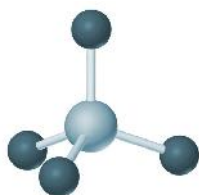


D & F BLOCK

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Chromate ion, CrO_4^{2-}



Dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$

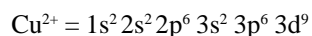
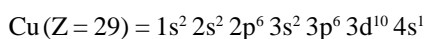
THEORY

1. INTRODUCTION

1.1 Definition

“The elements in which the last differentiating electron enters into the d-orbitals of the penultimate shell i.e. (n-1) d where n is the last shell are called d-block elements”.

A transition element may also be defined as the element which partially filled d-orbital in their ground state or most stable oxidation state.



(Cupric ion)

The properties of these elements are intermediate between the properties of s-block and p-block elements.

These elements represent a change or transition in properties from more electropositive elements (s-block) to less electropositive elements (p-block). Therefore these elements are called transition elements.

Position in the periodic table

The position of d-block element has been shown in periodic table as follows :

IA 1																	Zero 18
	IIA 2	d-block										IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	
		IIIB	IVB	VB	VIB	VII	VIII			IB	IIB						
		3	4	5	6	7	8	9	10	11	12						
		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	p-block					
		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd						
s-block		57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg						
		89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						
		f-block															

- (1) d-block elements lie in between ‘s’ and ‘p’ block elements, i.e. these elements are located in the middle of the periodic table.
- (2) d-block elements are present in,
 - 4th period (₂₁Sc to ₃₀Zn, 10 elements) → 1st Transition series.
 - 5th period (₃₉Y to ₄₈Cd, 10 elements) → 2nd Transition series.
 - 6th period (₅₁La, ₇₂Hf to ₈₀Hg, 10 elements) → 3rd Transition series.
 - 7th period (₈₉Ac, ₁₀₄Rf to ₁₁₂Uub, 10 elements) → 4th Transition series.

1.2 Electronic configuration

- (1) In d-block elements with increase in atomic number, the d-orbitals of penultimate shell i.e. (n-1) d are gradually filled by electrons. The general electronic configuration of d-block element is,

$$(n-1) d^{1-10}, ns^{0-2}.$$
- (2) Depending upon the d-orbitals of which penultimate shell i.e. n = 4, 5, 6, 7 are filled, four rows (called series) of ten elements each obtained. They correspond to 3d, 4d, 5d and 6d subshells.
- (3) Energy of ‘(n-1)d’ subshell is slightly greater than ‘ns’ subshell, hence orbital is filled first then (n - 1) d orbitals.
- (4) The general electronic configuration of d-block/d-series elements be shown as follows :

1. First (3d) Transition Series (Sc–Zn)

At. No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E.C.	$3d^1 4s^2, 3d^2 4s^2, 3d^3 4s^2, 3d^4 4s^1, 3d^5 4s^1, 3d^6 4s^2, 3d^7 4s^2, 3d^8 4s^2, 3d^9 4s^1, 3d^{10} 4s^2$									

2. Second (4d) Transition Series (Y–Cd)

At. No.	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd
E.C.	$4d^1 5s^2, 4d^2 5s^2, 4d^3 5s^1, 4d^4 5s^1, 4d^5 5s^1, 4d^6 5s^1, 4d^7 5s^1, 4d^8 5s^1, 4d^9 5s^1, 4d^{10} 5s^2$									

3. Third (5d) Transition Series (La–Hg)

At. No.	57	72	73	74	75	76	77	78	79	80
Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
E.C.	$5d^1 6s^2, 5d^2 6s^2, 5d^3 6s^2, 5d^4 6s^2, 5d^5 6s^2, 5d^6 6s^2, 5d^7 6s^2, 5d^8 6s^2, 5d^9 6s^1, 5d^{10} 6s^2$									

4. Fourth (6d) Transition Series

At. No.	89	104	105	106	107	108	109	110	111	112
Element	Ac	Ku	Ha	Sg	Bh	Hs	Mt	Uun	Uuu	Uub
	(Unh) (Uns) (Uno) (Une)									
E.C.	$6d^1 7s^2, 6d^2 7s^2, 6d^3 7s^2, 6d^4 7s^2, 6d^5 7s^2, 6d^6 7s^2, 6d^7 7s^2, 6d^8 7s^2, 6d^9 7s^1, 6d^{10} 7s^2$									

Exceptional configuration of Cr and Cu. The exceptions observed in the first series are in case of electronic configurations of chromium (Z = 24) and copper (Z = 29). It may be noted that unlike other elements, chromium and copper have a single electron in the 4s-orbital. This is due to the gain of additional stability by the atom by either having half-filled configuration (i.e., containing 5 electrons in the d-sublevel) or completely filled configuration, (i.e., containing 10 electrons in the d-sublevel). The 3d-level in case of chromium gets exactly half-filled with configuration $3d^5 4s^1$ and that in case of copper, it gets completely filled with configuration $3d^{10} 4s^1$. This can be explained on the basis of exchange energy

Thus, the electronic configuration of chromium ($Z = 24$) and copper ($Z = 29$) are $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ respectively.

1.3 Properties

1. Atomic Radii

- The atomic radii of the transition metals lie in-between those of s- and p-block elements.
- Generally the atomic radii of d-block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway.

Explanation

The atomic radius decreases with the increase in atomic number as the nuclear charge increases whereas the shielding effect of d-electron is small. After midway, as the electrons enter the last but one (penultimate) shell, the added d-electron shields (screens) the outermost electron. Hence, with the increase in the d-electrons, screening effect increases. This counterbalances the increased nuclear charge due to increase in atomic number. As a result, the atomic radii remain practically same after chromium. For example in Fe, the two opposing tendencies almost counterbalance and there is no change in the size from Mn to Fe.

- At the end of the period, there is a slight increase in the atomic radii.

Explanation

Near the end of series, the increased electron-electron repulsions between added electrons in the same orbitals are greater than the attractive forces due to the increased nuclear charge. This results in the expansion of the electron cloud and thus the atomic radius increases.

- The atomic radii increase down the group. This means that the atomic radii of second series are larger than those of first transition series. But the atomic radii of the second and third transition series are almost the same.

The atomic radii of the elements of the second and third transition metals are nearly same due to lanthanide contraction (or also called lanthanoid contraction) discussed later.

1.4 Ionic radii

- The trend followed by the ionic radii is the same as that followed by atomic radii.
- Ionic radii of transition metals are different in different oxidation states.
- The ionic radii of the transition metals are smaller than those of the representative elements belonging to the same period.

1.5 Metallic character

Except for mercury which is a liquid, all the transition elements have typical metallic structure. They exhibit all the characteristics of metals. ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Transition elements have relatively low ionization energies and have one or two electrons in their outermost energy level (ns^1 or ns^2). As a result, metallic bonds are formed. Hence, they behave as metals. Greater the number of unpaired d electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms.

1.6 Melting Point

Transition metals have high melting points which is due to their strong metallic bond. The metallic bond. The metallic bonding depends upon the number of unpaired e^- . The melting point first increases (Sc-Cr), reaches a maximum value (Cr) and then decreases (Fe-Zn)

- * Tungsten (W) has the highest melting point.
- * Mercury (Hg) has the lowest melting point.
- * Mn has the lowest melting point in 3d series typical transition elements.

1.7 Ionisation energies or Ionisation enthalpies

- The first ionisation enthalpies of d-block elements lie between s-block and p-block elements. They are higher than those of s-block elements and are lesser than those of p-block elements. The ionisation enthalpy gradually increases with increase in atomic number along a given transition series though some irregularities are observed

Explanation

- The increasing ionization enthalpies are due to increased nuclear charge with increase in atomic number which reduces the size of the atom making the removal of outer electron difficult.
- In a given series, the difference in the ionisation enthalpies between any two successive d-block elements is very much less than the difference in case of successive s-block or p-block elements.

Explanation

The addition of d electrons in last but one $[(n-1)]$ or penultimate shell with increase in atomic number provides a screening effect and thus shields the outer s electrons from inward nuclear pull. Thus, the effects of increased nuclear charge and addition of d electrons tend to oppose each other.

- The first ionization enthalpy of Zn, Cd and Hg are, however, very high because of the fully filled $(n-1) d^{10} ns^2$ configuration.
- Although second and third ionization enthalpies also, in general, increase along a period, but the magnitude of increase for the successive elements is much higher.

- (v) The high values of 3rd ionization enthalpies for Cu, Ni and Zn explain why they show a maximum oxidation state of +2.
- (vi) The first ionisation enthalpies of 5d elements are higher as compared to those of 3d and 4d elements. This is because the weak shielding of nucleus by 4f electrons in 5d elements results in greater effective nuclear charge acting on the outer valence electrons.

1.8. Oxidation state

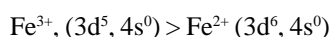
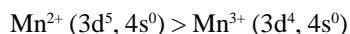
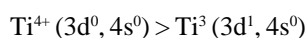
“The net numerical charge assigned to an atom of an element in its combined state is known as its Oxidation state or Oxidation number”.

- (1) With the exception of few elements, most of the d-block elements show more than one oxidation state i.e. they show variable oxidation states. The elements show variable oxidation state because of following reasons:
- (i) ‘(n-1) d’ and ‘ns’ orbitals in the atoms of d-block elements have almost same energies and therefore electron can be removed from ‘(n-1)d’ orbitals as easily as ‘s’ orbitals electrons.
- (ii) After removing ‘s’ electrons, the remainder is called Kernel of the metal cations. In d-block elements, the kernel is unstable and therefore it loses one or more electrons from (n – 1)d electrons. This results in formation of cations with different oxidation states.
- (2) All transition elements show variable oxidation state except last element in each series.
- (3) Minimum oxidation state = Total number of electrons in 4s lost. Maximum oxidation state = (Total number of electrons in 4s + number of unpaired electrons in 3d lost).

In ‘3d’ series all element contain 2 electrons in ‘4s’ and hence they all give a common minimum oxidation state of +2. (Except ‘Cr’ and ‘Cu’ where minimum oxidation state is +1.) The maximum oxidation state is given by Mn i.e. Mn^{+7} in which two electrons are removed from 4s and five unpaired electrons are removed from 3d orbitals.

- (4) The highest oxidation state is shown by Ruthenium (Ru) and Osmium (Os) i.e. +8.
- (5) Across the period oxidation state increases and it is maximum at the centre and then decreases even if atomic number increases. The element which shows highest oxidation state occur in the middle or near the middle of the series and then decreases.
- (6) Transition metals also show zero oxidation states in metal carbonyl complex. (Nickel tetracarbonyl).
Example : Ni in $Ni(CO)_4$ has zero oxidation state.
- (7) The bonding in the compounds of lower oxidation state (+2, +3) is mostly ionic and the bonding in the compounds of higher oxidation state is mostly covalent.
- (8) The relative stabilities of some oxidation states can be explained on the basis of rule extra stability, according to which d^0 , d^5 and d^{10} are stable configurations.

For example, the stability order of some ions is as follows:



- (9) Cu^{+2} is more stable than Cu^{+1} even when Cu^{+1} is $3d^{10}$ while Cu^{+2} is 3d due to high heat of hydration.

Variable oxidation states shown by 3d-series of d-block elements.

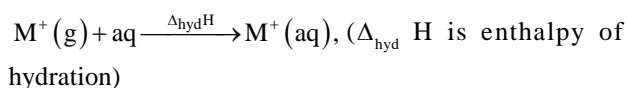
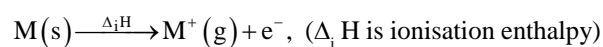
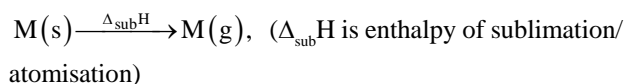
Oxidation States

ELECTRONIC CONFIGURATION	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	d^1s^2	d^2s^2	d^3s^2	d^4s^2	d^5s^2	d^6s^2	d^7s^2	d^8s^2	d^9s^2	$d^{10}s^2$
				d^5s^1					$d^{10}s^1$	
OXIDATION STATES				+1					+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
	+3	+3	+3	+3	+3	+3	+3	+3	+3	
		+4	+4	+4	+4	+4	+4	+4		
			+5	+5	+5	+5	+5			
				+6	+6	+6				
					+7					

1.9 Standard electrode potentials (E°) and chemical reactivity

Thermodynamic stability of the compounds of transition elements can be evaluated in terms of the magnitude of ionisation enthalpies of the metals — smaller the ionisation enthalpy of the metal, stabler is its compound.

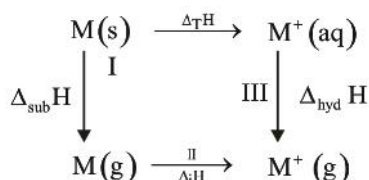
In solution, the stability of the compounds depends upon electrode potentials rather than ionization enthalpies. Electrode potential values depend upon factors such as enthalpy of sublimation (or atomisation) of the metal, the ionisation enthalpy and the hydration enthalpy, i.e.,



The total energy, $\Delta_T H$, for the process involving sublimation, ionisation and hydration simultaneously, i.e., for the process, $M(s) \longrightarrow M^+(aq) + e^-$, will be the sum of the three types of enthalpies, i.e.,

$$\Delta_T H = \Delta_{\text{sub}}H + \Delta_i H + \Delta_{\text{hyd}}H.$$

Thus, $\Delta_T H$, is the total enthalpy change when solid metal, M is brought in the aqueous medium in the form of monovalent ion, $M^+(aq)$.



Trends in the M^{2+}/M Standard Electrode Potentials

- There is no regular trend in the E° (M^{2+}/M) values. This is because their ionization enthalpies ($I_1 + IE_2$) and sublimation enthalpies do not show any regular trend.
- The general trend towards less negative E° values along the series is due to the general increase in the sum of first and second ionization enthalpies.
- Copper shows a unique behaviour in the series as it is the only metal having positive value for E° . This explains why it does not liberate H_2 gas from acids. It reacts only with the oxidizing acids (HNO_3 and H_2SO_4) which are reduced. The reason for positive E° value for copper is that the sum of enthalpies of sublimation and ionization is not balanced by hydration enthalpy.

- The values of E° for Mn, Ni and Zn are more negative than expected from the general trend. This is due to greater stability of half-filled d-subshell (d^5) in Mn^{2+} , and completely filled d-subshell (d^{10}) in Zn^{2+} . The exceptional behaviour of Ni towards E° value from the regular trend is due to its high negative enthalpy of hydration.

Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

- A very low value for E° (Sc^{3+}/Sc^{2+}) reflects the stability of Sc^{3+} ion which has a noble gas configuration.
- The highest value for Zn is on account of very high stability of Zn^{2+} ion with d^{10} configuration. It is difficult to remove an electron from it to change it into +3 state.
- The comparatively high value of E° (Mn^{3+}/Mn^{2+}) shows that Mn^{2+} is very stable which is on account of stable d^5 configuration of Mn^{2+} .
- The comparatively low value of E° (Fe^{3+}/Fe^{2+}) is on account of extra stability of Fe^{3+} (d^5), i.e., low third ionization enthalpy of Fe.
- The comparatively low value for V is on account of the stability of V^{2+} ion due to its half-filled t_{2g}^3 configuration (discussed in unit 9).

Chemical Reactivity and E° Values. The transition metals vary very widely in their chemical reactivity. Some of them are highly electropositive and dissolve in mineral acids whereas a few of them are 'noble', i.e., they do not react with simple acids. Some results of chemical reactivity of transition metals as related to their E° values are given below :

- The metals of the first transition series (except copper) are relatively more reactive than the other series. Thus, they are oxidized by H^+ ions though the actual rate is slow, e.g., Ti and V are passive to dilute non-oxidizing acids at room temperature.
- As already explained, less negative E° values for M^{2+}/M along the series indicate a decreasing tendency to form divalent cations.
- More negative E° values than expected for Mn, Ni and Zn show greater stability for Mn^{2+} , Ni^{2+} and Zn^{2+} .
- E° values for the redox couple M^{3+}/M^{2+} indicate that Mn^{3+} and Co^{3+} ions are the strongest oxidizing agents in aqueous solution whereas Ti^{2+} , V^{2+} and Cr^{2+} are strongest reducing agents and can liberate hydrogen from a dilute acid, e.g., $2 Cr^{2+}(aq) + 2 H^+(aq) \longrightarrow 2 Cr^{3+}(aq) + H_2(g)$

1.10 Catalytic Property

Most transition elements and their compounds have good catalytic properties because

- They possess variable oxidation state.

- (b) They provide a large surface area for the reactant to be absorbed.

Catalysts	Uses
$\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	Ziegler-Natta catalyst, used in polymerisation of ethylene
V_2O_5	Contact process $\text{SO}_2 \rightarrow \text{SO}_3$
Fe	Haber Bosch process
PdCl_2	Wacker's process for CH_3CHO manufacturing
Pd	Hydrogenation of alkene, alkyne etc
Pt/PtO	Adam's catalyst for selective reduction
Pt	Catalytic convertor, for cleaning car exhaust fumes
Pt/Rh	Ostwald's process : $\text{NH}_3 \rightarrow \text{NO}$
Cu	Oxidation of alcohols

1.11 Magnetic Behaviour

When a substance is placed in a magnetic field of strength H , the intensity of the magnetic field in the substance may be greater than or less than H . If the field in the substance is greater than H , the substance is a paramagnetic material and attracts line of force. If the field in the substance is less than H , the substance is diamagnetic. Diamagnetic materials tend to repel lines of force. The magnetic moment of a substance depends on the strength of magnetic field generated due to electronic spin, there is a change in electric flux which leads to induction of magnetic field. The electron is also under orbital angular momentum or orbital spin. It leads to generation of magnetic moment.

In first transition elements series the orbital angular magnetic moment is insignificant the orbital contribution is quenched by the electric fields of the surrounding atoms so magnetic moment is equal to the spin magnetic moment only.

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

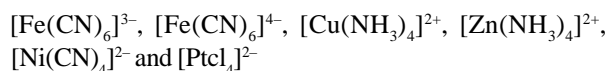
$n \rightarrow$ no. of unpaired electron.

Maximum transition elements and compounds are paramagnetic due to presence of unpaired electrons.

2. COMPLEX FORMATION

Transition metal ions form a large number of complex compounds. Complex compounds are those which have a metal ion linked to a number of negative ions (anions) or neutral molecules having lone pairs of electrons. These ions or molecules are called ligands. They donate lone pairs of electrons to the central transition metal ion forming coordinate bonds

A few examples are given below :



Such complex compounds are not formed by s - and p - block elements.

Explanation. The transition elements form complexes because of the following reasons :

- Comparatively smaller size of their metal ions.
- Their high ionic charges.
(Because of (i) and (ii), they have large charge/size ratio)
- Availability of vacant d-orbitals so that these orbitals can accept lone pairs of electrons donated by the ligands.

2.1 Interstitial Compounds

The transition metals form a large number of interstitial compounds in which small atoms such as hydrogen, carbon, boron and nitrogen occupy the empty spaces (interstitial sites) in their lattices (Fig.).

They are represented by formulae like TiC , TiH_2 , Mn_4N , Fe_3H , Fe_3C etc. However, actually they are non-stoichiometric materials, e.g., $\text{TiH}_{1.7}$, $\text{VH}_{0.56}$ etc. and the bonds present in them are neither typically ionic nor covalent. Some of their important characteristics are as follows:

- They are very hard and rigid, e.g., steel which is an interstitial compound of Fe and C is quite hard. Similarly, some borides are as hard as diamond.
- They have high melting points which are higher than those of the pure metals.
- They show conductivity like that of the pure metal.
- They acquire chemical inertness.

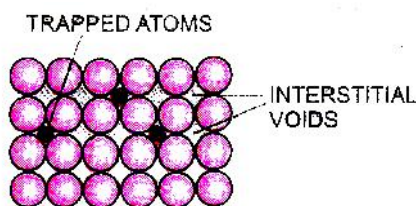
2.2 Alloy formation

Alloys are homogeneous solid solutions of two or more metals obtained by melting the components and then cooling the melt. These are formed by metals whose atomic radii differ by not more than 15% so that the atoms of one metal can easily take up the positions in the crystal lattice of the other (Fig.)

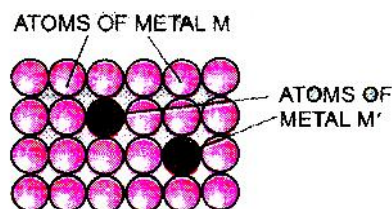
Now, as transition metals have similar atomic radii and

other characteristics, hence they form alloys very readily. Alloys are generally harder, have higher melting points and more resistant to corrosion than the individual metals.

The most commonly used are the ferrous alloys the metals chromium, vanadium, molybdenum, tungsten and manganese are used in the formation of alloy steels and stainless steels. Some alloys of transition metals with non-transition metals are also very common. e.g., brass (Cu + Zn) and bronze (Cu + Sn)



Formation of interstitial compounds.

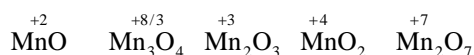


Formation of alloys.

3. COMPOUNDS OF TRANSITION ELEMENTS

3.1 Oxides

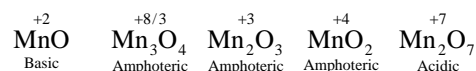
- (i) The metals of the first transition series form oxides with oxygen at high temperature.
- (ii) The oxides are formed in the oxidation, states +1 to +7 (as given in Table 8.10, page 8/14).
- (iii) The highest oxidation state in the oxides of any transition metal is equal to its group number, e.g., 7 in Mn_2O_7 . Beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Some metals in higher oxidation state stabilize by forming oxocations, e.g., V^{V} as VO_2^+ , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} .
- (iv) All the metals except scandium form the oxides with the formula MO which are ionic in nature. As the oxidation number of the metal increases, ionic character decreases, e.g., Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points.



- (v) In general, the oxides in the lower oxidation states of the metals are basic and in their higher oxidation states, they are acidic whereas in the intermediate oxidation state, the

oxides are amphoteric.

For example, the behaviour of the oxides of manganese may be represented as follows :

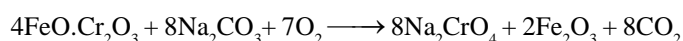


Thus, Mn_2O_7 dissolves in water to give the acid HMnO_4 .

3.2 KMnO_4 Potassium permanganate

It is prepared from the ore called chromite or ferrochrome or chrome iron, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The various steps involved are as follows :

- (i) Preparation of sodium chromate. The ore is finely powdered, mixed with sodium carbonate and quick lime and then roasted, i.e., heated to redness in a reverberatory furnace with free exposure to air when sodium chromate (yellow in colour) is formed and carbon dioxide is evolved. Quick lime keeps the mass porous and thus facilitates oxidation.



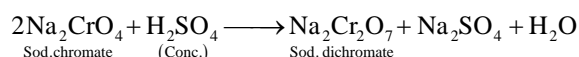
Chromite ore

Sod. chromate

Ferric oxide

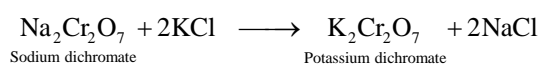
After the reaction, the roasted mass is extracted with water when sodium chromate is completely dissolved while ferric oxide is left behind. Ferric oxide is separated out by filtration.

- (ii) Conversion of sodium chromate into sodium dichromate. The filtrate containing sodium chromate solution is treated with concentrated sulphuric acid when sodium chromate is converted into sodium dichromate.



Sodium sulphate being less soluble crystallizes out as decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and is removed. The clear solution is then evaporated in iron pans to a specific gravity of 1.7 when a further crop of sodium sulphate is formed. It is removed and the solution is cooled when orange crystals of sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ separate on standing.

(iii) Conversion sodium dichromate into potassium dichromate. Hot concentrated solution of sodium dichromate is treated with calculated amount of potassium chloride when potassium dichromate, being much less soluble than sodium salt, crystallizes out on cooling as orange crystals.

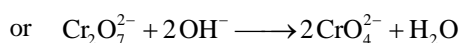
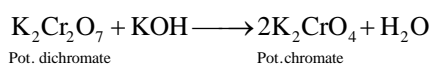


3.3 Properties

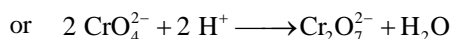
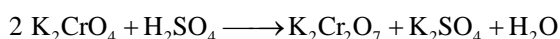
- Colour and Melting point.** It forms orange crystals which melt at 669 K.
- Solubility.** It is moderately soluble in cold water but freely soluble in hot water.
- Action of heat.** When heated to a white heat, it decomposes with the evolution of oxygen.



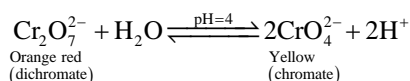
- Action of alkalis.** When an alkali is added to an orange red solution of dichromate, a yellow solution results due to the formation of chromate.



On acidifying, the colour again changes to orange red due to the reformation of dichromate.



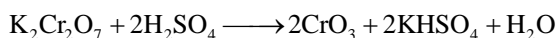
This interconversion is explained by the fact that in dichromate solution, the $\text{Cr}_2\text{O}_7^{2-}$ ions are invariably in equilibrium with CrO_4^{2-} ions at pH = 4, i.e.,



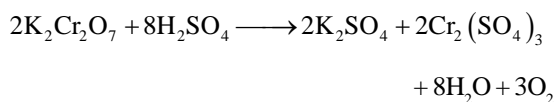
On adding an alkali (i.e., increasing the pH of the solution), the H^+ ions are used up and according to the law of chemical equilibrium, the reaction proceeds in the forward direction producing yellow chromate solution. On the other hand, when an acid is added (i.e., pH of the solution is decreased), the concentration of H^+ ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

5. Action of concentrated sulphuric acid

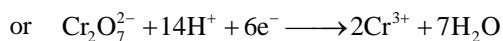
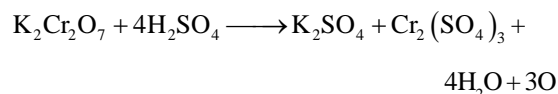
(a) In cold, red crystals of chromic anhydride (chromium trioxide) are formed.



(b) On heating the mixture, oxygen is evolved.

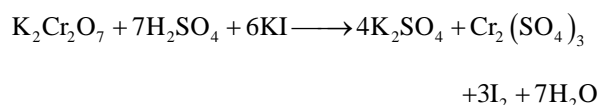


- Oxidising properties.** It is a powerful oxidising agent. In the presence of dilute sulphuric acid, one molecule of potassium dichromate furnishes 3 atoms of available oxygen as indicated by the equation :

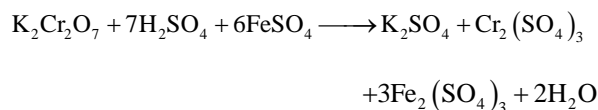


$$\therefore \text{Eq. wt. of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Mol. wt.}}{6} = \frac{294}{6} = 49$$

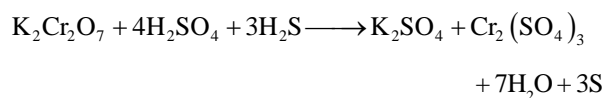
- It liberates I_2 from KI



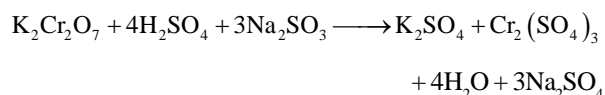
- It oxidises ferrous salts to ferric salts



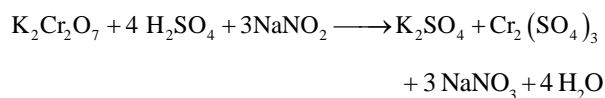
- It oxidises H_2S to sulphur



- It oxidises sulphites to sulphates and thiosulphates to sulphates and sulphur



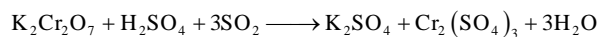
- It oxidises nitrites to nitrates



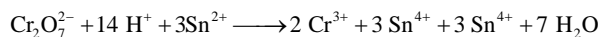
- It oxidises halogen acids to halogen



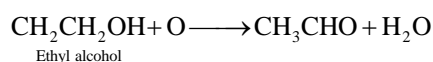
- It oxidises SO_2 to sulphuric acid

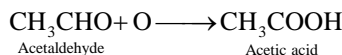


- It oxidises stannous salts to stannic salts



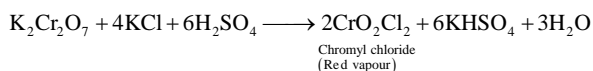
- It oxidises ethyl alcohol to acetaldehyde and acetic acid.



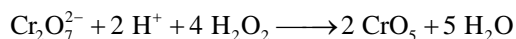


Test for a drunken driver. The above reaction helps to test whether a driver has consumed alcohol or not. he is asked to breathe into the acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution taken in a test tube. If the orange colour of the solution changes into green colour (due to $\text{Cr}_2(\text{SO}_4)_3$ formed in the reaction), the driver is drunk, otherwise not.

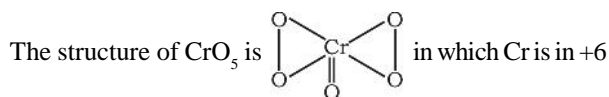
7. **Chromyl chloride test** (Reaction with a chloride and conc. sulphuric acid). When heated with concentrated hydrochloric acid or with a chloride and strong sulphuric acid, reddish brown vapours of chromyl chloride are obtained.



8. **Reaction with hydrogen peroxide.** Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of peroxo compound, $\text{CrO}(\text{O}_2)_2$.



The blue colour fades away gradually due to the decomposition of $\text{CrO}(\text{O}_2)_2$ into Cr^{3+} ions and oxygen.



oxidation state.

Uses.

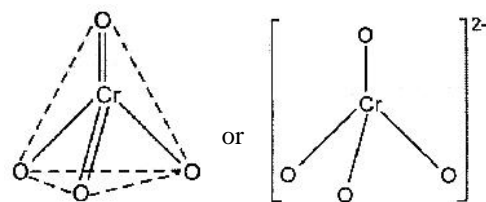
- (i) In volumetric analysis, it is used as a primary standard for the estimation of Fe^{2+} (ferrous ions) and I^- (iodides) in redox titrations.

Note

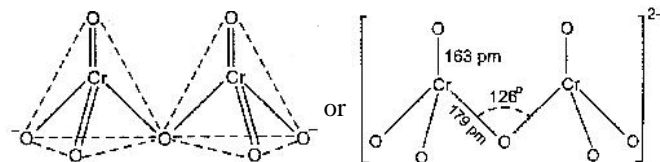
$\text{Na}_2\text{Cr}_2\text{O}_7$ is not used in volumetric analysis because it is deliquescent.

- (ii) In industry, it is used
- In chrome tanning in leather industry.
 - In the preparation of chrome alum $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ and other industrially important compounds such as Cr_2O_3 , CrO_3 , CrO_2Cl_2 , K_2CrO_4 , CrCl_3 etc.
 - In calico printing and dyeing.
 - In photography and in hardening gelatine film.
- (iii) In organic chemistry, it is used as an oxidising agent.

Structures of chromate and dichromate ions.



a Chromate ion-Tetrahedral structure



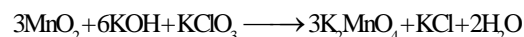
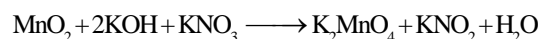
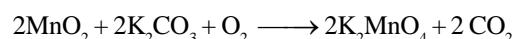
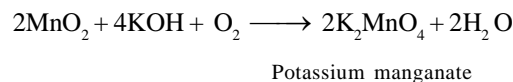
b Dichromate ion-Two tetrahedra sharing one oxygen atom at one corner

3.4 Potassium Permanganate (KMnO_4)

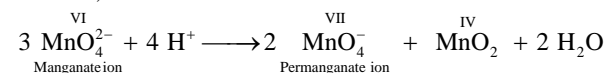
Preparation

On a large scale, it is prepared from the mineral, pyrolusite, MnO_2 . The preparation involves the following two steps:

- (i) Conversion of MnO_2 into potassium manganate. The finely powdered pyrolusite mineral is fused with potassium hydroxide or potassium carbonate in the presence of air or oxidising agent such as potassium nitrate or potassium chlorate when green coloured potassium manganate is formed.

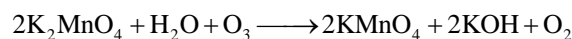
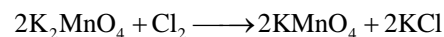


Potassium manganate thus formed undergoes disproportionation in the neutral or acidic solution as follows, if allowed to stand for some time :



- (ii) Oxidation of potassium manganate to potassium permanganate.

(a) Chemical oxidation. The fused mass is extracted with water and the solution after filtration is converted into potassium permanganate by bubbling carbon dioxide, chlorine or ozonised oxygen through the green solution.



The carbon dioxide process is uneconomical as one third of the original manganate is reconverted to manganese

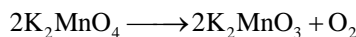
dioxide. However, this process has the advantage that the potassium carbonate formed as a by-product can be used for the oxidative fusion of manganese dioxide. In the chlorine process, potassium chloride obtained as a by-product is lost.

PROPERTIES

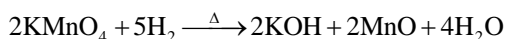
- 1. Colour.** Potassium permanganate exists as deep purple black prisms with a greenish lustre which become dull in air due to superficial reduction.
- 2. Solubility.** It is moderately soluble in water at room temperature and it is more soluble in hot water.
- 3. Action of heat.** When heated to 513 K, it readily decomposes giving oxygen.



At red heat, potassium manganate formed decomposes into potassium manganite (K_2MnO_3) and oxygen.

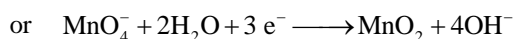
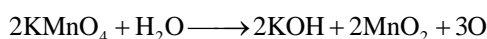


- 4. Action of heat in current of hydrogen.** When heated in a current of H_2 , solid KMnO_4 gives KOH , MnO and water vapours.



- 5. Oxidising property.** Potassium permanganate is powerful oxidising agent. The actual course of reaction depends on the use of the permanganate in (a) neutral (b) alkaline or (c) acidic solution.

- (a) **In neutral solution.** Potassium permanganate acts as a moderate oxidising agent in neutral aqueous solution because of the reaction :

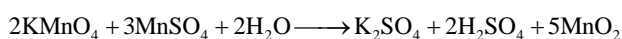


Thus, MnO_4^- ion gains 3 electrons. Also, according to the above equation, in neutral medium, from two moles of permanganate, three oxygen atoms are available. In fact, during the course of reaction, the alkali generated renders the medium alkaline even when we start with neutral solutions. Hence, Eq. wt. of KMnO_4 in neutral or weakly alkaline medium

$$= \frac{\text{Mol. wt.}}{3} = \frac{158}{3} = 52.67$$

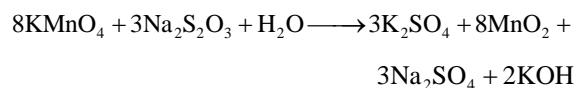
Some oxidizing properties of KMnO_4 in the neutral medium. These are given below :

- (i) It oxidises hot manganous sulphate to manganese dioxide.



Presence of ZnSO_4 or ZnO catalyses the oxidation.

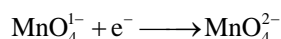
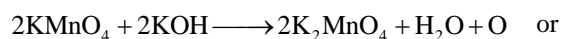
- (ii) It oxidises sodium thiosulphate to sodium sulphate.



- (iii) It oxidises hydrogen sulphide to sulphur.

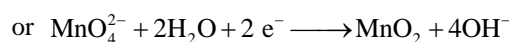
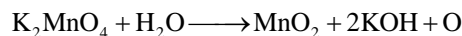


- (b) **In alkaline solution.** In strongly alkaline solution, MnO_4^{2-} (manganate) ion is produced.

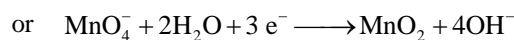
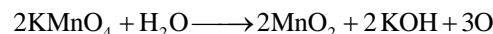


$$\therefore \text{Eq. wt. of } \text{KMnO}_4 = \frac{\text{Mol. wt.}}{1} = \frac{158}{1} = 158$$

Potassium manganate is also further reduced to MnO_2 when a reducing agent is present.



So the complete reaction is :

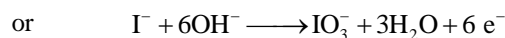
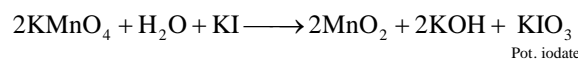


which is the same as that for neutral medium. Hence, equivalent weight of KMnO_4 in weakly alkaline medium is same as that in the neutral medium, viz., 52.67

Some oxidizing properties of KMnO_4 in the alkaline medium.

These are given below :

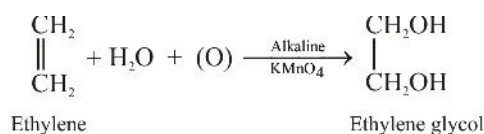
- (i) It oxidises potassium iodide to potassium iodate.



In this case, iodine is not liberated unlike the case of acidic medium.

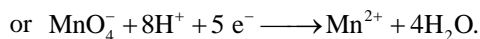
Similar reaction takes place with KBr .

- (ii) It oxidises olefinic compounds to glycols, i.e., when an olefinic compound is shaken with alkaline KMnO_4 , pink colour of KMnO_4 is discharged.



Alkaline KMnO_4 used for this test is known as Baeyer's reagent. It is used for oxidation of a number of organic compounds.

- (c) **In acidic medium.** Potassium permanganate in the presence of dil. sulphuric acid, i.e., in acidic medium, acts as a strong oxidising agent because of the reaction



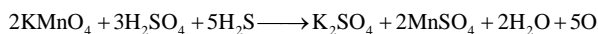
Since in the above reaction, MnO_4^- ion gains 5 electrons of five atoms of oxygen are available from two molecules of KMnO_4 . Hence.

$$\text{Eq. wt. of } \text{KMnO}_4 = \frac{\text{Mol. wt.}}{5} = \frac{158}{5} = 31.6$$

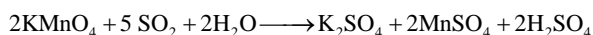
Some oxidizing properties of KMnO_4 in the acidic medium.

These are given below :

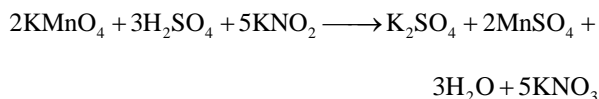
- (i) It oxidises H_2S to S .



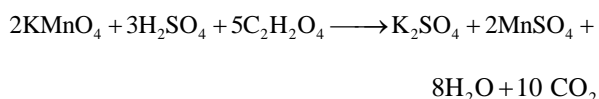
- (ii) It oxidises sulphur dioxide to sulphuric acid.



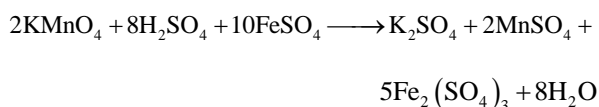
- (iii) It oxidises nitrites (NO_2^-) to nitrates (NO_3^-), arsenites (AsO_3^{3-}) to arsenates (AsO_4^{3-}) and sulphites and thiosulphates to sulphates.



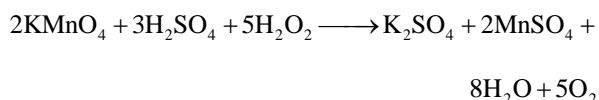
- (iv) It oxidises oxalates or oxalic acid to CO_2



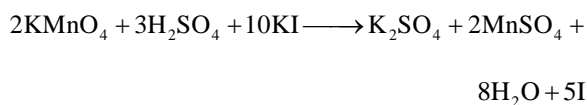
- (v) It oxidises ferrous sulphate to ferric sulphate (i.e., ferrous salt to ferric salt).



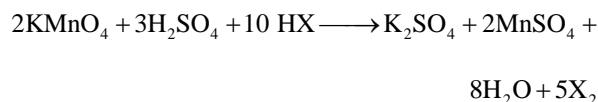
- (vi) It oxidises H_2O_2 to H_2O and O_2 . This is because acidified KMnO_4 is a stronger oxidising agent than H_2O_2 .



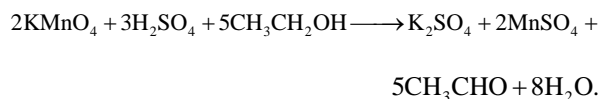
- (vii) It oxidises potassium iodide to iodine



- (viii) It oxidises HX (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) to X_2



- (ix) It oxidises ethyl alcohol to acetaldehyde



Uses.

- (i) It is often used in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and hydrogen peroxide. However, it is not a primary standard because it is difficult to obtain it in the pure state and free from traces of MnO_2 . It is, therefore, always first standardised with a standard solution of oxalic acid.

Remember that volumetric titrations involving KMnO_4 are carried out only in presence of dilute H_2SO_4 but not in the presence of HCl or HNO_3 . This is because oxygen produced from $\text{KMnO}_4 + \text{dill. H}_2\text{SO}_4$ is used only for oxidizing the reducing agent. Moreover, H_2SO_4 does not give any oxygen of its own to oxidize the reducing agent. In case HCl is used, the oxygen produced from $\text{KMnO}_4 + \text{HCl}$ is partly used up to oxidize HCl to chlorine and in case HNO_3 is used, it itself acts as oxidizing agent and partly oxidizes the reducing agent.

- (ii) It is used as a strong oxidising agent in the laboratory as well as in industry. It is a favourite and effective oxidising agent used in organic synthesis. Alkaline potassium permanganate is used for testing unsaturation in organic chemistry and is known as Baeyer's reagent.

- (iii) Potassium permanganate is also widely used as a disinfectant and germicide. A very dilute solution of permanganate is used for washing wounds and gargling for mouth sore. It is also used for purifying water of stinking wells.

- (iv) Because of its strong oxidizing power, it is also used for bleaching of wool, cotton, silk and other textile fibres and also for decolourisation of oils.

THE LANTHANIDE SERIES

1. INTRODUCTION

These elements are classified by the filling up of the antipenultimate 4f energy levels.

2. PHYSICAL PROPERTIES

Electronic Configuration and oxidation states

Element		Electronic Configuration	Electronic Configuration of M^{3+}	Oxidation States
Lanthanum	La	[Xe] 5d ¹ 6s ²	[Xe]	+3
Cerium	Ce	[Xe] 4f ¹ 5d ¹ 6s ²	[Xe] 4f ¹	+3 (+4)
Praseodymium	Pr	[Xe] 4f ³ 6s ²	[Xe] 4f ²	+3 (+4)
Neodymium	Nd	[Xe] 4f ⁴ 6s ²	[Xe] 4f ³	(+2) +3
Promethium	Pm	[Xe] 4f ⁵ 6s ²	[Xe] 4f ⁴	(+2) +3
Samarium	Sm	[Xe] 4f ⁶ 6s ²	[Xe] 4f ⁵	(+2) +3
Europium	Eu	[Xe] 4f ⁷ 6s ²	[Xe] 4f ⁶	(+2) +3
Gadolinium	Gd	[Xe] 4f ⁷ 5d ¹ 6s ²	[Xe] 4f ⁷	+3
Terbium	Tb	[Xe] 4f ⁹ 6s ²	[Xe] 4f ⁸	+3 (+4)
Dysprosium	Dy	[Xe] 4f ¹⁰ 6s ²	[Xe] 4f ⁹	+3 (+4)
Holmium	Ho	[Xe] 4f ¹¹ 6s ²	[Xe] 4f ¹⁰	+3
Erbium	Er	[Xe] 4f ¹² 6s ²	[Xe] 4f ¹¹	+3
Thulium	Tm	[Xe] 4f ¹³ 6s ²	[Xe] 4f ¹²	(+2) +3
Ytterbium	Yb	[Xe] 4f ¹⁴ 6s ²	[Xe] 4f ¹³	(+2) +3
Lutetium	Lu	[Xe] 4f ¹⁴ 5d ¹ 6s ²	[Xe] 4f ¹⁴	+3

2.1 Oxidation state

The sum of the first three ionization energies for each element are low. Thus the oxidation state (+III) is ionic and Ln^{3+} dominates the chemistry of these elements. The Ln^{2+} and Ln^{4+} ions that do occur are always less stable than Ln^{3+} .

Oxidation numbers (+II) and (+IV) do occur, particularly when they lead to :

1. a noble gas configuration e.g. Ce^{4+} (f^0)
2. a half filled f shell, e.g. Eu^{2+} and Tb^{4+} (f^7)
3. a completely filled f level, e.g. Yb^{2+} (f^{14}).

NOTE

The 4f electrons in the antipenultimate shell are very effectively shielded from their chemical environment outside the atom by the 5s and 5p electrons. Consequently the 4f electrons do not take part in bonding. They are neither removed to produce ions nor do they take any significant part in crystal field stabilization or complexes. Crystal field stabilization is very important with the d-block elements. The octahedral splitting of f orbitals Δ_o is⁻¹. Whether the f orbitals are filled or empty has little effect on the normal chemical properties. However, it does affect their spectra and their magnetic properties.

2.2 Atomic radius

In lanthanide series, with increasing atomic number, there is a progressive decrease in the atomic as well as ionic radii of trivalent ions from La^{3+} to Lu^{3+} . This regular decrease in the atomic and ionic radii with increasing atomic number is known as lanthanide contraction.

Atomic and Ionic radii (pm) of lanthanum and lanthanoids.

Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic Radii (Ln)	187	183	182	181	181	180	199	180	178	177	176	175	174	173	172
Ionic Radii (Ln^{3+})	106	103	101	99	98	96	95	94	92	91	90	89	88	87	86

2.3 Magnetic behaviour

Paramagnetism is shown by the positive ions of lanthanides except La^{3+} (lanthanum ion, f^0) and Lu^{3+} (lutetium ion, f^{14}). This property of the lanthanides is due to presence of unpaired electrons in the incomplete 4f subshell.

lanthanides differ from transition elements in the fact that their magnetic moments do not obey 'spin only' formula,

viz., $\mu_{\text{eff}} = \sqrt{n(n+2)}$ B.M. where n is the number of unpaired electrons. This because in case of transition elements, the orbital contribution is quenched by the electric field of the environment but in case of lanthanides, 4f orbitals lie too deep to be quenched. Hence, their magnetic moment is

As we move along the lanthanide series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (viz., 4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these f-orbitals. This imperfect shielding is unable to counterbalance the effect of the increased nuclear charge. Hence, the net result is a contraction in the size though the decrease is very small. It is interesting to note that in lanthanides, the decrease in the atomic radius for 14 elements [Ce (58) to Lu (71)] is only 11 pm (from 183 to 172 pm). Similarly, decrease in ionic radii from Ce^{3+} to Lu^{3+} is only 17 pm (103 to 86 pm).

The contraction is similar to that observed in any transition series. The cause is also similar, just as in the transition series where the contraction is due to imperfect shielding of one d electron by another. But the shielding of one 4f electron by another is less than one d electron by another with increase in nuclear charge along the series.

calculated by considering spin as well as orbital contribution, i.e.,

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

where S is spin quantum number and L is orbital quantum number.

NOTE

Separation of the Lanthanide Elements

Since the change in ionic radius is very small, the chemical properties are similar. This makes the separation of the element in pure state difficult. Separation is done by Ion Exchange methods which is based on the ionic size.

2.4 Colour

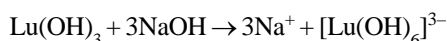
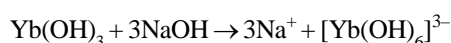
The Lanthanides are silvery white metals. However, most of the trivalent metal ions are coloured, both in the solid state and in aqueous solution. This is due to the partly filled-f-orbitals which permit f-f transition.

NOTE

Lanthanides ions with x f electrons have a similar colour to those with (14-x) f electrons e.g., La^{3+} and Lu^{3+} are colourless, Sm^{3+} and Dy^{3+} are yellow and Eu^{3+} and Tb^{3+} are pink.

2.5 Hydroxides

The hydroxides $\text{Ln}(\text{OH})_3$ are precipitated as gelatinous precipitates by the addition of NH_4OH to aqueous solutions. These hydroxides are ionic and basic. They are less basic than $\text{Ca}(\text{OH})_2$ but more basic than $\text{Al}(\text{OH})_3$ which is amphoteric. The metals, oxides and hydroxides all dissolve in dilute acids, forming salts. $\text{Ln}(\text{OH})_3$ are sufficiently basic to absorb CO_2 from the air and form carbonates. The basicity decreases as the ionic radius decreases from Ce to Lu. Thus $\text{Ce}(\text{OH})_3$ is the most basic, and $\text{Lu}(\text{OH})_3$, which is the least basic, is intermediate between Scandium and Yttrium in basic strength. The decrease in basic properties is illustrated by the hydroxides of the later elements dissolving in hot concentrated NaOH , forming complexes.



ACTINIDES SERIES

The elements and their Oxidation States

Atomic	Element	Symbol	Outer electronic structure	Oxidation states*
89	Actinium	Ac	$6d^1 7s^2$	+3
90	Thorium	Th	$6d^2 7s^2$	+3, +4
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	+3, +4, +5
92	Uranium	U	$5f^3 6d^1 7s^2$	+3, +4, +5, +6

93	Neptunium	Np	$5f^4 6d^1 7s^2$	+3, +4, +5, +6, +7
94	Plutonium	Pu	$5f^6 7s^2$	+3, +4, +5, +6, +7
95	Americium	Am	$5f^7 7s^2$	+2, +3, +4, +5, +6
96	Curium	Cm	$5f^7 6d^1 7s^2$	+3, +4
97	Berkelium	Bk	$5f^9 7s^2$	+3, +4
98	Californium	Cf	$5f^{10} 7s^2$	+2, +3
99	Einsteinium	Es	$5f^{11} 7s^2$	+2, +3
100	Fermium	Fm	$5f^{12} 7s^2$	+2, +3
101	Mendelevium	Md	$5f^{13} 7s^2$	+2, +3
102	Nobelium	No	$5f^{14} 7s^2$	+2, +3
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	+3
104	Rutherfordium	Rf	$4f^{14} 6d^2 7s^2$	

1. OXIDATION STATE

Unlike Lanthanides, Actinides show a large number of oxidation states. This is because of very small energy gap between 5f, 6d and 7s subshells. Hence, all their electrons can take part in bond formation. The dominant oxidation state of these element is +3 (similar to Lanthanides). Besides +3 state, Actinides also exhibit an oxidation state of +4. Some Actinides show still higher oxidation states. The maximum oxidation state first increases upto the middle of the series and then decreases, e.g., it increases from +4 from Th to +5, +6, and +7 for Pa, U and Np but decreases in the succeeding elements.

The Actinides resemble Lanthanides in having more compounds in +3 state than in the +4 state. However, the compounds in the +3 and +4 state tend to undergo hydrolysis.

Further, it may be noted that in case of Actinides, the distribution of oxidation states is so uneven that it is of no use to discuss their chemistry in terms of their oxidation states.

2. ATOMIC RADIUS

The Actinides show Actinide contraction (very much like Lanthanide contraction) due to poor shielding effect of the 5f-electrons. As a result, the radii of the atoms or ions of these metals decrease regularly across the series. The contraction is greater from element to element in this series due to poorer shielding by 5f electrons. This is because 5f orbitals extend in space beyond 6s and 6p orbitals whereas 4f orbitals are buried deep inside the atom.

3. MAGNETIC BEHAVIOUR

Like Lanthanides, the Actinides elements are strongly paramagnetic. The variation in magnetic susceptibility of Actinides with the increasing number of unpaired electrons is similar to that of Lanthanides but the values are higher for the Actinides than the Lanthanides.

4. COLOUR

These metals are silvery white. However, Actinide cations are generally coloured. The colour of the cation depends upon the number of 5f-electrons. The cations containing no 5f-electron or having seven 5f-electrons (i.e., exactly half-filled f-subshell) are colourless. The cations containing 2 to 6 electrons in the 5f-subshell are coloured both in the crystalline state as well as in aqueous solution. The colour arises due to f-f transition e.g. Ac^{3+} (5f⁰) = colourless, U^{3+} (5f³) = Red, Np^{3+} (5f⁴) = Blue, Pu^{3+} (5f⁵) = Violet, Am^{3+} (5f⁶) = Pink, Cm^{3+} (5f⁷) = Colourless, Th^{3+} (5f⁰) = Colourless as so on.

COMPARISON OF LANTHANIDES AND ACTINIDES

Similarities :

As both Lanthanides and actinides involve filling of f-orbitals, they show similarities in many respects as follows :

- (i) Both show mainly an oxidation state of +3.
- (ii) Both are electropositive and very reactive.
- (iii) Both exhibit magnetic and spectral properties.
- (iv) Actinides exhibit Actinide contraction like Lanthanide contraction shown by Lanthanides.

Differences :

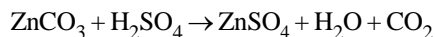
The show differences in some of their characteristics as follows :

Lanthanides	Actinides
(i) Besides + 3 oxidation state they show + 2 and +4 oxidation states only in few cases.	(i) Besides +3 oxidation state, they show higher oxidation states of +4, +5, +6, + 7 also.
(ii) Most of their ions are colourless	(ii) Most of their ions are coloured
(iii) They have less tendency towards complex formation	(iii) They have greater tendency towards complex formation.
(iv) Lanthanides compounds are less basic.	(iv) Actinides compounds are more basic
(v) Do not form oxocation	(v) Form oxocations e.g. UO_2^{2+} , PuO_2^{2+} and UO^+
(vi) Except promethium, they are non-radioactive	(vi) They are radioactive.
(vii) Their magnetic properties can be explained easily.	(vii) Their magnetic properties cannot be explained easily, as they are more complex.

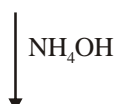
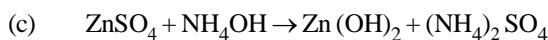
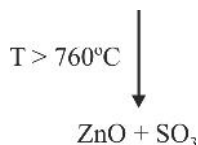
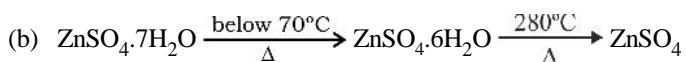
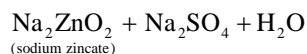
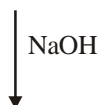
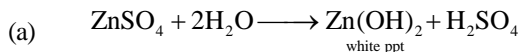
IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

1. ZINC SULPHATE (ZnSO₄ · 7H₂O - WHITE VITRIOL)

I PREPARATION:



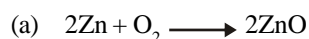
II REACTIONS:



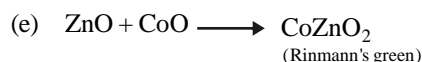
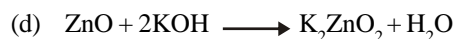
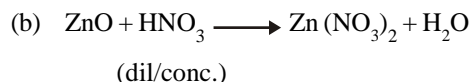
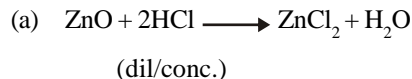
2. ZINC OXIDE, ZNO (CHINESE WHITE OR PHILOSPHER'S WOOL)

It found in nature as zincite or red zinc ore.

I PREPARATION:



II REACTIONS:



III USES:

- (i) As a white paint (It does not get tranished even in presence of H₂S because Zns is also white)
- (ii) For preparing Rinmann's green (Green Paint)
- (iii) As catalyst for preparation of methyl alcohol
- (iv) For making soft rubber
- (v) For making cosmetic powders, creams and in medicine

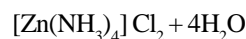
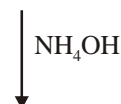
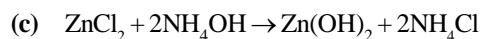
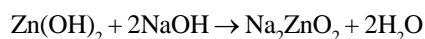
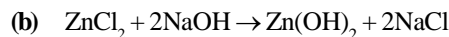
3. ZINC CHLORIDE ZnCl₂ · 2H₂O

Anhydride of zinc chloride cannot be obtained by heating its aqueous salt.

I PREPARATION:

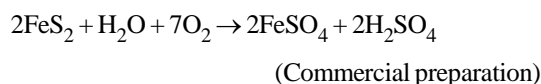
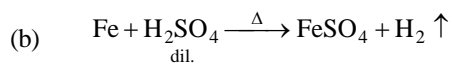
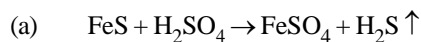


II PROPERTIES:

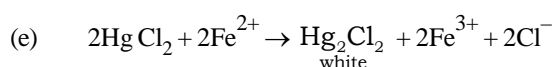
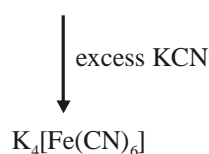
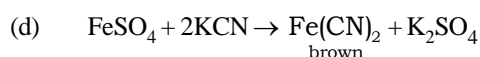
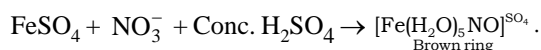
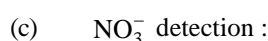
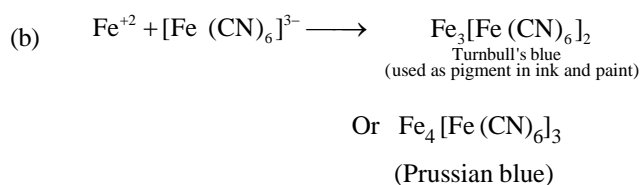
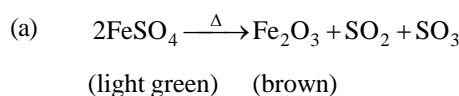


4. FERROUS SULPHATE ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - GREEN VITRIOL)

I PREPARATION:



II REACTIONS:

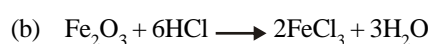
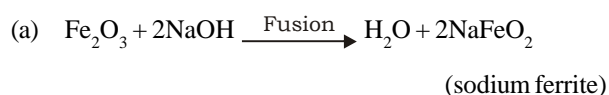


5. FERRIC OXIDE, Fe_2O_3

I PREPARATION:



II REACTIONS:



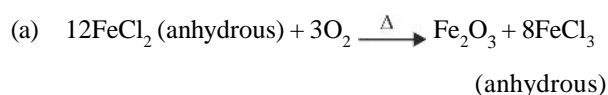
III USES:

- (i) As a red pigment
- (ii) As abrasive polishing powder
- (iii) As catalyst

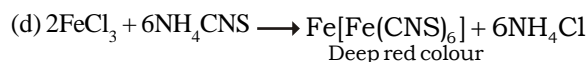
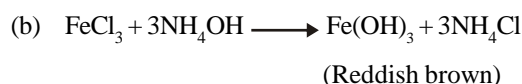
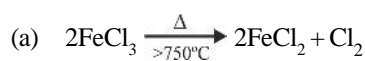
6. FERRIC CHLORIDE, FeCl_3

It is known in anhydrous and hydrated form. It is a red deliquescent solid.

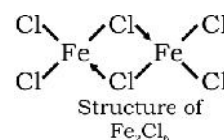
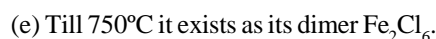
I PREPARATION:



II REACTIONS:



Deep red colouration is produced due to formation of complex.

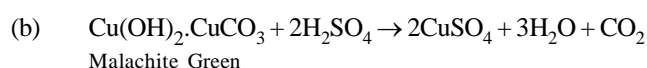
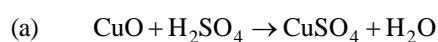


III USES:

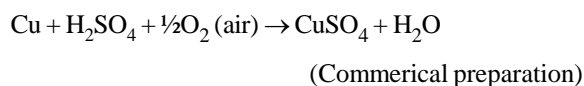
- (i) Its alcoholic solution is medicine, name (Tincture ferri perchloride)
- (ii) For detection of acetates and phenols
- (iii) For making prussian blue & as an oxidising agent

7. COPPER SULPHATE ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ - BLUE VITRIOL)

I PREPARATION:

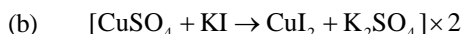
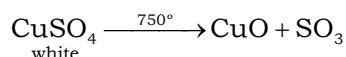
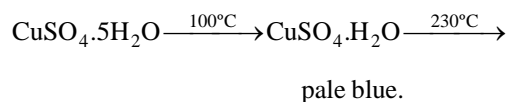


Copper scrape

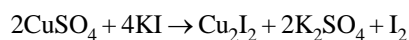
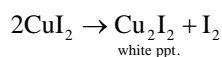


II REACTIONS:

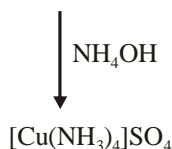
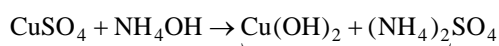
(a) Effect of heat



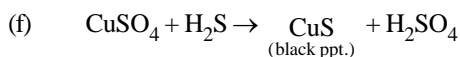
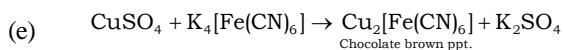
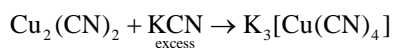
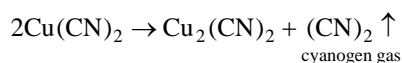
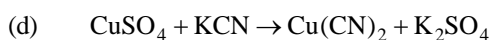
(Unstable
dirty white)



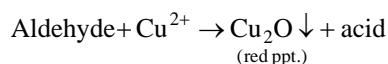
(c) Test of Cu^{2+}



Schwitzer's reagent
(Deep blue solution)



(g) In Fehling's test & Benedict's test



USES:

- (1) Bordeaux Mix $\rightarrow \text{CuSO}_4 + \text{CaO}$
(to kill fungi)

8. CUPRIC OXIDE, CuO

It is called black oxide of copper and is found in nature as tenorite.

I PREPARATION:

- (a) By heating Cu_2O in air or by heating copper for a long time in air (the temperature should not exceed above 1100°C)

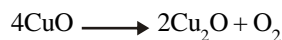


- (c) On a commercial scale, it is obtained by heating malachite which is found in nature.



II REACTIONS:

- (a) When heated to $1100\text{--}1200^\circ\text{C}$, it is converted into cuprous oxide with evolution of oxygen.

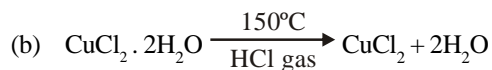
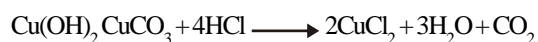
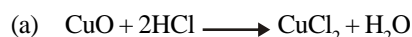


(Black) (Red)

Uses : Used to impart blue and green colour to glazes and glass.

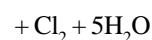
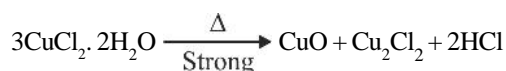
9. CUPRIC CHLORIDE, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

I PREPARATION:

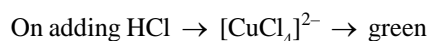
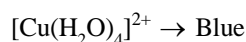


II REACTIONS:

- (a) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2

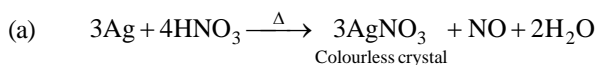


Dilute solution of CuCl_2 is blue but concentrated solution is green. Its dilute solution on adding HCl becomes yellow.

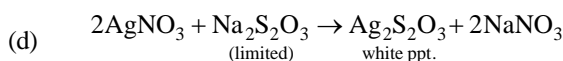
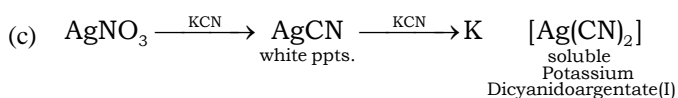
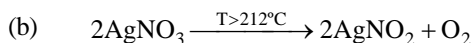
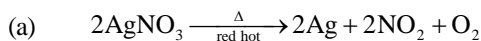


10. AgNO₃ (LUNAR CAUSTIC)

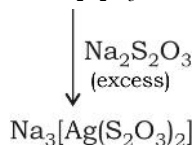
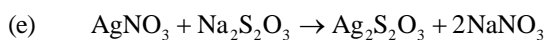
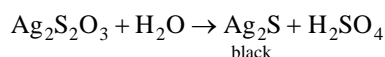
I Preparation :



II REACTION:

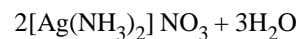
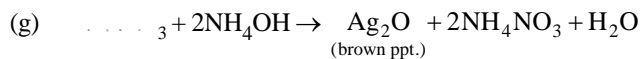
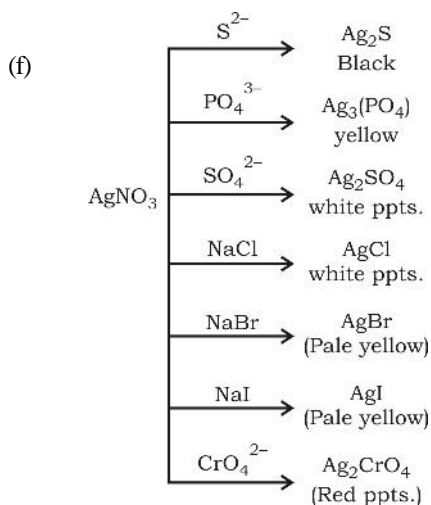


White ppt. of Ag₂S₂O₃ which gradually changes



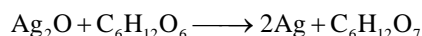
Sodium argentothio sulphate.

It is used in photography.

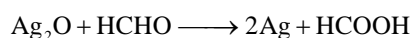


(h) Ammonical AgNO₃ → **Tollen's reagent** used to test aldehydes

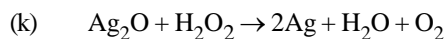
(i) It converts glucose to gluconic acid.



(j) It oxidises formaldehyde to formic acid



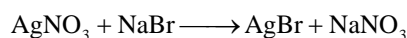
Very dilute solution of AgNO₃ is used as dental antiseptic.



11. SILVER BROMIDE, (AgBr)

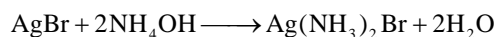
I PREPARATION:

It is prepared by the reaction of silver nitrate with a soluble bromide.



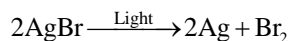
II PROPERTIES

(a) It is a pale yellow solid. It is insoluble in water and concentrated acids. It is partially soluble in strong solution of ammonium hydroxide due to complex formation.

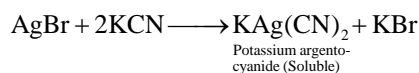


(b) On heating, it melts to a red liquid.

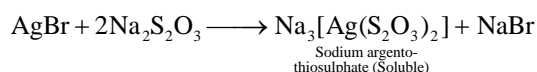
(c) It is most sensitive to light. It undergoes photoreduction.



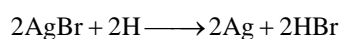
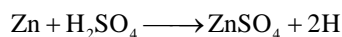
(d) It dissolves in potassium cyanide.



(e) It dissolves in sodium thiosulphate.



(f) AgBr is reduced to silver, when treated with zinc and dilute H₂SO₄.



All above reactions are also observed in the case of AgCl. However, it is white and fairly soluble in ammonium hydroxide. It is sensitive to light.

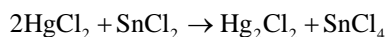
III. USES :

It is used for making photographic films and plates because it is sensitive to light.

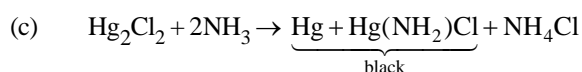
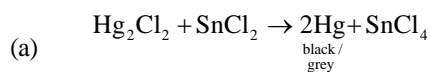
12. MERCURY CHLORIDES

12.1 Mercurous Chloride (Hg₂Cl₂ - Calomel)

I. PREPARATION :



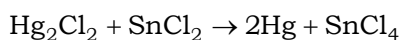
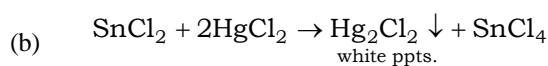
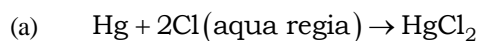
II. REACTIONS :



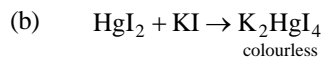
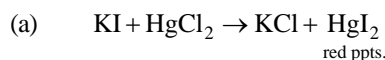
12.2 Mercuric Chloride (HgCl₂ - Corrosive sublimate)

I. PREPARATION :

It is highly corrosive, poisonous and hence is called as corrosive sublimate.

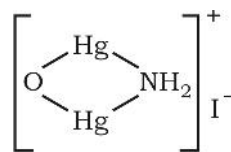
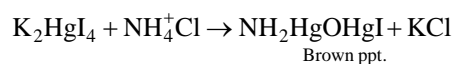


II. REACTION :

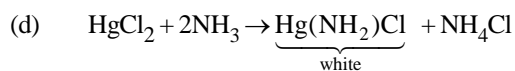


Basic solution of K₂HgI₄ (K₂HgI₄ + KOH) is called as Nessler's Reagent.

(c) Test for ammonium ion



Iodide of Millon's Base



(f) HgCl₂ is sparingly soluble in cold H₂O but readily in hot water.

SOLVED EXAMPLES

Example - 1

Silver atom has a completely filled d orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element ?

Silver ($Z = 47$) can exhibit +2 oxidation state wherein it will have incompletely filled d-orbitals ($4d$), hence a transition metal.

Example - 2

In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomisation of zinc is the lowest i.e., 26, kJ mol. Why ?

Sol. In the formation of metallic bonds no electrons from 3d-orbitals are involved in case of zinc, while in all other metals of the 3d series, electrons from the d-orbitals are always involved in the formation of metallic bonds.

Example - 3

Which of the 3d series of the transition metals exhibits the largest number of oxidation states and why ?

Sol. Manganese ($Z = 25$), as it atoms has the maximum number of unpaired electrons.

Example - 4

The $E^\circ (M^{2+}/M)$ value for copper is positive (+0.34 V). What is possibility the reason for this ?

Sol. Copper has high $\Delta_a H^\circ$ and low $\Delta_{hyd} H^\circ$.

Example - 5

How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements ?

Sol. Irregular variation of ionisation enthalpies in mainly attributed to varying degree of stability of different 3d-configurations (e.g., d^0 , d^5 , d^{10} are exceptionally stable).

Example - 6

Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

Sol. Because of small size and high electronegativity oxygen or fluorine can oxide the metal to its highest oxidation state.

Example - 7

Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why ?

Sol. Cr^{2+} is strong reducing agent than Fe^{2+} .

Reason : $d^4 \rightarrow d^5$ occurs in case of Cr^{2+} to Cr^{3+} .

But $d^6 \rightarrow d^5$ occurs in case of Fe^{2+} to Fe^{3+} . In a medium (like water) d^3 is more stable as compared to d^5 .

Example - 8

Calculate the 'spin only' magnetic moment of $M_{(aq)}^{2+}$ ion ($Z = 27$).

Sol. Atomic number (27) = $[Ar]3d^7 4s^2$

$$n = 1$$

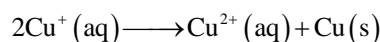
$$\mu = \sqrt{n(n+2)}$$

$$= \sqrt{1 \times 3} = 1.73 \text{ BM.}$$

Example - 9

Explain why Cu^+ ion is not stable in aqueous solutions ?

Sol. Cu^+ in aqueous solution undergoes disproportionation i.e.,



The E° , value for this is favourable.

Example - 10

Actinoid contraction is greater from element to element than lanthanoid contraction. Why ?

Sol. The 5f electrons are more effectively shielded from nuclear charge. In other words, the 5f electrons themselves provide poor shielding from element to element in the series.

Example - 11

On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not ?

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

Example - 12

Why Cr and Cu show exceptional configuration ?

Sol. By deviating from normal configuration, Cr and Cu acquires half-filled and fully filled configurations which gives them extra stability. Hence they show exceptional configuration.



Example - 13**Why are Zn, Cd and Hg softer and volatile metals ?**

Sol. Due to their completely filled d-orbitals, they have weak metallic bonding and least compact packing therefore they all are volatile in nature.

Example - 14**Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number ?**

Sol. In transition elements, there are greater horizontal similarities in the properties in contrast to the main group elements because of similar ns^2 common configuration of the outermost shell.

An examination of common oxidation states reveals that excepts scandium, the most common oxidation state of first row transition elements is +2 which arises from the loss of two 4s electrons. This means that after scandium, d-orbitals become more stable than the s-orbital.

Further, +2 state becomes more and more stable in the first half of first row transition elements with increasing atomic number because 3d orbitals acquire only one electron in each of five 3d orbitals (i.e. remains half filled) and electronic repulsion is the least and nuclear charge increases. In 2nd half of first row transition elements, electrons start pairing up in 3d orbitals.

(Ti^{2+} to Mn^{2+} electronic configuration changes from $3d^2$ to $3d^5$ but in 2nd half i.e. Fe^{2+} to Zn^{2+} it changes from d^6 to d^{10}).

Example - 15**To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements ? Illustrate your answer with example.**

Sol. One of the main characteristics of a transition element is that it can show large variety of oxidation states in its compounds. It is due to its characteristic electronic configuration i.e., $(n-1)d$ and ns electrons take part in bond formation either by losing or by sharing of electrons with other combining atoms.

The stability of oxidation state depends mainly on electronic configuration and also on the nature of other combining atom.

The elements which show largest number of oxidation states occur in or near the middle of series (i.e., $4s^23d^3$ to $4s^23d^7$ configuration). For example, Mn exhibits all oxidation states from +2 to +7 as it has $4s^23d^5$ configuration. The lesser number of oxidation states at extreme ends arise from either too few electrons to lose or share (e.g. Sc and Ti) or too many d electrons (hence

fewer orbitals available in which to share electrons with others) for higher elements at upper end of first transition series (i.e., Cu and Zn). Thus electronic configuration, to large extent, the existence and stability of oxidation states.

The other factors which determine stability of oxidation state are:

- (i) Enthalpy of atomisation (ii) Ionisation energy
- (iii) Enthalpy of solvation (iv) E.N. of other element.

Example - 16**What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$ and $3d^4$?**

Sol. The stable oxidation state of transition element with the d electron configuration in ground state of atoms are as follows :

S. No.	d-electron configuration	Symbol of element	Stable oxidation states
1.	$3d^3$	V($4s^23d^3$)	+2, +3, +5
2.	$3d^4$	Cr($4s^23d^4$)	+2, +3, +6
3.	$3d^5$	Mn($4s^23d^5$)	+2, +7
4.	$3d^8$	Ni($4s^23d^8$)	+2, +4

It should be noted that lower stable oxidation state generally leads to ionic bond and higher oxidation state corresponds to covalent bond.

Example - 17**Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.****Sol.**

Name of oxometal anion	Name of metal with oxidation state	Group no. to which metal belong
1. CrO_4^{2-} (chromate ion)	Cr in +6 state of oxidation	6th group of periodic table
2. MnO_4^- (permanganate ion)	Mn in +7 state	7th group

Example - 18**What is lanthanoid contraction ? What are the consequences of lanthanoid contraction ?**

Sol. A group of fourteen elements following lanthanum i.e. from $_{58}Ce$ to $_{71}Lu$ placed in 6th period of long form of periodic table is known as lanthanoids (or lanthanide series). These fourteen elements are represented by common general symbol 'Ln'. In these elements, the last electron enters the 4f-subshells (pre pen ultimate shell). It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level. However,

the electronic configuration of all the tripositive ions (the most stable oxidation state of all lanthanoids) are of the form $4f^n (n = 1 \text{ to } 14)$ with increasing atomic number). These elements constitute one of the two series of inner transition elements or f-block.

Lanthanoid contraction : In the lanthanoid series with the increase in atomic number, atomic radii and ionic radii decrease from one element to the other, but this decrease is very small. The regular small decrease in atomic radii and ionic radii of lanthanides with increasing atomic number along the series is called lanthanoid contraction.

Cause of lanthanoid contraction: When one moves from $_{58}\text{Ce}$ to $_{71}\text{Lu}$ along the lanthanide series nuclear charge goes on increasing by one unit every time. Simultaneously an electron is also added which enters to the inner f subshell. The shielding effect of f-orbitals is very poor due to their diffused shape. It results in the stronger force of nuclear attraction of the 4f electrons and the outer electrons causing decrease in size.

Consequences of lanthanoid contraction:

- Similarly in the properties of elements of second and third transition series e.g. Sr and Hf; Nb and Ta; Mo and W. This resemblance is due to the similarity in size due to the presence of lanthanoids in between.
- Similarity among lanthanoids : Due to the very small change in sizes, all the lanthanoids resemble one another in chemical properties.
- Decrease in basicity : With the decrease in ionic radii, covalent character of their hydroxides goes on increasing from $\text{Ce}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$ and so base strength goes on decreasing.

Example - 19

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

Sol. The important characteristics of transition metals are:

- All transition elements are metallic in nature, e.g., all are metals.
- These metals exhibit variable oxidation states.
- Transition metal atoms or ions generally form the complexes with neutral, negative and positive ligands.
- Compounds of transition metals are usually coloured.
- The compounds of these metals are usually paramagnetic in nature.
- Transition metals and their compounds act as good catalysts, i.e., they show catalytic activities.

(vii) These metals form various alloys with other metals of the series.

(viii) These metals form interstitial compounds with C, N, B and H.

The presence of partially filled d-orbitals in the electronic configuration of atomic and ionic species of these elements is responsible for the characteristic properties of transition elements. They are called transition elements because of their position in the periodic table. These elements lie in the middle of periodic table between s and p-block (i.e., between group 2 and group 13). A transition element may be defined as an element whose atom or at least one of its simple ions contain partially filled d-orbitals, e.g., iron, copper, chromium, nickel etc.

The general characteristic electronic configuration may be written as $(n - 1) d^{1-10} ns^{1-2}$.

The elements of group 12 i.e., Zinc, Cadmium, and Mercury are generally not regarded as transition elements as their atoms and all ions formed have completely filled d-orbitals i.e., these do not have partially filled d-orbitals in atomic state or common oxidation state (Zn^{2+} , Cd^{2+} , Hg^{2+})



Example - 20

In what way is the electronic configuration of the transition elements different from that of the non-transition elements ?

Sol. Transition elements have incomplete penultimate d-orbitals while penultimate orbitals of representative elements (s- and p-block elements) are completely filled up. The general valence shell configuration of s-block (group 1 and 2) elements is ns^{1-2} and for p-block elements (group 13 to 18) is $ns^2 np^{1-6}$. The valence shell configuration of transition elements can be written as $(n - 1) d^{1-9} ns^{1-2}$.

Example - 21

Explain giving reasons :

Sol.

- Transition metals and many of their compounds show paramagnetic behaviour.
- The enthalpies of atomisation of the transition metals are high.
- The transition metals generally form coloured compounds.
- Transition metals and their many compounds act as good catalysts.

Example - 22

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

Sol. Interstitial compounds are those which are formed when small atoms like H, C, N, B etc. are trapped inside the crystal lattices of metals. They are generally non-stoichiometric and neither typically ionic nor covalent.

Most of transition metals form interstitial compounds with small non-metal atoms such as hydrogen, boron, carbon and nitrogen. These small atoms enter into the void sites between the packed atoms of crystalline transition metals. For Example, steel and cast iron become hard by forming interstitial compound with carbon.

The existence of vacant $(n - 1)$ d orbitals in transition elements and their ability to make bonds with trapped small atoms in the main cause of interstitial compound formation. Other examples are : $\text{VH}_{0.56}$, $\text{TiH}_{1.7}$. Some main characteristics of these compounds are :

- They have high melting and boiling points, higher than those of pure metals.
- They are very hard. Some borides of transition elements approach diamond in hardness.
- They are chemically inert but retain metallic conductivity.

Example - 23

How is the variability in oxidation states of transition metals different from that of the non-transition metals ? Illustrate with examples

Sol. The variability in oxidation states is a fundamental characteristic of transition elements and it arises due to incomplete filling of d-orbitals in such a way that their oxidation states differ from each other by unity. For example, vanadium, V show the oxidation states of +2, +3, +4 and +5. Similarly, Cr shows oxidation states of +2, +3, +4, +5 and +6; Mn shows all oxidation states from +2 to +7.

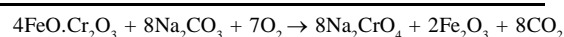
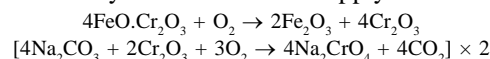
This is contrasted with variability of oxidation states of non-transition element where oxidation states generally differ by units of two. For example, S shows oxidation states of -2, +2, +4, +6 while P shows +3 and +5 oxidation states. Halogenes like Cl, Br and I show oxidation states of -1, +1, +3, +5 and +7 states. In non-transition elements variability of oxidation states is caused due to unpairing of electrons in ns or np orbitals and their promotion to np or nd vacant orbitals.

Example - 24

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

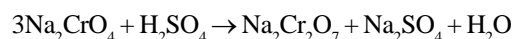
Sol. The following steps are involved in preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ from iron chromite (FeCr_2O_4) ore :

- (i) **Preparation of sodium chromate :** The chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is finely powdered and mixed with sodium carbonate and quick lime and then heated to redness in a reverberatory furnace with free supply of air.



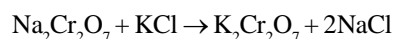
The mass is then extracted with water, when sodium chromate is completely dissolved while Fe_2O_3 is left behind.

- (ii) **Conversion of sodium chromate into sodium dichromate (NaCr_2O_7) :** The sodium chromate extracted with water in previous step is acidified.



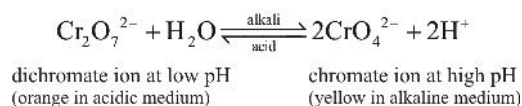
On cooling Na_2SO_4 separates out as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{Cr}_2\text{O}_7$ remains in solution.

- (iii) **Conversion of $\text{Na}_2\text{Cr}_2\text{O}_7$ into $\text{K}_2\text{Cr}_2\text{O}_7$:** The solution containing $\text{Na}_2\text{Cr}_2\text{O}_7$ is treated with KCl



Sodium chloride (NaCl) being less soluble separates out on cooling. On crystallising the remaining solution, orange coloured crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ separate out.

Effect of Change of pH : When pH of solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is increased slowly the medium changes from acidic to basic. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of solution.



At low pH (acidic medium), $\text{K}_2\text{Cr}_2\text{O}_7$ solution is orange coloured while at higher pH (alkaline medium) it changes to yellow due to formation of chromate ions.

Example - 25

Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with :

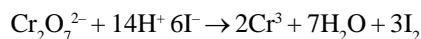
(a) iodide (b) iron (II) solution and (c) H_2S .

Sol. Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ is a strong oxidising agent and is used as a primary standard in volumetric analysis involving oxidation of iodides, ferrous ion and S^{2-} ions

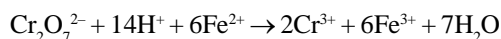
etc. In acidic solution, its oxidising action can be represented as follows :



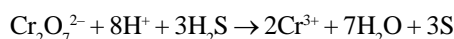
- (a) It oxidises potassium iodide to iodine.



- (b) It oxidises iron(II) salt to iron (III) salt



- (c) It oxidises H_2S to S

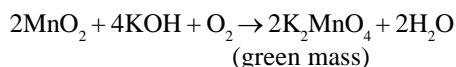


Example - 26

Describe the preparation of potassium permanganate. How does the acidified permanganate solution reacts with (a) iron(II) ions (b) SO_2 and (c) oxalic acid ? Write the ionic equations for the reactions.

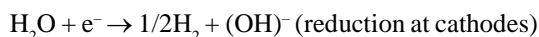
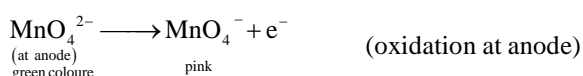
Sol. Preparation of KMnO_4 from pyrolusite ore (MnO_2) involves the following steps :

- (i) **Fusion of ore with alkali in presence of air :** Pyrolusite ore is fused with alkali in the presence of air when potassium manganate is obtained as green mass.

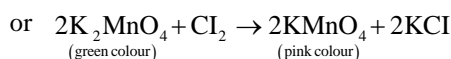


The green mass is dissolved in water to obtain aqueous solution of potassium manganate. The insoluble impurities of sand and other metal oxides are removed by filtration.

- (ii) **Oxidation of manganate into permanganate :** The aqueous solution of K_2MnO_4 is oxidised electrolytically or by using ozone or Cl_2 to obtain potassium permanganate. The process is carried out till green colour disappear and solution acquires distinct pink colour.



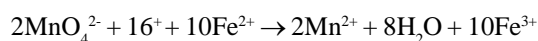
(at cathode)



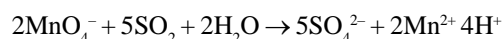
Potassium permanganate is crystallised out from the solution.

Oxidising Properties : It acts as a powerful oxidising agent in different media differently. In acidic medium, it oxidises iron(II) salts to iron(III) salts, SO_2 to H_2SO_4 and oxalic acid to CO_2 and H_2O .

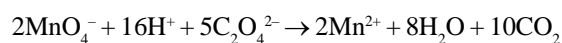
- (a) It oxidises iron(II) salt to iron(III) salts.



- (b) It oxidised sulphur dioxide to sulphuric acid.

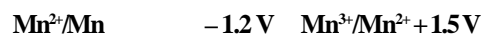
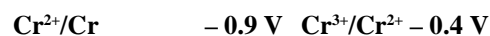


- (c) It oxidises oxalic acid to CO_2 and H_2O



Example - 27

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

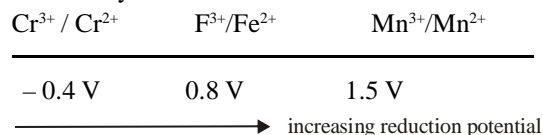


Use this data to comment upon

- (a) The stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and
- (b) In case with which iron can be oxidised as compared to the similar process for either chromium or manganese metal.

Sol.

- (a) We know that higher the reduction potential of a specie, there is larger tendency for its reduction to take place. Let us represent the reduction potential i.e., E° values of three $\text{M}^{3+}/\text{M}^{2+}$ systems on number line.



From values of reduction potentials, it is clear that the stability of Fe^{3+} in acid solution is more than that Cr^{3+} but less than that of Mn^{3+} .

- (b)
- | Mn^{2+}/Mn | Cr^{2+}/Cr | Fe^{2+}/Fe |
|----------------------------|----------------------------|----------------------------|
| -1.2 V | 0.9 V | -0.4 V 0V |

The lower the reduction potential of a species, its oxidation will take place more readily.

\therefore Mn is oxidised most readily to Mn^{2+} and Fe is oxidised least readily among given metals Mn, Cr and Fe.

Example - 28

Write the electronic configurations of the elements with the atomic numbers 61, 91, 101 and 109.

Sol. Atomic number (61) = $[\text{Xe}] 4f^5 6s^2$.

Atomic number (91) = $[\text{Rn}] 5f^2 6d^1 7s^2$

Atomic number (101) = $[\text{Rn}] 5f^{14} 7s^1$

Atomic number (109) = $[\text{Rn}] 5f^{14} 6d^7 7s^2$.

Example - 29

How would you account for the following :

- Of the d^4 species Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
- Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized.
- The d^1 configuration is very unstable in ions?

Sol.

- Of d^4 species, Cr^{2+} has 3 d^4 configuration and tends to loose one electron to acquire d^3 configuration as it is highly stable and best metallic specie available for complex formation. Cr^{3+} can accommodate six lone pair of electrons from ligands due to sp^3d^2 hybridisation e.g. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ Mn^{3+} although have d^4 configuration but tends to become Mn^{2+} stable specie by acquiring one electron to attain d^5 configuration. It becomes exactly half filled on one hand and more energy is released in gain of electron due to higher nuclear charge.
- Co^{2+} is stable in aqueous solution because it get surrounded and weakly bonded to water molecules. In presence of strong ligands and air it gets oxidised to Co(III) as strong ligands get co-ordinated more strongly with Co(III) . The electronic configuration of Co(II) and Co(III) are :

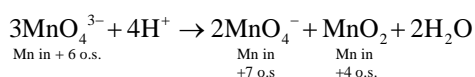
 $\text{Co(II)} = [\text{Ar}]_{18} 4s^0 3d^7$ and $\text{Co(III)} = [\text{Ar}]_{18} 4s^0 3d^6$

In Co(III) specie, 6 lone pairs of electrons from ligands are accommodated by sp^3d^2 hybridisation which is not possible in Co(II) .
- Some species with d^1 configuration are reducing and tends to loose one electron to acquire d^4 stable configuration. Some other species with d^1 configuration like Cr(V) and Mn(VI) undergo disproportionation.

Example - 30

What is meant by disproportionation ? Give two examples of disproportionation reaction in aqueous solution.

- Sol.** Some time transition metal species in same oxidation state undergo a chemical change in such a way that some species get oxidised and some other get reduced. For example, Cr(V) and Mn(VI) species undergo disproportionation reaction in acidic medium as follows:



Here, we can say that Cr in +5 oxidation state undergo disproportionation into its +6 and +3 states. Similarly, Mn in +6 oxidation state undergo disproportionation into +7 and +7 oxidation states.

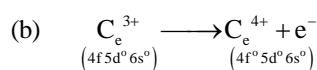
Example - 31

Give reasons for the following :

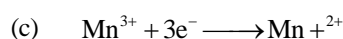
- Transition metals have high enthalpies of atomisation.
- Among the lanthenoids Ce(III) is easily oxidised to Ce(IV).
- $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple has less positive electrode potential than $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple.
- Copper (I) has d^{10} configuration while copper(II) has d^9 configuration, still copper(II) is more stable in aqueous solution than copper(I).
- The second and third transition series elements have almost similar atomic radii.

Sol.

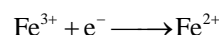
- The metallic bonds in transition elements are very strong due to participation of $(n - 1)$ d electrons along with valence s-electrons in the bond formation. Therefore, the cleavage of these bonds is extremely difficult and consequently, enthalpies of atomization are high.



Spontaneous oxidation due to more stability of Ce^{4+} ion as compared to Ce^{3+} ion due to more stable configuration of Ce^{4+} ion.



(more spontaneous due to higher stability of Fe^{3+})



(less spontaneous due to higher stability of Fe^{3+})

Due to stability of half filled d-orbitals, Mn^{2+} is more stable than Mn^{3+} and thus its reduction is more spontaneous. Similarly Fe^{3+} is more stable than Fe^{2+} and thus its reduction is less spontaneous.

- Copper (II) has lower reduction electrode potential than copper (I), hence. Copper(I) is oxidised to copper (II) in the presence of strong ligands and air.
- It is due to lanthanoid contraction. It arises due to poor shielding effect of d and f electrons.

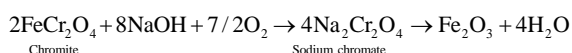
Example - 32

Indicate the steps in the preparation of :

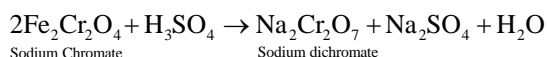
- (a) $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore
(b) KMnO_4 from pyrolusite ore.

Sol.

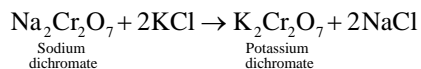
- (a) The preparation of potassium dichromate from chromite involves the following main steps :
- (i) The chromate ore is finely ground and heated strongly with molten alkali in the presence of air.



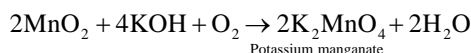
- (ii) The solution of sodium chromate is filtered and acidified with dilute sulphuric acid so that sodium dichromate is obtained.



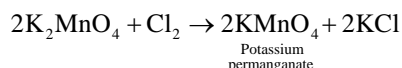
- (iii) A calculated quantity of potassium chloride is added to a hot concentrated solution of sodium dichromate. Potassium dichromate is less soluble therefore it crystallizes out first.



- (b) (i) Pyrolusite ore is fused with alkali in the presence of air when potassium manganate is formed.



- (ii) Potassium manganate is oxidised by using either CO_2 , ozone or chlorine to potassium permanganate.



- (iii) Potassium permanganate is crystallized from the solution.

Example - 33

What are alloys ? Mention an important alloy which contains some of the lanthanoid metals. Mention its uses.

Sol. An alloy is a mixture of a metal with other metals or non-metals.

An important alloy which contains some of the lanthanoid is mischmetall. Mischmetall consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al.

Uses : (i) Mischmetall is used in Mg based alloy to produce bullets, shell and lighter flint.

Some individual Ln oxides are used as phosphorus in television screens and similar fluorescing surfaces.

Example - 34

The Chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

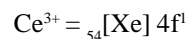
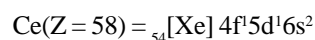
Sol. Among the actinoids, there is a greater range of oxidation states as compared to lanthanoids. This is in part due to the fact that 5f, 6d and 7s levels are of very much comparable energies and the frequent electronic transition among these three levels is possible. This 6d-5f transition and larger number of oxidation states among actinoids make their Chemistry more complicated particularly among the 3rd to 7th elements. following examples of oxidation states of actinoids. Justify the complex nature of their Chemistry.

- (i) Uranium exhibits oxidation states of +3, +4, +5, +6 in its compounds. However, the dominant oxidation state in actinoides is +3.
- (ii) Nobelium, No is stable in +2 state because of completely filled f^{14} orbitals in this state.
- (iii) Berkelium, BK in +4 oxidation state is more stable due to f^7 (exactly half filled) configuration.
- (iv) Higher oxidation states are exhibited in oxoions are UO_2^{2+} , PuO_2^{2+} , NpO^+ etc.

Example - 35

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

Sol. The electronic configuration of Ce and Ce^{3+} ion is :



The no. of unpaired electron = 1

'Spin only' formula for magnetic moment of a specie,

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

\therefore Magnetic moment of Ce^{3+}

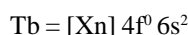
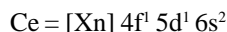
$$\mu = \sqrt{1(1+2)} \text{ B.M.}$$

$$= \sqrt{3} \text{ B.M.} = 1.732 \text{ B.M.}$$

Example - 36

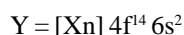
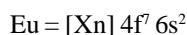
Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation state. Try to correlate this type of behaviour with the electronic configurations of these elements.

Sol. Cerium (Ce) and Terbium (Tb) show +4 oxidation state. Their electronic configurations are given below :



It is clear from the configuration of Ce that Ce^{+4} is favoured by its noble gas configuration i.e., $[\text{Xe}] 4f^0 5d^0 6s^0$, but can be easily converted into Ce^{3+} ($[\text{Xe}] 4f^1 5d^0 6s^0$). Due to this reason Ce^{+4} is an oxidising agent. Tb^{4+} ion is stabilized due to half filled f-subshell i.e., $[\text{Xe}] 4f^7$. It also acts as an oxidant.

Europium (63) and ytterbium (70) show +2 oxidation state, this acts as reducing agents because they can be converted into common oxidation state +3. The electronic configuration of Eu and Y are as follows :



Formation of Eu^{2+} ion leaves $4f^7$ configuration and Y^{2+} ion leaves $4f^{14}$ configuration. These configurations can be stable due to half filled and full filled f-subshell. Samarium, Sm (62) $4f^6 6s^2$ also shows both +2 and +3 oxidation states like europium.

Example - 37

Explain the following facts

- transition metals act as catalysts.
- chromium group elements have the highest melting points in their respective series.
- transition metals form coloured complexes.

Sol.

- The catalytic activity of transition metals is attributed to the following reasons :
 - Because of their variable oxidation states transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
 - In some cases, the transition metal provides a suitable large surface area with free valencies on which reactants are adsorbed.
- Because they have strong metallic bonds due to greater number of unpaired d electrons.
- this is due to d-d transition.

Example - 38

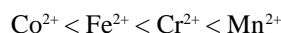
Discuss the relative stability in aqueous solutions of +2 oxidation state among the elements: Cr, Mn, Fe and Co. How would you justify this situation ?

(At. Nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

Sol. On the basis of electrochemical series the standard electrode potential shows the following order

$$E^\circ_{\text{Mn}^{2+}/\text{Mn}} < E^\circ_{\text{Cr}^{2+}/\text{Cr}} < E^\circ_{\text{Fe}^{2+}/\text{Fe}} < E^\circ_{\text{Co}^{2+}/\text{Co}}$$

Therefore Co^{2+} gets easily reduced to metallic cobalt while it is difficult to reduce Mn^{2+} . Hence Mn^{2+} will be most stable and the increasing stability order will be

**Example - 39**

Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why ?

Sol. Copper metal (Cu, at. no. 29) shows +1 oxidation state i.e., it exists as Cu^+ in large number of copper compounds e.g., cuprous oxide (Cu_2O), cuprous sulphide (Cu_2S); cuprous chloride (Cu_2Cl_2) etc. The electronic configuration of Cu^+ is $[\text{Ar}] 3d^{10} 4s^0$.

This configuration is very stable as all five 3d orbitals are fully filled.

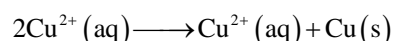
Example - 40

Assign a reason for each of the following :

- The third ionization energy of Mn (Z = 25) is higher than that of either Cr (Z = 24) or Fe (Z = 26).
- Simple copper (I) salts are not stable in aqueous solutions.

Sol.

- This is because Mn^{2+} is more stable as it has exactly half filled configuration $3d^5 4s^0$.
- Cu^{2+} (aq) is much more stable than Cu^+ (aq). This is because, although second ionization enthalpy of copper is large but for Cu^{2+} (aq) is much more negative than that of Cu^+ (aq) and therefore, it more compensate for the second ionisation enthalpy of copper. Therefore, Cu^+ ion aqueous solution undergoes disproportionation.



Example - 41

Describe the trends in the following properties of the first series of the transition elements:

(i) Oxidation states

(ii) Atomic sizes

(iii) Magnetic behaviour of dipositive gaseous ions (M^{2+}).

Sol.

- (i) As there is very little energy difference between 4s and 3d orbitals, electrons from both energy levels can be used for chemical bond formation. Therefore all elements except Sc and Zn, of the first transition series show a number of oxidation states as shown in table.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	
+3	+3	+3	+3	+3	+3	+3	+3	+2	+2
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- (ii) Atomic radii of the first transition series decreases from Sc to Cr, then remains almost constant till Ni and then increases from Cu to Zn.

The reason of this variation in atomic radii has been attributed to the increase in nuclear charge in the beginning of the series. But as the electrons continue to be filled in d-orbitals, they screen the outer 4s electrons from the influence of nuclear charge. When the increased nuclear charge and the increased screening effect balance each other in the middle of transition series, the atomic radii becomes almost constant (Mn to Fe). Towards the end of the series, the repulsive interaction between electrons in d orbitals become very dominant. As a result there is an expansion of the electron cloud; consequently, the atomic size increases.

- (iii) d^1 to d^9 , all other divalent gaseous ions of the first series of the transition elements contain unpaired electrons in their 3d subshell and are therefore paramagnetic in nature.

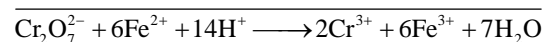
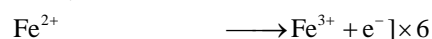
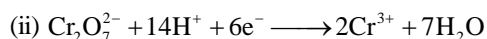
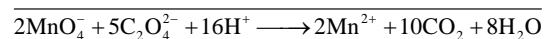
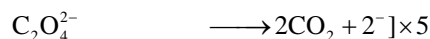
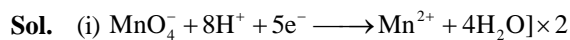
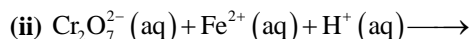
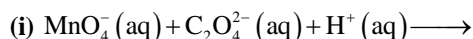
The magnetic moment (μ) of the elements of the first transition series can be calculated with the unpaired electrons (n) by the spin-only formula

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

Ion	Configuration	Unpaired electrons	Magnetic moment (μ) calculated
Mn^{2+}	$3d^5 4s^0$	5	$\sqrt{5(5+2)} = 5.92 \text{ B.M.}$
Cu^{2+}	$3d^9 4s^0$	1	$\sqrt{1(1+2)} = 1.73 \text{ B.M.}$
Zn^{2+}	$3d^{10} 4s^0$	0	$\sqrt{0(0+3)} = 0$

Example - 42

Complete the following chemical reaction equations:

**Example - 43**

How would you account for the following :

- Many of the transition elements and their compounds can act as good catalysts.
- The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.
- There is a greater range of oxidation states among the actinoids than among the lanthanoids.

Sol.

- The catalytic activity of transition metals is attributed to the following reasons:
 - Because of their variable oxidation states transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
 - In some cases, the transition metal provides a suitable large surface area with free vacancies on which reactants are adsorbed.
- This is due to filling of 4f orbitals which have poor shielding effect or due to lanthanoid contraction.
- This is due to comparable energies of 5f, 6d and 7s orbital in actinoids.

Example - 44

In transition series, with an increase in atomic number, the atomic radius does not change very much. Why is it so ?

- Sol.** With the increase in atomic number along a transition series the nuclear charge increases which tends to decrease the

size of the atom. But the addition of electrons in the d subshell increases the screening effect which counterbalances the increased nuclear charge. Hence, along a transition series the atomic radius does not change very much.

Example - 45

Decide giving reasons which one of the following pairs exhibits the property indicated:

(i) Sc^{3+} or Cr^{3+} exhibits paramagnetism.

(ii) V or Mn exhibits more number of oxidation states.

(Atomic Numbers: Sc = 21; Cr = 24; V = 23; Mn = 25)

Sol.

- (i) $^{3+}$ and Cr^{3+} are given below.



Because of the presence of three unpaired electrons in the 3d subshell Cr^{3+} is paramagnetic. Sc^{3+} is diamagnetic as it does not have any unpaired electrons.

- (ii) The electronic configurations of V and Mn are given below:



Mn exhibits more number of oxidation states than V because of the greater number of electrons in its valence shell.

Example - 46

Account for the following:

(i) Cerium (atomic number = 58) forms tetra positive ion, Ce^{4+} in aqueous solution.

(ii) The second and third members in each group of transition element have similar atomic radii.

Sol.

- (i) The electronic configuration of Ce ($Z = 58$) is $_{58}\text{Ce} = [\text{Xe}] 4f^1 5d^1 6s^2$

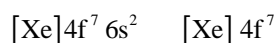
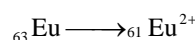
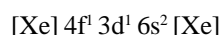
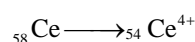
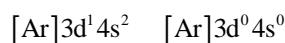
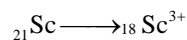
Cerium can lose four electrons ($4f^1 5d^1 6s^2$) in aqueous solution to acquire stable configuration of rare gas xenon. Moreover due to small size and high charge, Ce^{4+} ion has high hydration energy.

- (ii) The second and third members in each group of transition elements have very similar atomic radii due to lanthanoid contraction. It arises due to poor shielding effect of Δf electrons.

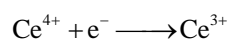
Example - 47

Among the ionic species Sc^{3+} , Ce^{4+} and Eu^{2+} which one is a good oxidising agent? Give a suitable reason for your answer. (Atomic numbers ; Sc = 21; Ce = 58; Eu = 63).

Sol. The electronic configurations of given species are:



Ce^{4+} is a good oxidising agent because it can readily change to the most stable +3 oxidation state by gaining one electron.



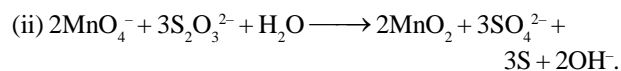
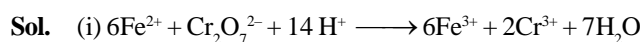
Because of their stable configuration Sc^{3+} and Eu^{2+} cannot gain electrons.

Example - 48

Write complete chemical equations for :

(i) Oxidation of Fe^{2+} by $\text{Cr}_2\text{O}_7^{2-}$ in acid medium.

(ii) Oxidation of $\text{S}_2\text{O}_3^{2-}$ by MnO_4^- in neutral aqueous solution.



Example - 49

What are the different oxidation states exhibited by the lanthanoids ?

Sol. The most common oxidation states shown by lanthanoids is +3. In some exceptional cases it may be +2 or +4 (+2 in Eu and Yb; +4 in Ce).

Example - 50

What is meant by 'lanthanoid contraction' ?

Sol. The regular decrease (contraction) in the atomic and ionic radii with increasing atomic number from lanthanum to lutetium along the lanthanoid series is called lanthanoid contraction.

Example - 51

How would you account for the following :

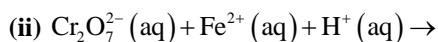
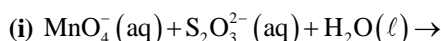
- (i) **Cr²⁺ is reducing in nature while with the same d-orbital configuration 9d⁴) Mn³⁺ is an oxidising agent.**
- (ii) **In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series.**

Sol.

- (i) E° value of Cr³⁺/Cr²⁺ is negative (−0.04V) while that of Mn³⁺/Mn²⁺ is positive (1.5 V). This means Cr²⁺ can lose electrons to form Cr³⁺ and thus is reducing in nature while Mn³⁺ can gain electrons to form Mn²⁺ and is thus oxidising in nature.
- (ii) In a transition series of maximum number of oxidation states are shown by that element which has maximum number of unpaired electrons. This is so in the element present in the middle of the series. That is why the metal in the middle of the series exhibits maximum number of oxidation states. For example, manganese, present in the middle of the first transition series exhibits maximum oxidation states i.e., +2, +3, +4, +5, +6, +7.

Example - 52

Complete the following chemical equations :

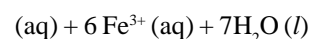
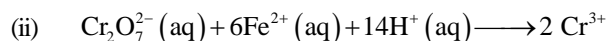
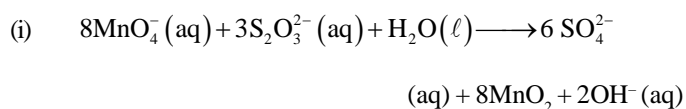


Or

State reasons for the following :

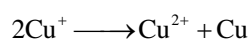
- (i) **Cu (I) ion is not stable in an aqueous solution.**
- (ii) **Unlike Cr³⁺, Mn²⁺, Fe³⁺ and the subsequent other M²⁺ ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species.**

Sol.



Or

- (i) Cu²⁺ (aq) is much more stable than Cu⁺ (aq). This is due to more negative Δ_{hyd} H more than compensates for Δ₁H₂. As a result Cu(I) is unstable in aqueous solution and undergoes disproportionation as below :



- (ii) The valence shell electronic configuration of Cr³⁺, Mn²⁺, Fe³⁺ is d³, d⁵ respectively. Due to symmetrical distribution of electrons (Either t_{2g}³ or t_{2g}³ e_g²) they form stable cationic complexes. The atomic radii of 4d and 5d transition metal at elements are more than those of 3d series. Hence, they generally do not form stable cationic complexes.

Example - 53

Explain giving reasons :

- (i) **Transition metals and their compounds generally exhibit a paramagnetic behaviour.**
- (ii) **The Chemistry (XII) (XII) of actinoids is not so smooth as that of lanthanoids.**

Sol.

- (i) Paramagnetism is a property due to presence of unpaired electrons. In case of transition metals, as they contain unpaired electrons in (n – 1) d orbitals, most of the transition metal ions and their compounds are paramagnetic.
- (ii) The general electronic configuration of lanthanoids is [Xe]⁵⁴ 4f⁰⁻⁴ 5d⁰⁻¹ 6s² and that of actinoids is [Rn]⁸⁶ 5f¹⁻¹⁴ 6d⁰⁻¹ 7s². Unlike 4f orbitals, 5f orbitals are not deeply buried and participate in bonding to a greater extent. In actinoids due to poor shielding effect of 5f orbitals, the effective nuclear charge experienced by valence shell electrons is more than those in lanthanoids. As a result the Chemistry (XII) (XII) of actinoids is not so smooth as that of lanthanoids.

Example - 54

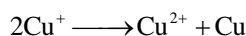
Assign reasons for the following :

- (i) **Copper (I) ion is not known in aqueous solution.**
- (ii) **Actinoids exhibit greater range of oxidation states than lanthanoids.**

Sol.

- (i) Cu (I) ion is not known in aqueous solution because Cu²⁺(aq) is much more stable than Cu⁺(aq). This is due to

more negative $\Delta_{\text{hyd}}H$ for $\text{Cu}^{2+}(\text{aq})$ than $\text{Cu}^{+}(\text{aq})$ although $\Delta_f H_2^\circ$ for Cu^{2+} is large. Thus, $\Delta_{\text{hyd}}H$ more than compensates for high value of $\Delta_f H_2^\circ$. As a result Cu(I) is unstable in aqueous solution and undergoes disproportionation as below :



- (ii) Actinoids exhibit greater range of oxidation states than lanthanoids. this is because of very small energy gap between 5f, 6d and 7s subshells. Hence, all their electrons can take part in bond formation.

Example - 55

Assign reasons for each of the following :

- (i) **Transition metals generally form coloured compounds.**
- (ii) **Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements.**

Sol.

- (i) Transition metals generally form coloured compounds. The colour of compounds of transition metals may be attributed to the presence of incomplete $(n-1)$ d subshell. In the compounds of transition metals the d-orbitals split into two sets- t_{2g} ($d_{x^2-y^2}, d_{z^2}$) of lower energy and e_g (d_{xy}, d_{yz}, d_{zx}) of high energy. The electron can jump from lower energy t_{2g} orbitals to higher energy e_g orbitals (d-d transition) by absorption of light of some particular wavelength from visible light. The remainder light is emitted as coloured light and the compound appears coloured.
- (ii) In a transition series the element with maximum oxidation state occurs in or near the middle of the transition series and maximum oxidation state exhibited is equal to sum of $(n-1)$ d and ns electrons. In Mn ($3d^5 4s^2$) the sum of $(n-1)$ d and (ns) electron is 7 and therefore it exhibits maximum o.s. of +7. The lesser no. of oxidation states on extreme ends are either due to too few electrons to lose or share or too many d-electrons so that fewer orbitals are available to share electrons with others.

Example - 56

Explain:

- (i) **CrO_4^{2-} is a strong oxidizing agent while MnO_4^{2-} is not.**
- (ii) **Zr and Hf have identical sizes.**
- (iii) **The lowest oxidation state of manganese is basic while the highest is acidic.**
- (iv) **Mn (II) shows maximum paramagnetic character amongst the divalent ions of the first transition series.**

Sol.

- (i) CuF_2 and CCl_2 compounds will be coloured because they incompletely filled d-orbitals and unpaired electrons, they

can undergo d-d transition by absorbing colour from visible region and radiating complementary colour.

- (ii) Zr and Hf have identical sizes because passing of electrons takes place in d-orbitals causing repulsion and effective nuclear charge does not increase appreciably.
- (iii) Manganese ($Z = 25$) exhibits the largest number of oxidation states because its atoms has the maximum number of npaired electrons. The lowest oxidation state of manganese is basic while the highest is acidic.
- (iv) Mn(II) shows maximum paramagnetic character amongst the divalent ions of the first transition series because it has the largest number of unpaired electrons.

Example - 57

Explain the following facts :

- (a) **Transition metals acts as catalyst.**
- (b) **Chromium group elements have highest melting points in their respectively series.**
- (c) **Transition metals form coloured complexes.**

Sol.

- (a) Transition metals acts as catalyst due to the following reasons :
- (i) Their partially empty d-orbitals provide surface area for reactant molecules.
 - (ii) They combine with reactant molecules to form transition states and lowers their activation energy.
 - (iii) They show multiple oxidation states and by giving electrons to reactants they form complexes and lower their energies.
 - (b) The melting point of chromium groups elements have the highest melting points in their respective series due to presence of strong intermetallic bonds (formed by valence electrons and covalent bonds formed due to d-d overlapping of impaired d-electrons.)
 - (c) Their colour due to the presence of incomplete d-subshell. The electrons can be excited from one energy level to another within the d-subshell. The energy required to cause such d-d promotions or transition falls within the visible range for all transition elements. When white light falls on an ion or compound, some of its wave lengths are absorbed due to d-d transition and others are reflected. Therefore, colour of the transition metal ion is that of the reflected light.

Example - 58

Give reasons :

- (i) Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.
- (ii) Ce^{4+} is used as an oxidising agent in volumetric analysis.
- (iii) Transition metals form a number of interstitial compounds.
- (iv) Zn^{2+} salts are white while Cu^{2+} salts are blue.

Sol.

- (i) Highest oxidation state is shown in fluorides and oxides because F_2 and O_2 are strong oxidising agents.
- (ii) $\text{Ce}^{4+} = [\text{Xe}], 4f^0, 5d^0, 6s^0$
 Ce^{4+} has the tendency to accept one electron to get the +3 oxidation state, hence Ce^{4+} is a good oxidising agent.
- (iii) In these compounds small size atoms like hydrogen, carbon, nitrogen, boron, etc. occupy the empty space of metal lattice (interstices). The small entrapped atom in the interstices form the bonds with metals due to which mobility and ductility of the metals decrease, when as tensile strength increases. Example : steel is the interstitial compound of iron and carbon.
- (iv) In Cu^{2+} salts ($3d^9$) d-d transition is possible. Therefore Cu^{2+} salts are coloured.
 In Zn^{2+} salts ($3d^{10}$) no. d-d transition is possible due to completely filled d-orbitals. Hence Zn^{2+} salts are white.

Example - 59

Write the main differences in lanthanides and actinides.

Sol.

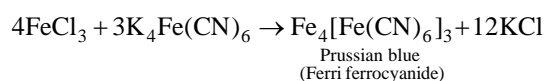
Lanthanides	Actinides
1. Lanthanides shows +3 oxidation state only except in few cases where it is +2 or +4. Oxidation states exhibited by lanthanides is never more than +4.	1. Actinides show higher oxidation states such as +4, +5, +6, +7 also in addition to +3.
2. Paramagnetic properties of lanthanides can be easily explained.	2. Paramagnetic properties are difficult to interpret.
3. Lanthanides do not form complexes.	3. They have a greater tendency to complex formation. Even p-complexes are formed by actinides.
4. Lanthanides do not form actinoid ions.	4. These in higher oxidation states form actinoid ions.
5. Except promethium, these are ion-radioactive	5. Such as UO_2^{2+} , NbO^+ , PuO_2^{2+} etc.

Example - 60

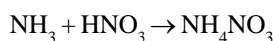
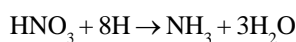
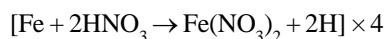
What happens when ?

- (i) Ferric chloride is added to potassium ferrocyanide.
- (ii) Iron reacts with cold dilute nitric acid.
- (iii) Potassium ferricyanide is added to ferrous sulphate.
- (iv) Excess of potassium iodide is added to mercuric chloride.
- (v) Green vitriol is strongly heated.
- (vi) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium.
- (vii) Zinc oxide is treated with excess of sodium hydroxide solution.
- (viii) Ammonium thiocyanate is added to ferric chloride solution.

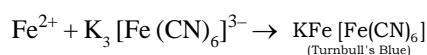
Sol. (i) Prussian blue is formed.



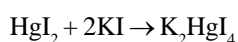
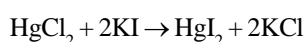
(ii) Ammonium nitrate is formed.



(iii) Ferrous ion is first oxidised to ferric ion while ferricyanide ion is reduced to ferrocyanide ion. Then, ferric ions react with ferrocyanide ions to form potassium ferric ferrocyanide (Turnbull's blue).



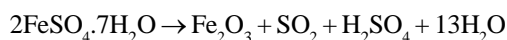
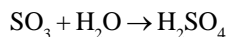
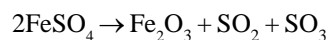
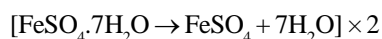
(iv) First scarlet precipitate is formed which then dissolves in excess of potassium iodide forming a complex.



Potassiumtetraiodomercurate(II)

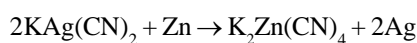
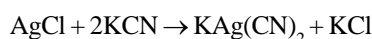
(colourless)

- (v) When heated strongly, a mixture of gases consisting of SO_2 and SO_3 is evolved and a red residue, Fe_2O_3 is formed.



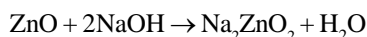
Green vitriol Red

- (vi) AgCl dissolves in KCN forming a complex, potassium argentocyanide. The addition of zinc precipitates silver.

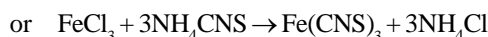
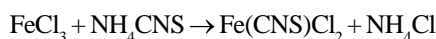


Potassium zincocyanide

- (vii) ZnO dissolves in NaOH forming sodium zincate.



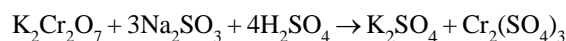
- (viii) Deep red colouration due to the formation of a complex is developed.



Example - 61

Explain the following :

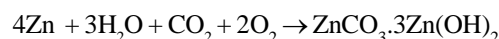
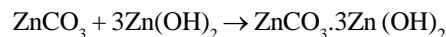
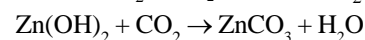
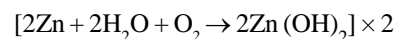
- Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution turns green when sodium sulphite is added to it.
- Zinc becomes dull in moist air.
- A little acid is always added in the preparation of aqueous ferrous sulphate solution.
- The addition of NaOH solution to a solution of zinc chloride produces a white precipitate which dissolves on further addition of NaOH .
- The addition of NH_4OH to ZnSO_4 solution produces white precipitate but no precipitate is formed if it contains NH_4Cl .
- Zinc and not copper is used for the recovery of silver from complex $[\text{Ag}(\text{CN})_2]^-$.
- Copper sulphate dissolves in NH_4OH solution but FeSO_4 does not.
- Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.



Green

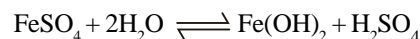


- (ii) When zinc is exposed to moist air, the surface is affected with the formation of a film of basic zinc carbonate on it. Due to this zinc becomes dull.



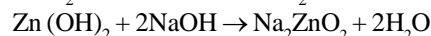
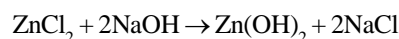
Basic zinc carbonate

- (iii) Ferrous sulphate is a salt of a weak base and a strong acid. Thus, its hydrolysis occurs when it is dissolved in water and solution becomes turbid due to formation of ferrous hydroxide.



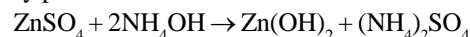
Addition of a small amount of acid shifts the equilibrium towards left and thus prevents hydrolysis.

- (iv) On addition of NaOH , a white precipitate of $\text{Zn}(\text{OH})_2$ is formed which dissolves in excess of NaOH forming sodium zincate.



Soluble

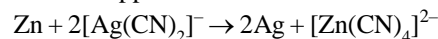
- (v) NH_4OH is a weak hydroxide. It ionises slightly furnishing OH^- ions. However, the OH^- ions are sufficient to cause the precipitation of $\text{Zn}(\text{OH})_2$ as its solubility product is exceeded.



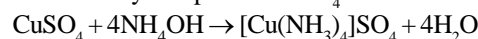
white ppt.

In presence of NH_4Cl , the ionisation of NH_4OH is further suppressed and sufficient OH^- ions are not available to cause precipitation as the solubility product is not exceeded.

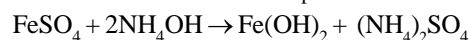
- (vi) Zinc is cheaper as well as stronger reducing agent in comparison to copper.



- (vii) Copper sulphate dissolves in the ammonium hydroxide due to formation of a copper complex. Ferrous sulphate reacts with NH_4OH to form insoluble $\text{Fe}(\text{OH})_2$. It does not form any complex with NH_4OH .

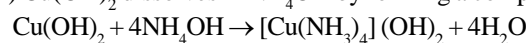


Deep blue solution



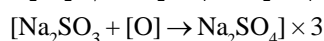
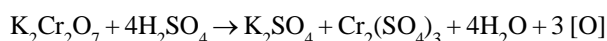
Insoluble

- (viii) $\text{Cu}(\text{OH})_2$ dissolves in NH_4OH by forming a complex.



$\text{Cu}(\text{OH})_2$ is insoluble in NaOH as no such complex is formed.

Sol. (i) Na_2SO_3 is a reducing agent. It reduces acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to chromic sulphate which is green in colour.



Example - 62

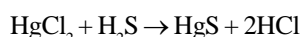
A metal chloride (x) shows the following reactions :

- When H_2S is passed in an acidified solution of (x) a black precipitate is obtained.
- The black precipitate is not soluble in ammonium sulphide.
- The solution of stannous chloride is added to an aqueous solution of (x), a white precipitate is obtained which turns grey on addition of more stannous chloride.
- When aqueous solution of KI is added to an aqueous solution of (x), a red precipitate is obtained which dissolves on addition of excess of KI.

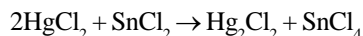
Identify (x) and write down the equations for the reactions.

Sol. The acidified solution of (x) gives a black sulphide with H_2S indicates that the chloride is of a basic cation of second group. The sulphide is insoluble in ammonium sulphide, hence, the cation belongs to IIA group of mixture analysis.

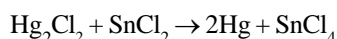
It gives white precipitate with SnCl_2 which turns to grey in excess of SnCl_2 suggests that (x) is HgCl_2 . It is further confirmed by the reaction with KI.

Reactions :

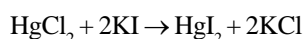
Black



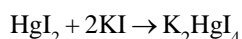
white



Grey



Red ppt.

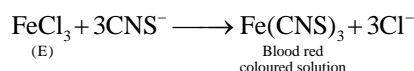
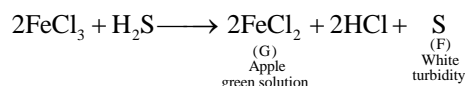
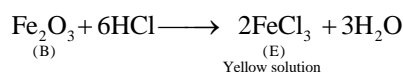
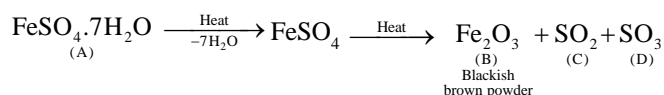


Soluble

Example - 63

A certain inorganic compound (A) on heating loses its water of crystallisation. On further heating, a blackish brown powder (B) and two oxides of sulphur (C and D) are obtained. The powder (B) on boiling with hydrochloric acid gives a yellow solution (E). When H_2S is passed in (E), a white turbidity (F) and apple green solution (G) are obtained. The solution (E) on treatment with thiocyanate ions gives a blood red coloured compound (H). Identify the compounds from (A) to (H).

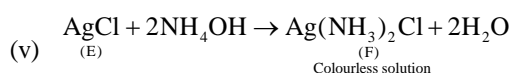
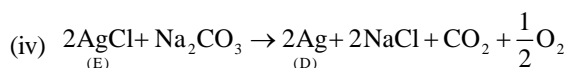
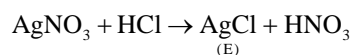
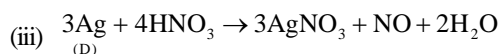
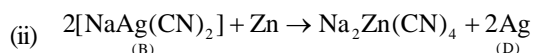
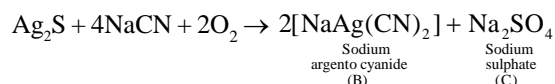
Sol. The compound (A) on strong heating gives two oxides of sulphur, it may be a sulphate. The solution (E) on treatment with thiocyanate ions gives blood red coloured compound (H) indicates that the solution (E) consists of Fe^{3+} ions. Thus, the compound (A) is ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Reactions :**Example - 64**

- A black mineral (A) on treatment with dilute sodium cyanide solution in presence of air gives a clear solution of (B) and (C).
- The solution (B) on reaction with zinc gives precipitate of a metal (D).
- (D) is dissolved in dilute HNO_3 and the resulting solution gives a white precipitate (E) with dilute HCl.
- (E) on fusion with sodium carbonate gives (D).
- (E) dissolves in ammonia solution giving a colourless solution of (F). Identify (A) to (F) and give chemical equations for reactions at steps (i) to (v).

Sol. On the basis of the given data, the black mineral (A) is silver glance, Ag_2S . It is confirmed by the following :

- It dissolves in sodium cyanide solution in presence of air.



- (A) = Silver glance, Ag_2S
 (B) = Sodium argentocyanide, $\text{NaAg}(\text{CN})_2$
 (C) = Sodium sulphate, Na_2SO_4
 (D) = Silver metal, Ag
 (E) = Silver chloride, AgCl
 (F) = Diamminsilver (I) chloride, $\text{Ag}(\text{NH}_3)_2\text{Cl}$

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

D & F Block

1. Transition elements have
 - (a) completely filled d levels
 - (b) completely filled s levels and d levels
 - (c) incompletely filled s levels and completely filled d levels
 - (d) incompletely filled d levels
2. The general electronic configuration of the transition elements is
 - (a) $(n-1)d^{10}(n+1)s^2$
 - (b) $(n-1)d^{1-10}(n+1)s^{1-2}$
 - (c) $(n-1)d^{1-10}np^6ns^2$
 - (d) $(n-1)d^{1-10}ns^{0-2}$
3. Which of the following transition elements has completely filled d orbitals (the d^{10} configuration)
 - (a) Co
 - (b) Cr
 - (c) Hg
 - (d) Ni
4. In which of the following transition elements are the d orbitals not completely filled ?
 - (a) Zn
 - (b) Hg
 - (c) Cd
 - (d) Ag
5. The electronic configurations of the first four members of the actinide series cannot be written accurately in a regular manner because of
 - (a) small difference in energy between 5f and 6d orbitals
 - (b) large difference in energy between 5f and 6d orbitals
 - (c) small difference in energy between 5f and 6s orbitals
 - (d) violation of the Pauli exclusion principle
6. The electronic configuration of silver is
 - (a) $[\text{Ar}]3d^{10}4s^1$
 - (b) $[\text{Ar}]4d^{10}4s^1$
 - (c) $[\text{Kr}]4d^{10}5s^1$
 - (d) $[\text{Kr}]4d^85s^2$
7. The electronic configuration of palladium is
 - (a) $[\text{Ar}]3d^84s^2$
 - (b) $[\text{kr}]4d^85s^2$
 - (c) $[\text{kr}]5d^86s^2$
 - (d) $[\text{Ar}]4d^{10}5s^0$
8. The electronic configuration of platinum is
 - (a) $[\text{Ar}]4f^{14}5d^96s^1$
 - (b) $[\text{Ar}]4f^{14}5d^{10}6s^2$
 - (c) $[\text{Ar}]4f^{14}6d^{10}7s^2$
 - (d) $[\text{Ar}]4f^{14}6d^97s^1$
9. Transition elements
 - (a) exhibit inert-pair effect
 - (b) show nonmetallic character
 - (c) do not form complex compounds
 - (d) exhibit variable oxidation states
10. The oxidation states shown by transition elements is related to their
 - (a) electropositive characters
 - (b) electronic configurations
 - (c) atomic weights
 - (d) atomic sizes
11. The electronic configuration of chromium is actually $[\text{Ar}]3d^54s^1$ instead of normally expected $[\text{Ar}]3d^44s^2$. This is because
 - (a) an exactly half-filled d level gives additional stability, according to the Hund rule of maximum multiplicity
 - (b) the 4s orbital has higher energy than the 3d orbitals
 - (c) the 4s orbitals has lower energy than the 3d orbitals
 - (d) the 3d and 4s orbitals have equal energies and hence electron migration occurs readily
12. Identify the species having an atom in +6 oxidation state.
 - (a) MnO_4^-
 - (b) $\text{Cr}(\text{CN})_6^{3-}$
 - (c) NiF_6^{3-}
 - (d) CrO_2Cl_2
13. Which of the following is not true about the transition elements ?
 - (a) They show variable oxidation states
 - (b) Their ions have a strong tendency to form complexes
 - (c) Their compounds usually do not absorb ultraviolet and visible lights
 - (d) Their ions and complex ions usually possess magnetic moments.
14. What of the following is an incorrect statement?
 - (a) The lowest oxide of a transition metal is acidic whereas the highest one is usually basic.
 - (b) A transition metal usually exhibits higher oxidation states in its fluorides than in its iodides.
 - (c) Transition metal halides become more covalent with the increasing oxidation state of the transition metal and are more susceptible to hydrolysis.
 - (d) The highest oxide of a transition metal is acidic whereas the lowest one is usually basic.
15. Which of the following transition metals does not show variable oxidation states ?
 - (a) Mercury
 - (b) Zinc
 - (c) Gold
 - (d) Silver
16. Which of the following ions is colourless in solution ?
 - (a) V^{3+}
 - (b) Cr^{3+}
 - (c) Co^{2+}
 - (d) Sc^{3+}
17. Which of the following ions has the maximum number of unpaired d electrons ?
 - (a) Fe^{3+}
 - (b) V^{3+}
 - (c) Ti^{3+}
 - (d) Mg^{2+}
18. Which of the following ions possesses the maximum number of unpaired electrons ?
 - (a) Ni^{2+}
 - (b) Fe^{2+}

- (c) Cu^+ (d) Zn^{2+}
19. Which of the following does not possess unpaired electrons ?
 (a) Co^{3+} (b) Cu^{2+}
 (c) Ti^{2+} (d) Hg^{2+}
20. Which one of the following ionic species will impart colour to an aqueous solution ?
 (a) Ti^{4+} (b) Cu^+
 (c) Zn^{2+} (d) Cr^{3+}
21. Which of the following elements shows the maximum number of different oxidation states in its compounds ?
 (a) Eu (b) La
 (c) Gd (d) Am
22. Which of the following electronic configurations represents Fe^{3+} ?
 (a) $[\text{Ar}]3d^64s^2$ (b) $[\text{Ar}]3d^54s^1$
 (c) $[\text{Ar}]3d^54s^2$ (d) $[\text{Ar}]3d^54s^0$
23. The last electron of a d-block element occupies the orbital
 (a) $(n-1)d$ (b) nd
 (c) np (d) $(n-1)s$
24. Which of the following ions is expected to be coloured in solution ?
 (a) Cu^+ (b) Cu^{2+}
 (c) Ti^{4+} (d) Sc^{3+}
25. Which of the following compounds is expected to be coloured ?
 (a) Ag_2SO_4 (b) CuF_2
 (c) MgF_2 (d) CuCl
26. The covalent radii of transition metals decrease from left to right in a period because
 (a) the densities of the metals decrease with increasing atomic number due to poor shielding of electrons
 (b) the screening of nuclear charge by d electrons is poor and hence the nuclear charge attracts all the electrons strongly, causing a decrease in size
 (c) the ionization energies also decrease correspondingly
 (d) the metallic character decreases as the atomic number increases
27. The highest possible oxidation state shown by osmium in its compounds is
 (a) +4 (b) +8
 (c) +6 (d) +10
28. Which of the following oxides of chromium is amphoteric in nature ?
 (a) CrO (b) CrO_3
 (c) Cr_2O_3 (d) CrO_5
29. Permanent magnets are generally made from the alloy of
 (a) Co (b) Zn
 (c) Al (d) Pb
30. CrO_3 dissolves in aqueous NaOH to give
 (a) CrO_4^{2-} (b) $\text{Cr}(\text{OH})_2$
 (c) $\text{Cr}_2\text{O}_7^{2-}$ (d) $\text{Cr}(\text{OH})_3$
31. Lanthanide elements have
 (a) similar lattice energies but widely different solvation and ionization energies
 (b) similar lattice and solvation energies but widely different ionization energies
 (c) similar lattice and ionization energies but widely different hydration energies
 (d) similar lattice energies, solvation energies and ionization energies
32. Among the transition metals, the melting points of Zn, Cd and Hg are relatively low because
 (a) their d shells are not completely filled
 (b) their d electrons do not participate in metallic bonding
 (c) their densities are higher
 (d) of all the above
33. The noble character of platinum and gold is favoured by
 (a) high enthalpies of sublimation, high ionization energies and low enthalpies of solvation
 (b) high enthalpies of sublimation, low ionization energies and low enthalpies of solvation
 (c) low enthalpies of sublimation, high ionization energies and low enthalpies of solvation
 (d) high enthalpies of sublimation, high ionization energies and high enthalpies of solvation
34. The transition elements are
 (a) more reactive than group 1 elements
 (b) more reactive than group 2 elements
 (c) less reactive than group 1 elements but more reactive than group 2 elements
 (d) less reactive than group 1 and 2 elements
35. Transition metals
 (a) form only ionic compounds
 (b) form exclusively covalent compounds
 (c) may form either ionic or covalent compounds depending on the condition
 (d) exclusively form coordination compounds but no simple compounds
36. Which of the following statements is incorrect ?
 (a) The compounds formed by the 3d transition metals in lower valence states are ionic but those in higher valence states are covalent.
 (b) The 4d and 5d transition metals form less ionic compounds than do the 3d transition metals.
 (c) The compounds formed by the 3d transition metals are less ionic than the corresponding compounds formed by the 4d and 5d transition metals.
 (d) The ionization energies of 3d, 4d and 5d transition metals are greater than those of group 1 and 2 metals.

37. Which of the following compounds is colourless?
 (a) K_2MnO_4 (b) HgI_2
 (c) ZnSO_4 (d) FeSO_4
38. The compound ZnSO_4 is white because
 (a) charge is transferred from the metal to the oxygen atoms
 (b) electron transfer to d level does not occur as the level is already filled to capacity in zinc
 (c) Zn^{2+} has d^{10} configuration and d–d transition occurs easily
 (d) Zn^{2+} ions absorb light of the visible range
39. Which of the following compounds is green in colour ?
 (a) KMnO_4 (b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 (c) MnO_2 (d) K_2MnO_4
40. $\text{Cr}_2\text{O}_7^{2-}$ reacts with OH^- as

$$\text{Cr}_2\text{O}_7^{2-} + 2(\text{OH}^-) \rightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$$
 The change in oxidation number of Cr is
 (a) +6 (b) +3
 (c) zero (d) +4
41. CrO_4^{2-} reacts with H^+ as

$$2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$
 The change in oxidation number of Cr is
 (a) +5 (b) +7
 (c) +6 (d) zero
42. Which of the following ions is paramagnetic ?
 (a) Zn^{2+} (b) N^{3-}
 (c) Mn^{4+} (d) Cu^+
43. Which of the following ions is diamagnetic ?
 (a) Ni^{2+} (b) Ti^{4+}
 (c) Cr^{3+} (d) Co^{3+}
44. The value of magnetic moment (μ spin only) for Cu^{2+} in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is
 (a) 5.92 BM (b) 4.92 BM
 (c) 2.83 BM (d) 1.73 BM
45. For a given ion, the magnetic moment is 2.83 BM. The total spin (s) of all the unpaired electrons is
 (a) 2 (b) 1
 (c) $3/2$ (d) $1/2$
46. The transition metals sometimes form nonstoichiometric compounds. These compounds have
 (a) definite structures and definite proportions
 (b) indefinite structures and definite proportions
 (c) definite structures and indefinite proportions
 (d) indefinite structures and indefinite proportions
47. Which of the following statements is correct ?
 (a) The second-row elements have smaller radii than the corresponding third-row ones.
 (b) Because of lanthanide contraction, the radii of the third-row elements are almost the same as those of the first-row elements.
 (c) Because of lanthanide contraction, the radii of the third-row elements are almost the same as those of the second-row elements.
 (d) Because of lanthanide contraction, the separation of second-row elements from one another is easier.
48. Sodium chromate is prepared by
 (a) fusing chromite (FeCr_2O_4) with sodium chloride in air
 (b) fusing chromite (FeCr_2O_4) with sodium hydroxide in air
 (c) fusing $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ with sodium hydrogen sulphate in nitrogen
 (d) fusing sodium dichromate with carbon
49. When hydrogen peroxide is added to an acidic solution of a dichromate, the most probable product is
 (a) K_2CrO_4 (b) CrO_3
 (c) Cr_2O_3 (d) $\text{CrO}(\text{O}_2)_2$
50. Which of the following statements is incorrect for CrO_3 ?
 (a) It is a bright orange solid.
 (b) It is commonly called chromic acid.
 (c) It is prepared by adding concentrated H_2SO_4 to a saturated solution of sodium dichromate.
 (d) The colour arises due to d–d transition.
51. Chromyl chloride, CrO_2Cl_2 , is prepared by heating a mixture of
 (a) NaCl , $\text{K}_2\text{Cr}_2\text{O}_7$ and NaOH
 (b) NaCl , $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4
 (c) NaCl , $\text{K}_2\text{Cr}_2\text{O}_7$ and MnO_2
 (d) CrO_3 and NaCl
52. Deep red-yellow vapour of CrO_2Cl_2 is passed into an aqueous solution of NaOH . The solution turns
 (a) yellow due to the formation of $\text{Na}_2\text{Cr}_2\text{O}_7$
 (b) yellow due to the formation of Na_2CrO_4
 (c) green due to the formation of CrCl_3
 (d) red due to the formation of Na_2CrO_4
53. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ on treatment with KI produces
 (a) KIO_3 (b) I_2
 (c) KIO_4 (d) I_3^-
54. Na_2CrO_4 on treatment with lead acetate gives a precipitate. This precipitate is dried and the solid is used as a pigment for road signs and markings. The solid is known as
 (a) white lead (b) chrome green
 (c) chrome yellow (d) red lead
55. Which of the following oxides of manganese is amphoteric ?
 (a) MnO (b) Mn_2O_3
 (c) Mn_2O_7 (d) MnO_2

56. Which of the following oxides of manganese is stable as well as strongly acidic ?
 (a) MnO_2 (b) Mn_2O_7
 (c) MnO_3 (d) Mn_2O_3
57. KMnO_4 is manufactured on a large scale by
 (a) fusing MnO_2 with KOH and then oxidizing the fused mixture with KNO_3
 (b) fusing MnO_2 with Na_2CO_3 in the presence of O_2
 (c) fusing MnO_2 with KOH and KNO_3 to form K_2MnO_4 which is then electrolytically oxidized in an alkaline solution
 (d) fusing MnO_2 with KNO_3 and then acidifying the fused mixture
58. MnO_4^- is prepared by treating a solution containing Mn^{2+} ions with a very strong oxidizing agent such as
 (a) PbO_2 (b) $\text{C}_2\text{O}_4^{2-}$
 (c) I_2 (d) Fe^{3+}
59. Which of the following is an incorrect statement ?
 (a) In a redox reaction in acidic medium, KMnO_4 produces Mn^{2+} ions.
 (b) In a redox reaction in strongly alkaline medium, KMnO_4 produces MnO_4^{2-} ions.
 (c) In a redox reaction in neutral medium, KMnO_4 produces MnO_2 .
 (d) In a redox reaction in alkaline medium, KMnO_4 produces Mn_2O_7 .
60. KMnO_4 in an acidic medium oxidizes
 (a) CrO_4^{2-} to CO_2 (b) N_2H_4 to N_2
 (c) $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-} (d) all of these
61. KMnO_4 in an acidic medium will not oxidize
 (a) NO_2^- (b) SO_4^{2-}
 (c) HN_3 (d) H_2O_2
62. Which one of the following oxides of chromium is amphoteric in nature ?
 (a) CrO (b) Cr_2O_3
 (c) CrO_3 (d) CrO_5
63. The electronic configuration of f-block elements is represented by
 (a) $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$
 (b) $(n-2)f^{1-14} (n-1)d^{0-5} ns^{0-2}$
 (c) $(n-2)f^{1-14} (n-1)d^{0-10} ns^{1-2}$
 (d) $(n-2)f^{1-14} (n-1)d^{0-2} (n-1)s^2$
64. Lanthanides are characterized by the filling of the
 (a) penultimate 4f energy level
 (b) antepenultimate 4f energy level
 (c) penultimate 3f energy level
 (d) antepenultimate 3f energy level
65. The electronic configuration of cerium is
 (a) $[\text{Xe}]4f^1 5d^1 6s^2$ (b) $[\text{Xe}]4f^2 5d^0 6s^1$
 (c) $[\text{Xe}]4f^1 5d^2 6s^2$ (d) $[\text{Xe}]4f^2 5d^0 6s^2$
66. Which of the following statements is correct for the lanthanoids ?
 (a) The 4f electrons do not take part in bonding.
 (b) The 4f electrons can neither be removed to produce ions nor be made to take part in crystal field stabilization of complexes.
 (c) The 4f electrons in the antepenultimate shell are very effectively shielded by the 5s and 5p electrons.
 (d) All of these
67. The most common and stable oxidation state of a lanthanide is
 (a) +II (b) +IV
 (c) +VII (d) +III
68. The atomic and ionic radii (M^{3+} ions) of lanthanide elements decrease with increasing atomic number. This effect is called
 (a) lanthanide contraction
 (b) lanthanide expansion
 (c) actinide contraction
 (d) none of these
69. Lanthanide contraction occurs because
 (a) the 4f electrons, which are gradually added, create a strong shielding effect
 (b) the 4f orbitals are greater in size than the 3d and 3f orbitals
 (c) the 5f orbitals strongly penetrate into the 4f orbitals
 (d) the poor shielding effect of 4f electrons is coupled with increased attraction between the nucleus and the added electrons
70. The hardness, melting point and boiling point of elements increase from Ce to Lu because
 (a) the attraction between the atoms increases as the size increases
 (b) the attraction between the atoms decreases as the size increases
 (c) the attraction between the atoms increases as the size decreases
 (d) the attraction between the atoms remains the same as the size increases

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

1. Arrange Ce^{+3} , La^{+3} , Pm^{+3} and Yb^{+3} in increasing order of their ionic radii. (2002)
 - (a) $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{Ce}^{+3} < \text{La}^{+3}$
 - (b) $\text{Ce}^{+3} < \text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3}$
 - (c) $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3}$
 - (d) $\text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3} < \text{Yb}^{+3}$
2. When KMnO_4 acts as an oxidising agent and ultimately forms $[\text{MnO}_4]^{2-}$, MnO_2 , Mn_2O_3 , Mn^{+2} then the number of electrons transferred in each case respectively is (2002)
 - (a) 4, 3, 1, 5
 - (b) 1, 5, 3, 7
 - (c) 1, 3, 4, 5
 - (d) 3, 5, 7, 1
3. The radius of La^{3+} (Atomic number of La = 57) is 1.06 Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71) ? (2003)
 - (a) 1.40 Å
 - (b) 1.06 Å
 - (c) 0.85 Å
 - (d) 1.60 Å
4. Ammonia forms the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solutions. What is the reason for it ? (2003)
 - (a) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
 - (b) In alkaline solutions insoluble $\text{Cu}(\text{OH})_2$ is precipitated which is soluble in excess of any alkali
 - (c) Copper hydroxide is an amphoteric substance
 - (d) In acidic solutions hydration protects copper ions
5. A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is (2003)
 - (a) HgI_2
 - (b) HgO
 - (c) Pb_3O_4
 - (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
6. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid ? (2003)
 - (a) $\text{Cr}_2\text{O}_7^{2-}$ and H_2O are formed
 - (b) CrO_4^{2-} is reduced to +3 state of Cr
 - (c) CrO_4^{2-} is oxidized to +7 state of Cr
 - (d) Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ are formed
7. Heating mixture of Cu_2O and Cu_2S will give (2005)
 - (a) Cu_2SO_3
 - (b) $\text{CuO} + \text{CuS}$
 - (c) $\text{Cu} + \text{SO}_3$
 - (d) $\text{Cu} + \text{SO}_2$
8. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives (2005)
 - (a) HgO
 - (b) Hg_2O
 - (c) $\text{NH}_2 - \text{Hg} - \text{Hg} - \text{Cl}$
 - (d) $\text{Hg NH}_2 \text{Cl}$
9. The lanthanide contraction is responsible for the fact that (2005)
 - (a) Zr and Zn have the same oxidation state
 - (b) Zr and Hf have about the same radius
 - (c) Zr and Nb have similar oxidation state
 - (d) Zr and Y have about the same radius
10. Which of the following factors may be regarded as the main cause of lanthanide contraction ? (2005)
 - (a) Greater shielding of 5d electrons by 4f electrons
 - (b) Poorer shielding of 5d electrons by 4f electrons
 - (c) Effective shielding of one of 4f electrons by another in the subshell
 - (d) Poor shielding of one of 4f electron by another in the subshell
11. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion ? (2006)
 - (a) One
 - (b) Two
 - (c) Six
 - (d) Three
12. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence (2007)
 - (a) $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$
 - (b) $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
 - (c) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$
 - (d) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$
13. Identify the incorrect statement among the following :
 - (a) 4f and 5f orbitals are equally shielded.
 - (b) d-Block elements show irregular and erratic chemical properties among themselves.
 - (c) La and Lu have partially filled d-orbitals and no other partially filled orbitals.
 - (d) The chemistry of various lanthanoids is very similar.

14. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because (2007)
- The 5f orbitals extend further from the nucleus than the 4f orbitals
 - The 5f orbitals are more buried than the 4f orbitals
 - There is a similarity between 4f and 5f orbitals in their angular part of the wave function
 - The actinoids are more reactive than the lanthanoids.
15. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being (2007)
- 4f orbitals more diffused than the 5f orbitals
 - lesser energy difference between 5f and 6d than between 4f and 5d orbitals
 - more energy difference between 5f and 6d than between 4f and 5d orbitals
 - more reactive nature of the actinoids than the lanthanoids
16. Amount of oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 . The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl (2008)
- gets oxidised by KMnO_4 to chlorine
 - furnishes H^+ ions in addition to those from oxalic acid
 - reduces permanganate to Mn^{2+}
 - Oxidises oxalic acid to carbon dioxide and water
17. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? (2009)
- The ionic size of Ln (III) decrease in general with increasing atomic number
 - Ln (III) compounds are generally colourless.
 - Ln (III) hydroxide are mainly basic in character.
 - Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
18. The correct order of $E_{\text{M}^{2+}/\text{M}}^\circ$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is (2010)
- $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$
 - $\text{Cr} > \text{Fe} > \text{Mn} > \text{Co}$
 - $\text{Fe} > \text{Mn} > \text{Cr} > \text{Co}$
 - $\text{Cr} > \text{Mn} > \text{Fe} > \text{Co}$
19. The outer electron configuration of Gd (At. No. 64) is (2011)
- $4f^3 5d^5 6s^2$
 - $4f^8 d^0 6s^2$
 - $4f^4 5d^4 6s^2$
 - $4f^7 5d^1 6s^2$
20. In context of the lanthanoids, which of the following statements is not correct? (2011)
- There is a gradual decrease in the radii of the members with increasing atomic number in the series.
 - All the member exhibit +3 oxidation state.
 - Because of similar properties the separation of lanthanoids is not easy.
 - Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.
21. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? (2012)
- Ferrous oxide is more basic in nature than the ferric oxide.
 - Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
 - Ferrous compounds are less volatile than the corresponding ferric compounds.
 - Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.
22. Which of the following arrangements does not represent the correct order of the property stated against it? (2013)
- $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: paramagnetic behaviour
 - $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: ionic size
 - $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: stability in aqueous solution
 - $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: number of oxidation states
23. The color of KMnO_4 is due to : (2015)
- $\text{L} \rightarrow \text{M}$ charge transfer transition
 - $\sigma - \sigma^*$ transition
 - $\text{M} \rightarrow \text{L}$ charge transfer transition
 - d – d transition
24. Which of the following compounds is metallic and ferromagnetic? (2016)
- CrO_2
 - VO_2
 - MnO_2
 - TiO_2
25. In the following reactions, ZnO is respectively acting as a/an (2017)
- $\text{ZnO} + \text{Na}_2\text{O} \longrightarrow \text{Na}_2\text{ZnO}_2$
 - $\text{ZnO} + \text{CO}_2 \longrightarrow \text{ZnCO}_3$
- base and acid
 - base and base
 - acid and acid
 - acid and base

JEE MAINS ONLINE QUESTION

- Which of the following is not formed when H_2S reacts with acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solution? **Online 2014 SET (1)**
 (a) CrSO_4 (b) $\text{Cr}_2(\text{SO}_4)_3$
 (c) K_2SO_4 (d) S
- Consider the following equilibrium

$$\text{AgCl} \downarrow + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$$
 White precipitate of AgCl appears on adding which of the following? **Online 2014 SET (2)**
 (a) aqueous HNO_3 (b) aqueous NaCl
 (c) aqueous NH_4Cl (d) NH_3
- Copper becomes green when exposed to moist air for a long period. This is due to: **Online 2014 SET (3)**
 (a) the formation of a layer of cupric oxide on the surface of copper.
 (b) the formation of basic copper sulphate layer on the surface of the metal
 (c) the formation of a layer of cupric hydroxide on the surface of copper.
 (d) the formation of a layer of basic carbonate of copper on the surface of copper.
- Which one of the following exhibits the largest number of oxidation states? **Online 2014 SET (3)**
 (a) Mn (25) (b) Ti (22)
 (c) Cr (24) (d) V (23)
- Which of these statements is not true ? B is always covalent in its compounds **Online 2014 SET (4)**
 (a) In aqueous solution the Tl^+ ion is much more stable than $\text{Tl}(\text{III})$
 (b) LiAlH_4 is a versatile reducing agent in organic synthesis.
 (c) NO^+ is not isoelectronic with O_2
 (d) None of these
- Which of the following statements is false ? **Online 2015 SET (1)**
 (a) $\text{Na}_2\text{Cr}_2\text{O}_7$ is less soluble than $\text{K}_2\text{Cr}_2\text{O}_7$
 (b) $\text{Na}_2\text{Cr}_2\text{O}_7$ is primary standard in volumetry
 (c) CrO_4^{2-} is tetrahedral in shape
 (d) CrO_7^{2-} has a Cr–O–Cr bond
- A pink coloured salt turns blue on heating. The presence of which cation is most likely? **Online 2015 SET (1)**
 (a) Co^{2+} (b) Cu^{2+}
 (c) Zn^{2+} (d) Fe^{2+}
- Which one of the following species is stable in aqueous solution **Online 2016 SET (1)**
 (a) Cr^{2+} (b) Cu^+
 (c) MnO_4^{3-} (d) MnO_4^{2-}
- Sodium extract is heated with concentrated HNO_3 before testing for halogens because : **Online 2016 SET (2)**
 (a) Silver halides are totally insoluble in nitric acid.
 (b) Ag_2S and AgCN are soluble in acidic medium.
 (c) S^{2-} and CN^- , if present, are decomposed by conc. HNO_3 and hence do not interfere in the test.
 (d) Ag reacts faster with halides in acidic medium
- Which of the following ions does not liberate hydrogen gas on reaction with dilute acids ? **Online 2017 SET (2)**
 (a) Ti^{2+} (b) V^{2+}
 (c) Cr^{2+} (d) Mn^{2+}
- In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively : **Online 2018 SET (3)**
 (a) sp^3d , trigonal bipyramidal
 (b) sp^3 , tetrahedral
 (c) dsp^2 , square planar
 (d) d^2sp^3 , octahedral
- When XO_2 is fused with an alkali metal hydroxide in presence of an oxidizing agent such as KNO_3 ; a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is : **Online 2018 SET (3)**
 (a) Ti (b) V
 (c) Cr (d) Mn

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked “S” are single choice questions
2. All questions marked “M” are multiple choice questions
3. All questions marked “C” are comprehension based questions
4. All questions marked “A” are assertion–reason type questions
 - (A) If both assertion and reason are correct and reason is the correct explanation of assertion.
 - (B) If both assertion and reason are true but reason is not the correct explanation of assertion.
 - (C) If assertion is true but reason is false.
 - (D) If reason is true but assertion is false.

D & F Block

1. (S) Chemically philosopher of wool is :
 - (a) ZnO
 - (b) BaO
 - (c) HgCl
 - (d) Hg₂Cl₂
2. (S) Boiling CuCl₂ with Cu in conc. HCl gives :
 - (a) CuCl
 - (b) CuCl₂
 - (c) H[CuCl₂]
 - (d) Cu₂Cl
3. (S) Thermal decomposition of zinc nitrate give :
 - (a) Zn
 - (b) ZnO
 - (c) Zn(NO₃)₂
 - (d) NO
4. (S) Malachite and azurite are used respectively are :
 - (a) Blue and green pigment
 - (b) Red and green pigment
 - (c) Green and blue pigment
 - (d) Green and red pigment
5. (S) Mercury is transported in the containers made of :
 - (a) Ag
 - (b) Pb
 - (c) Al
 - (d) Fe
6. (S) Calomel is the name of :
 - (a) HgCl₂
 - (b) Hg₂Cl₂
 - (c) HgCl₂ + Hg
 - (d) Hg₂Cl₂ + Hg
7. (S) ZnO shows yellow colour on Heating due to :
 - (a) d-d transition
 - (b) C-T spectra
 - (c) Higher polarisation caused by Zn²⁺ ion
 - (d) F-centres
8. (S) When steam is passed over red hot iron, the substances formed are :
 - (a) Fe₂O₃ + H₂
 - (b) Fe₃O₄ + H₂
 - (c) FeO + H₂
 - (d) FeO + H₂ + O₂
9. (S) Verdigris is :
 - (a) Basic copper acetate
 - (b) Basic lead acetate
 - (c) Basic lead
 - (d) None
10. (S) Which of the following is the correct formula for a compound of scandium and oxygen ?
 - (a) Sc₂O
 - (b) ScO
 - (c) Sc₃O₂
 - (d) Sc₂O₃
11. (S) Mercury on heating with aqua-regia gives :
 - (a) Hg(NO₃)₂
 - (b) HgCl₂
 - (c) Hg(NO₂)₂
 - (d) Hg₂Cl₂
12. (S) Chloroplatinic acid is :
 - (a) monobasic
 - (b) dibasic
 - (c) tribasic
 - (d) tetrabasic
13. (S) Fe is made passive by :
 - (a) dil. H₂SO₄
 - (b) dil. HCl
 - (c) conc. HNO₃
 - (d) conc. H₂SO₄
14. (S) Na₂CO₃ + Fe₂O₃ → A + CO₂ what is A in the reaction ?
 - (a) NaFeO₂
 - (b) Na₃FeO₃
 - (c) Fe₃O₄
 - (d) Na₂FeO₂

15. (S) Ferrous sulphate on heating gives :

- (a) SO_2 and SO_3 (b) SO_2 only
(c) SO_3 only (d) H_2S only

16. (S) Iron is protected by coating it with a thin layer of :

- (a) Cu (b) Zn
(c) Pb (d) Mg

17. (S) The formula of azurite is :

- (a) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (b) $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
(c) $\text{CuCO}_3 \cdot 2\text{Cu}(\text{OH})_2$ (d) $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$

18. (S) Oxide of metal cation which is not amphoteric?

- (a) Al^{3+} (b) Cr^{3+}
(c) Fe^{3+} (d) Zn^{2+}

19. (S) Philosopher's wool when heated with BaO at 1100°C gives the compound :

- (a) BaCdO_2 (b) $\text{Ba} + \text{ZnO}_2$
(c) $\text{BaO}_2 + \text{Zn}$ (d) BaZnO_2

20. (S) Gold dissolves in an aqua-regia forming :

- (a) Auric chloride (b) Aurous chloride
(c) Chloroauric acid (d) Aurous nitrate

21. (S) The solubility of silver bromide in hypo solution is due to the formation of :

- (a) Ag_2SO_3 (b) $\text{Ag}_2\text{S}_2\text{O}_3$
(c) $[\text{Ag}(\text{S}_2\text{O}_3)]^-$ (d) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

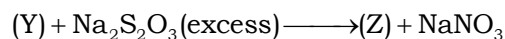
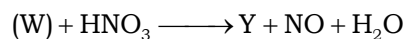
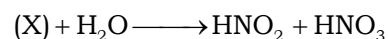
22. (S) Sodium thiosulphate is used to remove the unexposed AgBr from photographic films by forming a complex. In this complex of silver, the coordination number of silver is :

- (a) 2 (b) 4
(c) 6 (d) 8

23. (S) The false statement about iron (III) hydroxide is that :

- (a) it is a weaker base than $\text{Fe}(\text{OH})_2$
(b) with concentrated KOH, it forms a complex $\text{K}_3[\text{Fe}(\text{OH})_6]$
(c) it gradually loses water and transforms into Fe_2O_3
(d) it exhibits amphoteric properties with acid ones predominating

24. (S) $\text{AgNO}_3 \xrightarrow{\Delta} (\text{W}) + (\text{X}) + \text{O}_2$



Identify (W) to (Z).

- (a) $\text{W} = \text{Ag}$ $\text{X} = \text{N}_2\text{O}$ $\text{Y} = \text{AgNO}_3$ $\text{Z} = \text{Na}_2[\text{Ag}(\text{S}_2\text{O}_3)_2]$
(b) $\text{W} = \text{Ag}_2\text{O}$ $\text{X} = \text{NO}$ $\text{Y} = \text{AgNO}_3$ $\text{Z} = \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$
(c) $\text{W} = \text{Ag}$ $\text{X} = \text{NO}_2$ $\text{Y} = \text{AgNO}_3$ $\text{Z} = \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$
(d) $\text{W} = \text{Ag}_2\text{O}$ $\text{X} = \text{N}_2$ $\text{Y} = \text{AgNO}_3$ $\text{Z} = \text{Na}[\text{Ag}(\text{S}_2\text{O}_3)_2]$

25. (S) The oxidation state of copper changes when aqueous copper (II) ions react with :

- (I) $\text{NaOH} (\text{aq})$ (II) $\text{Fe}(\text{s})$
(III) $\text{KI} (\text{aq})$
(a) I, II, III (b) II only
(c) II, III (d) I only

26. (S) A blood red colour is obtained when ferric chloride solution reacts with :

- (a) KCN (b) KSCN
(c) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (d) $\text{K}_3[\text{Fe}(\text{CN})_6]$

27. (S) The compound in which nickel has the lowest oxidation state is :

- (a) $\text{Ni}(\text{CO})_4$ (b) $(\text{CH}_3\text{COO})_2\text{Ni}$
(c) NiO (d) $\text{NiCl}_2(\text{PPh}_3)_2$

28. (S) Spiegeleisen is an alloy of :

- (a) $\text{Cu} + \text{Zn} + \text{Ni}$ (b) $\text{Ni} + \text{Cr}$
(c) $\text{Mn} + \text{Fe} + \text{C}$ (d) $\text{Fe} + \text{Cr} + \text{Ni}$

29. (S) HgCl_2 is a covalent compound, sparingly soluble in water, the solubility increases by the addition of chloride ions due to :

- (a) common ion effect
(b) formation of complex $[\text{HgCl}_4]^{2-}$
(c) weakening of $\text{Hg} - \text{Cl}$ bonds
(d) strong ion – dipole forces

30. (S) Silver nitrate solution is kept in brown bottles in laboratory because :

- (a) it reacts with ordinary white bottles
(b) brown bottles cut the passage of light through
(c) brown bottles do not react with it
(d) ordinary bottles catalyse its decomposition

- 31. (S)** Copper is very slowly oxidised on the surface in moist air, giving a green coating of verdigris. Verdigris is :
- (a) Cu_2O (b) CuCO_3
 (c) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2$
 (d) CuSO_4
- 32. (S)** $\text{Fe}(\text{OH})_2$ is precipitated from $\text{Fe}(\text{II})$ solutions as a white solid but turns dark green and then brown due to the formation of :
- (a) $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$
 (b) only $\text{Fe}(\text{OH})_3$
 (c) $\text{Fe}_2\text{O}_3 \cdot (\text{H}_2\text{O})_n$ (d) $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
- 33. (S)** Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.
- (I) Sulphide ions reacts with $\text{Na}_2 [\text{Fe}(\text{CN})_5(\text{NO})]$ to form a purple coloured compound $\text{Na}_4 [\text{Fe}(\text{CN})_5(\text{NOS})]$. In the reaction, the oxidation state of iron changes .
 (II) $\text{Pt}(\text{IV})$ compounds are relatively more stable than $\text{Ni}(\text{IV})$ compounds
 (III) The welding of magnesium can be done in the atmosphere is Helium
 (IV) LiAlH_4 on hydrolysis will give H_2
- (a) FFTT (b) FTTF
 (c) TFTF (d) TFFT
- 34. (S)** Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is used in photography to :
- (a) Reduce the silver bromide to metallic silver
 (b) Convert the metallic silver to silver salt
 (c) remove underexposed AgBr as soluble silver thiosulphate complex
 (d) remove reduced silver
- 35. (S)** When AgNO_3 comes in contact with skin, it leaves a black stain. This is because of :
- (a) HNO_3 produced by hydrolysis of AgNO_3
 (b) AgOH produced by hydrolysis of AgNO_3
 (c) Its reduction of silver
 (d) Its oxidation to silver oxide
- 36. (S)** Mark the correct statements :
- (a) Hg forms an amalgam with iron
 (b) Hg vapour is non-poisonous
 (c) Hg is monovalent in mercurous compound
 (d) Oxysalts of mercury are thermally unstable
- 37. (S)** Mercury is the only metal which is liquid at 0°C . This is due to its :
- (a) Very high ionisation energy and weak metallic bond
 (b) Low ionisation potential
 (c) High atomic weight
 (d) High vapour pressure
- 38. (S)** A white precipitate of AgCl dissolves in excess of :
- (I) $\text{NH}_3(\text{aq})$ (II) $\text{Na}_2\text{S}_2\text{O}_3$
 (III) NaCN
 (a) III only (b) I, II, III
 (c) I, II (d) I only
- 39. (S)** Which of the following statements regarding copper salts is not true ?
- (a) Copper (I) disproportionates to copper and copper (II) ion in aqueous solution
 (b) Copper (I) can be stabilised by the formation of insoluble complex compounds such as CuCl_2^- and $\text{Cu}(\text{CN})_2^-$
 (c) Copper (II) oxide is red powder
 (d) The water of crystallization of copper sulphate is five
- 40. (S)** Zinc (II) ion on reaction with NaOH first give a white precipitate which dissolves in excess of NaOH due to the formation of :
- (a) ZnO (b) $\text{Zn}(\text{OH})_2$
 (c) $[\text{Zn}(\text{OH})_4]^{2-}$ (d) $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$
- 41. (M)** Mercury is a liquid at 0°C because of :
- (a) very high ionisation energy
 (b) weak metallic bonds
 (c) high heat hydration
 (d) high heat of sublimation
- 42. (M)** An element of 3d-transition series shown two oxidation states x and y, differ by two units then:
- (a) compounds in oxidation state x are ionic if $x > y$
 (b) compounds in oxidation state x are ionic if $x < y$
 (c) compounds in oxidation state y are covalent if $x < y$
 (d) compounds in oxidation state y are covalent if $y < x$
- 43. (M)** The metal oxide which decomposes on heating is/are :
- (a) ZnO (b) Al_2O_3
 (c) Ag_2O (d) HgO

44. (M) Which of the following acids attack(s) on copper and silver ?

- (a) dilute HNO_3 (b) dilute HCl
(c) conc. H_2SO_4 (d) aqua regia

45. (M) Identify the correct statements :

- (a) Iron belongs to first transition series of the periodic table
(b) The purest form of commercial iron is wrought iron
(c) Anhydrous ferrous sulphate is called as yellow vitriol
(d) Iron is the most abundant transition metal

46. (M) Which statements about mercury are correct?

- (a) Hg is a liquid metal
(b) Hg forms two series of salts
(c) Hg forms no amalgam with iron and platinum
(d) Anhydrous Hg does not show variable valency

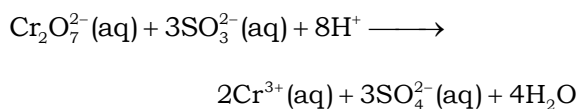
47. (M) To an acidified dichromate solution, a pinch of Na_2O_2 is added and shaken. What is observed?

- (a) Blue colour
(b) Orange colour changing to green
(c) Copious evolution of oxygen
(d) Bluish-green precipitate

48. (M) Pick out the correct statement(s) :

- (a) MnO_2 dissolves in conc. HCl , but does not form Mn^{4+} ions
(b) Decomposition of acidic KMnO_4 is not catalysed by sunlight
(c) MnO_4^{2-} is strongly oxidising and stable only in very strong alkali. In dilute alkali, water or acidic solutions it disproportionates
(d) KMnO_4 does not act as oxidising agent in alkaline medium

49. (M) Choose correct statement(s) regarding the following reaction.



- (a) $\text{Cr}_2\text{O}_7^{2-}$ is oxidising agent
(b) SO_3^{2-} is reducing agent
(c) The oxidation number of per 'S' atom in 3SO_3^{2-} is increase by two
(d) The oxidation number of per 'Cr' atom in $\text{Cr}_2\text{O}_7^{2-}$ is decreased by three

50. (A) **Assertion :** Melting point of Mn is more than that of Fe.

Reason : Mn has higher number of unpaired e^- than Fe in atomic state.

- (a) A (b) B
(c) C (d) D

51. (A) **Assertion :** Cu^+ has less stable than Cu^{2+} but Fe^{3+} is more stable than Fe^{2+} .

Reason : Half filled and completely filled subshells are more stable.

- (a) A (b) B
(c) C (d) D

52. (A) Zn gives H_2 gas with dil. HCl and also with dil. H_2SO_4 .

Reason : NO_3^- ion is reduced in preference to hydronium ion.

- (a) A (b) B
(c) C (d) D

53. (A) **Assertion :** KMnO_4 has different equivalent weights in acid, neutral or alkaline medium.

Reason : In different medium, change in oxidation number shown by manganese is altogether different.

- (a) A (b) B
(c) C (d) D

54. (A) **Assertion :** Cu^{2+} is more stable than Cu^+ .

Reason : Electrode potential is more important in determining stable oxidation state than electronic configuration.

- (a) A (b) B
(c) C (d) D

55. (A) **Assertion :** KMnO_4 is purple in colour to charge transfer.

Reason : There is no electron present in d-orbitals of manganese in MnO_4^- .

- (a) A (b) B
(c) C (d) D

56. (A) **Assertion :** CrO_3 reacts with HCl to form chromyl chloride gas.

Reason : Chromyl chloride (CrO_2Cl_2) has tetrahedral shape.

- (a) A (b) B
(c) C (d) D

57. (A) **Assertion :** Hg is the only metal which is liquid at 0°C.

Reason : It has very high I.P. and weak metallic bond.

- (a) A (b) B
(c) C (d) D

58. (A) **Assertion :** $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are blue and green colour compounds respectively.

Reason : Both compounds have their specific colour due to phenomenon of polarisation of anion.

- (a) A (b) B
(c) C (d) D

59. (A) **Assertion :** $\text{Zn}(\text{OH})_2$ is dissolved in both NH_4OH and NaOH solution.

Reason : Both NaOH and NH_4OH being basic can dissolve amphoteric $\text{Zn}(\text{OH})_2$.

- (a) A (b) B
(c) C (d) D

60. (A) **Assertion :** AgNO_3 reacts with KCN to form white ppt. of AgCN . This white ppt. disappears when excess KCN is added.

Reason : AgCN decomposes to form silver-carbide and evolve N_2 gas.

- (a) A (b) B
(c) C (d) D

Comprehension

A white substance 'X' when heated in a test tube, produces a colourless, odourless gas leaving a residue, yellow when hot and white when cold. The residue was dissolved in dil. HCl , made alkaline with NH_4Cl and NH_4OH and H_2S gas was passed through it. A white ppt 'Y' was formed. It was dissolved in dil. HCl to give 'Z' which on treatment with $\text{K}_4[\text{Fe}(\text{CN})_6]$ gave bluish white precipitate.

61. (C) 'X' is

- (a) ZnO (b) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
(c) Cu_2Cl_2 (d) ZnCO_3

62. (C) 'Y' and 'Z' are respectively

- (a) ZnO , ZnSO_4 (b) ZnS , ZnCl_2
(c) ZnCl_2 , $\text{Zn}(\text{OH})_2$ (d) ZnO , ZnS

63. (C) Bluish white precipitate formed is

- (a) $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ (b) $\text{K}_2[\text{Zn}(\text{CN})_4]$

- (c) $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (d) None of these

Comprehension

A certain metal (X) is boiled in dilute HNO_3 to give a salt (Y) and an oxide of nitrogen (Z). An aqueous solution of (Y) with brine solution gives a white precipitate (P). When (Y) was treated with $\text{Na}_2\text{S}_2\text{O}_3$ solution a white precipitate (Q) was obtained which on standing turns to a black compound (R).

64. (C) Salt (Y) and the oxide of nitrogen (Z) is

- (a) $\text{AgNO}_3 + \text{NO}_2$ (b) $\text{AgNO}_3 + \text{NO}$
(c) $\text{AgNO}_3 + \text{N}_2$ (d) $\text{AgNO}_3 + \text{NH}_3$

65. (C) The precipitate (Q) formed is

- (a) Ag_2S (b) $\text{Ag}_2\text{S}_2\text{O}_3$
(c) Ag_2O (d) Ag_2SO_3

66. (C) The compound (R) formed is

- (a) Ag_2O (b) Ag
(c) Ag_2S (d) Ag_2SO_3

67. (S) Wilkinson's catalyst consists of

- (a) $(\text{C}_2\text{H}_5)_3\text{Al}$ and TiCl_4
(b) RhCl_3 and Ph_3P
(c) $\text{HCo}(\text{CO})_4$
(d) $\text{trans} - [(\text{Rh}(\text{CO})(\text{H})(\text{PPh}_3)_3)]$

68. (S) Which of the following mixture is known as Fenton's reagent ?

- (a) $\text{FeSO}_4 + \text{K}_4[\text{Fe}(\text{CN})_6]$ (b) $\text{FeSO}_4 + \text{PdCl}_2$
(c) $\text{FeSO}_4 + \text{H}_2\text{O}_2$ (d) $\text{TiCl}_4 + (\text{C}_6\text{H}_5)_3\text{P}$

69. (S) Which of the following is known as Adams catalyst ?

- (a) Pt/PtO (b) $\text{V}_2\text{O}_5/\text{TiCl}_4$
(c) Cu/V (d) Pt/Rh

70. (S) Which of the following ores is known as pyrolusite ?

- (a) Fe_2O_3 (b) SnO_2
(c) MnO_2 (d) PbS

71. (S) Dilute and slightly alkaline KMnO_4 is called

- (a) Fenton's reagent (b) Lucas reagent
(c) Baeyer's reagent (d) Tollens reagent

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

Objective Questions (Only one correct option)

1. When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of hydrogen evolved is **(1979)**
 (a) 1 : 1 (b) 1 : 2
 (c) 2 : 1 (d) 9 : 4
2. Which of the following is the weakest base **(1980)**
 (a) NaOH (b) $\text{Ca}(\text{OH})_2$
 (c) KOH (d) $\text{Zn}(\text{OH})_2$
3. One of the constituent of German silver is **(1980)**
 (a) Ag (b) Cu
 (c) Mg (d) Al
4. Which of the following dissolves in hot conc. NaOH solution **(1980)**
 (a) Fe (b) Zn
 (c) Cu (d) Ag
5. How many unpaired electrons are present in Ni^{2+} ? **(1981)**
 (a) 0 (b) 2
 (c) 4 (d) 8
6. Sodium thiosulphate is used in photography because of its **(1981)**
 (a) reducing behaviour
 (b) oxidising behaviour
 (c) complex forming behaviour
 (d) reaction with light
7. Iron is rendered passive by treatment with concentrated **(1982)**
 (a) H_2SO_4 (b) H_3PO_4
 (c) HCl (d) HNO_3
8. In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in **(1982)**
 (a) slag (b) gangue
 (c) metallic calcium (d) calcium carbonate
9. Zinc-copper couple that can be used as a redcuing agent is obtained by : **(1984)**
 (a) mixing zinc dust and copper gauze
 (b) zinc coated with copper
 (c) copper coated with zinc
 (d) zinc and copper wires welded together
10. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by **(1988)**
 (a) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (d) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
11. The reaction which proceed in the forward direction is **(1991)**
 (a) $\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$
 (b) $\text{NH}_3 + \text{H}_2\text{O} + \text{NaCl} \rightarrow \text{NH}_4\text{Cl} + \text{NaOH}$
 (c) $\text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 \rightarrow \text{SnCl}_2 + 2\text{HgCl}_2$
 (d) $2\text{CuI} + \text{I}_2 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 4\text{KI}$
12. Which one is solder ? **(1995)**
 (a) Cu & Pb (b) Zn & Cu
 (c) Pb & Sn (d) Fe & Zn
13. Which pair gives Cl_2 at room temperature ? **(1995)**
 (a) $\text{HCl}(\text{conc}) + \text{KMnO}_4$ (b) $\text{NaCl} + \text{H}_2\text{SO}_4(\text{conc})$
 (c) $\text{NaCl} + \text{MnO}_2$ (d) $\text{NaCl} + \text{HNO}_3(\text{conc})$
14. An aqueous solution of FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are :
 (a) a colourless filtrate and a green residue
 (b) a yellow filtrate and a green residue
 (c) a yellow filtrate and a brown residue
 (d) a green filtrate and a brown residue
15. Among the following, the compound that is both paramagnetic and coloured is **(1997)**
 (a) $\text{K}_2\text{Cr}_2\text{O}_7$ (b) $(\text{NH}_4)_2(\text{TiCl}_6)$
 (c) CoSO_4 (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$
16. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is **(1997)**
 (a) CrO_3 (b) Cr_2O_3
 (c) Cr (d) $\text{CrO}(\text{O}_2)$
17. The number of moles of KMnO_4 that will be needed to react with one mole of sulphite ion in acidic solution is **(1997)**
 (a) $\frac{2}{5}$ (b) $\frac{3}{5}$
 (c) $\frac{4}{5}$ (d) 1

18. Which of the following is an organometallic compound ? (1997)
 (a) Lithium methoxide (b) Lithium acetate
 (c) Lithium dimethylamide (d) Methyl lithium
19. Which of the following compounds is expected to be coloured ? (1997)
 (a) Ag_2SO_4 (b) CuF_2
 (c) MgF_2 (d) CuCl
20. In the dichromate anion, (1999)
 (a) 4 Cr – O bonds are equivalent
 (b) 6 Cr – O bonds are equivalent
 (c) all Cr – O bonds are equivalent
 (d) all Cr – O bonds are nonequivalent
21. On heating ammonium dichromate, the gas evolved is (1999)
 (a) oxygen (b) ammonia
 (c) nitrous oxide (d) nitrogen
22. Amongst the following, identify the species with an atom in +6 oxidation state (2000)
 (a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$
 (c) NiF_6^{2-} (d) CrO_2Cl_2
23. In the process of extraction of gold.

$$\text{Roasted gold ore} + \text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$$

$$[\text{X}] + \text{Zn} \longrightarrow [\text{Y}] + \text{Au}$$
 Identify the complexes [X] and [Y] (2003)
 (a) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
 (b) $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$, $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$
 (c) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$
 (d) $\text{X} = [\text{Au}(\text{CN})_4]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
24. When MnO_2 is fused with KOH , a coloured compound is formed, the product and its colour is (2003)
 (a) K_2MnO_4 , purple green (b) KMnO_4 , purple
 (c) Mn_2O_3 , brown (d) Mn_3O_4 , black
25. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating gives a gas which is also given by (2004)
 (a) heating NH_4NO_2 (b) heating NH_4NO_3
 (c) $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O}$ (d) $\text{Na}(\text{comp.}) + \text{H}_2\text{O}_2$
26. The pair of compounds having metals in their highest oxidation state is (2004)
 (a) MnO_2 , FeCl_3 (b) $[\text{MnO}_4]^-$, CrO_2Cl_2
 (c) $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_3]$ (d) $[\text{NiCl}_4]^{2-}$, $[\text{CoCl}_4]^-$
27. When I^- is oxidised by MnO_4^- in alkaline medium, I^- converts into (2004)
 (a) IO_3^- (b) I_2
 (c) IO_4^- (d) IO^-
28. Which of the following pair is expected to exhibit same colour in solution ? (2005)
 (a) VOCl_2 ; FeCl_2 (b) CuCl_2 ; VOCl_2
 (c) MnCl_2 ; FeCl_2 (d) FeCl_2 ; CuCl_2
29. Which of the following will not be oxidised by O_3 ? (2005)
 (a) KI (b) FeSO_4
 (c) KMnO_4 (d) K_2MnO_4
30. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of (2008)
 (a) nitrogen (b) oxygen
 (c) carbon dioxide (d) argon
31. Among the following, the coloured compound is (2008)
 (a) CuCl (b) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (c) CuF_2 (d) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$
32. The colour of light absorbed by an aqueous solution of CuSO_4 is (2011)
 (a) orange-red (b) blue-green
 (c) yellow (d) violet
33. Which of the following combination will produce H_2 gas ? (2018)
 (a) Fe metal and conc. HNO_3
 (b) Cu metal and conc. HNO_3
 (c) Au metal and $\text{NaCN}(\text{aq})$ in the presence of air
 (d) Zn metal and $\text{NaOH}(\text{aq})$

Objective Questions (One or more than one correct option)

34. Potassium manganate (K_2MnO_4) is formed when (1988)
- chlorine is passed into aqueous $KMnO_4$ solution
 - manganese dioxide is fused with KOH in air
 - formaldehyde reacts with potassium permanganate in presence of strong alkali
 - potassium permanganate reacts with conc. H_2SO_4
35. The aqueous solutions of the following salts will be coloured in the case of (1990)
- $Zn(NO_3)_2$
 - $LiNO_3$
 - $Co(NO_3)_2$
 - $CrCl_3$
36. Which of the following alloys contains(s) Cu and Zn ? (1993)
- Bronze
 - Brass
 - Gun metal
 - Type metal
37. Which of the following statement (s) is/are correct when a mixture of $NaCl$ and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ? (1998)
- a deep red vapours is formed
 - vapours when passed into $NaOH$ solution gives a yellow solution of Na_2CrO_4
 - chlorine gas is evolved
 - chromyl chloride is formed
38. Which of the following statement (s) is/are correct ? (1998)
- The electronic configuration of Cr is $[Ar] 3d^5 4s^1$
(Atomic number of Cr = 24)
 - The magnetic quantum number may have a negative value
 - In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (Atomic number of Ag = 47)
 - The oxidation state of nitrogen in HN_3 is - 3
39. The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) [Atomic numbers of Cr = 24 and Mn = 25] (2015)
- Cr^{2+} is a reducing agent
 - Mn^{3+} is an oxidizing agent
 - Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
 - When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

40. Fe^{3+} is reduced to Fe^{2+} by using (2015)
- H_2O_2 in presence of $NaOH$
 - Na_2O_2 in water
 - H_2O_2 in presence of H_2SO_4
 - Na_2O_2 in presence of H_2SO_4

Assertion and Reason

- (A) If both ASSERTION and REASON are true and reason is the correct explanation of the assertion.
- (B) If both ASSERTION and REASON are true but reason is not the correct explanation of the assertion.
- (C) If ASSERTION is true but REASON is false.
- (D) If both ASSERTION and REASON are false.
- (E) If ASSERTION is false but REASON is true.
41. **Assertion :** To a solution of potassium chromate if a strong acid is added, it changes its colour from yellow to orange.
Reason : The colour change is due to the change in oxidation state of potassium chromate. (1988)
- A
 - B
 - C
 - D
 - E
42. **Assertion :** Zn^{2+} is diamagnetic.
Reason : The electrons are lost from 4s orbital to form Zn^{2+} . (1998)
- A
 - B
 - C
 - D
 - E

Fill in the Blanks

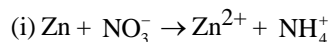
43. Mn^{2+} can be oxidized to MnO_4^- by (SnO_2 , PbO_2 , BaO_2) (1981)
44. The salts and are isostructural. ($FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$) (1990)
45. Fehling's solution A consists of an aqueous solution of copper sulphate while Fehling's solution B consists of an alkaline solution of (1990)
46. The outermost electronic configuration of Cr is (1994)
47. The compound $YBa_2Cu_3O_7$ which show super conductivity has copper in oxidation state assuming that the rare earth element Yttrium in its usual +3 oxidation state. (1994)

True/False

48. Copper metal reduces Fe^{2+} in an acid medium. (1982)
49. Dipositive zinc exhibit paramagnetism due to loss of two electrons from 3d orbitals of neutral atom. (1987)

Subjective Questions

50. Complete and balance the following reactions (1983)



51. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.

“Potassium permanganate from manganese dioxide”

(1983)

52. Show with balanced equations for the reactions when

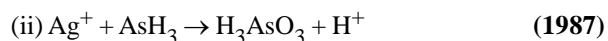
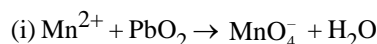
(i) Potassium permanganate interacts with manganese dioxide in presence of potassium hydroxide.

(ii) Potassium ferricyanide is heated with concentrated sulphuric acid. (1985)

53. Give reason in one or two sentences.

“Most transition metal compounds are coloured.” (1986)

54. Complete and balance the following reactions

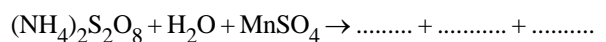


55. Write the balanced chemical equations for the following reactions

(i) A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4 .

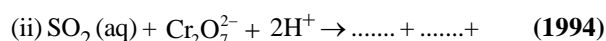
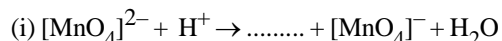
(ii) Potassium permanganate is added to a hot solution of manganous sulphate. (1990)

56. Complete and balance the following reaction



(1993)

57. Complete and balance the following reactions



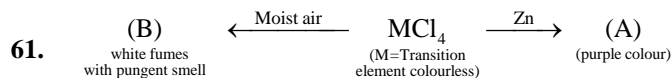
58. Write balanced equations for the following

(i) Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.

(ii) Reaction of zinc with dilute nitric acid. (1997)

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

60. Give reason : CrO_3 is an acid anhydride. (1999)



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

62. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is (2016)

ANSWER KEY

Exercise - 1 (Basic Objective Questions)

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

Exercise - 2 (Previous Year JEE Mains Questions)

1. (a)	2. (c)	3. (c)	4. (a)	5. (a)	6. (a)	7. (d)	8. (d)	9. (b)	10. (d)
11. (a)	12. (d)	13. (a)	14. (a)	15. (b)	16. (c)	17. (b)	18. (a)	19. (d)	20. (d)
21. (d)	22. (a)	23. (a)	24. (a)	25. (d)					

JEE Mains Online

1. (a)	2. (a)	3. (d)	4. (a)	5. (a)	6. (b)	7. (a)	8. (d)	9. (b)	10. (d)
11. (c)	12. (d)								

Exercise-3 (Advanced Objective Questions)

1. (a)	2. (a)	3. (b)	4. (c)	5. (d)	6. (b)	7. (d)	8. (b)	9. (a)	10. (d)
11. (b)	12. (b)	13. (c)	14. (a)	15. (a)	16. (b)	17. (b)	18. (c)	19. (a)	20. (c)
21. (c)	22. (b)	23. (d)	24. (c)	25. (c)	26. (b)	27. (a)	28. (c)	29. (b)	30. (b)
31. (c)	32. (c)	33. (a)	34. (c)	35. (c)	36. (d)	37. (a)	38. (b)	39. (c)	40. (c)
41. (a,b)	42. (b,c)	43. (c,d)	44. (a,c,d)	45. (a,b,d)	46. (a,b,c,d)		47. (a,c)	48. (a,c)	
49. (a,b,c,d)	50. (d)	51. (b)	52. (b)	53. (a)	54. (a)	55. (b)	56. (b)	57. (a)	58. (c)
59. (c)	60. (c)	61. (d)	62. (b)	63. (a)	64. (b)	65. (b)	66. (c)	67. (b)	68. (c)
69. (a)	70. (c)	71. (c)							

Exercise - 4 (Previous Year JEE Advanced Questions)

1. (a)	2. (d)	3. (b)	4. (b)	5. (b)	6. (c)	7. (d)	8. (a)	9. (a)	10. (b)
11. (a)	12. (c)	13. (a)	14. (c)	15. (c)	16. (b)	17. (a)	18. (d)	19. (b)	20. (b)
21. (d)	22. (d)	23. (a)	24. (a)	25. (a)	26. (b)	27. (a)	28. (b)	29. (c)	30. (b)
31. (c)	32. (a)	33. (d)	34. (b, c)	35. (c,d)	36. (b,c)	37. (a, b, c, d)		38. (a, b, c)	
39. (a,b,c)	40. (c,d)	41. (c)	42. (b)	43. PbO_2	44. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$		45. Rochelle salt		
46. $3d^5 4s^1$	47. $x = +\frac{7}{3}$	48. False	49. False	62. (0006)					