Zn and Ni

33. Which of the following has lowest percentage of carbon ?
(a) Cast iron
(b) Wrought iron
(c) Steel iron
(d) All have same percentage.

34. Black jack is an ore of :
(a) Cr (b) Sn
(c) Zn (d) Ni

35. Which one of the following is coinage metal ?
(a) Zn (b) Cu
(c) Sn (d) Pb.

36. When excess of $SnCl_2$ is added to a solution of $HgCl_2$, a white precipitate turning to grey is obtained. This grey colour is due to the formation of
(a) Hg_2Cl_2 (b) $SnCl_4$
(c) Sn (d) Hg.

37. Bronze is an alloy of :
(a) Pb + Sn + Zn (b) Cu + Sn
(c) Pb + Zn (d) Cu + Zn

38. The treatment of Cu with dilute HNO_3 gives :
(a) N_2O (b) NO
(c) NH_4^+ (d) NO_2

39. White vitriol has the formula :
(a) $CaSO_4.2H_2O$ (b) $CuSO_4.5H_2O$
(c) $ZnSO_4.7H_2O$ (d) $FeSO_4.7H_2O$

40. Addition of iron fillings to $CuSO_4$ solution caused precipitation of Cu owing to the
(a) Reduction of Cu^{2+} (b) Oxidation of Cu^{2+}
(c) Reduction of Fe (d) Reduction of Fe^{3+}

41. The final products formed on the addition of KI to copper sulphate solution are :
(a) K_2SO_4, CuI_2 and I_2 (b) K_2SO_4, Cu_2I_2 and I_2
(c) K_2SO_4 and Cu_2O (d) K_2SO_4, CuO and I_2

42. $KMnO_4$ (acidic/alkaline) is not decolourised by
(a) mohr salt (b) oxalic acid
(c) benzene (d) propene

43. Bessemer converter is used in the manufacture of
(a) Pig iron (b) Steel
(c) Wrought (d) Cast iron.

44. Among the lanthanoides the one obtained by synthetic method is
(a) Lu (b) Pm
(c) Pr (d) Gd

45. Both acid and base may react with which of the following oxides ?
(a) CaO (b) Na_2O_2
(c) ZnO (d) Mn_3O_4.

46. The lanthanoide contraction is responsible for the fact that
(a) Zr and Y have about the same radius
(b) Zr and Nb have similar oxidation state
(c) Zr and Hf have about the same radius
(d) Zr and Zn have the same oxidation state
(Atomic numbers : Zr = 40, Y = 39, Nb = 41, Hf = 72, Zn = 30)

47. Which one of the following elements shows maximum number of different oxidation states in its compounds?
(a) Eu (b) La
(c) Gd (d) Am

48. Among the following which is used as an electrolyte in electroplating a base metal with gold ?
(a) NH_4Cl (b) $K[Au(CN)_2]$
(c) HgCN (d) AgCN

49. Cuprous chloride is used in gas analysis to absorb?
(a) CO_2 (b) CO
(c) H_2 (d) CH_4

50. Lanthanoids are
(a) 14 elements in the sixth period (atomic no. = 90 to 103) that are filling 4*f* sublevel
(b) 14 elements in the seventh period (atomic no. = 90 to 103) that are filling 5*f* sublevel
(c) 14 elements in the sixth period (atomic no. = 58 to 71) that are filling 4*f* sublevel
(d) 14 elements in the seventh period (atomic no. = 58 to 71) that are filling 4*f* sublevel

51. Aufbau principle does not give the correct arrangement of filling up of atomic orbitals in :
(a) Cu and Zn (b) Co and Zn
(c) Mn and Cr (d) Cu and Cr

52. The radius of La^{3+} (Atomic number of La = 57) is 1.06Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71) ?
(a) 1.40 Å (b) 1.06 Å
(c) 0.85 Å (d) 1.60 Å

53. Which of the following compounds is formed when a mixture of $K_2Cr_2O_7$ and NaCl is heated with conc. H_2SO_4 ?
(a) CrO_2Cl_2 (b) $CrCl_3$
(c) $Cr_2(SO_4)_3$ (d) Na_2CrO_4

54. Which of the following factors may be regarded as the main cause of lanthanoide contraction?
(a) Greater shielding of 5*d* electrons by 4*f* electrons
(b) Poorer shielding of 5*d* electrons by 4*f* electrons
(c) Effective shielding of one of 4*f* electrons by another in the subshell
(d) Poor shielding of one of 4*f* electron by another in the subshell

55. For making Ag from $AgNO_3$, which of the following is used
(a) PH_3 (b) phosphonium iodide
(c) Na_2CO_3 (d) NH_3

56. The titanium (atomic number 22) compound that does not exist is
(a) TiO (b) TiO_2
(c) K_2TiF_6 (d) K_2TiO_4

57. The Ce (Z = 58) belongs to IIIrd group of periodic table. If it furnish one α particle to form an element 'X', then X belongs to
(a) IIIrd group (b) IInd group
(c) Ist group (d) zero group

58. Lanthanum is grouped with *f*-block elements because
(a) it has partially filled *f*-orbitals
(b) it is just before Ce in the periodic table
(c) it has both partially filled *f* and *d*-orbitals
(d) properties of lanthanum are very similar to the elements of *f*-block

59. The approximate percentage of iron in mischmetal is
(a) 10 (b) 20
(c) 50 (d) 5

60. Which of the following is not an actinide ?
(a) Curium (b) Californium
(c) Uranium (d) Terbium

61. A reduction in atomic size with increase in atomic number is a characteristic of elements of
(a) high atomic masses (b) *d*-block
(c) *f*-block (d) Radioactive series

62. Identify the product and its colour when MnO_2 is fused with solid KOH in the presence of O_2.
(a) $KMnO_4$, purple (b) K_2MnO_4, dark green
(c) MnO, colourless (d) Mn_2O_3, brown

63. Which one of the following ions is the most stable in aqueous solution?
(a) V^{3+} (b) Ti^{3+}
(c) Mn^{3+} (d) Cr^{3+}
(At.No. Ti = 22, V = 23, Cr = 24, Mn = 25)

64. Identify the incorrect statement among the following :
(a) Lanthanoid contraction is the accumulation of successive shrinkages.
(b) As a result of lanthanoid contraction, the properties of 4*d* series of the transition elements have no similarities with the 5*d* series of elements.
(c) Shielding power of 4*f* electrons is quite weak.
(d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

65. The correct order of decreasing second ionisation enthalpy of Ti (22), V(23), Cr(24) and Mn (25) is :
(a) Cr > Mn > V > Ti (b) V > Mn > Cr > Ti
(c) Mn > Cr > Ti > V (d) Ti > V > Cr > Mn

66. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states?
(a) $3d^5 4s^1$ (b) $3d^5 4s^2$
(c) $3d^2 4s^2$ (d) $3d^3 4s^2$

67. Which one of the following ions has electronic configuration [Ar] $3d^6$?
(a) Ni^{3+} (b) Mn^{3+}
(c) Fe^{3+} (d) Co^{3+}
(At. Nos. Mn = 25, Fe = 26, Co = 27, Ni = 28)

68. Which of the following pairs has the same size?
(a) Fe^{2+}, Ni^{2+} (b) Zr^{4+}, Ti^{4+}
(c) Zr^{4+}, Hf^{4+} (d) Zn^{2+}, Hf^{4+}

69. Which of the following oxidation states is the most common among the lanthanoids?
(a) 3 (b) 4
(c) 2 (d) 5

70. For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order?
(a) Mn > Fe > Cr > Co (b) Fe > Mn > Co > Cr
(c) Co > Mn > Fe > Cr (d) Cr > Mn > Co > Fe

71. Acidified $K_2Cr_2O_7$ solution turns green when Na_2SO_3 is added to it. This is due to the formation of :
(a) $Cr_2(SO_4)_3$ (b) CrO_4^{2-}
(c) $Cr_2(SO_3)_3$ (d) $CrSO_4$

72. Which of the statements is not true?
(a) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed.
(b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis.
(c) $K_2Cr_2O_7$ solution in acidic medium is orange.
(d) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7.

73. Which one of the following does not correctly represent the correct order of the property indicated against it?
(a) Ti < V < Cr < Mn : increasing number of oxidation states
(b) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$: increasing magnetic moment
(c) Ti < V < Cr < Mn : increasing melting points
(d) Ti < V < Mn < Cr : increasing 2nd ionization enthalpy

74. The catalytic activity of transition metals and their compounds is mainly due to :
(a) their magnetic behaviour
(b) their unfilled *d*-orbitals
(c) their ability to adopt variable oxidation state
(d) their chemical reactivity

75. Which of the following exhibit only + 3 oxidation state ?
(a) U (b) Th (c) Ac (d) Pa

EXERCISE - 2
Applied Questions

1. To an aqueous solution containing anions a few drops of acidified $KMnO_4$ are added. Which one of the following anions, if present will not decolourise the $KMnO_4$ solution?

(a) I^- (b) CO_3^{2-}
(c) S^{2-} (d) NO_2^-

2. Consider the following statements

(I) $La(OH)_3$ is the least basic among hydroxides of lanthanides.
(II) Zr^{4+} and Hf^{4+} posses almost the same ionic radii.
(III) Ce^{4+} can as an oxidizing agent.

Which of the above is/are true ?

(a) (I) and (III) (b) (II) and (III)
(c) (II) only (d) (I) and (II)

3. The basic character of the transition metal monoxides follows the order

(Atomic Nos., Ti = 22, V = 23, Cr = 24, Fe = 26)

(a) $TiO > VO > CrO > FeO$ (b) $VO > CrO > TiO > FeO$
(c) $CrO > VO > FeO > TiO$ (d) $TiO > FeO > VO > CrO$

4. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is

(a) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$
(b) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
(c) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
(d) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$

(Atomic nos. Y = 39, La = 57, Eu = 63, Lu = 71)

5. Which one of the following metals has a different lattice from those of the others?

(a) Fe (b) Co
(c) Ni (d) Cu

6. Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is (At. nos. Ti = 22; V = 23; Cr = 24; Mn = 25)

(a) $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$
(b) $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{7+}$
(c) $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$
(d) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$

7. A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is

(a) HgI_2 (b) HgO
(c) Pb_3O_4 (d) $(NH_4)_2Cr_2O_7$

8. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown-red vapours of :

(a) CrO_3 (b) $CrCl_3$
(c) CrO_2Cl_2 (d) Cr_2O_3

9. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them ?

(a) $(n-1)d^3 ns^2$ (b) $(n-1)d^5 ns^1$
(c) $(n-1)d^8 ns^2$ (d) $(n-1)d^5 ns^2$

10. When a small amount of $KMnO_4$ is added to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Compound may be :

(a) $MnSO_4$ (b) Mn_2O_7
(c) MnO_2 (d) Mn_2O_3

11. For *d* block elements the first ionization potential is of the order :

(a) $Zn > Fe > Cu > Cr$ (b) $Sc = Ti < V = Cr$
(c) $Zn < Cu < Ni < Co$ (d) $V > Cr > Mn > Fe$

12. A blue colouration is not obtained when

(a) ammonium hydroxide dissolves in copper sulphate
(b) copper sulphate solution reacts with $K_4[Fe(CN)_6]$
(c) ferric chloride reacts with sod. ferrocyanide
(d) anhydrous $CuSO_4$ is dissolved in water

13. Which of the following combines with Fe (II) ions to form a brown complex?

(a) NO (b) N_2O
(c) N_2O_3 (d) N_2O_5

14. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

15. A solution of sodium thiosulphate on addition of few drops of ferric chloride gives violet colour due to the formation of

(a) $Na_2S_4O_6$ (b) $Fe_2(SO_4)_3$
(c) $Fe_2(S_2O_3)_3$ (d) $Fe_2(S_2O_3)_2$

16. Precipitate of AgCl is soluble in liquid NH_3, the compound forms

(a) $Ag(NH_4)_2OH$ (b) $Ag(NH_4)_2Cl$
(c) $Ag(NH_3)_2OH$ (d) $Ag(NH_3)_2Cl$

17. Philosopher's wool is :

(a) $ZnCl_2$ (b) ZnS
(c) $Zn(NO_3)_2$ (d) ZnO

18. Zinc and mercury do not show variable valency like *d*-block elements because

(a) they are soft
(b) their *d*-shells are complete
(c) they have only two electrons in the outermost subshell
(d) their *d*-shells are incomplete

19. Silver nitrate produces a black stain on skin due to

(a) being a strong reducing agent
(b) its corrosive action
(c) formation of complex compound
(d) its reduction to metallic silver

20. KI and $CuSO_4$ solutions on mixing produce :

(a) $Cu_2I_2 + K_2SO_4$ (b) $Cu_2I_2 + I_2 + K_2SO_4$
(c) $CuI_2 + K_2SO_4$ (d) $CuI_2 + I_2 + K_2SO_4$

21. Which one is most acidic?

(a) Cr_2O_3 (b) V_2O_5
(c) Mn_2O_7 (d) Fe_2O_3

22. Which of the following statement is incorrect ?

(a) Across a period from Sc to Cu the densities increase with increasing atomic number.

(b) The melting point of transition elements rise to a maximum from Sc to Cr and then decreases from Fe to Zn.

(c) Transition elements have high enthalpies of atomization and in 3*d* series increase regularly from Sc to Cu.

(d) On going down a group from 3*d* to 6d series the stability of higher oxidation state increases with increasing atomic number.

23. Lithopone is a mixture of :

(a) $ZnCO_3$, $BaCO_3$ (b) ZnS, Na_2SO_4

(c) $ZnSO_4$, $BaSO_4$ (d) ZnS, $BaSO_4$

24. Out of TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (*Z* of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are:

(a) Cu_2Cl_2 and $NiCl_4^{2-}$ (b) TiF_6^{2-} and Cu_2Cl_2

(c) CoF_6^{3-} and $NiCl_4^{2-}$ (d) TiF_6^{2-} and CoF_6^{3-}

25. Which of the following ions will exhibit colour in aqueous solutions?

(a) La^{3+} (Z = 57) (b) Ti^{3+} (Z = 22)

(c) Lu^{3+} (Z = 71) (d) Sc^{3+} (Z = 21)

26. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

(a) II, III in haematite and III in magnetite

(b) II, III in haematite and II in magnetite

(c) II in haematite and II, III in magnetite

(d) III in haematite and II, III in magnetite

27. Which of the following arrangements does not represent the correct order of the property stated against it ?

(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

28. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{M^{3+}/M^{2+}}$ value ?

(a) Cr(Z = 24) (b) Mn(Z = 25)

(c) Fe(Z = 26) (d) Co(Z = 27)

29. Identify the incorrect statement among the following:

(a) 4*f* and 5*f* orbitals are equally shielded.

(b) *d*-Block elements show irregular and erratic chemical properties among themselves.

(c) La and Lu have partially filled *d*-orbitals and no other partially filled orbitals.

(d) The chemistry of various lanthanoids is very similar.

30. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being

(a) 4*f* orbitals more diffused than the 5*f* orbitals

(b) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals

(c) more energy difference between 5f and 6d than between 4f and 5d orbitals

(d) more reactive nature of the actionids than the lanthanoids

31. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl

(a) gets oxidised by oxalic acid to chlorine

(b) furnishes H^+ ions in addition to those from oxalic acid

(c) reduces permanganate to Mn^{2+}

(d) oxidises oxalic acid to carbon doxide and water

32. Knowing that the chemistry of lanthanoids(Ln) is dominated by its + 3 oxidation state, which of the following statements is incorrect?

(a) The ionic size of Ln (III) decrease in general with increasing atomic number

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

(c) Ln (III) hydroxide are mainly basic in character.

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

33. In context of the lanthanoids, which of the following statements is not correct?

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

(b) All the members exhibit +3 oxidation state.

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

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

34. The outer electron configuration of Gd (Atomic No. : 64) is :

(a) $4f^3\,5d^5\,6s^2$ (b) $4f^8\,5d^0\,6s^2$

(c) $4f^4\,5d^4\,6s^2$ (d) $4f^7\,5d^1\,6s^2$

35. Iron exhibits +2 and + 3 oxidation states. Which of the following statements about iron is incorrect ?

(a) Ferrous oxide is more basic in nature than the ferric oxide.

(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.

(c) Ferrous compounds are less volatile than the corresponding ferric compounds.

(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

36. Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential $\left(E^\circ_{M^{2+}/M}\right)$ value has a positive sign?

(a) Co (Z = 27) (b) Ni (Z = 28)

(c) Cu (Z = 29) (d) Fe (Z = 26)

37. Which of the following species is/are paramagnetic?

Fe^{2+}, Zn^0, Hg^{2+}, Ti^{4+}

(a) Fe^{2+} only (b) Zn^0 and Ti^{4+}

(c) Fe^{2+} and Hg^{2+} (d) Zn^0 and Hg^{2+}

38. The titanium (atomic number 22) compound that does not exist is

(a) TiO (b) TiO_2

(c) K_2TiF_6 (d) K_2TiO_4

39. The colour of the following ions V^{2+}, V^{3+}, V^{4+}, Fe^{2+}, Fe^{3+} are respectively
(a) green, violet, blue, green, yellow
(b) yellow, green, violet, green, blue
(c) violet, green, yellow, green, blue
(d) yellow, green, blue, green, violet

40. Which of the following is not a characteristic of interstitial compounds of transition elements?
(a) The formulae of these compounds do not correspond to any normal oxidation state
(b) They have melting points higher than those of pure elements
(c) They are very hard and some compounds approach diamond in hardness
(d) They are insulators in contrast to the transition metals

41. In the following salts the lowest value of magnetic moment is observed in
(a) $MnSO_4 . 4H_2O$ (b) $CuSO_4.5H_2O$
(c) $FeSO_4.6H_2O$ (d) $ZnSO_4.7H_2O$

42. Which one of the following transition elements does not exhibit variable oxidation state?
(a) Ni (b) Cu
(c) Fe (d) Sc

43. Identify the product and its colour when MnO_2 is fused with solid KOH in the presence of O_2.
(a) $KMnO_4$, purple (b) K_2MnO_4, dark green
(c) MnO, colourless (d) Mn_2O_3, brown

44. Which one of the following ions has the maximum magnetic moment?
(a) Sc^{3+} (b) Ti^{3+}
(c) Cr^{3+} (d) Fe^{3+}

DIRECTIONS for Qs. 45 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.
(a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

45. **Statement-1 :** Magnetic moment values of actinides are lesser than the theoretically predicted values.
Statement-2 : Actinide elements are strongly paramagnetic.

46. **Statement-1 :** Cu^{2+} and Cd^{2+} are separated from each other by first adding KCN solution and then passing H_2S gas.
Statement-2 : KCN reduces Cu^{2+} to Cu^+ and forms a complex with it.

47. **Statement-1 :** Cuprous ion (Cu^+) has unpaired electrons while cupric ion (Cu^{++}) does not.
Statement-2 : Cuprous ion (Cu^+) is colourless whereas cupric ion (Cu^{++}) is blue in the aqueous solution

48. **Statement-1 :** Transition metals show variable valency.
Statement-2 : Transition metals have a large energy difference between the ns^2 and $(n-1)d$ electrons.

49. **Statement-1 :** Transition metals are good catalysts.
Statement-2 : V_2O_5 or Pt is used in the preparation of H_2SO_4 by contact process.

50. **Statement-1 :** Magnetic moment values of actinides are lesser than the theoretically predicted values.
Statement-2 : Actinide elements are strongly paramagnetic.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number?
(a) 25 (b) 26
(c) 27 (d) 24

2. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct.
(a) Cu(II) is more stable
(b) Cu(II) is less stable
(c) Cu(I) and Cu(II) are equally stable
(d) Stability of Cu(I) and Cu(II) depends on nature of copper salts

3. Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(a) Fe (b) Ni
(c) Co (d) Cu

4. Generally, transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?
(a) Ag_2SO_4 (b) CuF_2
(c) ZnF_2 (d) Cu_2Cl_2

5. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.
(a) Mn_2O_7 (b) MnO_2
(c) $MnSO_4$ (d) Mn_2O_3

6. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
(a) $3d^7$ (b) $3d^5$
(c) $3d^8$ (d) $3d^2$

7. Which of the following oxidation state is common for all lanthanoids?
(a) +2 (b) +3
(c) +4 (d) +5

8. Which of the following reactions are disproportionation reactions?

(i) $Cu^+ \rightarrow Cu^{2+} + Cu$

(ii) $3MnO_4^- + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(iii) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(iv) $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

(a) (i) (b) (i), (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (i) and (iv)

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

(a) CO_2 is formed as the product
(b) reaction is exothermic
(c) MnO_4^- catalyses the reaction
(d) Mn^{2+} acts as autocatalyst

10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

(a) U (b) Np
(c) Tm (d) Fm

11. $KMnO_4$ acts as an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$
(c) $\frac{4}{5}$ (d) $\frac{1}{5}$

12. Which of the following oxides are amphoteric?

$Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4$

(a) V_2O_5, Cr_2O_3 (b) Mn_2O_7, CrO_3
(c) CrO, V_2O_5 (d) V_2O_5, V_2O_4

13. Gadolinium belongs to 4*f* series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

(a) $[Xe]4f^7 5d^1 6s^2$ (b) $[Xe]4f^6 5d^2 6s^2$
(c) $[Xe]4f^8 6d^2$ (d) $[Xe]4f^9 5s^1$

14. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

(a) They have high melting points in comparison to pure metals
(b) They are very hard
(c) They retain metallic conductivity
(d) They are chemically very reactive

15. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is

(a) 2.87 BM (b) 3.87 BM
(c) 3.47 BM (d) 3.57 BM

16. $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to ....

(a) I_2 (b) IO^-
(c) IO_3^- (d) IO_4^-

17. Which of the following statements is not correct?

(a) Copper liberates hydrogen from acids
(b) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine
(c) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution
(d) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution

18. When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salt then Sn^{2+} changes to

(a) Sn (b) Sn^{3+}
(c) Sn^{4+} (d) Sn^+

19. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because

(a) fluorine is more electronegative than oxygen
(b) fluorine does not possess *d*-orbitals
(c) fluorine stabilises lower oxidation state
(d) in covalent compounds, fluorine can form single bond only while oxygen forms double bond

20. Although zirconium belongs to 4*d* transition series and hafnium to 5*d* transition series even then they show similar physical and chemical properties because ....

(a) both belong to *d*-block
(b) both have same number of electrons
(c) both have similar atomic radius
(d) both belong to the same group of the periodic table

21. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?

(a) Both HCl and $KMnO_4$ act as oxidising agents
(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent
(c) $KMnO_4$ is a weaker oxidising agent than HCl
(d) $KMnO_4$ acts as a reducing agent in the presence of HCl

NEET/AIPMT (2013-2017) Questions

22. Which of the following lanthanoid ions is diamagnetic ?
(At nos. Ce = 58, Sm = 62, Eu = 63, Yb = 70) ***[2013]***

(a) Sm^{2+} (b) Eu^{2+}
(c) Yb^{2+} (d) Ce^{2+}

23. $KMnO_4$ can be prepared from K_2MnO_4 as per the reaction:

$$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^{2-} + MnO_2 + 4OH^-$$

The reaction can go to completion by removing OH^- ions by adding. ***[2013]***

(a) KOH (b) CO_2
(c) SO_2 (d) HCl

24. The outer electronic configuration of Gd (At. No. 64) is: ***[1997, NEET Kar. 2013]***

(a) $4f^4 5d^5 6s^1$ (b) $4f^5 5d^4 6s^1$
(c) $4f^7 5d^1 6s^2$ (d) $4f^3 5d^5 6s^2$

25. Sc (Z = 21) is a transition element but Zn (Z = 30) is not because ***[NEET Kar. 2013]***

(a) both Sc and Zn do not exhibit variable oxidation states
(b) both Sc^{3+} and Zn^{2+} ions are colourless and form white compounds

(c) in case of Sc, 3*d* orbitals are partially filled but in Zn these are completely filled
(d) last electron is assumed to be added to 4s level in case of Zn

26. The pair of compounds that can exist together is: ***[2014]***
(a) $FeCl_3, SnCl_2$ (b) $HgCl_2, SnCl_2$
(c) $FeCl_2, SnCl_2$ (d) $FeCl_3$, KI

27. In acidic medium, H_2O_2 changes $Cr_2O_7^{-2}$ to CrO_5 which has two (–O–O) bonds. Oxidation state of Cr in CrO_5 is:- ***[2014]***
(a) +5 (b) +3
(c) +6 (d) – 10

28. The reaction of aqueous $KMnO_4$ with H_2O_2 in acidic conditions gives: ***[2014]***
(a) Mn^{4+} and O_2 (b) Mn^{2+} and O_2
(c) Mn^{2+} and O_3 (d) Mn^{4+} and MnO_2

29. Magnetic moment 2.83 BM is given by which of the following ions ? ***[2014]***
(At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28):-
(a) Ti^{3+} (b) Ni^{2+}
(c) Cr^{3+} (d) Mn^{2+}

30. Reason of lanthanoid contraction is:- ***[2014]***
(a) Negligible screening effect of '*f*' orbitals
(b) Increasing nuclear charge
(c) Decreasing nuclear charge
(d) Decreasing screening effect

31. Magnetic moment 2.84 B.M. is given by :- ***[2015]***
(At. nos, Ni = 28, Ti = 22, Cr = 24, Co = 27)
(a) Ti^{3+} (b) Cr^{2+}
(c) Co^{2+} (d) Ni^{2+}

32. The number of *d*-electrons in Fe^{2+} (Z = 26) is not equal to the number of electrons in which one of the following? ***[2015]***
(a) *p*-electrons in Cl (Z = 17)
(b) *d*-electrons in Fe (Z = 26)
(c) *p*-electrons in Ne (Z = 10)
(d) *s*-electrons in Mg (Z = 12)

33. Which of the following processes does not involve oxidation of iron ? ***[2015]***
(a) Decolourization of blue $CuSO_4$ solututíon by iron
(b) Formation of $Fe(CO)_5$ from Fe
(c) Liberation of H_2 from steam by iron at high temperature
(d) Rusting of iron sheets

34. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii ? (Numbers in the parenthesis are atomic numbers). ***[2015]***
(a) Zr (40) and Nb (41) (b) Zr (40) and Hf (72)
(c) Zr (40) and Ta (73) (d) Ti (22) and Zr (40)

35. The angular momentum of electron in 'd' orbital is equal to : ***[2015]***
(a) $\sqrt{2}\,\hbar$ (b) $2\sqrt{3}\,\hbar$
(c) $0\hbar$ (d) $\sqrt{6}\,\hbar$

36. Assuming complete ionization, same moles of which of the following compounds will require the least amount of acidified $KMnO_4$ for complete oxidation ***[2015 RS]***
(a) $FeSO_4$ (b) $FeSO_3$
(c) FeC_2O_4 (d) $Fe(NO_2)_2$

37. Gadolinium belongs to 4f series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium ? ***[2015 RS]***
(a) $[Xe]4f^8 6d^2$ (b) $[Xe]4f^9 5s^1$
(c) $[Xe]\,4f^7 5d^1 6s^2$ (d) $[Xe]\,4f^6 5d^2 6s^2$

38. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium ? ***[2015 RS]***
(a) $3s\ 4s\ 3p\ 3d$ (b) $4s\ 3s\ 3p\ 3d$
(c) $3s\ 3p\ 3d\ 4s$ (d) $3s\ 3p\ 4s\ 3d$

39. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution ? ***[2016]***
(a) The solution turns blue
(b) The solution is decolourized
(c) SO_2 is reduced
(d) Green $Cr_2(SO_4)_3$ is formed

40. The electronic configurations of Eu(Atomic No. 63), Gd(Atomic No. 64) and Tb (Atomic No. 65) are ***[2016]***
(a) $[Xe]4f^7 6s^2$, $[Xe]4f^8\,6s^2$ and $[Xe]4f^8 5d^1 6s^2$
(b) $[Xe]4f^7 5d^1 6s^2$, $[Xe]4f^7\,5d^1\,6s^2$ and $[Xe]4f^9 6s^2$
(c) $[Xe]4f^6 5d^1 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^8 5d^1 6s^2$
(d) $[Xe]4f^7 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^9 6s^2$

41. Which copper is heated with conc. HNO_3 it produces ***[2016]***
(a) $Cu(NO_3)_2$ and NO_2
(b) $Cu\,(NO_3)_2$ and NO
(c) $Cu(NO_3)_2$, NO and NO_2
(d) $Cu(NO_3)_2$ and N_2O

42. Name the gas that can readily decolourise acidified $KMnO_4$ solution : ***[2017]***
(a) SO_2 (b) NO_2
(c) P_2O_5 (d) CO_2

43. The reason for greater range of oxidation states in actinoids is attributed to :- ***[2017]***
(a) actinoid contraction
(b) 5*f*, 6*d* and 7*s* levels having comparable energies
(c) 4*f* and 5*d* levels being close in energies
(d) the redioactive nature of actinoids

Hints & Solutions

EXERCISE - 1

1. (b) The transition metal oxides in which metal is in lower oxidation states are basic and in which metal is in higher oxidation states are acidic while with intermediate oxidation states are amphoteric.

$$\overset{+6}{Cr}O_3 \quad \overset{+6}{Mo}O_3 \quad \overset{+6}{W}O_3$$

So, the given transition metal oxides are acidic in nature.

2. (c) Potassium dichromate dissociates with evolution of O_2 on heating.

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

So, X is Cr_2O_3.

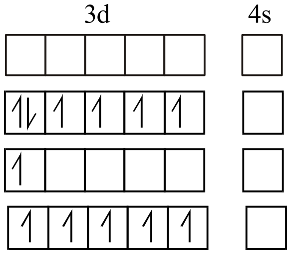
3. (d)

4. (a) $Sc^{3+} \rightarrow 3d^0 4s^0$

$Fe^{2+} \rightarrow 3d^6\ 4s^0$

$Ti^{3+} \rightarrow 3d^1 4s^0$

$Mn^{2+} \rightarrow 3d^5\ 4s^0$



In Sc^{3+} there is/are no unpaired electrons. So the aqueous solution of Sc^{3+} will be colourless.

5. (c) Tin on reaction with conc. HNO_3 to form meta stannic acid and nitrogen dioxide.

$$\underset{\text{tin}}{Sn} + \underset{\substack{\text{nitric}\\\text{acid}\\\text{(conc.)}}}{4HNO_3} \longrightarrow \underset{\substack{\text{Meta}\\\text{stannic}\\\text{acid}}}{H_2SnO_3} + \underset{\substack{\text{nitrogen}\\\text{dioxide}}}{4NO_2} + H_2O$$

6. (d) Sc^{3+} : $1s^2, 2s^2p^6, 3s^2p^6d^0, 4s^0$; no unpaired electron.
Cu^+ : $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^0$; no unpaired electron.
Ni^{2+}: $1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^0$;
unpaired electrons are present.
Ti^{3+} : $1s^2, 2s^2p^6, 3s^2p^6d^1, 4s^0$;
unpaired electron is present
Co^{2+} : $1s^2, 2s^2p^6, 3s^2p^6d^7, 4s^0$;
unpaired electrons are present
So from the given options the only correct combination is Ni^{2+} and Ti^{3+}.

7. (a) Mn^{++} –5 unpaired electrons
Fe^{++} – 4 unpaired electrons
Ti^{++} – 2 unpaired electrons
Cr^{++} – 4 unpaired electrons
Hence maximum no. of unpaired electron is present in Mn^{++}.
Magnetic moment $\propto$ number of unpaired electrons

8. (d) The ions with unpaired electrons are colourled and those with paired electrons are colourless.

$$\underset{(\text{No. of } e^-\text{s} = 28)}{Zn^{2+}} = 1s^2, 2s^2p^6, 3s^2\,p^6\,d^{10}$$

$$\underset{(\text{No. of } e^-\text{s} = 21)}{Cr^{3+}} = 1s^2, 2s^2p^6, 3s^2\,p^6\,d^3$$

$$\underset{(\text{No. of } e^-\text{s} = 26)}{Ni^{2+}} = 1s^2, 2s^2p^6, 3s^2\,p^6\,d^8$$

Thus Zn^{2+}, Cr^{3+} and Ni^{2+} have zero, 3 and 2 unpaired electrons respectively.

9. (b) Copper reacts with H_2SO_4 to produce SO_2

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

But Cu does not displace H_2 from dilute H_2SO_4 as it is less reactive than H_2 (comes below H_2 in electrochemical series)

10. (b) Zn is volatile metal

11. (d) The ion having all electrons paired is not coloured.
(a) $Ti^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^0$
(b) $Fe^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^0$
(c) $V^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^0$
(d) $Cu^+ = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^0$
$\because$ Only Cu^+ does not have any unpaired electron, it is not coloured.

12. (b) Zirconium (Z = 40).

13. (c) Cerium (Ce) belongs to lanthanide series and is member of inner-transition metals.

14. (b) Configuration of Fe ($Z = 26$)
$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

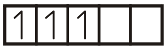
15. (a) German silver is
Cu = 25 - 50%
Zn = 25 - 35%
Ni = 10 - 35%
Used as utensils, resistance wire.

16. (c) Due to d^5 configuration, Mn has exactly half filled d-orbitals. As a result the electronic configuration is stable means $3d$ electrons are more tightly held by the nucleus and this reduces the delocalization of electrons resulting in weaker metallic bonding.

17. (c) $Mn^{3+} = [Ar]3d^4$

= [Ar] 

Number of unpaired electrons = 4
$Cr^{3+} = [Ar]3d^3$

= [Ar] 

No. of unpaired electrons = 3
$V^{3+} = [Ar]3d^2$

= [Ar] 

No. of unpaired electrons = 2

18. (a) Among the given options Ga is the only liquid metal which expands on solidification. It has an unusual structure. Each metal atom has one close neighbour at a distance of 2.43Å, and six more neighbours at distances within range of 2.70Å to 2.79Å. Due to this structure it exists as discrete diatomic molecules rather than a metallic structure in crystal form which is less dense than its liquid form. As its solid form is heated to 30°C, due to weak metallic bonds this unusual structure no longer exists and melts to liquid. This property is unique to Ga, Ge and Bi.

19. (d) Strength of metallic bond directly depends on the number of unpaired electrons. More is number of unpaired electrons stronger is metallic bond. Hence, metallic bond is strongest in Cr having maximum of 6 unpaired electrons among the given options, i.e., Sc (1 unpaired electron), V (3 unpaired electrons) and Fe (4 unpaired electrons).

20. (d)

21. (b) CuF_2 is both paramagnetic and coloured.

22. (d)

	Eu	La	Gd	Am
O.S =	+2 ,+3	+3	+3	+3,+4,+5,+6

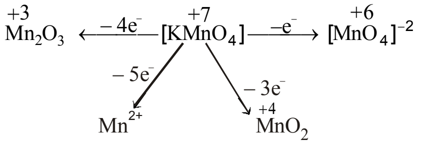
23. (a) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

Hence CrO_4^{2-} ion is obtained.

24. (b) $CrO_3 + 2NaOH \rightarrow Na_2CrO_4 + H_2O$

25. (c) Galvanisation is the process of deposition of zinc metal on the surface of Fe to prevent corrosion.

26. (c)



27. (a) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 3I_2 + 7H_2O + 2Cr^{3+}$

oxidation state of Cr is +3.

28. (a) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

1 mole atom of zinc produces the same amount of H_2 (2 g) in each case.

29. (d) $Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg_2NH_2Cl + NH_4Cl + 2H_2O$

30. (b) $2Cu + H_2O + CO_2 + O_2 \longrightarrow CuCO_3.Cu(OH)_2$
(green coloured basic carbonate of copper is formed)

31. (a) Cu is more electropositive than Ag therefore, it displaces Ag from their salt solution $AgNO_3$.
$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$

32. (c) Gun metal is an alloy of Cu, Zn and Sn. It contains 88% Cu, 10% Sn and 2% Zn.

33. (b) Wrought iron is the purest form of iron containing lowest percentage of C (0.2-0.5%).

34. (c) Black jack or Zinc blende is ZnS. It is ore of Zn.

35. (b) Cu, Ag and Au are called coinage metals.

36. (d) $2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White ppt}}{HgCl_2} + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{grey}}{2Hg} + SnCl_4$

37. (b) Bronze is an alloy of Cu and Sn.

38. (b) $3Cu + (dil)\ 8\ HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

39. (c) $ZnSO_4.7H_2O$ is White vitriol
$FeSO_4.7H_2O$ is Green vitriol
$CuSO_4.5H_2O$ is Blue vitriol

40. (a) Addition of iron filling to $CuSO_4$ solution caused ppt. of Cu owing to the reduction of Cu^{2+} e.g.

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$$

(reduction of copper).

41. (b) $2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + Cu_2I_2 + I_2$

42. (c) Benzene does not decolourise $KMnO_4$ (acidic/alkaline). It is due to the delocalization of π-electron in benzene. Mohr's salt and oxalic acid gives redox reaction with $KMnO_4$. Propene decolorises $KMnO_4$ due to presence of $C = C$ bond.

43. (b) Bessemer converter is used in the manufacture of steel.

44. (b) Pm is obtained by synthetic method.

45. (c) ZnO is amphoteric and dissolves in both acids and bases

$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

46. (c) A regular decrease in the size of the atoms and ions in lanthanoid series from La^{3+} to Lu^{3+} is called lanthanide contraction. The similarity in size of the atoms of Zr and Hf is due to the lanthanide contraction.

47. (d) We know that lanthanides La, Gd shows +3, oxidation state, while Eu shows oxidation state of +2 and + 3. Am shows +3, +4, +5 and +6 oxidation states. Therefore Americium (Am) has maximum number of oxidation states.

48. (b) Complex soluble salts of the metal to be deposited are usually employed as electrolytes in electroplating. Hence $K[Au(CN)_2]$ is used as an electrolyte in gold plating.

49. (b) A solution of CuCl in NH_4OH is often used to measure the amount of CO in gas samples, by measuring the change in volume of the gas.

50. (c) Lanthanides are 4*f*-series elements starting from cerium (*Z* = 58) to lutetium (*Z* = 71). These are placed in the sixth period and in third group.

51. (d) Electronic configuration of Cr is $[Ar]\ 3d^5 4s^1$ because this gives it a stable half filled d^5 configuration. Similarly, electronic configuration of Cu is $[Ar] 3d^{10} 4s^1$. This filling of electrons is not in accordance with Aufbau principle.

52. (c) Ionic radii $\propto \frac{1}{z}$

Thus, $\frac{z_2}{z_1} \Rightarrow \frac{1.06}{(\text{Ionic radii of } Lu^{3+})} = \frac{71}{57}$

$\Rightarrow$ Ionic radii of $Lu^{3+} = 0.85$ Å

53. (a) $K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \xrightarrow{\text{Heat}}$

$2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$

54. (b) In lanthanides, there is poorer shielding of 5*d* electrons by 4*f* electrons resulting in greater attraction of the nucleus over 5*d* electrons and contraction of the atomic radii.

55. (a) When $AgNO_3$ reacts with PH_3, then Ag is obtained.

$$\underset{\text{silver nitrate}}{6AgNO_3} + \underset{\text{phosphene}}{2PH_3} \longrightarrow 6Ag + \underset{\text{phosphorous acid}}{2H_3PO_3} + 6NO_2$$

56. (d) Oxidation state of Ti in the given compounds.
as follows:
TiO – $+2$
TiO_2 – $+4$
$TiCl_3$ – $+3$
K_2TiF_6 – $+4$
K_2TiO_4 – $+6$
The oxidation states exhibited by Ti is + 2, + 3, + 4. So K_2TiO_4 does not exist.

57. (b) $_{58}Ce$ is lanthanide. Lanthanides are from 57 to 71 all present in IIIrd group. Hence $_{58}Ce$ forms $_{56}X$ element on emission of one α particle with belongs to IInd group.

58. (d)

59. (d) Mischmetal is an alloy which contains rare earth elements (94-95%), iron (5%) and traces of sulphur, carbon, silicon, calcium and aluminium. It is used in gas lighters, tracer bullets and shells.

60. (d) Terbium is lanthanide as it belongs to $4f$ – series having configuration $[Xe]4s^9 6s^2$. However the remaining members belong to $5f$ – series (actinides).

61. (c) Lanthanide contraction results into decrease in atomic and ionic radii.

62. (b) $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{dark green}}{2K_2MnO_4} + 2H_2O$

63. (d) For chromium ion + 3 oxidation state is most stable.

64. (b) As a result of lanthanoid contraction change in ionic radii on going from elements of $4d$ to $5d$ transition series is very small. Thus chemical properties of $4d$ and $5d$ series of transition elements are similar.

65. (a) Ti ; Z (22) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
V ; Z (23) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Cr ; Z (24) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Mn ; Z (25) is $1s^2 2s^2 2p^6 3s^2 3d^5 4s^2$
The second electron in all the cases (except Cr) has to be removed from $4s$-orbital and for Cr it has to be removed from completely half filled $3d$-orbital which have extra stability thus $I.E_2$ is highest for Cr. Now among rest elements more will be the nuclear charge more will be the value of $I.E_2$. As nuclear charge depends upon atomic number. Therefore correct order of $I.E_2$ is Mn > V > Ti.
i.e. Cr > Mn > V > Ti. So correct answer is (a).

66. (b) Mn - $3d^5\ 4s^2$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}$
The no. of various oxidation states possible are + 2, + 3, + 4, + 5, + 6 and + 7.

67. (d) Ni^{3+} : [Ar] $3d^7$
Mn^{3+} : [Ar] $3d^4$
Fe^{3+} : [Ar] $3d^5$
Co^{3+} : [Ar] $3d^6$

68. (c) Due to lanthanide contraction, the size of Zr and Hf (atom and ions) become nearly similar

69. (a) 70. (a)

71. (a) The green colour appears due to the formation of Cr^{+++} ion

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

72. (b) $Na_2Cr_2O_7$ is hygroscopic.

73. (c) The melting points of the transition element first rise to a maximum and then fall as the atomic number increases manganese have abnormally low melting point.

74. (c) The transition metals and their compounds are used as catalysts. Because of the variable oxidation states they may form intermediate compound with one of the readtants. These intermediate provides a new path with lowe activation energy. $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$
$2V_2O_4 + O_2 \rightarrow 2V_2O_5$

75. (c) Ac (89) = [Rn] [$6d^1$] [$7s^2$]

EXERCISE - 2

1. (b) Thus they decolourise the $KMnO_4$ solution.
Except CO_3^{2-} all other ions I^-, S^{2-}, NO_2^-, Cl^- are oxidised by acidified $KMnO_4$ forming I_2, S, NO_3^- and Cl_2 respectively.
$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$.
S^{2-} is oxidised to S in presence of $KMnO_4$
$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$.
Nitrites are oxidised to nitrates
$2KMnO_4 + 5KNO_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$
Chloride is oxidised to chlorine
$2KMnO_4 + 3H_2SO_4 + 10HCl \rightarrow K_2SO_4 + 2MnSO_4 + 5Cl_2 + 8H_2O$
CO_3^{2-} is not oxidised by $KMnO_4$ because in CO_3^{2-}, C is already in its highest + 4 oxidation state. Thus CO_3^{2-} does not decolourise $KMnO_4$ solution.

2. (b) As a result of lanthanide contraction Zr^{4+} and Hf^{4+} possess almost the same ionic radii. Ce^{4+} is an oxidising agent. Ce^{4+} gains electron to acquire more stable Ce^{3+} state. $La(OH)_3$ is the most basic among lanthanide hydroxides.

3. (a) The order of basic character of the transition metal monoxide is TiO > VO > CrO > FeO because basic character of oxides decreases with increase in atomic number.

4. (c) In lanthanide series there is a regular decrease in the atomic as well as ionic radii of trivalent ions (M^{3+}) as the atomic number increases. Although the atomic radii

do show some irregularities but ionic radii decreases from La(103 pm) to Lu (86pm). Y^{3+} belong to second transition series there fore have greater ionic radii then other ions of third transition series.

5. (a) Fe has hcp lattice while all other given metals have ccp lattice.

6. (d) The electronic configuration of different species given in the question are :

(a) $_{22}Ti^{3+} : 1s^2 2s^2 p^6 3s^2 p^6 d^1$

(b) $_{22}Ti^{+} : 1s^2 2s^2 p^6 3s^2 . p^6 d^2 4s^1$

(c) $_{22}Ti^{4+} : 1s^2 2s^2 p^6 3s^2 p^6$

(d) $_{22}Ti^{2+} : 1s^2 2s^2 p^6 3s^2 p^6 d^2$

Thus options (a) and (c) are discarded; now let us observe the second point of difference.

$_{23}V^{4+} : 1s^2 2s^2 p^6 3s^2 p^6 d^1$

Thus option (b) is discarded

$_{23}V^{3+} : 1s^2 2s^2 p^6 3s^2 p^6 d^2$

$_{24}Cr^{4+} : 1s^2 2s^2 p^6 3s^2 p^6 d^2$

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

7. (a) $$\underset{\substack{\text{red, solid}\\\text{(insoluble)}}}{HgI_2} + 2KI \rightarrow \underset{\text{(soluble)}}{K_2[HgI_4]}$$

$$HgI_2 \rightleftharpoons Hg + \underset{\text{(violet vapours)}}{I_2}$$

8. (c) Solid potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride gives orange red vapours of a volatile oily liquid CrO_2Cl_2

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{chromyl chloride}}{2CrO_2Cl_2}$$

9. (d) $(n-1)d^5ns^2$ attains the maximum O.S. of $+7$.

10. (b) $KMnO_4$ reacts with H_2SO_4 to form Mn_2O_7 which is highly explosive substance.

$$2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Mn_2O_7 + H_2O$$

11. (a) The ionisation energies increase with increase in atomic number. However, the trend is some irregular among *d*-block elements. On the basis of electronic configuration, the

Zn : $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2$

Fe : $1s^2 2s^2 p^6 3s^2 p^6 d^6 4s^2$

Cu : $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^1$

Cr : $1s^2 2s^2 p^6 3s^2 p^6 d^5 4s^1$

IE_1 follows the order : $Zn > Fe > Cu > Cr$

12. (b) $$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate ppt.}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

13. (a) We know that when nitrogen oxide (NO) combines with Fe (II) ions, a brown complex is formed. This reaction is called brown ring test.

14. (d) (i) Haematite is Fe_2O_3 in which Fe is present in III oxidation state.

(ii) Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3.
Oxidation state of Fe in FeO is II.
Oxidation state of Fe in Fe_2O_3 is III.

15. (c) The reaction can be represented as

$$3Na_2S_2O_3 + 2FeCl_3 \rightleftharpoons \underset{\text{(Violet)}}{Fe_2(S_2O_3)_3} + 6NaCl$$

16. (d) $$AgCl + 2NH_3 \longrightarrow \underset{\text{diammine silver (I) chloride}}{Ag(NH_3)_2Cl}$$

17. (d) Philosopher's wool is ZnO

18. (b) $_{30}Zn$ and $_{80}Hg$ have their d orbitals completely filled so they do not show any variable valency.

19. (d) Its reduction to metallic silver.

$$2AgNO_3 \rightarrow \underset{\text{black stain}}{2Ag} + N_2 + 3O_2$$

20. (b) $$\begin{array}{l} [2KI + CuSO_4 \rightarrow CuI_2 + K_2SO_4] \times 2 \\ 2CuI_2 \rightarrow Cu_2I_2 + I_2 \\ \hline 4KI + 2CuSO_4 \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2 \end{array}$$

21. (c) As the oxidation state of metal associated with oxygen increases, the acidic character of oxide increases. So Mn_2O_7 is most acidic as it has highest +7, oxidation state.

22. (c) (a), (b) and (d) are correct statements.

(c) There is drop in enthalpy of atomization at manganese because of half filled stable electronic configuration leading to less mobilisation of electrons. This results in weaker metallic bonds.

23. (d) Lithopone is a mixture of $ZnS + BaSO_4$ which is a white paint.

24. (b) The colour exhibited by transition metal ions is due to the presence of unpaired electrons in *d*-orbitals which permits the *d* - *d* excitation of electrons.

In TiF_6^{2-} – Ti is in + 4 O.S. ; $3d^0$ = colourless

In CoF_6^{3-} – Co is in + 3 O.S ; $3d^5$ = coloured

In Cu_2Cl_2 – Cu is in +1 O.S. ; $3d^{10}$ – colourless

In $NiCl_4^{2-}$ – Ni is in + 2 O.S ; $3d^8$ – coloured

25. (b) La^{3+} : $54\ e^- = [Xe]$

Ti^{3+} : $19\ e^- = [Ar]\ 3d^1$ (Coloured)

Lu^{3+} : $68\ e^- = [Xe]\ 4f^{14}$

Sc^{3+} : $18\ e^- = [Ar]$

26. (d) (i) Haematite is Fe_2O_3 in which Fe is present in III oxidation state.

(ii) Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3.
Oxidation state of Fe in FeO is II.
Oxidation state of Fe in Fe_2O_3 is III.

27. (a)

(a) $V = 3d^3\,4s^2;\quad V^{2+} = 3d^3 = 3$ unpaired electrons
$Cr = 3d^5\,4s^1;\quad Cr^{2+} = 3d^4 = 4$ unpaired electrons
$Mn = 3d^5\,4s^2;\quad Mn^{2+} = 3d^5 = 5$ unpaired electrons
$Fe = 3d^6\,4s^2;\quad Fe^{2+} = 3d^6 = 4$ unpaired electrons
Hence the correct order of paramagnetic behaviour
$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(b) For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series. hence the order is
$Mn^{++} > Fe^{++} > Co^{++} > Ni^{++}$

(c) In solution, the stability of the compound depends upon electrode potentials, SEP of the transitions metal ions are given as
$Co^{3+} / Co = +1.97, Fe^{3+} / Fe = +0.77;$
$Cr^{3+} / Cr^{2+} = -0.41$, Sc^{3+} is highly stable as it does not show + 2 O. S.

(d) Sc – (+ 2), (+ 3)
Ti – (+ 2), (+ 3), (+ 4)
Cr – (+ 1), (+ 2), (+ 3), (+ 4), (+ 5), (+ 6)
Mn – (+ 2), (+ 3), (+ 4), (+ 5), (+ 6), (+ 7)
i.e. Sc < Ti < Cr = Mn

28. (d) $E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41\ V \quad E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\ V$

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57\ V,\ E^\circ_{Co^{3+}/Co^{2+}} = +1.97\ V$

29. (a) 4*f* orbital is nearer to nucleus as compared to 5*f* orbital therefore, shielding of 4*f* is more than 5*f*.

30. (b) The main reason for exhibiting larger number of oxidation states by actinoids as compared to lanthanoids is lesser energy difference between 5*f* and 6*d* orbitals as compared to that between 4*f* and 5*d* orbitals.
In case of actinoids we can remove electrons from 5*f* as well as from *d* and due to this actinoids exhibit larger number of oxidation state than lanthanoids. Thus the correct answer is option (b)

31. (c) The titration of oxalic acid with $KMnO_4$ in presence of HCl gives unsatisfactory result because of the fact that $KMnO_4$ can also oxidise HCl along with oxalic acid. HCl on oxidation gives Cl_2 and HCl reduces $KMnO_4$ to Mn^{2+}

32. (b) Most of the Ln^{3+} compounds except La^{3+} and Lu^{3+} are coloured due to the presence of *f*-electrons.

33. (d)

34. (d) The configuration of Gd is [xe] $4f^7\,5d^1\,6s^2$.

35. (d) Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.

36. (c) $E^o_{Cu^{+2}/Cu} = 0.34\ V$

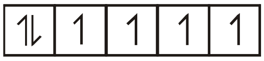
other has – ve $E^o_{R.P.}$

$E^o_{Co^{++}/Co} = -0.28\ V$

$E^o_{Ni^{++}/Ni} = -0.25V$

$E^o_{Fe^{++}/Fe} = -0.44V$

37. (a) The outermost electronic configuration of Fe is
$Fe = [Ar]\ 3d^6\,4s^2$
$Fe^{2+} = [Ar]\ 3d^6\,4s^0$



Since Fe^{2+} has 4 unpaired electrons it is paramagnetic in nature.
$Zn = [Ar]\ 3d^{10}\,4s^2$ —— no unpaired e^-
$Hg^{2+} = [Ar]\ 4f^{14}\,5d^{10}$ —— no unpaired e^-
$Ti^{4+} = [Ar]\ 3d^0\,4s^0$ —— no unpaired e^-

38. (d) Oxidation state of Ti in the given compounds. as follows:

TiO	–	+2
TiO_2	–	+4
$TiCl_3$	–	+3
K_2TiF_6	–	+4
K_2TiO_4	–	+6

The oxidation states exhibited by Ti is + 2, + 3, + 4. So K_2TiO_4 does not exist.

39. (d) V^{2+} – violet, V^{3+} – green V^{4+} – blue
Fe^{2+} – green Fe^{3+} – yellow

40. (d) Interstitial compounds of transition metal exhibit metallic conductivity.

41. (a) $Mn^{++} = 3d^5$ i.e. no. of unpaired $e^- = 5$
$Cu^{++} = 3d^9$ i.e. no. of unpaired $e^- = 1$
$Fe^{++} = 3d^6$ i.e. no. of unpaired $e^- = 4$
$Zn^{++} = 3d^{10}$ i.e. no. of unpaired $e^- = 0$
$Ni^{++} = 3d^8$ i.e. no. of unpaired $e^- = 3$
Higher the number of unpaired electrons higher will be the magnetic moment. Hence Mn^{++} having maximum unpaired electrons will have the maximum magnetic moment.

42. (d) Sc does not show variable valency.

43. (b) $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{dark green}}{2K_2MnO_4} + 2H_2O$

44. (d) $Fe^{3+}(d^5)$ has 5 unpaired electrons therefore magnetic moment $= \sqrt{n(n+2)} = \sqrt{5(5+2)} = 5.91$ which is maximum among given options. As Sc^{3+}, Ti^{3+}, Cr^{3+}, V^{3+} contains 0, 1, 3, and 2 number of unpaired electrons respectively.

45. (b) The magnetic moments are lesser than the theoetically predicted values. This is due to the fact that 5*f* electrons of actinides are less effectively shielded which result in quenching of orbital contribution.

46. (b) KCN forms complexes with Cu^+ and Cd^{2+} as $K_3[Cu(CN)_4]$ and $K_2[Cd(CN)_4]$ respectively. On passing H_2S, only Cd^{2+} complex is decomposed to give yellow CdS precipitate.

47. (d)

48. (c) The statement-1 is correct but the statement-2 is false. Actually transition metal show variable valency due to very small difference between the ns^2 and $(n-1)d$ electrons.

49. (b) Due to larger surface area and variable valencies to form intermediate absorbed complex easily, transition metals are used as catalysts.

50. (b) The magnetic moments are lesser than the fact that 5*f* electrons of actinides are less effectively shielded which results in quenching of orbital contribution.

EXERCISE - 3

Exemplar Questions

1. (b) Electronic configuration of X^{3+} is $[Ar]3d^5$
Atomic number of $X = 18 + 5 + 3 = 26$

2. (a) Anion carrying a higher charge and smaller size is associated with greater lattice and hydration energy but it is expected on the basis of electronic. configuration Cu^+ should be more stable because it has completely filled orbitals. But the lattice and hydration energy factors dominate and as a result Cu^{2+} is more stable.

3. (d) Along the period, decrease in metallic radius is coupled with increase in atomic mass therefore results in increase in density of metal. Hence, Cu will exhibit highest density.

4. (b) CuF_2 is coloured in solid state because Cu(II) has d^9 configuration thus, due to the presence of unpaired electron, it exists as a coloured salts.

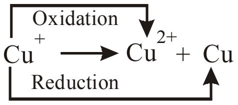
5. (a) The compound formed can be explained by the following reaction :
$$2KMnO_4 + 2H_2SO_4\,(conc.) \rightarrow \underset{\text{(green oily)}}{Mn_2O_7} + 2KHSO_4 + H_2O$$

6. (b) Greater the number of unpaired electrons, higher will be the value of magnetic moment.

Configuration	No. of Unpaired e^{s}s
$3d^7$	3
$3d^5$	5
$3d^8$	2
$3d^2$	2

7. (b) Lanthanoids show common oxidation state of +3.

8. (a) The reaction in which oxidation as well as reduction of same metal occur is known as disproportionation reaction.



$$Cu^+ \longrightarrow Cu^{2+} + Cu$$

9. (d) Mn^{2+} acts as autocatalyst.
$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

10. (c) Tm ; Thulium Z = 69 do not belong to actinoid series.

11. (a) Reaction $KMnO_4$ with sulphide ions in acidic medium is as follows :
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$\underline{H_2S + [O] \rightarrow H_2O + S] \times 5}$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$
5 moles of S^{2-} ions react with 2 moles of $KMnO_4$ thus,
1 mole of S^{2-} ion will react with $\frac{2}{5}$ moles of $KMnO_4$.

12. (a) Amphoteric oxide react with alkalies as well as acids.
$$V_2O_5 \xrightarrow{\text{alkali}} VO_4^{3-}$$
$$V_2O_5 \xrightarrow{\text{acid}} VO_4^+$$
$$Cr_2O_3 \xrightarrow{\text{acid}} [Cr(H_2O)_6]^{3+}$$
$$Cr_2O_3 \xrightarrow{\text{alkali}} [CrO_2]^-$$

13. (a) The E.C. of gadolinium is :
$Gd = [Xe]4f^7 5d^1 6s^2$

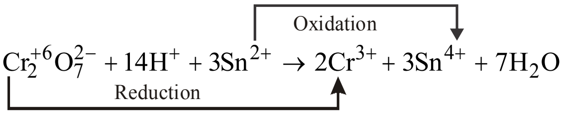
14. (d) Interstitial compounds are chemicaly inter.

15. (b) Spin only magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM
$$= \sqrt{3(3+2)} = \sqrt{15}$$
$$= 3.87 \text{ BM}$$

16. (c) When alkaline $KMnO_4$ oxidising agent is treated with KI, iodide ion is oxidised to IO_3^-.
$$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$$

17. (a) Copper lies below hydrogen in the electrochemical series and hence does not liberate H_2 from acids.

18. As mentioned in the reaction below Sn^{2+} changes to Sn^{4+} :

(c) 

$$\overset{+6}{Cr_2}O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

19. (d) In covalent compounds fluorine can form only single bond while oxygen forms double bond.

20. (c) Zr and Hf possess almost same atomic and ionic radii because of lanthanoid contraction. Hence they exhibit similar properties.

21. (b) HCl is not used in oxidation reactions of $KMnO_4$ in acidic medium because $KMnO_4$ + HCl produce nascent oxygen which will partly oxidise HCl to Cl_2. So the end point will not be correct in the titration.

NEET/AIPMT (2013-2017) Questions

22. (c)

$Sm^{2+}(Z = 62)$	$[Xe]4f^6\,6s^2$ – 6 unpaired e^-
$Eu^{2+}(Z = 63)$	$[Xe]4f^7\,6s^2$ – 7 unpaired e^-
$Yb^{2+}(Z = 70)$	$[Xe]4f^{14}\,6s^2$ – 0 unpaired e^-
$Ce^{2+}(Z = 58)$	$[Xe]4f^1\,5d^1\,6s^2$ – 2 unpaired e^-

Only Yb^{2+} is diamagnetic.

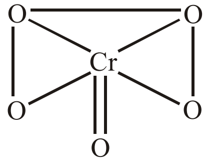
23. (b) HCl and SO_2 are reducing agents and can reduce MnO_4^-. CO_2 which is neither oxidising and nor reducing will provide only acidic medium. It can shift reaction in forward direction and reaction can go to completion.

24. (c) $Gd\,[64] = [Xe]\,4f^7 5d^1 6s^2$

25. (c) A transition element must have incomplete *d*-subshell. Zinc have completely filled *d* subshell having $3d^{10}$ configuration. Hence do not show properties of transition elements to any appreciable extent except for their ability to form complexes.

26. (c) Both are reducing agents.

27. (c) The structure of CrO_5 is



Hence CrO_5 has two proxy linkage.

Now suppose the oxi. no. of Cr is x then

$x + (-1 \times 4) + (-2) = 0$

$\therefore \quad x = +6$

28. (b) $2\,KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

i.e., Mn^{++} ion and O_2.

29. (b) Magnetic moment

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

$2.83 = \sqrt{n(n+2)}$

On solving n = 2

Ni^{2+} have two unpaired electron.

30. (a) The shape of *f*-orbitals is very much diffused and they have poor shielding effect. The effective nuclear charge increases which causes the contractiion in the size of electron charge cloud. This contraction in size is quite regular and known as lanthanoid contraction.

31. (d) Magnetic moment = 2.84 B.M. This indicates that 2 unpaired electrons are present.

For $Ni^{+2} = 4s^0\,3d^8$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

Number of unpaired electrons (n) = 2

Hence Ni^{2+} gives magnetic moment 2.84 B.M.

32. (a) $Fe^{+2} = 3d^6$ (number of '*d*' electrons = 6)

In $Cl = 1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

total *p* electrons = 11, which are not equal to number of '*d*' electrons in Fe^{+2}

p-electrons in $Ne = 1s^2\,2s^2\,2p^6 = 6$

s-electrons in $Mg = 1s^2\,2s^2\,2p^6\,3s^2 = 6$

33. (b) Formation of $Fe(CO)_5$ from Fe involves no change in oxidation state of iron.

34. (b) Due to lanthanoid contraction atomic radii of Zr and Hf is almost similar.

35. (d) Orbital angular momentum $= \sqrt{\ell(\ell+1)}.\hbar$

For *d*-orbital $\ell = 2$

angular momentum $= \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$

36. (a) Considering the same moles of compounds $Fe^{2+}\,SO_4^{2-}$ only Fe^{2+} is oxidised by $KMnO_4$. $\overset{(+6)}{SO_4^{2-}}$ in which sulphur is in highest oxidation state cannot be oxidised.

$Fe^{2+}\,SO_3^{2-} \longrightarrow Fe^{2\oplus}$

$\overset{(+4)}{SO_3^{2-}} \longrightarrow \overset{(+6)}{SO_4^{2-}} + 2e^-$

Sulphur can be oxidised to (+6) i.e to SO_4^{2-}

In $FeC_2O_4 \longrightarrow Fe^{2\oplus}$

Carbon can be oxidised to (+IV) i.e to CO_2

$Fe(NO_2)_2 \longrightarrow Fe^{2\oplus}$

$+\,2\overset{(+3)}{NO_2^{\ominus}} \downarrow 2NO_3^- + 2e^-$, $\underset{(+5)}{\uparrow}$ Nitrogen can be oxidised to (+V) state

37. (c) $Gd\,(64) = [Xe]4f^7\,5d^1\,6s^2$

38. (d) (n + l) rule can be used. Titanium is a multi electron system

$$\begin{array}{ccccccccc} (n+l) & 3s & < & 3p & < & 4s & < & 3d \\ & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ & (3+0) & & (3+1) & & (4+0) & & (3+2) \\ & \parallel & & \parallel & & \parallel & & \parallel \\ & 3 & & 4 & & 4 & & 5 \end{array}$$

If (n + l) values are same, than value of "n" has to be considered.

39. (d) $K_2Cr_2O_7 + SO_2 + H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{green colour}}{Cr_2(SO_4)_3} + H_2O$

40. (d) $Eu\,(63) = [Xe]\,4f^7\,6s^2$
$Gd\,(64) = [Xe]\,4f^7\,5d^1\,6s^2$
$Tb\,(65) = [Xe]\,4f^9\,6s^2$

41. (a) Less active metals like Cu, Ag etc react with conc acid and form nitrate and nitrogen dioxide.

42. (a) Potassium permanganate has a purple colour. When sulphur dioxide reacts with potassium permanganate the solution decolourizes.
$SSO_2 + 2KMnO_4 + 2H_2O \rightarrow 2H_2SO_4 + 2MnSO_4 + K_2SO_4$

43. (b) Minimum or comparable energy gap between 5f, 6d and 7s subshell makes electron excitation easier, hence there is a greater range of oxidation states in actinoids.