08

d- and *f*-Block Elements

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- Potassium Dichromate
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- *f*-Block Elements

These are the elements having completely filled outermost shell and incomplete filled inner shell. If last electron enters in penultimate shell, i.e. $(n-1)$ d-orbital, the elements are called ***d*-block elements** when it enters in $(n-2)$ f-orbital, the elements are called ***f*-block elements**.

d-Block Elements

These are the elements in which the differentiating electron (i.e. the last electron) enters in the d-subshell. They are place from group 3 to 12 (i.e. IB to VIIB and VIII) are placed between s- and p-blocks. They have properties intermediate between those of s- and p-block elements. That's why, these elements are also called **transition elements.**

Zinc, cadmium and mercury, have completely filled $(n-1)$ d-subshell in their elementary as well as in combined state that's why these elements do not show much resemblance with other d-block elements (except for their ability to form complexes with ligands such as NH_3, RNH_2 and halides). Nevertheless, these are studied with the d-block elements. These elements are also called **non-typical transition elements.**

Elements of IIIB group (i.e. Sc, Y, La and Ac) also differ in their properties from rest of the members, e.g. they form compounds only in +3 oxidation state. Unlike the compounds of other members, these are diamagnetic and colourless.

Classification of *d*-Block Elements

These elements make up three complete rows of ten elements and an incomplete fourth row in periodic table. These rows are named as $3d$, $4d$, $5d$ and $6d$-series respectively.

Different Series of d-Block Elements

Series name	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8 (VIII)	9 (VIII)	10 (VIII)	11 (IB)	12 (IIB)
3d-series	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
4d-series	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
5d-series	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
6d-series	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds		

General and Physical Properties

The general and physical properties of d-block elements and their trends are discussed below

1. Electronic Configuration

The general electronic configuration of these metals is $(n-1)\,d^{1\text{-}10}\,ns^{1\text{-}2}$. Here, it is obvious that the electronic configuration of these elements differ only in the number of electrons in their penultimate shell (i.e. in d-orbital). Thus, they do not show a regular trend of physical and chemical properties like s- and p-block elements.

Half and completely filled sets of orbitals are relatively more stable. e.g. Cr (24) = [Ar] $3d^5\ 4s^1$ and
Cu (29) = [Ar] $3d^{10}\ 4s^1$.

The electronic configurations of Zn, Cd and Hg are represented by the general formula $(n-1)\,d^{10}ns^2$.

2. Atomic Radii

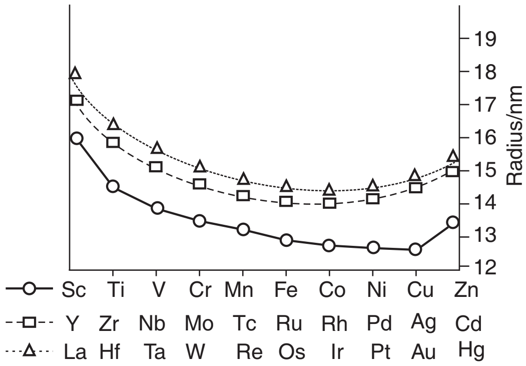
In a given series, the atomic radii of these elements generally decreases from group 3 to group 10 and after that increases again towards the end of the series. This is because the nuclear charge increases with increase in atomic number.

Due to this, the electron clouds are attracted more strongly and results in decreased size. However, the decrease in the radii across the period is not uniform. e.g. The radii of elements from Cr to Cu are very close to one another.

This is due to the effective screening of outer ns-electrons by the electrons of $(n-1)\,d$ subshell. The reason for the anomalous increase in atomic radii towards the end of the series is due to predominant repulsion between the added electrons. Presence of completely filled d-orbitals also decreases the force of attraction.

On moving downwards in the groups, the atomic radii increases although the increase is not as significant as in the case of s- and p-block elements.

The members of 4d and 5d-series exhibit near about similar radii which is due to **lanthanide contraction** (filling of 4f electrons before 5d results in decrease of atomic size with increase in atomic number).



Plot of radii with atomic number of transition elements

Hence, Zr—Hf, Nb—Ta, Mo—W and Tc—Re are called **chemical twins**. Zr and Hf have very similar physical and chemical properties because of their similar radii (Zr = 160 pm, Hf = 159 pm) which makes their separation difficult.

3. Ionic Radii

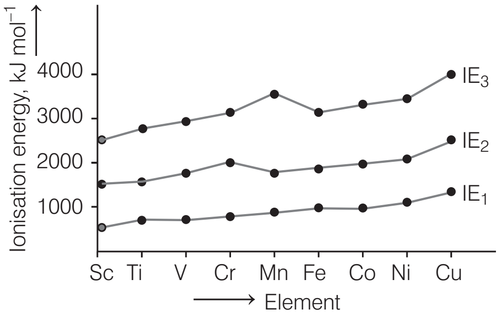
The ionic radii of these elements follow the same trend as their atomic radii. In case of ions carrying identical charges, the ionic radius decreases slowly with increase in atomic number in a series. The ionic radii decrease with increase in oxidation state. For the same oxidation state, ionic radii generally decreases with increase in nuclear charge.

4. Molar Volume and Density

The molar volumes of d-block elements are much lower than those of s-elements of neighbouring groups. It is due to the reason that as inner orbitals gets filled, the increased nuclear charge pulls the electrons inward. Due to such decrease in molar volumes, an increase in density is seen. In a series from left to right density increases. On moving down a group,density increases.

5. Ionisation Energy

Since, the atoms are smaller in size, their ionisation energies are fairly high. The values in most cases lie in between those of p- and s-block elements, thus indicating that transition metals are less electropositive than the elements of s-block.



Variation of the IE_1, IE_2 and IE_3 for the first transition metals

In a series, the IE increases from left to right but the increase is not so pronounced as in the case of s-and p-block elements. The IE, of $5d$-series elements is higher than the elements of $4d$ and $3d$-series.

This is due to the greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by $4f$-electrons.

IE_2 of the first transition series increases almost regularly with increase in atomic number. However, the value for Cr and Cu are sufficiently higher than those of their neighbours. This is due to their stable electronic configurations. The ionisation energy of Zn, Cd and Hg are abnormally higher due to their completely filled orbitals.

Ionisation Energies of *d*-block Elements

Elements of $3d$-series	**Ionisation energies** (kJ mol^{-1})	**Elements of $4d$-series**	**Ionisation energies** (kJ mol^{-1})	**Elements of $5d$-series**	**Ionisation energies** (kJ mol^{-1})
Sc	631	Y	616	La	541
Ti	656	Zr	674	Hf	760
V	650	Nb	664	Ta	760
Cr	653	Mo	685	W	770
Mn	717	Tc	703	Re	759
Fe	762	Ru	711	Os	840
Co	758	Rh	720	Ir	900
Ni	736	Pd	804	Pt	870
Cu	745	Ag	731	Au	889
Zn	906	Cd	876	Hg	1007

The sum of first three ionisation energies for Sc is a little less than the sum for Al. Thus, the properties of Sc are similar in some ways to those of Al.

The magnitude of ionisation energies give an idea about the relative stabilities of various oxidation states of transition elements. e.g. Ni (II) compounds are thermodynamically more stable than platinum (II) while platnium (IV) compounds are relatively more stable than nickle (IV) compounds.

	$IE_1 + IE_2$	$IE_3 + IE_4$	Total
Ni	2.49×10^3	8.80×10^3	11.29×10^3
Pt	2.66×10^3	6.70×10^3	9.36×10^3

Example 1. *For d-block elements, correct first ionisation potential order will be*

(a) Zn > Fe > Cu > Cr (b) Sc = Ti < V = Cr

(c) Zn < Cu < Ni < Co (d) V > Cr > Mn > Fe

Sol. (a) The ionisation energies increase with increasing atomic number. The trend is irregular among d-block elements.

Zn > Fe > Cu > Cr is correct order.

6. Nature of Bond

Unlike alkali and alkaline earth metals, the transition elements have tendency to form covalent bond along with the ionic bonds. Generally, the compounds in which smaller valency is exercised are ionic while those in which higher valency form covalent compounds.

7. Metallic Character

All transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lusture (except Hg, which is a liquid at room temperature).

With the exception of Zn, Cd and Hg, all the transition elements are much harder and less volatile. Zn, Cd and Hg do not contain any unpaired electron.

Cr, Mo and W contain maximum number of unpaired electrons and as such these are hardest metals in their respective periods.

Although, hardness and brittleness are associated with covalent bonding between metal atoms, the existence of metallic bonding cannot be denied. While the overlapping of unfilled d-orbitals of metals causes covalent bonding, Cu, Ag and Au are particularly outstanding in their thermal and electrical conductivities.

8. Enthalpy of Atomisation

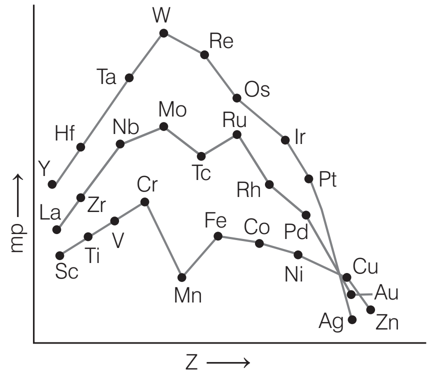
The atoms of transition elements are closely packed. They are held together by strong metallic bonds because of the presence of large number of unpaired electrons in their atoms, these possess high enthalpy of atomisation.

The metals of 2nd and 3rd series have greater enthalpies of atomisation than the corresponding elements of the first series.

9. Melting and Boiling Points

Their melting and boiling points are high which is attributed to strong interatomic bonding involving participation of ns and $(n-1)$ d-electron, i.e. **metallic bonding is stronger in them.** In any row, the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.

However, Zn, Cd and Hg due to the presence of completely filled $(n-1)$ d-orbital are not expected to have covalent bonding, thus their melting and boiling points are relatively low, as compared to the other elements of this block.



Melting point of 3*d*, 4*d* and 5*d*-series elements (not according to scale)

10. Oxidation State

Transition elements show a large number of oxidation states differing usually by unit of one. This is due to the fact that $(n-1)$ d-electrons may get involved along with ns-electrons in bonding as electrons in $(n-1)$ d-orbitals are in an energy state comparable to ns-electrons.

The stability of a given oxidation state depends on the nature of the element with which the transition metal is combined.

The highest oxidation states are found in the compounds of fluorides and oxides because of the most electronegative nature of F and O.

The different oxidation states of 3*d*-series have been given below

Oxidation States of First Transition Series

Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, + 3, +4
V	$3d^3 4s^2$	+2, + 3, + 4, +5
Cr	$3d^5 4s^1$	+1, + 2, + 3, + 4, + 5, + 6
Mn	$3d^5 4s^2$	+2, +3, +4, + 5, + 6, + 7
Fe	$3d^6 4s^2$	+2, + 3, + 4, + 5, + 6
Co	$3d^7 4s^2$	+2, + 3, + 4
Ni	$3d^8 4s^2$	+2, + 3, + 4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

The oxidation states of elements of 2nd and 3rd transition series are

Oxidation States of Second Transition Series

Elements	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Oxidation states									+1	
						+2		+2	(+2)	+2
	+3		+3	+3		+3	+3	(+3)	(+3)	
		+4		+4	+4	+4	+4	(+4)		
			+5	+5		+5				
				+6	(+6)	+6	+6			
					+7	(+7)				
						(+8)				

Oxidation States of Third Transition Series

Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Oxidation states									+1	+1
				(+2)		(+2)	(+2)	+2		+2
	+3			(+3)	(+3)	(+3)	+3	(+3)	+3	
		+4	(+4)	+4	+4	+4	+4	+4		
			+5	+5	+5	+5				
				+6	+6	+6	+6			
					+7					
						+8				

First member of each transition series does not show variable valency. It generally shows only + 3 oxidation state. Except scandium, the most common oxidation state of first row transition elements is (+ 2) which arises due to the loss of two 4*s* electrons.

- In (II) and (III) oxidation states, bonds formed are mostly ionic. In the compounds of the higher oxidation states (MnO_4^-), the bonds formed are essentially covalent. Some transition elements also show an oxidation of zero in their compounds, e.g. $[Ni(CO)_4]$ and $[Fe(CO)_5]$.
- In general for the first four elements of a transition series, higher oxidation states are more stable than lower oxidation states. For the next five elements lower oxidation states are more stable than higher oxidation states, e.g. Cr (III) is more stable than Cr(II) but Mn (II) is more stable than Mn (III). Among the group of *d*-block elements, the higher oxidation states are favoured by heavier members (the opposite is true in *p*-block), e.g. in group 6 Mo (VI) and W (VI) are found to be more stable than Cr (VI).

Thus, Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent whereas MoO_3 and WO_3 are not. Only Ru and Os show + 8 oxidation states in their compounds.

Remember All Cu (II) halides are known except the iodide as Cu^{2+} oxidises I^- to I_2. However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation

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

The stability of Cu^{2+} (*aq*) rather than Cu^+(*aq*) is due to much more negative ΔH° of Cu^{2+} (*aq*) than Cu^+, which is more than that compensates form the second ionisation enthalpy of Cu.

While solving problems based on oxidation state, always keep in mind

- Atomic number of the elements and their electronic configuration.
- Minimum oxidation state is generally + 2 but it is + 3 for Sc and Cr and +1 for Cu and Ag.
- For d-block elements up to 7 group, maximum oxidation state = $nse^- + (n-1)\,d$ unpaired e^-.
- Transition elements in lower oxidation state (+2 and +3) form ionic compounds while those in higher oxidation states form covalent compounds.
- The maximum oxidation state for any transition element is found in its compounds with F and oxygen as these have very small size and are most electronegative.
- Lower oxidation states are found when a complex compound has ligands like CO, which is capable of π-acceptor character is addition to its σ-bonding.

Example 2. *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

Sol. *(d)* (a) $FeO > Fe_2O_3$ (basic). Thus, it is correct statement.

(b) $FeCl_2 > FeCl_3$ (ionic), larger the charge greater the polarising power. Thus, greater the covalent nature. Thus, the given statement is correct.

(c) Fe^{2+} salts are more ionic thus less volatile than Fe^{3+} salts. Thus, given statement is correct.

(d) Greater the covalent nature, more easily they are hydrolysed. Thus, $FeCl_3$ is more easily hydrolysed than $FeCl_2$.
Thus, statement (d) is incorrect.

11. Standard Electrode Potentials

The $E°$ values of all the transition metals (except Cu) is lower (negative) than that of hydrogen (taken as zero). Thus, all the transition elements, with negative reduction potential, liberate hydrogen from dilute acids.

$E°$ Values for First Row Transition Metals

Elements	V	Cr	Mn	Fe	Co	Ni	Cu
$E°(M^{2+}/M)$ in volts	–1.18	– 0.91	–1.18	– 0.44	– 0.28	–0.5	+0.34

Most transition metals are inert towards acids or react slowly with them because of a protective layer of oxide. In case of Cr, despite a negative $E°$, it is quite inert chemically because of the formation of chromium (III) oxide, Cr_2O_3 on its surface. $E°\,(M^{2+}/M)$ values are not regular for 3d series elements.

It can be explained from the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and also the sublimation enthalpies which are relatively much less for Mn and V.

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

Example 3. *Which one of the following is a stronger reducing agent ?*

(a) Cr^{2+} (b) Fe^{2+}
(c) Cu (d) None of these

Sol. *(a)* Cr^{2+} is a stronger reducing agent than Fe^{2+} and Cu because $E°$ values for (Cr^{3+}/Cr^{2+}) are more negative than that of $E°$ for Fe^{3+}/Fe^{2+}. Further more, transition $\underset{(3d^4)}{Cr^{2+}} \longrightarrow \underset{(3d^3)}{Cr^{3+}}$ is easier than $\underset{(3d^6)}{Fe^{2+}} \longrightarrow \underset{(3d^5)}{Fe^{3+}}$ because in latter, an electron is removed from the paired orbital.

12. Reducing Property

All these elements (of 3d-series) except Cu has SRP (standard reducing potential) lower than H, hence, all of them (except Cu) are good reducing agents. However, they are not as good reducing agents as the metals of 1st, 2nd and 13th group.

13. Coloured Compounds or Complexes

Most of the compounds of transition metals are coloured in solid state or solutions. The colour of transition metal ions arises from the excitation of electron from d-orbitals of lower energy to d-orbitals of higher energy, i.e. d-d transition.

The transition metal ions which have either completely filled d-orbitals or completely empty d-orbitals are colourless because these are not capable of showing d-d transition.

- The colour of a transition metal complex is dependent on how big the energy difference in between the two d-levels.
- Depends on the nature of the ligand.
- The type of the complex formed.

The colour which we see is the colour of the transmitted wavelength and is complimentary colour absorbed by the complex.

In the series Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+} and Mn^{7+} all have empty d-orbitals, hence, d-d spectra are impossible and as such their compounds should be colourless.

But $VO_2^{2+}(V^{5+})$, $CrO_4^{2-}\,(Cr^{6+})$ and $MnO_4^-\,(Mn^{7+})$ ions in aqueous solution are coloured. The colour arise due to charge transfer.

Example 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

Sol. (*b*) In Ag_2SO_4, Ag is in + 1 oxidation state ($4d^{10}$), so colourless. In CuF_2, Cu is in + 2 oxidation state ($3d^9$), so it is coloured. In ZnF_2, Zn is in +2 oxidation state ($3d^{10}$) colourless.

In Cu_2Cl_2, Cu is in + 1 oxidation state ($3d^{10}$), so it is colourless. The transition metal ions having d^1 to d^9 configuration are coloured whereas the transition metal ions having d^0 and d^{10} configuration are colourless. Thus, among the given only CuF_2 is coloured.

14. Magnetic Properties

Many of the transition metal ions are paramagnetic due to the presence of unpaired electrons in them. Each such unpaired electron have a magnetic moment associated with its spin angular momentum and orbital angular momentum.

In transition elements compounds, the orbital motion of unpaired electron is severely disturbed by the electrons of surrounding ligands.

Therefore, the contribution of spin angular momentum becomes much more significant than orbital angular momentum contribution, i.e. μ-orbital contribution may be neglected.

Thus, effective magnetic moment (μ_{eff}) is given by the expression,

$$\mu_{\text{eff}} \approx \mu_{\text{spin}} \approx \sqrt{n\,(n+2)}$$

where, n is the number of unpaired electrons.

Magnetic moment ∝ number of unpaired electrons.

Species having unpaired electrons are paramagnetic whereas the species having all paired electrons are diamagnetic.

Magnetic moment is given in Bohr-Magneton (BM) which is given by the expression

$$\text{BM} = \frac{eh}{4\pi mc}$$

where, h = Planck's constant, e = electronic charge

c = velocity of light, m = mass of electron

Example 5. *Which of the following compounds is metallic and ferromagnetic?* **(JEE Main 2016)**

(a) CrO_2 (b) VO_2
(c) MnO_2 (d) TiO_2

Sol. (*a*) Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. CrO_2 is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

Example 6. *The pair having the same magnetic moment is [at. no. Cr = 24, Mn = 25, Fe = 26 and Co = 27]* **(JEE Main 2016)**

(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
(c) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$
(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

Sol. (*a*)

Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (*n*)
$[Cr(H_2O)_6]^{2+}$	Cr^{2+} ; [Ar] $3d^4$	↑ ↑ ↑ ↑ ↑ ; 4
$[Fe(H_2O)_6]^{2+}$	Fe^{2+} ; [Ar] $3d^6$	⇅ ↑ ↑ ↑ ↑ ; 4
$[Mn(H_2O)_6]^{2+}$	Mn^{2+} ; [Ar] $3d^5$	↑ ↑ ↑ ↑ ↑ ; 5
$[CoCl_4]^{2-}$	Co^{2+} ; [Ar] $3d^7$	⇅ ⇅ ↑ ↑ ↑ ; 3

15. Catalytic Property

- Most of the transition metals and their compounds have good catalytic properties, e.g. Pt, Fe, V_2O_5, Ni etc.
- According to modern theory of catalysis, a catalytic substance is capable of forming an unstable intermediate which readily decomposes yielding the product and regenerating the catalyst, i.e.

$$A + B + \text{catalyst} \longrightarrow \underset{\substack{\text{Intermediate}\\ \text{(unstable)}}}{AB\ \text{catalyst}} \longrightarrow C + \text{catalyst}$$

  Transition elements on account of their variable oxidation states have the ability to form intermediate compounds readily thus, acting as good catalysts.
- In many cases transition metals provide a suitable surface to the reactants for reaction to take place completely. The reactants are adsorbed on the surface of catalyst where reaction occurs.

16. Complex Formation

The transition metals are almost unique in their tendency to form coordination complexes. This is due to their

(i) very small size,
(ii) high positive charge density,
(iii) vacant or partially filled orbitals with suitable energy to accept lone pair of electrons.

17. Alloy Formation

Since, transition elements have almost similar radii. Due to this reason, these have a tendency to replace each other from their lattice and form solid solutions over an appreciable composition range. These as solutions are called **alloy**. These are hard and have high melting points as compared to the host metal.

Some important alloys of copper and zinc, etc., along with their properties and uses are tabulated in the table.

Some Alloys of Copper

Name	Composition	Important properties	Uses
Brass	Cu = 60-80% Zn = 20-40%	Harder, paler and more brittle with more zinc, can be moulded, malleable and ductile, high tensile strength	Domestic utensils, condensers, tubes, casting cartridges.
Bronze	Cu = 75-90% Sn = 10-25%	Hard, brittle, tenacious, durable, resistant to corrosion, takes high polish.	Statues, coins, utensils, bells, machine parts, propellers, blades.
Aluminium bronze	Cu = 90% Al = 10%	Light, strong, tenacious, resistant to corrosion, golden yellow.	Utensils, coins, frames, statues, jewellery, bearings and castings.
Phosphorus bronze	Cu = 85% Sn = 13% P = 2%	Very hard, tough, elastic, resistant to corrosion.	Suspension wire instrument, gears, aerials, ships, propellers.
Silica bronze	Cu = 97% Sn = 2% Si = 1%	Very hard, tensile, tough, non-corrosive, good conductor.	Telephone and telegraph wires, suspension wires.
German silver or nickel silver	Cu = 50% Zn = 30% Ni = 20%	White shining, malleable and ductile, tough, resistance to corrosion.	Utensils, plates, ornaments.
Gun metal	Cu = 88% Sn = 10% Zn = 2%	Strength increases with the increase of the percentage of Sn, very hard and strong, resistant to corrosion.	For making cannons, guns, machine parts.
Monel metal	Cu = 30% Ni = 67% Fe + Mn = 3%	Very resistant to chemical action, high tensile strength.	Alkali industry resistance wires, domestic wires, valves, automobile engine parts.

18. Interstitial Compounds

Transition elements also have some tendency to trap small atoms like H, B, C, N etc., in the interstitial space and thus, forming some interstitial or non-stoichiometric compounds. FeC, Fe_8N are the examples of interstitial compounds. $Fe_{0.98}O, Ni_{0.98}O, TiH_{1.7}$ are the examples of both interstitial as well as non-stoichiometric compounds.

The principal physical and chemical characteristics of these compounds are as follows

- Melting points are higher than that of pure metals.
- They are very hard, e.g. some borides (a binary compounds of boron with a metallic elements) approach diamond in hardness.
- They are chemically inert.
- They retain metallic conductivity.

19. Reactivity

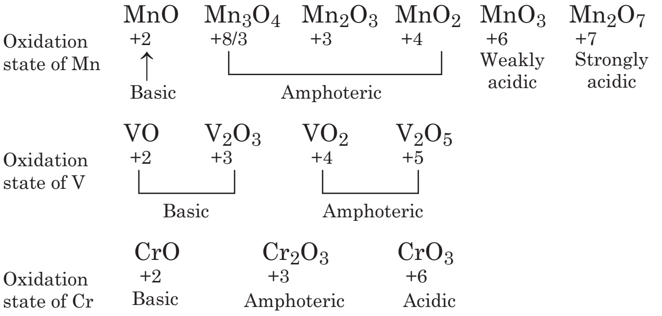
The transition elements have small tendency to react due to their high heats of sublimation, high ionisation energies and low heats of hydration.

They have rather a tendency to remain unreactive or **noble**.

20. Nature of Oxides

While moving along a period from Sc and Zn, basic nature of oxides decreases and acidic nature increases. Behaviour differs when oxidation states are different. Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, MnO_2 and ZnO are amphoteric while Fe_2O_3, Co_2O_3, NiO and CuO are basic.

With increase in the oxidation state of a given transition metal, the covalent character of its compound increases and thus, acidic character also increases.



The basic and amphoteric oxides dissolve in non-oxidising acids and form hexaquo ions $[M(H_2O)_6]^{n+}$. The acidic oxides like CrO_3 and Mn_2O_3 dissolve in water to form oxyacids. These oxides also react with bases to form oxosalts.

$$2CrO_3 + H_2O \longrightarrow H_2Cr_2O_7 \text{ (dichromic acid)}$$

$$2CrO_3 + 2KOH \longrightarrow K_2Cr_2O_7 + H_2O$$

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4 \text{ (permanganic acid)}$$

$$Mn_2O_7 + 2KOH \longrightarrow 2KMnO_4 + H_2O$$

Remember Mercury can't form any hydroxide, because alkali, dilute non-oxidising acids and water or steam have no effect on mercury.

Potassium Dichromate

Its chemical formula is $K_2Cr_2O_7$. It contains ionic as well as covalent bonds.

Methods of Preparation

$K_2Cr_2O_7$ is manufactured from chromite ore, $FeO \cdot Cr_2O_3$.

The steps involve in this process are as follows

***Step* I Conversion of the finely powdered chromite ore into Na_2CrO_4** (roasting of the concentrated ore). Concentrated chromite ore is fused with molten Na_2CO_3 in the presence of air when Na_2CrO_4 and Fe_2O_3 are formed.

$$4FeCr_2O_4 + \underset{\text{Molten}}{8Na_2CO_3} + 7O_2 \xrightarrow{1100^\circ C} \underset{\text{Water soluble}}{8Na_2CrO_4} + \underset{\text{Water insoluble}}{2Fe_2O_3} + 8CO_2 \uparrow$$

Instead of Na_2CO_3, NaOH can also be used here.

***Step* II Conversion of Na_2CrO_4 into $Na_2Cr_2O_7$.**

Aqueous solution of Na_2CrO_4 is acidified to obtain $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + \underset{\text{Dil.}}{H_2SO_4} \longrightarrow Na_2Cr_2O_7 + H_2O$$

***Step* III Conversion of** $Na_2Cr_2O_7$ **to** $K_2Cr_2O_7$. Hot solution of $Na_2Cr_2O_7$ obtained as above in step (III) is treated with the calculated quantity of KCl whereby less soluble $K_2Cr_2O_7$ separates out from the solution on crystallisation.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{More soluble}}{2NaCl} + \underset{\text{Less soluble}}{K_2Cr_2O_7}$$

Physical and Chemical Properties

General properties exhibited by $K_2Cr_2O_7$ are as follows

- $K_2Cr_2O_7$ forms orange-red prismatic crystals which melt at 396°C.
- It is moderately soluble in cold water and freely soluble in hot water.
- When heated to a white heat, it decomposes to give potassium chromate, $K_2Cr_2O_7$ and O_2 gas is evolved.

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

- $K_2Cr_2O_7$ is a powerful oxidising agent. In the presence of dil. H_2SO_4, one molecule of this compound gives three atoms of oxygen as shown below

$$\underset{\text{Orange}}{K_2Cr_2O_7} + \underset{\text{(Dil.)}}{4H_2SO_4} \longrightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + 4H_2O + 3O$$

Thus, in presence of dil. H_2SO_4, it liberates I_2 from KI solution, oxidises Fe(+2) salts to Fe(+3) salts, H_2S to S, SO_2 to H_2SO_4 as

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

- With cold H_2SO_4, red crystals of chromium trioxide, CrO_3 are formed.

$$K_2Cr_2O_7 + H_2SO_4(\text{cold}) \longrightarrow \underset{\text{Red crystals}}{2CrO_3} + K_2SO_4 + H_2O$$

When $K_2Cr_2O_7$ is heated with H_2SO_4, O_2 gas is evolved.

$$2K_2Cr_2O_7 + 8H_2SO_4 \xrightarrow{\Delta} 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2 \uparrow$$

- **Chromyl chloride test** When solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4 and a soluble chloride like NaCl, deep red vapours of chromyl chloride, CrO_2Cl_2 are produced.

$$K_2Cr_2O_7 + 4NaCl + \underset{\text{(Concentrated)}}{6H_2SO_4} \xrightarrow{\Delta} \underset{\text{Red vapours}}{2CrO_2Cl_2} + 2KHSO_4 + 4NaHSO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{(Yellow solution)}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + CH_3COOH + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Yellow ppt.)}}{PbCrO_4} + \text{Other products}$$

When vapours of chromyl chloride are passed into aqueous NaOH solution, yellow colour solution of Na_2CrO_4 is obtained, which is on reaction with acetic acid and lead acetate gives yellow ppt. of $PbCrO_4$. This test is called **chromyl chloride test**. It is used to identify Cl^- in inorganic salt analysis.

- When $K_2Cr_2O_7$ is heated with conc. HCl, Cl_2 is given off and chromic chloride ($CrCl_3$) is obtained.

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

When Zn metal is added to the above solution, nascent hydrogen is evolved which reduces $CrCl_3$ to blue chromous chloride, $CrCl_2$.

$$CrCl_3 + \underset{\text{(From Zn /HCl)}}{H} \longrightarrow CrCl_2 + HCl$$

When a saturated solution of CH_3COONa is added to the blue solution of $CrCl_2$ obtained as above, a red precipitate of chromous acetate, $(CH_3COO)_2Cr$ is obtained.

$$CrCl_2 + 2CH_3COONa \longrightarrow \underset{\text{Red ppt.}}{(CH_3COO)_2Cr \downarrow} + 2NaCl$$

- When an alkali is added to an orange-red solution of $K_2Cr_2O_7$, a yellow solution is obtained.

$$\underset{\text{Orange-red}}{K_2Cr_2O_7} + 2KOH \longrightarrow \underset{\text{Yellow}}{2K_2CrO_4} + H_2O$$

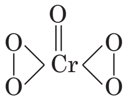
or $$\underset{\text{Orange-red}}{K_2Cr_2O_7} + 2NaOH \longrightarrow \underset{\text{Yellow}}{K_2CrO_4} + H_2O + Na_2CrO_4$$

- When H_2O_2 is added to an acidified solution of a dichromate, a complicated reaction occurs.
  The products depend on the pH and concentration of Cr(VI) ion.

  A deep blue-violet coloured chromic peroxide is formed which is decomposed rapidly in aqueous solution into Cr^{3+} and oxygen.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow \underset{\substack{\text{Chromic peroxide}\\ \text{(Deep blue-violet)}}}{2CrO(O_2)_2} + 5H_2O$$

Structure of chromic peroxide



(Oxidation state + 6 due to the presence of two peroxide linkages)

Uses of $K_2Cr_2O_7$

- Potassium dichromate finds extensive use in dyeing, calico-printing and chrome-tanning.
- It is used as an oxidising agent and in the preparation of various chromium compounds like Cr_2O_3, CrO_3 $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O, CrO_2Cl_2$, K_2CrO_4, $CrCl_3$, $Cr(CH_3COO)_2$ etc.
- It is also used in photography.
- A mixture of $K_2Cr_2O_7$ and conc. H_2SO_4, usually known as chromic acid mixture, has strong oxidising properties and is used as a cleaning agent for glassware etc.
- It is also used in leather industry (chrome tanning).

Example 7. *Consider the following reaction,*

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are, respectively

(JEE Main 2013)

(a) 5, 2 and 16 (b) 2, 5 and 8

(c) 2, 5 and 16 (d) 5, 2 and 8

Sol. (c) The half equations of the reaction are

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$C_2O_4^{2-} \longrightarrow CO_2$$

The balanced half equations are

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

On equating number of electrons, we get

$$2MnO_4^- + 16\,H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$
$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

On adding both the equations, we get

$$2MnO_4^- + 5C_2O_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 2 \times 5CO_2 + \frac{16}{2}H_2O$$

Thus, x, y and z are 2, 5 and 16 respectively.

Example 8. *The colour of* $KMnO_4$ *is due to* ***(JEE Main 2015)***

(a) $M \to L$ charge transfer transition

(b) $d - d$ transition

(c) $L \to M$ charge transfer transition

(d) $\sigma - \overset{*}{\sigma}$ transition

Sol. (c) $KMnO_4 \longrightarrow K^+ + MnO_4^-$

$\therefore$ In MnO_4^-, Mn has $+7$ oxidation state having no electron in d-orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur $L \to M$ charge transfer, because ligand is able to donate the electrons into the vacant d- orbital of metal.

Since, charge transfer is Laporte as well as spin allowed, therefore, it shows colour.

Interconversion of K_2CrO_4 and $K_2Cr_2O_7$

On acidifying, the yellow colour of K_2CrO_4 again changes to orange-red due to the reformation of K_2CrO_4.

$$\underset{\text{Yellow}}{2K_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{Orange red}}{K_2Cr_2O_7} + K_2SO_4 + H_2O$$

This interconversion is explained on the basis of the fact that in K_2CrO_4 solution, orange-red $Cr_2O_7^{2-}$ ions are in equilibrium with yellow CrO_4^{2-} ions.

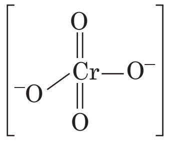
$$\underset{\text{Orange red}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+$$

On adding an alkali, the concentration of H^+ ions decreases and hence, the above reaction proceeds in the forward direction producing yellow coloured solution containing CrO_4^{2-} ions.

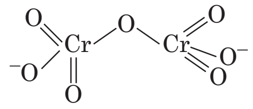
On the other hand, when an acid is added, the concentration of H^+ ions increases and hence, the above reaction proceeds in the backward direction producing the orange coloured solution containing $Cr_2O_7^{2-}$ ions

Structures of Chromate and Dichromate Ions

The structure of chromate ion and dichromate ion as shown below



Tetrahedral (chromate ion)



(Dichromate ion)

In $Cr_2O_7^{2-}$ two CrO_3 units have been joined by O.

The above description makes it evident that since both $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are present in a dichromate solution, $K_2Cr_2O_7$ will precipitate a salt of lower solubility product with Pb^{2+} or Ba^{2+} ions.

Thus, when $K_2Cr_2O_7$ is treated with $Pb(NO_3)_2$, $PbCrO_4$ is precipitate out and not$PbCr_2O_7$. This is because of the fact that $PbCrO_4$ has less solubility product than $PbCr_2O_7$.

$$K_2Cr_2O_7 + 2Pb(NO_3)_2 + H_2O \longrightarrow 2PbCrO_4 + 2KNO_3 + 2HNO_3$$

Remember In less acidic solution $K_2Cr_2O_7$ and H_2O_2 give violet coloured diamagnetic salt $[CrO(O_2)(OH)]^-$. In alkaline solution with 30% H_2O_2, a red brown compound K_3CrO_8 is formed. $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ in volumetric analysis as $Na_2Cr_2O_7$ is deliquescent.

Estimation of $Cr_2O_7^{2-}$

- $K_2Cr_2O_7$ can be estimated volumetrically by iodometric titration. Acidified $K_2Cr_2O_7$ is treated with KI and liberated I_2.
- This I_2 is titrated using hypo ($Na_2S_2O_3$ solution) with starch as an indicator.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

$$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I^- \equiv 6e^-$$

$$\text{Equivalent weight of } K_2Cr_2O_7 = \frac{\text{Molecular wt.}}{6} = \frac{294}{6}$$

$$2S_2O_3^{2-} \equiv I_2 \equiv 2I^- \equiv 2e^-$$

$$\text{Equivalent weight of } Na_2S_2O_3 \cdot 5H_2O = \frac{248}{1}$$

Potassium Permanganate

Its formula is $KMnO_4$. It is the salt of permanganic acid, $HMnO_4$ which is an unstable acid and exists only in solution.

Methods of Preparation

- It may be prepared by acidifying the solution of potassium manganate, K_2MnO_4 by H_2SO_4.

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

- On a large scale, it is generally prepared from the mineral **pyrolusite,** MnO_2. The finely powdered pyrolusite mineral is fused with KOH in presence of air or an oxidising agent like KNO_3, $KClO_3$, etc. This treatment gives us fused green coloured potassium manganate, K_2MnO_4.

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

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

$$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

The fused K_2MnO_4 obtained as above is extracted with water and the solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods

(i) In **Stadeler's process** Cl_2 is passed through the green solution of K_2MnO_4 until it becomes purple due to the formation of $KMnO_4$. Here, Cl_2 oxidises K_2MnO_4 into $KMnO_4$.

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

(ii) By passing CO_2 or O_3 through the green solution of K_2MnO_4 until it becomes purple.

$$\underset{\text{Green}}{3K_2MnO_4} + 2H_2O + 4CO_2 \longrightarrow \underset{\text{Purple}}{2KMnO_4} + MnO_2 + 4KHCO_3$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow \underset{\text{Purple}}{2KMnO_4} + 2KOH + O_2$$

(iii) Now-a-days the conversion of K_2MnO_4 into $KMnO_4$ is done by **the electrolytic oxidation process** in alkaline medium.

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

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

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

At cathode, $2H + 2e^- \longrightarrow H_2\uparrow$

Physical and Chemical Properties

- Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution.
- It is isomorphous with potassium perchlorate, $KClO_4$.
- Its solubility in water at 20°C is only about 7% while it dissolves more at higher temperature (25% at 63°C).
- It gives off O_2 at 200°C.

$$2KMnO_4 \xrightarrow[200^\circ C]{\Delta} K_2MnO_4 + MnO_2 + O_2\uparrow$$

At red heat, K_2MnO_4 formed as above is decomposed into permanganite, K_2MnO_3 and O_2.

$$2K_2MnO_4 \rightleftharpoons 2K_2MnO_3 + O_2\uparrow$$

- When an alkaline solution of $KMnO_4$ is heated, O_2 is evolved.

$$4KMnO_4 + 4KOH \xrightarrow{\Delta} 4K_2MnO_4 + 2H_2O + O_2\uparrow$$

- When heated in a current of H_2, solid $KMnO_4$ gives KOH, MnO and steam.

$$2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + \underset{\text{(Steam)}}{4H_2O}$$

- A mixture of $KMnO_4$ with sulphur and charcoal burns when heated, and explodes like a gun powder when rubbed.
- A well-powdered mixture of $KMnO_4$ and oxalic acid catches fire spontaneously in a few seconds.

Oxidising Nature of $KMnO_4$

$KMnO_4$ is a powerful oxidising agent. The course of reaction depends on whether the oxidation takes place in alkaline, neutral or acid solution.

(i) **In alkaline solution**, MnO_4^- ion (Mn = +7) is first reduced to MnO_4^{2-} ion (Mn = +6) and then to insoluble MnO_2 (Mn = + 4). The solution first changes from purple (due to MnO_4^-) to green (due to MnO_4^{2-}) and finally it becomes colourless (MnO_2).

$$\underset{\substack{\text{Purple}\\(\text{Mn} = +7)}}{2KMnO_4} + 2KOH \longrightarrow \underset{\substack{\text{Green}\\(\text{Mn} = +6)}}{2K_2MnO_4} + H_2O + O \quad \text{...(i)}$$

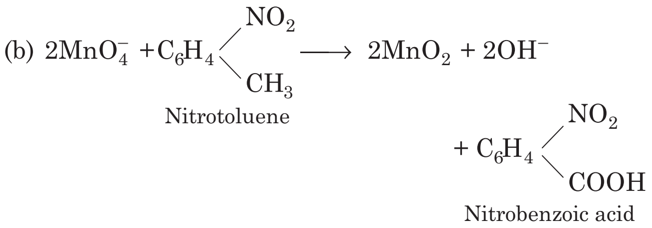
$$\underset{\substack{\text{Green}\\ (\text{Mn}=+6)}}{2K_2MnO_4} + 2H_2O \longrightarrow \underset{\substack{\text{Colourless}\\ (\text{Mn}=+4)}}{2MnO_2} + 4KOH + 2O \quad \text{...(ii)}$$

$$\underset{\substack{\text{Purple}\\ (\text{Mn}=+7)}}{2KMnO_4} + H_2O \longrightarrow \underset{\substack{\text{Colourless}\\ (\text{Mn}=+4)}}{2MnO_2} + 2KOH + 3O \quad (1)$$

: Change in oxidation number of Mn = 3

: In alkaline medium, $KMnO_4$ oxidises iodides (I^-) to iodates (IO_3^-), NH_3 to N_2 and nitrotoluene to nitrobenzoic acid in following way

(a) $2MnO_4^- + H_2O + I^- \xrightarrow{\text{Alkali}} 2MnO_2 + 2OH^- + IO_3^-$



(b) $2MnO_4^- + C_6H_4\begin{cases}NO_2\\ CH_3\end{cases} \longrightarrow 2MnO_2 + 2OH^- + C_6H_4\begin{cases}NO_2\\ COOH\end{cases}$

(c) $2MnO_4^- + 2NH_3 \longrightarrow 2MnO_2 + 2OH^- + N_2\uparrow + 2H_2O$

(ii) **In neutral solution**, $KMnO_4$ is directly reduced to MnO_2.

$$2K\overset{+7}{Mn}O_4 + H_2O \longrightarrow 2KOH + 2\overset{+4}{Mn}O_2 + 3[O]$$

Change in oxidation number of Mn = 3

In neutral medium, $KMnO_4$ oxidises Mn^{2+} salt to MnO_2, $Na_2S_2O_3$ to Na_2SO_4 and H_2S to S in following way

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

(b) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(c) $2MnO_4^- + 4H_2S \longrightarrow 2MnS + S + SO_4^{2-} + 4H_2O$

(iii) **In acidic medium** (dil. H_2SO_4), MnO_4^- ion is reduced to Mn^{2+} ion and five O-atoms are rendered from two MnO_4^- ions as

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

In acidic medium, $KMnO_4$ oxidises Fe (II) salts to Fe (III) salts, oxalic acid to CO_2, H_2S to S, SO_2 to H_2SO_4, sulphites to sulphates, KI to I_2, H_2O_2 to O_2, halogen acids to halogens as,

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

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

$$2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

$$2MnO_4^- + 16H^+ + 10X^- \longrightarrow 2Mn^{2+} + 5X_2 + 8H_2O$$

Equivalent Weight of $KMnO_4$

In different mediums, equivalent weight of $KMnO_4$ is different.

1. **In alkaline medium** From the equation (1), it is evident that two molecules of $KMnO_4$ in alkaline solution give three oxygen atoms (i.e. six equivalents). Therefore, the equivalent weight of $KMnO_4$ as an oxidising agent in alkaline solution is one-third of its molecular weight.

   $$\text{Eq. wt. of } KMnO_4 = \frac{\text{mol. wt.}}{3} = \frac{158}{3} = 52.67$$

   (Change in oxidation no = 3)

2. **In neutral medium** Equation (2) is the same as for alkaline medium. Evidently, in neutral medium as well, the equivalent weight of $KMnO_4$ is one-third of its molecular weight.

   $$\text{Eq. wt. of } KMnO_4 = \frac{\text{mol. wt.}}{3} = \frac{158}{3} = 52.67$$

   (Change in oxidation number = 3)

3. **In acidic medium** It is obvious that in acid solution, the equivalent weight of $KMnO_4$ is one-fifth of its molecular weight.

   $$\text{Eq. wt. of } KMnO_4 = \frac{\text{mol. wt.}}{5} = \frac{158}{5} = 31.6$$

   (Change in oxidation number of Mn = 5)

Example 9. *MnO_4^{2-} changes to MnO_2 and MnO_4^- in acidic medium. The equivalent wt. of MnO_4^{2-} will be*

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

Sol. (c) $3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow \overset{+4}{Mn}O_2 + 2\overset{+7}{Mn}O_4^- + 2H_2O$

(disproportionation reaction) Eq. wt. of the species undergoing disproportionation = eq. wt. (in oxidation) + eq. wt. (in reduction)

$$\overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+4}{Mn}O_2;\quad \text{Eq. wt. (reduction)} = \frac{M}{2}$$

$$\overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+7}{Mn}O_4^-;\quad \text{Eq. wt. (oxidation)} = \frac{M}{1}$$

$$\therefore\ \text{Eq. wt. of } MnO_4^{2-} = \frac{M}{2} + \frac{M}{1} = \frac{3M}{2}$$

Uses of Potassium Permanganate

It is used

- as an oxidising agent in the laboratory as well as in industry.
- in volumetric estimations of ferrous salts, oxalic acid, H_2O_2 etc.
- as a disinfectant and a germicide on account of its oxidising property.
- in qualitative analysis for detecting halides and oxalates.

- in the manufacture of saccharin, benzoic acid, acetaldehyde etc.
- for bleaching waxes.
- for the detection of double bond in organic compounds. (For this purpose alkaline $KMnO_4$ solution under the name Baeyer's reagent is used.)
- as a source of reactive form of MnO_2 which is used in place of pyrolusite in the manufacture of dry cells.

f-Block Elements

The elements in which last electron enters into *f*-orbitals of the anti-penultimate (inner to the penultimate shell), i.e. $(n-2)$ shell, are called *f*-block elements. Since, these constitute transition series within transition series and the last electron occupies the antipenultimate shell, these are named as **inner-transition elements.**

These all have been kept in III-B group (group 3) of periodic table. In these elements, both the *d* and *f* subshells are incomplete. The general outer electronic configuration of these elements is $(n-2)f^{1-14}, (n-1)d^{10}ns^2$.

Depending upon the nature of *f*-orbital of the antipenultimate shell, in which the differentiating electron enters, these are further divided into two series, viz., 4*f* and 5*f* series.

4*f*-Series or First Inner-Transition Series or Lanthanoids

In this series, the last electron occupies the 4*f*-orbital. This series includes next fourteen elements after lanthanum $(Z = 57)$, i.e. from cerium $(Z = 58)$ to lutetium $(Z = 71)$. These are commonly called **lanthanoides** or **lanthanons** or **rare earths.**

The name lanthanides or lanthanons was given because they are closely related with lanthanum ($_{57}La$) in their properties. However, the name rare earth was given because these elements were difficult to obtain and are found in small quantities.

General and Physical Properties

The general characteristics of lanthanoids are as follows

1. Electronic Configuration

General electronic configuration of these elements is $[Xe]\,4f^{1\text{-}14}, 5d^{0\text{-}1}, 6s^2$.

Electronic Configuration of Lanthanides

Name	Symbol	Atomic no.	Configuration
Cerium	Ce	58	$[Xe]\,4f^2 5d^0 6s^2$
Praseodymium	Pr	59	$[Xe]\,4f^3 5d^0 6s^2$
Neodymium	Nd	60	$[Xe]\,4f^4 5d^0 6s^2$
Promethium	Pm	61	$[Xe]\,4f^5 5d^0 6s^2$
Samarium	Sm	62	$[Xe]\,4f^6 5d^0 6s^2$
Europium	Eu	63	$[Xe]\,4f^7 5d^0 6s^2$
Gadolinium	Gd	64	$[Xe]\,4f^7 5d^1 6s^2$
Terbium	Tb	65	$[Xe]\,4f^9 5d^0 6s^2$
Dysprosium	Dy	66	$[Xe]\,4f^{10} 5d^0 6s^2$
Holmium	Ho	67	$[Xe]\,4f^{11} 5d^0 6s^2$
Erbium	Er	68	$[Xe]\,4f^{12} 5d^0 6s^2$
Thulium	Tm	69	$[Xe]\,4f^{13} 5d^0 6s^2$
Ytterbium	Yb	70	$[Xe]\,4f^{14} 5d^0 6s^2$
Lutetium	Lu	71	$[Xe]\,4f^{14} 5d^1 6s^2$

2. Physical State

All of them are silvery white soft metals with high density and high melting point. These get tarnished off readily in air. The hardness of these metals increases with rise in atomic number. These are good conductors of heat and electricity.

3. Atomic and Ionic Radii

In 4*f*-series, as the atomic number increases from La to Lu, the atomic and ionic radii decreases gradually. This decrease in atomic and ionic size from lanthanum (at. no. 57) to lutetium (at. no. 71) is a unique feature and is known as **lanthanide contraction.** This contraction is attributed to imperfect shielding of electrons of *f*-orbital. It is even less than the shielding shown by *d*-electron.

As a result of lanthanide contraction, the normal increase in size from $Sc \rightarrow Y \rightarrow La$ disappears after the lanthanide and the pairs of elements such as Zr—Hf, Nb—Ta and Mo—W have nearly same size. The properties of these elements are very similar.

The similarities in properties within these pairs make separation of lanthanoids very difficult.

Due to lanthanide contraction, the elements of 5*d* and 4*d*-series resemble each other much more closely than do the elements of 4*d* and 3*d*-series.

4. Oxidation State

All of them show variable valency or oxidation state. However, +3 oxidation state is most stable. Some of these elements also exhibit +2 and +4 oxidation states along with +3 oxidation state. Higher oxidation states are not possible because there is a large energy gap beween 4*f* and 5*d* subshells.

Following stable ions also exist as,

$$4f^0 = La^{3+}$$

$$4f^7 = Eu^{2+}, Gd^{3+}, Tb^{4+}$$

$$4f^{14} = Yb^{2+}, Lu^{3+}$$

Stability of these ions depend on (i) ionisation energy, (ii) sublimation energy and (iii) lattice energy

5. Electronegativity

There is slight increase in electronegativity of trivalent ions from La to Lu.

6. Colour

- Many trivalent lanthanide ions are coloured in both solid state as well as aqueous solutions (not shown by La^{+}, Ce^{3+}, Gd^{3+}, Yb^{3+} and Lu^{3+}). The colour of these ions is because of *f*-*f* transition due to the presence of partly filled *f*-orbitals.
- Ce^{4+} is orange red ($4f^0$, isoelectronic to La^{3+}) and Yb^{2+} is yellow ($4f^{14}$ isoelectronic to Lu^{3+}).

7. Magnetic Properties

Except Lu^{3+}, Yb^{3+} and Ce^{4+}, all other lanthanoid ions are paramagnetic. However, the point of difference from transition elements is that here, both spin as well as orbital moments give contribution.

The μ_{eff} is calculated as, $\mu_{eff} = \sqrt{4S(S+1) + L(L+1)}$ BM

The paramagnetism increases to maximum in neodymium (Nd) (atomic number 60).

8. Ionisation Energy

These elements have low ionisation energy and thus, have high electropositive character.

9. Complex Formation

Lanthanoids have very less tendency to form complexes this is because of their low charge density. They form complexes with strong chelating agents like EDTA oxime but not with π-bonding ligands. Tendency to form complexes increases from La^{3+} to Lu^{3+} as size decreases.

10 Alloy Formation

They form alloy with other metals like iron, e.g. misch metal which consists of lanthanoid metal (~ 95%), iron (~ 5%) and traces of S, C, Ca, Al, etc.

11.Reactivity

- As far as their chemical behaviour is concerned, their earlier members are quite reactive (similar in behaviour to Ca) but with increasing atomic number they behave more like Al.
- These elements easily combine with hydrogen forming hydrides.
- The carbides (with C) of the type A_2C, A_2C_3 and AC_2 are reported (where, A = lanthanide). They liberate H$_2$ with dilute acids and form halides with halogens.

12. Basic Nature

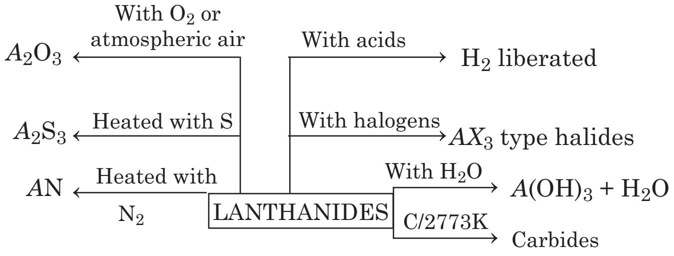
Their oxides (M_2O_3) and hydroxides [$M(OH)_3$] are stable. The hydroxides are ionic and basic. These are less basic than Ca(OH)$_2$ but more basic than amphoteric Al(OH)$_3$. The basic strength decreases from Ce(OH)$_3$ to Lu(OH)$_3$.

Other Properties

Other important properties are as follows

- Carbonyls are not formed by lanthanides due to non-availability of *d*-electrons for π-bonding. However, an unstable Nd(CO)$_6$ has been prepared.
- Ce and Tb give CeF$_4$ and TbF$_4$ instead of CeF$_3$ and TbF$_3$ respectively.
- Eu and Yb dissolve in liquid ammonia and form blue solution (which give characteristic spectra of M^{2+} and ammoniated electrons). The solution decolourises slowly but the concentrated solution appear golden.

Their generalised reactions can be summarised as



Here, A = *lanthanides*

Example 10. *Match the property given in Column I with the element given in Column II.*

	Column I (Property)		**Column II** (Element)
I.	Lanthanoid which shows +4 oxidation state	A.	Pm
II.	Lanthanoid which can show +2 oxidation state	B.	Ce
III.	Radioactive lanthanoid	C.	Lu
IV.	Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state	D.	Eu
V.	Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state	E.	Gd
		F.	Dy

Codes

(a) I-B, II-D, III-A, IV-E, V-C (b) I-B, II-C, III-E, IV-A, V-D

(c) I-E, II-F, III-C, IV-A, V-D (d) I-F, II-A, III-B, IV-C, V-D

Sol. (a) Ce = + 4 oxidation state ; Eu = + 2 oxidation state;
Pm = radioactive lanthanoid ; Gd^{3+} = $4f^7$: electronic configuration;
Lu^{3+} = $4f^{14}$: electronic configuration

5*f*-Series or Second Inner-Transition Series or Actinoids

If the last electron (i.e. the differentiating electron) occupies 5*f*-orbital, the element is said to belong **5*f*-series**. This series also includes fourteen elements but here, the elements are after actinium, (Z = 89), i.e. from thorium (Z = 90) to lawrencium (Z = 103). These are called **actinides** or **actinones** because of their close resemblance in properties with actinium.

Thorium, protactinium and uranium all are radioactive. Except them all other actinides are synthetic elements (i.e. man-made elements).

Important characteristics of actinides are

1. **Electronic Configuration**

Their general electronic configuration these elements is [Rn] $5f^{1\text{-}14}6d^{0\text{-}1}7s^2$. These elements along with their electronic configuration are tabulated below

Electronic Configuration of Actinides

Name	Symbol	Atomic no.	Configuration
Thorium	Th	90	[Rn] $5f^0 6d^2 7s^2$
Protactinium	Pa	91	[Rn] $5f^2 6d^1 7s^2$
Uranium	U	92	[Rn] $5f^3 6d^1 7s^2$
Neptunium	Np	93	[Rn] $5f^4 6d^1 7s^2$
Plutonium	Pu	94	[Rn] $5f^6 6d^0 7s^2$
Americium	Am	95	[Rn] $5f^7 6d^0 7s^2$
Curium	Cm	96	[Rn] $5f^7 6d^1 7s^2$
Berkelium	Bk	97	[Rn] $5f^8 6d^1 7s^2$
Californium	Cf	98	[Rn] $5f^{10} 6d^0 7s^2$
Einsteinium	Es	99	[Rn] $5f^{11} 6d^0 7s^2$
Fermium	Fm	100	[Rn] $5f^{11} 6d' 7s^2$
Mendelevium	Md	101	[Rn] $5f^{13} 6d^0 7s^2$
Nobelium	No	102	[Rn] $5f^{14} 6d^0 7s^2$
Lawrencium	Lr	103	[Rn] $5f^{14} 6d^1 7s^2$

2. **Physical State**

These metals are silvery white in appearance and display a variety of structures. Except thorium and americium, all actinides have high density. Actinoids like lanthanoids have high melting and boiling points but these do not show any regular trend for this.

3. **Oxidation State**

For them, there is a greater range of oxidation states (i.e. +4, +5, +6 along with +3) The reason for having variable oxidation state is that the $5f$, $6d$ and $7s$ levels are of comparable energy. The maximum oxidation state increases from + 4 in Th to + 5 in Pa, + 6 in U and + 7 in Np and Pu and then decreases in succeding elements. However, here also the predominant oxidation state is +3, which is more stable in case of heavier elements.

4. **Atomic and Ionic Radii**

There is seen a gradual decrease in the size of atoms or ions (actinide contraction) which is like lanthanide contraction but less prone. The contraction is infact attributed to the shielding effect of $5f$-electrons.

5. **Magnetic Property**

The magnetic properties of them are even more complex than those of lanthanides. These are also paramagnetic in nature due to the presence of unpaired $5f$-electrons.

6. **Colour**

Actinides are also coloured compounds. This is because of f-f transition, from the f-orbital of lower energy to the f-orbital of higher energy. The ions having $5f^0$, $5f^7$ and $5f^{14}$ are colourless. The colour of some other ions are as,

$$U^{3+}\,(5f^3): \text{Red};\ Np^{3+}\,(5f^4): \text{ Bluish}$$

$$Pu^{3+}\,(5f^5): \text{Blue};\ Am^{3+}\,(5f^6): \text{Pink}$$

7. **Ionisation Energies**

Their ionisation energies are lower then those of lanthanoids. But they have high electropositive character and behave as strong reducing agents.

In actinoids $5f$ electrons are more effectively shielded from the nuclear charge than $4f$ electrons of corresponding lanthanoids. Hence, outer electrons are less firmly held and they are available for bonding in the actinoids.

8. **Complex Formation**

Because of their higher nuclear charge and small size, these elements form complex.

9. **Reactivity**

Actinoids metals are reactive. Their reactivity increase with increase in atomic number. They tarnish rapidly. Protective covering is formed only in case of Th.
Conc. HCl reacts rapidly with these metals but conc. HNO_3 makes Th, U and Pu passive. They exhibit variety of structures due to irregularities in metallic radii.

10. **Basic Nature**

Actinoids are basic in nature and hence these do not react with alkalies such as NaOH. Actinoids react with non-metals (like O, H, halogens etc.) at moderate temperature. Their hydrides are non-stoichiometric. These react with boiling water to give a mixture of oxide and hydride.

Uses of Actinoids

The three most important actinoids which find uses as such or in the form of their compounds are Th, U and Pu.

- Th is used in atomic reactors and in the treatment of cancer. Its salts are used in making incandescent gas mantles.
- U is used as nuclear fuel. It salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
- Pu is used as fuel for atomic reactors as well as for making atomic bombs.

Comparison of Lanthanoids with Actinoids

	Lanthanoids	Actinoids
(i)	Besides +3 oxidation state, they show +2 and +4 oxidation states only in few cases.	Besides +3 oxidation state, they show higher states of +4, + 5, + 6, +7 also.
(ii)	Lanthanoid compounds are less basic.	Actinoid compounds are more basic.
(iii)	They have less tendency towards complex formation.	They have greater tendency towards complex formation.
(iv)	Most of their ions are colourless.	Most of their ions are coloured.
(v)	Except promethium, they are non-radioactive.	They are radioactive.
(vi)	Their magnetic properties can be explained easily.	Their magnetic properties cannot be explained easily, as they are more complex.

Practice Exercise

ROUND I Topically Divided Problems

Characteristics of Transition Elements

1. Transition elements exhibit variable valencies because they release electrons from the following orbits

(a) ns (b) ns and np

(c) $(n-1)d$ and ns (d) $(n-1)\,d$

2. The valence shell electronic configuration of Cr^{2+} ion is

(a) $4s^0, 3d^4$ (b) $3p^6, 4s^2$

(c) $4s^2, 3d^2$ (d) $4s^2, 3d^0$

3. Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration ?

(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) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$

4. Zinc does not show variable valency like d-block elements because

(a) it is low melting

(b) its d-orbital is completely filled

(c) it is a soft metal

(d) two electrons are present in the outermost orbit

5. Which one of the following arrangement of ions in order of increasing strength as a reducing agent is correct?

(a) $Cr_2O_7^{2-} < Cr^{3+} < Cr^{2+}$ (b) $Cr_2O_7^{2-} < Cr^{2+} < Cr^{3+}$

(c) $Cr^{3+} < Cr^{2+} < Cr_2O_7^{2-}$ (d) $Cr^{2+} < Cr^{3+} < Cr_2O_7^{2-}$

6. Which of the following statements is not correct? *(NCERT Exemplar}*

(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

7. Transition elements are coloured

(a) due to unpaired d-electrons

(b) due to small size

(c) due to metallic nature

(d) All of the above

8. Cuprous ion is colourless, while cupric ion is coloured because

(a) both have half-filled p and d-orbitals

(b) cuprous ion has a completely filled d-orbital and cupric ion has incomplete d-orbital

(c) cuprous ion has incomplete d-orbital and cupric ion has a complete d-orbital

(d) both have unpaired electrons in d-orbital

9. Of the ions Zn^{2+}, Ni^{2+} and Cr^{3+}, (atomic number of $Zn = 30, Ni = 28, Cr = 24$)

(a) all three are coloured

(b) all three are colourless

(c) only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured

(d) only Ni^{2+} is coloured and Ni^{2+} and Cr^{3+} are colourless

10. Which of the following ionic species will impart colour to an aqueous solution?

(a) Cu^{+} (b) Zn^{2+}

(c) Cr^{3+} (d) Ti^{4+}

11. Colour of Cu^{+} compound would be

(a) white (b) blue

(c) orange (d) yellow

12. Ti^{2+} is purple whereas Ti^{4+} is colourless, because

(a) there is no crystal field effect in Ti^{4+}

(b) Ti^{2+} has $3d^2$ configuration

(c) Ti^{4+} has $3d^2$ configuration

(d) Ti^{4+} is a very small cation when compared to Ti^{2+} and hence, does not absorb any radiation

13. Which of the following elements has the maximum first ionisation potential?

(a) V (b) Ti

(c) Mn (d) Cr

14. The correct statement about ionisation energies of Cu and Zn is/are

(a) IE_1 of Cu is less than that of Zn

(b) IE_2 of Cu is more than that of Zn

(c) IE_2 of Zn is more than that of Cu

(d) Both (a) and (b)

15. Paramagnetism is given by the relation $\mu = 2\sqrt{s(s+1)}$ magnetons where 's' is the total spin. On this basis, the paramagnetism of Cu^+ ion is

(a) 3.88 magnetons (b) 2.83 magnetons
(c) 1.41 magnetons (d) zero

16. Magnetic moment of Cr ($Z = 24$), Mn^+ ($Z = 25$) and Fe^{2+} ($Z = 26$) are x, y, z. They are in order

(a) $x < y < z$ (b) $x = y < z$
(c) $z < x = y$ (d) $x = y = z$

17. Which of the following has the maximum number of unpaired d-electrons?

(a) Fe^{2+} (b) Cu^+ (c) Zn (d) Ni^{3+}

18. Which of the following ions has the highest magnetic moment?

(a) Ti^{3+} (b) Sc^{3+} (c) Mn^{2+} (d) Zn^{2+}

19. Which one of the following is a diamagnetic ion?

(a) Co^{2+} (b) Cu^{2+}
(c) Mn^{2+} (d) Sc^{3+}

20. The magnetic moment of Mn in MnO_4^- is

(a) Zero BM (b) $\sqrt{3}$ BM
(c) $\sqrt{8}$ BM (d) $\sqrt{15}$ BM

21. The compound which is not paramagnetic out of the following

(a) $Cr(ClO_4)_3$ (b) $KMnO_4$
(c) $TiCl_3$ (d) $VOBr_2$

22. Which of the following ions exhibits largest magnetic moment ?

(a) V^{3+} (b) Cr^{3+} (c) Fe^{3+} (d) Co^{2+}

23. Match the following columns.

	Column I		Column II
(i)	Cr^{3+}	p.	$\sqrt{35}$
(ii)	Fe^{2+}	q.	$\sqrt{30}$
(iii)	Ni^{2+}	r.	$\sqrt{20}$
(iv)	Mn^{2+}	s.	$\sqrt{15}$
		t.	$\sqrt{8}$

Codes

(a) (i)-p, (ii)-r, (iii)-t, (iv)-s
(b) (i)-q, (ii)-r, (iii)-t, (iv)-p
(c) (i)-s, (ii)-r, (iii)-t, (iv)-p
(d) (i)-s, (ii)-t, (iii)-r, (iv)-p

24. VO_2 is an amphoteric oxide and in acidic medium it forms

(a) VO^{2+} (b) VO_2^+ (c) V^{3+} (d) VO_2^{2+}

25. Which oxide of manganese is amphoteric?

(a) MnO (b) MnO_2
(c) Mn_2O_7 (d) Mn_2O_3

26. The transition elements are more metallic than the representative elements because they have

(a) electron pairs in d-orbitals
(b) availability of d-orbitals for bonding
(c) the electron in d-orbitals
(d) unpaired electron in metallic orbitals

27. In which of the following metallic bond is strongest?

(a) V (b) Fe
(c) Cr (d) Sc

28. Coinage metals show the properties of

(a) inert elements (b) normal elements
(c) typical elements (d) transition elements

29. Which of the following is correct?

(a) Duralumin : Al + Cu + Mg + Ag
(b) German silver : Cu + Zn + C
(c) Gun metal : Cu + Zn + Sn
(d) Solder : Pb + Al

30. Transition metals form alloys easily. The reason for this is

(a) their occurrence (b) similar size
(c) magnetic nature (d) do not form easily

31. The catalytic activity of the transition metals and their compounds is ascribed to their

(a) magnetic behaviour
(b) chemical reactivity
(c) ability to adopt multiple oxidation states and their complexing ability
(d) unfilled d-orbitals

32. Select the incorrect statement.

(a) The melting point of Mn is lower than that of Cr and Fe
(b) The melting point of Tc is higher than that of Mo but lower than that of Ru
(c) The melting point of W is highest in $5d$-series
(d) The order of melting point of $3d, 4d$ and $5d$-series is $5d > 4d > 3d$

33. The order of reactivity of halogens with transition metals is

(a) $F_2 > Cl_2 > Br_2 > I_2$ (b) $F_2 > Br_2 > Cl_2 > I_2$
(c) $F_2 > Cl_2 > I_2 > Br_2$ (d) $F_2 > I_2 > Br_2 > Cl_2$

34. Select the incorrect statement about transition elements.

(a) The last electron enters in the d-orbital
(b) Their properties are in between s and p-block elements
(c) Scandium is the transition element with smallest atomic radii
(d) Their common oxidation state is +3

35. Select the incorrect statement from the following.

(a) Higher oxidation state for *d*-block elements is most stable with F

(b) The bond strength order of the following ions will be $Zn_2^{2+} > Hg_2^{2+} > Cd_2^{2+}$

(c) The ionic size of the following ions would be : $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$

(d) Mn_2O_7 exist but MnF_2 does not exist

Compounds of Transition Elements

36. $K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + O_2 + X$. In the above reaction X is

(a) CrO_3 (b) Cr_2O_7 (c) Cr_2O_3 (d) CrO_5

37. One of the product formed when $K_2Cr_2O_7$ reacts with conc. H_2SO_4 in cold is

(a) CrO_3 (b) $Cr_2(SO_4)_3$ (c) Cr_2O_3 (d) CrO_4Cl_2

38. The reaction of $K_2Cr_2O_7$ with NaCl and conc. H_2SO_4 gives

(a) CrO_2Cl_2 (b) Cr_2O_3 (c) $CrCl_3$ (d) $CrOCl_2$

39. $Cr_2O_7^{2-} \xrightarrow{pH = x} CrO_4^{2-} \xrightarrow{pH = y} Cr_2O_7^{2-}$ pH values x and y can be

(a) 4 and 5 (b) 4 and 8

(c) 8 and 4 (d) 8 and 9

40. What are the species A and B in the following

$$CrO_3 + H_2O \longrightarrow A \xrightarrow{OH^-} B$$

(a) $H_2CrO_4, H_2Cr_2O_7$ (b) $H_2Cr_2O_7, Cr_2O_3$

(c) $CrO_4^{2-}, Cr_2O_7^{2-}$ (d) H_2CrO_4, CrO_4^{2-}

41. The common positive oxidation states for an element with atomic number 24, are *(JEE Main 2021)*

(a) + 2 to + 6

(b) + 1 and + 3 to + 6

(c) + 1 and + 3

(d) + 1 to + 6

42. When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salts, then Sn^{2+} changes to

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

43. CrO_3 dissolves in aqueous NaOH to give

(a) $Cr_2O_7^{2-}$ (b) CrO_4^{2-}

(c) $Cr(OH)_3$ (d) $Cr(OH)_2$

44. Thermal decomposition of ammonium dichromate gives

(a) N_2, H_2O and Cr_2O_3 (b) N_2, NH_3 and CrO

(c) $(NH_4)_2CrO_4$ and H_2O (d) N_2, H_2O and CrO_3

45. The gas produced from thermal decomposition of $(NH_4)_2Cr_2O_7$ is

(a) oxygen (b) nitric oxide

(c) ammonia (d) nitrogen

46. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium? ***(NCERT Exemplar)***

(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 that HCl

(d) $KMnO_4$acts as a reducing agent in the presence of HCl

47. In dilute alkaline solution, MnO_4^- changes to

(a) MnO_4^{2-} (b) MnO_2 (c) Mn_2O_3 (d) MnO

48. Black coloured solid $(A) \xrightarrow[\Delta]{KNO_3 + KOH}$

Green colour solution $(B) \xrightarrow{CO_2} \underset{\text{Pink}}{(C)} + (A)$

Pink compound (C) is decolourised by Fe^{2+}. The compound A, B and C are

(a) $MnO_2, K_2MnO_4, KMnO_4$

(b) $MnO_2, KMnO_4, K_2MnO_4$

(c) $KMnO_4, MnO_2, K_2MnO_4$

(d) $K_2MnO_4, MnO_4, KMnO_4$

Inner-Transition Elements

49. Lanthanum is grouped with f-block elements because

(a) it has partially filled f-orbitals

(b) it has both partially filled f and d-orbitals

(c) the properties of lanthanum are very similar to the elements of 4f-block

(d) it is just before Ce in the periodic table

50. Cerium (Z = 58) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?

(a) The common oxidation states of cerium are +3 and +4

(b) Cerium (IV) acts as an oxidising agent

(c) The +4 oxidation state of cerium is not known in solutions

(d) The +3 oxidation state of cerium is more stable than the +4 oxidation state

51. Which one of the following acts as an oxidising agent?

(a) Np^{4+} (b) Sm^{2+} (c) Eu^{2+} (d) Yb^{2+}

52. Gadolinium belongs to 4f series, atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? ***(NCERT Exemplar}***

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

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

53. Which of the following oxidation state is common for all lanthanoids? *(NCERT Exemplar}*

(a) $+2$ (b) $+3$ (c) $+4$ (d) $+5$

54. Across the lanthanide series, the basicity of lanthanide hydroxides

(a) increases
(b) decreases
(c) first increases and then decreases
(d) first decreases and then increases

55. Which of the following trivalent ion has the largest atomic radii in the lanthanide series?

(a) Ce (b) Pm (c) La (d) Lu

56. The $+3$ ion of which one of the following has half-filled $4f$ subshell?

(a) La (b) Lu (c) Gd (d) Ce

57. Lanthanide contraction occurs because

(a) f-orbitals are incompletely filled
(b) f-orbital electrons are easily lost
(c) f-orbital do not come out on the surface of atom and are buried inside
(d) f-orbital electrons are poor shielders of nuclear charge

58. The colour of $_{62}Sm^{3+}$ is yellow. The expected colour of $_{66}Dy^{3+}$ is

(a) yellow (b) red (c) blue (d) green

59. The lanthanoids contraction relateds to

(a) atomic radii
(b) atomic as well as M^{3+} radii
(c) valence electrons
(d) oxidation states

60. In aqueous solution Eu^{2+} ion acts as

(a) an oxidising agent (b) a reducing agent
(c) an acid (d) All of these

61. Which of the following statement is not correct?

(a) $La(OH)_3$ is less basic than $Lu(OH)_3$
(b) In lanthanide series ionic radius of Ln^{3+} ions decreases
(c) Zn, Cd, Hg are colourless and are diamagnetic
(d) Mn shows maximum oxidation state +7

62. Which one of the following elements shows maximum number of different oxidation states in its compounds?

(a) Eu (b) La (c) Gd (d) Am

63. CeI_2 has metallic lustre. It is explained by formulating it as

(a) Ce (III), $2I^-$, e^- (b) Ce(II), $2I^-$
(c) Ce (IV), $2I^-$, $2e^-$ (d) None of these

64. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Number in parenthesis are atomic numbers)

(a) Zr (40) and Hf (72)
(b) Zr (40) and Ta (73)
(c) Ti (22) and Zr (40)
(d) Zr (40) and Nb (41)

65. Identify the incorrect statement of among the following.

(a) Shielding power of $4f$-electrons is quite weak
(b) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu
(c) As a result of lanthanoid contraction, the properties of $4d$ series of the transition elements have no similarities with the $5d$ series of elements
(d) (a) and (b) both statements are correct

66. Consider the following statements with respect of lanthanoids :

I. The basic strength of hydroxides of lanthanoids increases from $La(OH)_3$ to $Lu(OH)_3$
II. The lanthanoid ions Lu^{3+}, Yb^{2+} and Ce^{4+} are diamagnetic

Which of the statements given above is/are correct ?

(a) Only I (b) Only II
(c) Both I and II (d) Neither I nor II

67. Which of the following lanthanoid ions is diamagnetic? (At. no. Ce = 58, Sm = 62, Eu = 63, Yb = 70)

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

68. Which one of the following statements related to lanthanons is incorrect?

(a) Europium shows + 2 oxidation state.
(b) The basicity decreases as the ionic radius decreases from Pr to Lu.
(c) All the lanthanons are much more reactive than aluminium.
(d) Ce(+ 4) solutions are widely used as oxidising agent in volumetric analysis.

69. There are 14 elements in actionoid series. Which of the following elements does not belong to this series? *(NCERT Exemplar}*

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

70. Which of the following ion is diamagnetic?

(a) Nd^{3+} (b) La^{3+}
(c) Tb^{3+} (d) Er^{3+}

ROUND II Mixed Bag

1. Which of the following pair will have equal effective magnetic moment ?
(a) Ti^{2+} and V^{2+} (b) Cr^{2+} and Fe^{2+}
(c) Cr^{3+} and Mn^{2+} (d) V^{2+} and Sc^{3+}

2. Most basic hydroxide among the following is
(a) $Lu(OH)_3$ (b) $Eu(OH)_3$
(c) $Yb(OH)_3$ (d) $Ce(OH)_3$

3. When MnO_2 is fused with KOH, a coloured compound is formed. The product and its colour is
(a) K_2MnO_4, purple colour (b) Mn_2O_3, brown
(c) Mn_2O_4, black (d) $KMnO_4$, purple

4. Which of the following weighs less when weighted in magnetic field?
(a) $ScCl_3$ (b) $FeCl_3$ (c) $TiCl_3$ (d) VCl_3

5. An element is in M^{3+} form. Its electronic configuration is $[Ar]3d^1$, the ion is
(a) Ca^{2+} (b) Sc^+ (c) Ti^{4+} (d) Ti^{3+}

6. Transuranic elements begins with
(a) Np (b) Cm (c) Pu (d) U

7. Which among the following metals does not dissolve in *aqua-regia*?
(a) Pt (b) Pd (c) Au (d) Ir

8. Which lanthanoid compound is used as a most powerful liquid lasers after dissolving it in selenium oxychloride?
(a) Cerium oxide
(b) Neodymium oxide
(c) Promethium sulphate
(d) Ceric sulphate

9. In aqueous solutions Eu^{2+} acts as
(a) an oxidising agent
(b) a reducing agent
(c) can act oxidising as well as reducing agent
(d) cannot act as oxidising as well as reducing agent

10. Which of the following is not amphoteric ?
(a) Al^{3+} (b) Cr^{3+}
(c) Fe^{3+} (d) Zn^{2+}

11. Which of the following compounds are coloured?
(a) $KMnO_4$ (b) $Ce(SO_4)_2$
(c) $TiCl_4$ (d) Both (a) and (b)

12. Which of the following will not act as oxidising agents? ***(NCERT Exemplar)***
(a) CrO_3 (b) MoO_3
(c) WO_3 (d) Both (b) and (c)

13. Arrange Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} in increasing order of their ionic radii.
(a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
(c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
(d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

14. The basic character of the transition metal monoxide follows the order
(At. no. of 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

15. If M is element of actinoids series, the degree of complex formation decreases in the order
(a) $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^{+}$
(b) $MO_2^{+} > MO_2^{2+} > M^{3+} > M^{4+}$
(c) $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$
(d) $MO_2^{2+} > MO_2^{+} > M^{4+} > M^{3+}$

16. The electronic configuration of actinoids cannot be assigned with degree of certainty because of
(a) overlapping of inner orbitals
(b) free movement of electrons over all the orbitals
(c) small energy difference between $5f$ and $6d$ levels
(d) None of the above

17. 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

18. Which series of reactions correctly represents chemical relations related to iron and its compound ? ***(JEE Main 2014)***

(a) $Fe \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$

(b) $Fe \xrightarrow{O_2, \text{ Heat}} FeO \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{Heat}} Fe$

(c) $Fe \xrightarrow{Cl_2, \text{ Heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{Zn} Fe$

(d) $Fe \xrightarrow{O_2, \text{ Heat}} Fe_3O_4 \xrightarrow{CO, \ 600°C} FeO \xrightarrow{CO, \ 700°C} Fe$

19. Although, $+3$ is the characteristic oxidation state for lanthanoids but cerium also shows $+4$ oxidation state because *(NCERT Exemplar}*

(a) it has variable ionisation enthalpy

(b) it has a tendency to attain noble gas configuration

(c) it has a tendency to attain f^0 configuration

(d) Both (b) and (c)

20. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment? *(NCERT Exemplar}*

(a) Co^{2+} (b) Cr^{2+}

(c) Cr^{3+} (d) Both (a) and (c)

21. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium but Mo (VI) in MoO_3 and W (VI) in WO_3 are not because *(NCERT Exemplar}*

(a) Cr (VI) is more stable than Mo(VI) and W(VI)

(b) Mo(VI) and W(VI) are more stable than Cr(VI)

(c) Higher oxidation states of heavier members of group 6 of transition series are more stable

(d) Both (b) and (c)

22. In which case there is a change in oxidation number of Cr ?

(a) Aqueous solution of CrO_4^{2-} is acidified

(b) SO_2 gas is passed into $Cr_2O_7^{2-}/H^+$

(c) $Cr_2O_7^{2-}$ solution is made alkaline

(d) CrO_2Cl_2 is dissolved in NaOH

23. Most transition metals are inert towards acids or react slowly with them because of

(a) negative standard reduction potential

(b) protective layer of oxide

(c) Both (a) and (b)

(d) None of the above

24. Consider the following statements.

I. Colour of a transition metal complex is dependent on energy difference between two d-levels.

II. Colour of the complex is dependent on the nature of the ligand and the type of complex formed.

III. $ZnSO_4$ and TiO_2 are white as in both d-d spectra are impossible.

Select the correct statements.

(a) I, II, III (b) I, II (c) II, III (d) I, III

25. MnO_4^- is of intense pink colour, though Mn is in $(+7)$ oxidation state. It is due to

(a) oxygen gives colour to it

(b) charge transfer when oxygen gives its electron to Mn making it Mn (+ VI) hence, coloured

(c) charge transfer when Mn gives its electron to oxygen

(d) None of the above is correct

26. Match the following Columns.

	Column I		Column II
A.	K_2MnO_4	1.	Transition metal is $+6$ oxidation state
B.	$KMnO_4$	2.	Paramagnetic
C.	$K_2Cr_2O_7$	3.	Manufactured from pyrolusite ore
D.	K_2CrO_4	4.	Manufactured from chromite ore

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	3	2	1
(c)	1,2,3	3	1,4	4	(d)	2	3	1	4

27. Match the following Columns

	Column I		Column II
A.	Highest oxidation state	1.	Cr
B.	Highest density	2.	Os
C.	Element with maximum number of unpaired electrons	3.	Tc
D.	Radioactive transition element	4.	Ru

Codes

	A	B	C	D		A	B	C	D
(a	1	2	3	4	(b)	4	3	2	1
(c)	2, 4	2	1	3	(d)	2	4	1	3

Numeric Value Questions

28. The oxidation state of Cr in butterfly structure is ……… .

29. Out of the following

Ti O, Sc_2O_3, Ti_2O_3, VO, V_2O_5, Cr_2O_3, CuO, TiO_2

The number of basic oxides will be ……… .

30. When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide the ratio of volumes of hydrogen evolved is $x : y$. The value of $x + y$ will be ……… .

31. The magnetic moment of a metal ion of first transition series is 2.83 BM. Therefore, it will have unpaired electrons ……… .

32. In the reduction of dichromate by Fe(II), the number of electrons involved per chromium atom is ……… .

33. Consider the following oxides.

Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4.

Among them the number of amphoteric oxides are ……… .

34. When 35 mL of 0.15 M lead nitrate solution is mixed with 20 mL of 0.12 M chromic sulphate solution ……$\times 10^{-5}$ moles of lead sulphate precipitate out. *(JEE Main 2021)*

35. Consider the following reaction

$$a\mathrm{Cr_2O_7^{2-}} + b\mathrm{H^+} + c\mathrm{H_2O_2} \longrightarrow d\mathrm{CrO(O_2)_2} + e\mathrm{H_2O}$$

The value of $a + b + c + d + e$ will be ……… .

36. Number of moles of iodine are liberated when 1 mole of potassium dichromate reacts with potassium iodide.

37. On complete reaction of $\mathrm{FeCl_3}$ with oxalic acid in aqueous solution containing KOH, resulted in the formation of product A. The secondary valency of Fe in the product A is …… . *(JEE Main 2021)*

38. The number of electrons required to reduce chromium completely in $\mathrm{Cr_2O_7^{2-}}$ to $\mathrm{Cr^{3+}}$ in acidic medium, is

39. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is

40. x moles of potassium dichromate oxidises 1 mole of ferrous oxalate, in acidic medium. Here, x is …… .

Answers

Round I

1. (c)	**2.** (a)	**3.** (d)	**4.** (b)	**5.** (a)	**6.** (a)	**7.** (a)	**8.** (b)	**9.** (c)	**10.** (c)
11. (a)	**12.** (d)	**13.** (c)	**14.** (d)	**15.** (d)	**16.** (c)	**17.** (a)	**18.** (c)	**19.** (d)	**20.** (b)
21. (b)	**22.** (c)	**23.** (c)	**24.** (a)	**25.** (b)	**26.** (b)	**27.** (c)	**28.** (d)	**29.** (c)	**30.** (b)
31. (c)	**32.** (b)	**33.** (a)	**34.** (c)	**35.** (b)	**36.** (c)	**37.** (a)	**38.** (a)	**39.** (c)	**40.** (d)
41. (a)	**42.** (c)	**43.** (b)	**44.** (a)	**45.** (d)	**46.** (b)	**47.** (a)	**48.** (c)	**49.** (c)	**50.** (c)
51. (a)	**52.** (a)	**53.** (b)	**54.** (b)	**55.** (c)	**56.** (c)	**57.** (d)	**58.** (a)	**59.** (b)	**60.** (b)
61. (a)	**62.** (d)	**63.** (c)	**64.** (a)	**65.** (d)	**66.** (b)	**67.** (d)	**68.** (c)	**69.** (c)	**70.** (b)

Round II

1. (b)	**2.** (d)	**3.** (a)	**4.** (a)	**5.** (d)	**6.** (a)	**7.** (d)	**8.** (b)	**9.** (b)	**10.** (c)
11. (d)	**12.** (d)	**13.** (a)	**14.** (a)	**15.** (a)	**16.** (c)	**17.** (a)	**18.** (d)	**19.** (d)	**20.** (d)
21. (d)	**22.** (b)	**23.** (b)	**24.** (a)	**25.** (b)	**26.** (c)	**27.** (c)	**28.** (4)	**29.** (4)	**30.** (2)
31. (2)	**32.** (3)	**33.** (2)	**34.** (525)	**35.** (14)	**36.** (3)	**37.** (6)	**38.** (6)	**39.** (3)	**40.** (0.5)

Solutions

Round I

1. Transition elements release electrons from $(n-1)\,d$ and ns-orbitals.

2. In Cr electrons are withdrawn from 4s to make $\mathrm{Cr^{+2}}$.

3. $\mathrm{Ti} \rightarrow 3d^2 4s^2$, $\mathrm{Ti^{2+}} \rightarrow 3d^2$

$\mathrm{V} \rightarrow 3d^3, 4s^2$, $\mathrm{V^{3+}} \rightarrow 3d^2$

$\mathrm{Cr} \rightarrow 3d^4 4s^2$, $\mathrm{Cr^{4+}} \rightarrow 3d^2$

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

4. Electronic configuration of $_{30}\mathrm{Zn} \longrightarrow [\mathrm{Ar}]\,3d^{10}4s^2$

Its d-orbital is completely filled.

Therefore, it does not show variable valency.

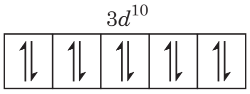
5. $\mathrm{Cr_2O_7^{2-}} < \mathrm{Cr^{3+}} < \mathrm{Cr^{2+}}$

Smaller the oxidation state of element in the ion, greater the reducing nature.

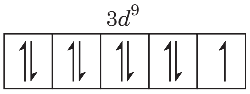
6. Copper does not liberate hydrogen from acids because it has positive $E°$.

7. Transition elements are coloured due to d-d transition.

8. Cuprous ion $(\mathrm{Cu^+})\,3d^{10}$ (completely filled d-subshell)



Cupric ion $(\mathrm{Cu^{2+}})\,3d^9$ (one unpaired electron)



9. $\mathrm{Ni^{2+}}$ and $\mathrm{Cr^{3+}}$ are coloured due to the presence of unpaired electrons. But $\mathrm{Zn^{2+}}$ is colourless because of the absence of unpaired electrons.

11. Colour of a compound of transition element is due to the *d*-*d* transition. The configuration of $\mathrm{Cu^+}$ is $3d^{10}, 4s^0$ and such no electron is available for excitation and hence $\mathrm{Cu^+}$ will be colourless or white in colours.

12. $\mathrm{Ti}\ (22) = [\mathrm{Ar}]\, 4s^2 3d^2$

$\mathrm{Ti^{2+}} = [\mathrm{Ar}]\, 3d^2$

$\mathrm{Ti^{4+}} = [\mathrm{Ar}]\, 3d^0$

$\mathrm{Ti^{2+}}$ has two unpaired electrons in $3d$ and thus, *d*-*d* transition is possible due to absorption of light in visible region.

13. Among the given, manganese has the most stable electronic configuration, thus it is very hard to remove an electron from its outer shell. Therefore, manganese has the maximum first ionisation potential.

14. $\mathrm{IE_1}$ of Cu ($3d^{10}4s^1$) is less than that of Zn($3d^{10}4s^2$) because it is easy to remove an electron from a half-filled *s*-orbital as compared to fully-filled *s*-orbital. However, in case of $\mathrm{IE_2}$, the electron is lost from $3d$-orbital of Cu and $4s$-orbital of Zn and loss of electron from $4s$-orbital is easier as compared to fully-filled $3d$-orbital

15. $\mathrm{Cu^+} = [\mathrm{Ar}]\, 3d^{10}$

No unpaired electron, thus $s = 0$. Paramagnetism of ion is also zero.

16. Magnetic moment, $\mu = \sqrt{N(N+2)}$ BM

where, N = unpaired electrons

$\mathrm{Cr}(24) = [\mathrm{Ar}]\, 3d^5, 4s^1; \quad N = 6, \mu = \sqrt{48}$ BM $= x$

$\mathrm{Mn^+} = [\mathrm{Ar}]\, 3d^5\, 4s^1; \quad N = 6, \mu = \sqrt{48}$ BM $= y$

$\mathrm{Fe^{2+}} = [\mathrm{Ar}]\, 3d^6; \quad N = 4, \mu = \sqrt{24}$ BM $= z$

Thus, $z < x = y$

17. $\mathrm{Fe^{2+}} = [\mathrm{Ar}]\, 3d^6 4s^0 \Rightarrow 4$ unpaired electrons

$\mathrm{Cu^+} = [\mathrm{Ar}]\, 3d^{10} 4s^0 \Rightarrow 0$ unpaired electron

$\mathrm{Zn} = [\mathrm{Ar}]\, 3d^{10} 4s^2 \Rightarrow 0$ unpaired electron

$\mathrm{Ni^{3+}} = [\mathrm{Ar}]\, 3d^7 4s^0 \Rightarrow 3$ unpaired electrons

18. $\mathrm{Ti^{3+}} \longrightarrow 3d^1, 4s^0$

$\mathrm{Sc^{3+}} \longrightarrow 3d^0$

$\mathrm{Mn^{2+}} \longrightarrow 3d^5, 4s^0$

$\mathrm{Zn^{2+}} \longrightarrow 3d^{10}, 4s^0$

In $\mathrm{Mn^{2+}}$ number of unpaired electrons = 5. So, it has maximum magnetic moment, i.e. 5.91 BM, according to the formula

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

20. Oxidation number of Mn in $\mathrm{MnO_4^-} = +7$

So, it should have [Ar] configuration and it should be colourless and diamagnetic.

But one electron is transferred to Mn from oxygen and thus Mn in $\mathrm{MnO_4^-}$ has one unpaired electron making it paramagnetic.

Magnetic moment $= \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3}$ BM

21. Mn in $\mathrm{KMnO_4}$ has + 7 oxidation state. Its general electronic configuration is $3d^5 4s^2$. In + 7 state Mn does not have any unpaired electron and hence, it will be diamagnetic.

22. The electronic configuration of

$\mathrm{V^{3+}} \rightarrow 3d^2,$

$\mathrm{Cr^{3+}} \rightarrow 3d^3,$

$\mathrm{Fe^{3+}} \rightarrow 3d^4,$

$\mathrm{Co^{3+}} \rightarrow 3d^7$

So, maximum number of unpaired electrons are present in $\mathrm{Fe^{3+}}$ and hence it will have largest magnetic moment.

23. For $\mathrm{Cr^{3+}}$ $n = 3, \mu = \sqrt{15}$

$\mathrm{Fe^{2+}}$ $n = 4, \mu = \sqrt{24}$

$\mathrm{Ni^{2+}}$ $n = 2, \mu = \sqrt{8}$

$\mathrm{Mn^{2+}}$ $n = 5, \mu = \sqrt{35}$

24. $\mathrm{VO_2 + 2H^+ \longrightarrow VO^{2+} + H_2O}$

25. $\mathrm{MnO_2}$ is a amphoteric oxide.

26. Transition elements are more metallic than representative elements due to the availability of *d*-orbitals for bonding.

27. Strength of metallic bond depends upon number of unpaired electrons. As number of unpaired electrons increases, the bond strength increases. So, Cr, Mo, W show stronger bonding due to maximum number of unpaired electrons. Thus, option (c) is correct.

28. Coinage metals (Cu, Ag, Au) shows the properties of transition elements as in their common oxidation states they possess partially filled *d*-subshells.

29. Gun metal is $\mathrm{Cu} + Zn + Sn$ alloy.

30. Transition metals are quite similar in atomic size. Therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture, solution of two or more transition metals, i.e. smooth solid alloy, is formed.

31. The ability of transition elements to adopt multiple oxidation states and complexing ascribed their catalytic activity.

32. Actually, melting point of Tc is lower than that of Mo as Mo contains maximum number of unpaired electrons. Tc has configuration $4d^5 5s^2$ while Mo has configuration $4d^5 5s^1$ (6 unpaired e^-).

33. The reactivity depends upon the electronegativity value of halogens, i.e. greater the electronegativity of halogens more will be the reactivity.

34. Variable valency is due to the participation of electron from $(n-1)d$ and ns levels in bond formation.

35. The correct order for (b) shall be : $Hg_2^{2+} > Cd_2^{2+} > Zn_2^{2+}$.

Due to ineffective shielding of $4f$ electrons, bond strength is maximum for Hg_2^{2+}.

In (c) along $3d$-series size decreases due to increase in Z_{eff}.

Option (d) is correct. Due to ability of oxygen to form $(p\pi - d\pi)$ multiple bonds.

36. Potassium dichromate on heating gives oxygen and chromic oxide (Cr_2O_3).

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

37. $K_2Cr_2O_7 + 2H_2SO_4 \xrightarrow{\text{Cold}} 2CrO_3 + 2KHSO_4 + H_2O$

CrO_3 is highly acidic and oxidising. It is called chromic acid.

38. $4NaCl + \underset{\text{(Conc.)}}{3H_2SO_4} + K_2Cr_2O_7 \longrightarrow \underset{\text{Chromyl chloride}}{2CrO_2Cl_2} + K_2SO_4$

$+ 2Na_2SO_4 + 3H_2O$

39. $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$ $\quad pH > 7 (x > 7)$

$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ $\quad pH < 7 (y < 7)$

40. $CrO_3 + H_2O \longrightarrow \underset{(A)}{H_2CrO_4} \xrightarrow{OH^-} \underset{(B)}{CrO_4^{2-}}$

41. Cr $(Z = 24)$

$[Ar]\, 4s^1\, 3d^5$ Cr shows common oxidation states starting from +2 to + 6.

42. $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

43. $CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$

44. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + Cr_2O_3 + 4\,H_2O$

45. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2\uparrow + 4H_2O$

So, N_2 gas is evolved.

46. Because hydrochloric acid is oxidised to chlorine.

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

48. Black colour compound is $MnO_2(A)$.

When it is fused with KOH and KNO_3, potassium manganate (K_2MnO_4) is formed. It is indicated by its green colour.

In acidic medium, K_2MnO_4 is unstable and disproportionates

$$\underset{(A)}{MnO_2} + KOH + (KNO_3) \xrightarrow{\Delta} \underset{\text{Green colour } (B)}{K_2MnO_4}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$$

(disproportionation reaction)

51. All those inner-transition elements having +2 oxidation state, changes to +3, and act as reducing agents. While those having +4 oxidation state tend to change to +3 oxidation state and act as oxidising agents. Therefore, Np^{4+} acts as an oxidising agent.

52. Gadolinium, $Gd = 4f^7\, 5d^1\, 6s^2$

56. $Gd = [Xe]\, 4f^7 5d^1 6s^2$,

$Gd^{3+} = [Xe]\, 4f^7$ (half-filled)

57. The size of lanthanides are smaller than expected. This is associated with the filling up of $4f$-orbitals which must be filled before the $5d$-orbitals.

The electrons in f-orbitals are not effective in screening other electrons from the nuclear charge.

58. The electronic configuration of $_{62}Sm^{3+}$ is $4f^5$ and that of $_{66}Dy^{3+}$ is $4f^9$. The colour of f^n and f^{14-n} are often identical.

59. Lanthanide contraction relates to decrease in atomic as well as ionic size of M^{3+} ions.

61. $La(OH)_3$ is more basic than $Lu(OH)_3$ This is because ionic size of La^{3+} ion is more than Lu^{3+} ion.

62. Oxidation states of americium are + 3, + 4, + 5 and + 6.

63. CeI_2 is supposed to have metal excess defect due to anion vacancies and the electrons associated with anions are left behind trapped in the vacancies. Thus, CeI_2 is formulated as Ce (IV), $2I^-$, $2e^-$. Due to the presence of these trapeed electrons, the compound shows metallic lustre.

64. Zr and Hf have nearly same atomic radii due to lanthanoid contraction.

65. As a result of lanthanoid contraction, the sizes of elements of $4d$ transition series are almost similar to those of $5d$ transition series. Hence, they show similarities in properties.

66. $Ce = [Xe]\, 4f^1 5d^1 6s^2$; $Ce^{4+} = [Xe]$, $Yb = [Xe]\, 4f^{14} 6s^2$; $Yb^{2+} = [Xe]\, 4f^{14}$, $Lu = [Xe]\, 4f^{14} 5d^1 6s^2$; $Lu^{3+} = [Xe]\, 4f^{14}$. The given ions contain no unpaired electrons and therefore, all are diamagnetic.

67. Yb^{2+} has an electronic configuration of $[Xe]\, 4f^{14}$. Thus, all the electrons are paired up and hence, it is diamagnetic in nature.

68. The first few members of the lanthanons are quite reactive like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium.

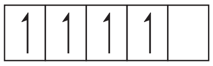
69. Tm(thulium) does not belong to actinoides.

70. Paramagnetism is shown by the positive ions of lanthanides except $La^{3+}(4f^0)$ and $Lu^{3+}(4f^{14})$. These ions are diamagnetic.

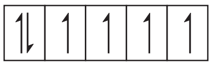
Round II

1. Cr^{2+} and Fe^{2+}

$Cr^{2+} - 3d^4$ (4 unpaired electrons)



$Fe^{2+} - 3d^6$ (4 unpaired electrons)



2. Due to lanthanide contraction, the size of M^{3+} ions (i.e. Lu^{3+}, Eu^{3+}, Yb^{3+} and Ce^{3+}) decreases and thus, the basic strength of their hydroxides decreases.

The order of size of given M^{3+} ions is

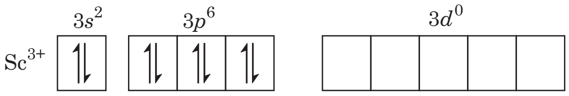
$$Ce^{3+} > Eu^{3+} > Yb^{3+} > Lu^{3+}$$

∴ The order of basic strength of their hydroxides is

$$\underset{\text{(Most basic)}}{Ce(OH)_3} > Eu(OH)_3 > Yb(OH)_3 > Lu(OH)_3$$

3. $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{Purple green}}{2K_2MnO_4} + 2H_2O$

4. $ScCl_3 \longrightarrow Sc^{3+} + 3Cl^-$



No unpaired electron, so will show diamagnetic character so, will weigh less in magnetic field.

Other have unpaired electron thus, they are paramagnetic, so they weigh less in magnetic field Fe^{3+} have 5, Ti^{3+} have 1, V^{3+} have 2 unpaired electrons.

5. Electronic configuration of M^{3+} is $[Ar]3d^1$. It is Ti which have this electronic configuration in its ionic form (Ti^{3+}).

6. Transuranic elements start after uranium and begin with Np (Neptunium).

7. Ir does not dissolve in *aqua-regia*.

8. Neodymium oxide (Nd_2O_3) dissolved in selenium oxychloride is one of the most powerful liquid lasers known so far.

9. In aqueous solution, Eu^{2+} acts like a reducing agent as it losses its electrons to get itself oxidised to more stable Eu^{3+}.

10. Al^{3+}, Cr^{3+} and Zn^{2+} are amphoteric as Al_2O_3, Cr_2O_3 and ZnO dissolve both in acid as well as alkalies.

Fe^{3+} is mainly basic as Fe_2O_3 dissolves only in acids.

11. $KMnO_4$ and $Ce(SO_4)_2$ are coloured due to charge transfer spectra.

12. In group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). (Higher oxidation state is more stable in heavier members, the opposite is true in *p*-block.) Thus, Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

13. Due to lanthanoid contraction order will be

$$Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$$

14. Basic character of oxides decreases from left to right in a period of periodic table.

15. The higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$.

The higher tendency of complex formation of MO_2^{2+} as compared to M^{3+} is due to high concentration of charge on metal atom M in MO_2^{2+}.

16. There is very small difference in energies of $5f$, $6d$ and $7s$-orbitals of actinoids, therefore their electronic configuration cannot assigned with a degree of certainty.

17. V^{2+} = 3 unpaired electrons

Cr^{2+} = 4 unpaired electrons

Mn^{2+} = 5 unpaired electrons

Fe^{2+} = 4 unpaired electrons

Hence, the order of paramagnetic behaviour should be

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

(b) Ionic size decreases from left to right in the same period.

(c) $Co^{3+}/Co^{2+} = 1.97$; $Fe^{3+}/Fe^{2+} = 0.77$;

$Cr^{3+}/Cr^{2+} = -0.41$

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

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

18. The correct reactions are as follows

(a) $Fe + \text{Dil. } H_2SO_4 \longrightarrow FeSO_4 + H_2\uparrow$

$$H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3(s) + 3SO_3\uparrow$$

The given reaction is incorrect in question.

(b) $Fe \xrightarrow{O_2} FeO$ (It could also be Fe_2O_3 or Fe_3O_4)

$$FeO + H_2SO_4 \xrightarrow{\Delta} FeSO_4 + H_2O$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

This is also a incorrect reaction.

(c) $Fe \xrightarrow[Cl_2]{\Delta} FeCl_3 \xrightarrow[\text{Air}]{\Delta} \text{No reaction}$

(It cannot give $FeCl_2$)

(d) $Fe \xrightarrow[\Delta]{O_2} Fe_3O_4 \xrightarrow[600°C]{CO} FeO \xrightarrow[700°C]{CO} Fe$

This is correct reaction.

19. $Ce = [Xe]4f^1 5d^1 6s^2$

$Ce^{4+} = [Xe]4f^0$

Ce also shows + 4 oxidation state because it has the tendency to attain noble gas configuration and $4f^0$ configuration.

20. $Co^{2+} = 3d^7, Cr^{2+} = 3d^4$ and $Cr^{3+} = 3d^3$

Co^{2+} and Cr^{3+} have same number of unpaired electrons, i.e. 3 therefore these ions have almost same spin only magnetic moment.

21. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium. But Mo (VI) in MoO_3 and W (VI) in WO_3 are not because Mo (VI) and W (VI) are more stable than Cr (VI).

Further more, in heavier members of group 6 higher oxidation states are more stable.

22. (a) $2\overset{+6}{Cr}O_4^{2-} + 2H^+ \longrightarrow \overset{+6}{Cr_2}O_7^{2-} + H_2O$

(No change in oxidation state of Cr.)

(b) $\overset{+6}{Cr_2}O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$

(Oxidation state of Cr changes from + 6 to + 3 in this reaction.)

(c) $\overset{+6}{Cr_2}O_7^{2-} + 2OH^- \longrightarrow 2\overset{+6}{Cr}O_4^{2-} + H_2O$

(No change in oxidation state of Cr)

(d) $\overset{+6}{Cr}O_2Cl_2 + 2NaOH \longrightarrow Na_2\overset{+6}{Cr}O_4 + 2HCl$

(No change in oxidation state of Cr)

26. In K_2MnO_4, the oxidation state of Mn is +6 and it is paramagnetic due to presence of unpaired e^-

$KMnO_4$ is manufactured from pyrolusite ore.

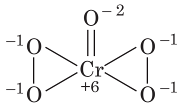
In $K_2Cr_2O_7$, the oxidation state of Cr is +6 and it is manufactured from chromite ore.

K_2CrO_4 is manufactured from chromite ore.

27. Os and Ru show maximum/highest oxidation state of + 8 Os has highest density.

Cr contains maximum number (6) of unpaired electrons. Tc is radioactive transition element.

28. Butterfly structure is shown by CrO_5.



29. TiO, Sc_2O_3, Ti_2O_3 and VO are basic oxides.

30. $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2\uparrow$

Therefore, the value of x and y is 1 and value of $x + y = 2$.

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

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

$$(2.83)^2 = n(n+2)$$

$$8 = n^2 + 2n$$

$$n^2 + 2n - 8 = 0$$

$$n^2 + 4n - 2n - 8 = 0$$

$$n(n+4) - 2(n+4) = 0$$

$$(n-2)(n+4) = 0$$

$$n = 2 \text{ or } -4.$$

But, −4 cannot be possible. Thus, the unpaired of electrons are 2.

32. $Cr_2O_7^{4-} + 16e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Electron per Cr-atom = 3.

33. V_2O_5 and Cr_2O_3 are amphoteric oxides because both reacts with alkalies as well as acids. (In lower oxides, the basic character is predominant while in higher oxides, the acidic character is predominant).

34. $3Pb(NO_3)_2 + Cr_2(SO_4)_3 \longrightarrow 3PbSO_4 + 2Cr(NO_3)_3$

35 mL 20 mL

0.15 M 0.12 M

$= 5.25$ m.mol $= 2.4$ m.

$= 5.25 \times 10^{-3}$ mol

therefore moles of $PbSO_4$ formed $= 5.25 \times 10^{-3}$

$= 525 \times 10^{-5}$

35. $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \rightarrow \underset{\substack{\text{Chromic peroxide} \\ \text{(deep blue-violet)}}}{2CrO(O_2)_2} + 5H_2O$

The value of $a + b + c + d + e = 1 + 2 + 4 + 2 + 5$

$= 14$

36.
$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$
$$\underline{2KI + H_2SO_4 + (O) \longrightarrow K_2SO_4 + I_2 + H_2O] \times 3}$$
$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

Thus, 1 mole of $K_2Cr_2O_7$ reacts with KI to give 3 moles of I_2.

37. $Fe^{3+} + 3K^+ + 3C_2O_4^{2-} \longrightarrow \underset{(A)}{K_3[Fe(C_2O_4)_3]}$

Secondary valency of Fe in 'A' is 6.

38. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$

Thus, Cr^{VI} in $Cr_2O_7^{2-}$ requires 6 e^- to undergo reduction completely to Cr^{3+} in acidic medium.

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

Thus, final oxidation state of Cr is + 3.

40. Potassium dichromate oxidises ferrous oxalate in acidic medium in following way

$$2FeC_2O_4 + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Fe^{3+} + 2Cr^{3+} + 4CO_2 + 7H_2O$$

Since, 2 moles of FeC_2O_4 are oxidised by 1 mole of $Cr_2O_7^{2-}$ therefore, 1 mole of FeC_2O_4 will be oxidised by 0.5 mole of $Cr_2O_7^{2-}$.