

# d-Block Elements

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## Syllabus

### d-Block Elements

Transition elements (3d series): Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment; Preparation and properties of the following compounds: Oxides and chlorides of tin and lead. Oxides, chlorides and sulphates of  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ; Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate

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# TRANSITION ELEMENTS (d-BLOCK ELEMENTS) & THEIR COMPOUNDS

## INTRODUCTION :

- (i) The elements lying between s- & p - block element of the periodic table are collectively known as transition or transitional elements.
- (ii) Their properties are transitional between the highly electropositive s- block element to least electropositive p - block elements.
- (iii) In d-block elements, the last differentiating electron is accommodated to the penultimate shell, expanding it from 8 to 18 electrons.
- (iv) The general electronic configuration of transition element is  $(n-1) d^{1-10} ns^{0, 1 \text{ or } 2}$
- (v) These elements either in their atomic state or in any of their common oxidation state have partly filled  $(n-1)$  d- orbitals of  $(n-1)^{\text{th}}$  main shell.
- (vi) The configuration clearly show that strictly, according to the definition of d- block elements, Cu, Ag & Au should be excluded from d- block element. Since these elements, both in their atomic state [With configuration  $(n-1) d^{10} ns^1$ ] & in their +1 oxidation state [ with configuration  $(n-1) d^{10}$ ], do not have partly filled  $(n-1)$  d- orbitals.
- (vii) Similarly Zn, Cd & Hg which both in their atomic state [  $(n-1) d^{10} ns^2$ ] & in + 2 oxidation state [  $(n-1) d^{10}$  ] do not contain partly filled  $(n-1)$  d orbitals should be excluded from d- block elements..
- (viii) Yet, in order to maintain a rational classification of the elements; these elements (viz. Cu, Ag, Au, Zn, Cd & Hg) are also generally studied with d- block elements.
- (ix) There are four complete rows ( called series) of ten elements each corresponding to the filling of 3d, 4d, 5d & 6d orbitals respectively.
- (x) The irregularities in the observed configuration of Cr ( $3d^5 4s^1$  instead of  $3d^4 4s^2$ ), Cu ( $3d^{10} 4s^1$ ), Mo ( $4d^5 4s^1$ ), Pd ( $[Kr] 4d^{10} 5s^0$ ), Au ( $[Xe] 4f^{14} 5d^{10} 4s^1$ ), Ag ( $[Kr] 4d^{10} 5s^1$ ) are explained on the basis of the concept that half- filled and completely filled d- orbitals are relatively more stable than other d- orbitals.

There are greater horizontal similarities in the properties of the transition elements. However, some group similarities also exist.

## GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

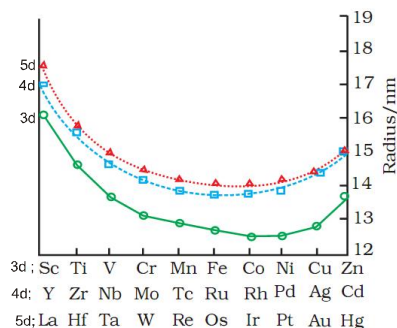
### Size of atoms and ions :

The atomic radii of the transition metals lie in-between those of s- and p-block elements. The covalent radii of the elements decreases from left to right across a row in the transition series, until near the end when the size increases slightly. The decrease in size is small after mid way. In the beginning, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), where as the shielding effect of d-electrons is small. After mid way as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.

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

The atomic radii, in general, increase down the group. The atomic radii of second series are larger than those of first transition series. In the atoms of the second transition series, the number of shells are more than those of the 1st transition series. As a result, the atoms of 2nd transition series are larger than those of the elements of the first transition series. But the atomic radii of the second and third transition series are almost the same.

This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called.



Trends in atomic radii of transition elements

**Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

The trend followed by the ionic radii is same as that followed by atomic radii. The ionic radii of transition metals are different in different oxidation states.

**Density :**

The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high. The densities of the second row are high and third row values are even higher. Elements with the highest densities are osmium  $22.57 \text{ g cm}^{-3}$  and irridium  $22.61 \text{ g cm}^{-3}$ .

Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities also increase across a period.

The last element zinc is an exception, having large atomic volume and hence lower density.

**Ionisation energies or Ionisation enthalpies :**

The first ionisation energies of d-block elements are intermediate between those of the s- and p-blocks. This suggests that the transition elements are less electropositive than groups 1 and 2 and may form either ionic

or

covalent bonds depending on the conditions. Generally, the lower valent states are ionic and the higher valent states are covalent. Across a period from left to right ionisation energies gradually increase with increase in

atomic number

along the period. Consequently making the removal of outer electron difficult.

In a given series, the difference in the ionisation energies between any two successive d-block elements is very

much less than the difference in case of successive s-block or p-block elements. The effect of increased nuclear

charge and screening effect of the added d-electrons tend to oppose each other. Hence due to these two counter

effects, the difference in the ionisation energies of two successive transition elements is very small on moving

across a period.

The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled  $(n-1)d^{10}ns^2$  configuration.  $II^{nd}$  and  $III^{rd}$  ionisation energies also increase along a period.

$II^{nd}$  ionisation energy of  $Cr > Mn$  and  $Cu > Zn$

This is because after the removal of 1<sup>st</sup> electron Cr and Cu acquire stable configurations ( $d^5$  &  $d^{10}$ ) and the removal of  $II^{nd}$  electron thus become very difficult.

Similarly the  $IE_2$  of  ${}_{23}V < {}_{24}Cr > {}_{25}Mn$  and  ${}_{28}Ni < {}_{29}Cu > {}_{30}Zn$

The third ionization energy of Mn is very high because the third electron has to be removed from the stable half-filled 3d orbital.

The first ionisation energies of the 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 higher effective nuclear charge

acting on the outer valence electrons.

The magnitude of ionization enthalpy gives the amount of energy required to remove electrons to form a particular oxidation state of the metal in a compound. Thus, the value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states. Smaller the ionisation enthalpy of the metal, the stable is its compound. For example, the first four ionisation enthalpies of nickel and platinum are given below :

Ionisation enthalpies	Ni	Pt
$IE_1 + IE_2$	$2.49 \times 10^3 \text{ kJ mol}^{-1}$	$2.66 \times 10^3 \text{ kJ mol}^{-1}$
$IE_3 + IE_4$	$8.80 \times 10^3 \text{ kJ mol}^{-1}$	$6.70 \times 10^3 \text{ kJ mol}^{-1}$
Total	$11.29 \times 10^3 \text{ kJ mol}^{-1}$	$9.36 \times 10^3 \text{ kJ mol}^{-1}$

It is clear from the above table that the sum of first two ionization enthalpies is less for nickel than for platinum.



Therefore, ionization of nickel to  $\text{Ni}^{2+}$  is energetically favourable as compared to that of platinum. Thus, the nickel (II) compounds are thermodynamically more stable than platinum (II) compounds. On the other hand, the sum of first four ionisation enthalpies is less for platinum than for nickel as :



Thus, the platinum (IV) compounds are relatively more stable than nickel (IV) compounds. Therefore,  $\text{K}_2\text{PtCl}_6$  [having Pt (IV)] is a well-known compound whereas the corresponding nickel compound is not known.

However, in solutions the stability of the compounds depends upon electrode potentials.

### Metallic character :

In d-block elements the last but one (i.e. the penultimate) shell of electrons is expanding. Thus they have many physical and chemical properties in common.

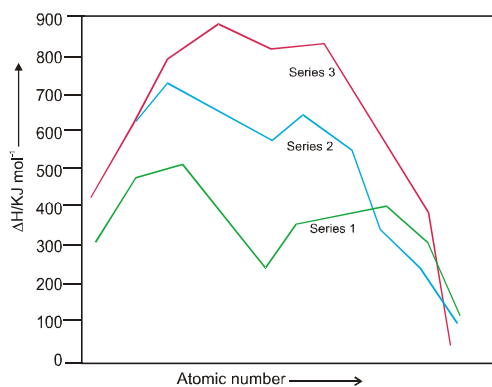
Hence nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

The transition elements (with the exception of copper) are very much hard and have low volatility.

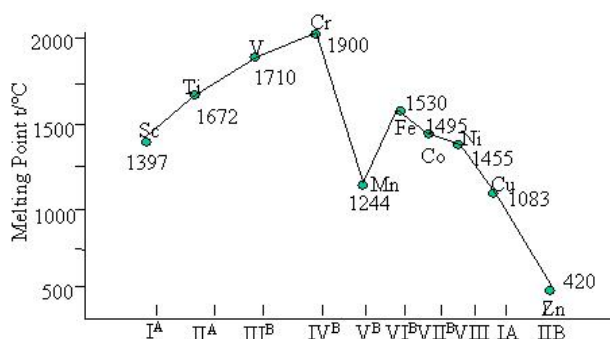
They have high enthalpies of atomisation which are shown in figure given below. The maxima at about the middle of each series indicate that one unpaired electron per d orbital is particularly favourable of strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomization.

Hence the metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions.

The metals of the second, 4d and third, 5d series have greater enthalpies of atomisation than the corresponding elements of the first series, 3d and this is an important factor indicating for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.



Graph showing Trends in enthalpies of atomisation of transition elements



Graphic representation m.p. of 3d-series elements

### Melting and boiling points :

The melting and boiling points of the transition series elements are generally very high. The melting points of the transition elements rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points. Strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points. In a particular series, the metallic strength increases upto the middle with increasing number of unpaired electrons i.e up to  $d^5$ . After chromium, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons.

The dip in melting points of Mn and Tc can be attributed to their stable electronic configurations (half filled  $3d^5$  and fully filled  $4s^2$ ). Due to this stable electronic configuration, the delocalisation of electrons may be less and thus the metallic bond is much weaker than preceding elements.

### Oxidation states :

The transition metals exhibit a large number of oxidation states. With the exception of a few elements, most of these show variable oxidation states. These different oxidation states are related to the electronic configuration of their atoms.

The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner  $(n - 1)$  d-electrons in addition to outer ns-electrons because, the energies of the ns and  $(n - 1)$  d-sub-shells are nearly same. For example, scandium has the outer electronic configuration  $3d^1 4s^2$ . It exhibits an oxidation state of +2 when it uses both of its 4s-electrons for bonding but it can also show oxidation state of +3 when it uses its two s-electrons and one d-electron. Similarly, the other atoms can show oxidation states equal to ns-and  $(n - 1)$  d-electrons.

#### Different oxidation states of first transition series.

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

Oxidation states given in parenthesis are unstable.

It may be noted that the stability of a given oxidation state depends upon the nature of the elements with which the metal is combined. The highest oxidation states are found in compounds of fluorides and oxides because fluorine and oxygen are most electronegative elements.

The examination of the common oxidation states exhibited by different transition metals reveals the following facts :

- (i) The variable oxidation states of transition metals are due to participation of inner  $(n - 1)d$  and outer ns-electrons. The lowest oxidation state corresponds to the number of ns-electrons. For example, in the first transition series, the lowest oxidation states of Cr ( $3d^5 4s^1$ ) and Cu ( $3d^{10} 4s^1$ ) are +1 while for others, it is +2 ( $3d^{1-10} 4s^2$ ).
- (ii) Except scandium, the most common oxidation state of the first row transition elements is +2 which arises due to loss of two 4s-electrons. This means that after scandium 3d-orbitals become more stable and, therefore, are lower in energy than the 4s-orbitals. As a result, electrons are first removed from 4s-orbitals.

- (iii) The elements which show the greater number of oxidation states occur in or near the middle of the series. For example, in the first transition series, manganese exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states in the beginning of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a fewer orbitals are available in which the electron can share with other for higher valence. The highest oxidation state shown by any transition metal is +8.
- (iv) In the +2 and +3 oxidation states, the bonds formed are mostly ionic. In the compounds of higher oxidation states (generally formed with oxygen and fluorine), the bonds are essentially covalent. Thus, the bonds in +2 and +3 oxidation states are generally formed by the loss of two or three electrons respectively while the bonds in higher oxidation states are formed by sharing of d-electrons. For example, in  $\text{MnO}_4^-$  (Mn in +7 state) all the bonds are covalent.
- (v) Within a group, the maximum oxidation state increase with atomic number. For example, iron (group 8) shows common oxidation states of +2 and +3 but ruthenium and osmium in the same group form compounds in the +4, +6 and +8 oxidation states.
- (vi) Transition metals also form compounds in low oxidation states such as +1 and 0 or negative. The common examples are  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$  in which nickel and iron are in zero oxidation state.
- (vii) The variability of oxidation states in transition elements arises because of incomplete filling of the d-orbitals in such a way that their oxidation states differ by unity such as  $\text{V}^{\text{II}}$ ,  $\text{V}^{\text{III}}$ ,  $\text{V}^{\text{IV}}$  and  $\text{V}^{\text{V}}$ . This behaviour is in contrast with the variability of oxidation states of non-transition elements (p-block elements), where oxidation states normally differ by a unit of two such as  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{In}^+$ ,  $\text{In}^{3+}$ , etc.
- (viii) Unlike p-block elements where the lower oxidation states are favoured by heavier members (due to inert pair effect), the higher oxidation states are more stable in heavier transition elements. For example, in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). Therefore, Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent whereas  $\text{MoO}_3$  and  $\text{WO}_3$  are not.

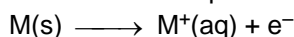
#### Oxidation states in Oxides and Oxoions :

The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides coincides with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides,  $\text{Sc}_2\text{O}_3$  whereas the highest oxidation state of manganese of group 7 is +7, in  $\text{Mn}_2\text{O}_7$ . However beyond group 7, no higher oxides of iron above  $\text{Fe}_2\text{O}_3$  are known. Although higher oxidation state such as +6 is shown in ferrates such as  $\text{FeO}_4^{2-}$  in alkaline medium, but they readily decompose to  $\text{Fe}_2\text{O}_3$  and  $\text{O}_2$ . Besides the oxides, oxocation of the metals also stabilise higher oxidation states. For example,  $\text{V}^{\text{V}}$  as  $\text{VO}_2^+$ ,  $\text{V}^{\text{IV}}$  as  $\text{VO}^{2+}$  and  $\text{Ti}^{\text{IV}}$  as  $\text{TiO}^{2+}$ . It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ . This is due to the fact that oxygen has great ability to form multiple bonds to metals. In the covalent oxide,  $\text{Mn}_2\text{O}_7$ , each Mn is tetrahedrally surrounded by oxygen atoms and has Mn–O–Mn bridge. The tetrahedral  $[\text{MO}_4]^{n-}$  ions are also known for vanadium (V), chromium (VI), manganese (VI) and manganese (VII).

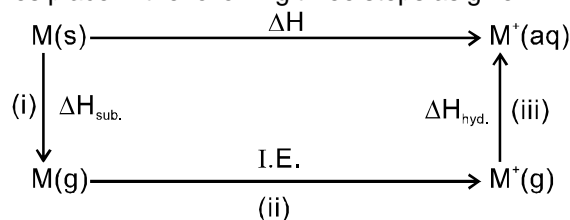
The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g., in  $\text{MnO}_4^-$  all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn,  $\text{Mn}_2\text{O}_7$  is a covalent green oil. In these higher oxides the acidic character is predominant. Thus  $\text{CrO}_3$  gives  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$  and  $\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$ .  $\text{V}_2\text{O}_5$  is, however amphoteric though mainly acidic and with alkalis as well as acids gives  $\text{VO}_4^{3-}$  and  $\text{VO}_2^+$  respectively.

#### Electrode potentials :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:



This process actually takes place in the following three steps as given in following flowchart :





- (i) In the first step, the atoms get isolated from one another and become independent in the gaseous state. This converts solid metal to the gaseous state. The energy needed for this step is known as enthalpy of sublimation.



- (ii) In the second step, the outer electron is removed from the isolated atom. The energy required for this change is ionisation enthalpy.



- (iii) In the third step the gaseous ion gets hydrated. In this process, energy known as hydration enthalpy, is liberated.

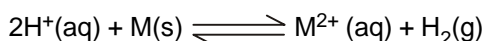


The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is

$$\Delta H = \Delta_{\text{sub}}H^{\ominus} + \text{IE} + \Delta_{\text{hyd}}H$$

Thus,  $\Delta H$  gives the enthalpy change required to bring the solid metal,  $M$  to the monovalent ion in aqueous medium,  $M^+$  (aq). An exactly similar cycle may be constructed for the formation of an anion in solution except that the ionization enthalpy may be replaced by electron gain enthalpy when the gaseous atom goes to gaseous anion.  $\Delta H$  helps to predict the stability of a particular oxidation state. The smaller the values of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are a measure of total energy change. Qualitative, the stability of the transition metal ions in different oxidation states can be determined on the basis of electrode potential data. The lower the electrode potential i.e., more negative the standard reduction potential of the electrode, the more stable is the oxidation state of the transition metal in the aqueous solution.

The electrode potentials of different metals can also be measured by forming the cell with standard hydrogen electrode. For the measurement of electrode potential of  $M^{2+} | 1M$ , the e.m.f. of the cell in which the following reaction occurs is measured :



Knowing the potential of  $2H^+(aq) | H_2(g)$ , it is possible to determine the potential of  $M^{2+}(aq) | M$ .

### Trends in the $M^{3+} | M^{2+}$ Standard Electrode Potentials

Except copper and zinc, all other elements of first transition series show +3 oxidation states also to form  $M^{3+}$  ions in aqueous solutions. The standard reduction potentials for  $M^{3+} | M^{2+}$  redox couple are given below:

	Ti	V	Cr	Mn	Fe	Co
$E (M^{3+}(aq)   M^{2+}(aq))$ (in Volt)	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97

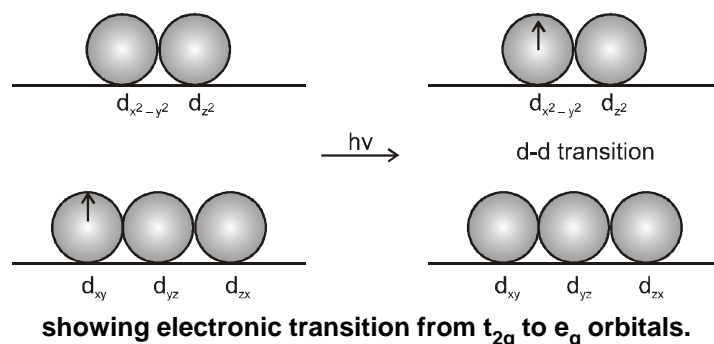
These values reveal the following facts :

- The low value of scandium reflects the stability of  $Sc^{3+}$  which has a noble gas configuration.
- The comparatively high value for Mn shows that  $Mn^{2+}$  ( $d^5$  configuration) is particularly stable. On the other hand comparatively low value for Fe shows the extra stability of  $Fe^{3+}$  ( $d^5$  configuration).
- The comparatively low value of V is related to the stability of  $V^{2+}$  (due to half filled  $t_{2g}^3$  energy level of 3d orbitals in octahedral crystal field splitting).
- The  $E^{\ominus}$  value for  $Mn^{3+}/Mn^{2+}$  couple much more positive than for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$ . This is because of the much larger III<sup>rd</sup> ionisation energy of Mn (removal of electron from  $d^5$  configuration).

### Formation of Coloured Ions :

Most of the compounds of transition metals are coloured in the solid form or solution form. The colour of the compounds of transition metals may be attributed to the presence of incomplete  $(n - 1)$  d-sub-shell. In the case of compounds of transition metals, the energies of the five d-orbitals in the same sub-shell do not remain equal. Under the influence of approaching ions towards the central metal ion, the d-orbitals of the central metal split into different energy levels. This phenomenon is called crystal field splitting. For example, when the six ions or molecules approach the metal ion (called octahedral field), the five d-orbitals split up into two sets : one set consisting of two d-orbitals ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) of higher energies and the other set consisting of three d-orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) of lower energies.

In the case of the transition metal ions, the electron can be easily promoted from one energy level to another in the same d-sub-shell. These are called **d-d transitions**. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub-shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on a transition metal compound, some of its energy corresponding to a certain colour, is absorbed and the electron gets raised from lower energy set of orbitals to higher energy set of orbitals as shown below :



The excess of other colours constituting white light are transmitted and the compound appears coloured. The observed colour of a substance is always complementary colour of the colour which is absorbed by the substance. For example,  $Ti^{3+}$  compounds contain one electron in d-sub-shell ( $d^1$ ). It absorbs green and yellow portions from the white light and blue and red portions are emitted. Therefore,  $Ti^{3+}$  ions appear purple. Similarly, hydrated cupric compounds absorb radiations corresponding to red light and the transmitted colour is greenish blue (which is complementary colour to red colour). Thus, cupric compounds have greenish-blue colour.

**Colour of different hydrated transition metal ions.**

Ion	Outer Configuration	Colour of the ion
Sc (III), Ti (IV)	$3d^0$	Colourless
Ti (III)	$3d^1$	Purple
V (IV)	$3d^1$	Blue
V (III)	$3d^2$	Green
Cr (III)	$3d^3$	Green
Mn (III)	$3d^4$	Violet
Cr (II)	$3d^4$	Blue
Mn (II)	$3d^5$	Pink
Fe (III)	$3d^5$	Yellow
Fe (II)	$3d^6$	Green
Co (III)	$3d^6$	Blue
Co (II)	$3d^7$	Pink
Ni (II)	$3d^8$	Green
Cu (II)	$3d^9$	Blue
Cu (I)	$3d^{10}$	Colourless
Zn (II)	$3d^{10}$	Colourless

### Magnetic Properties

It is interesting to note that when the various substances are placed in a magnetic field, they do not behave in a similar way i.e., they show different behaviour which are known as magnetic behaviour.

These are classified as :

- (i) **Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.
- (ii) **Diamagnetic substances.** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals. Most of the compounds of transition elements are paramagnetic in nature and are attracted by the magnetic field. The transition elements involve the partial filling of d-sub-shells. Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration  $d^1$  to  $d^9$ ) and therefore, they give rise to paramagnetic character. The magnetic character is expressed in terms of magnetic moment. The larger the number of unpaired electrons in a substance, the greater is the paramagnetic character and larger is the magnetic moment. The magnetic moment is expressed in Bohr magnetons abbreviated as B.M.



### Calculated and observed magnetic moment of ions of first transition series.

Ion	Outer Configuration	Number of unpaired electrons	Magnetic moment (B.M.)	
			Calculated	observed
Sc <sup>3+</sup>	3d <sup>0</sup>	0	0	0
Ti <sup>3+</sup>	3d <sup>1</sup>	1	1.73	1.75
Ti <sup>2+</sup>	3d <sup>2</sup>	2	2.84	2.76
V <sup>2+</sup>	3d <sup>3</sup>	3	3.87	3.86
Cr <sup>2+</sup>	3d <sup>4</sup>	4	4.90	4.80
Mn <sup>2+</sup>	3d <sup>5</sup>	5	5.92	5.96
Fe <sup>2+</sup>	3d <sup>6</sup>	4	4.90	5.3 - 5.5
Co <sup>2+</sup>	3d <sup>7</sup>	3	3.87	4.4 - 5.2
Ni <sup>2+</sup>	3d <sup>8</sup>	2	2.84	2.9 - 3.4
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73	1.8 - 2.2
Zn <sup>2+</sup>	3d <sup>10</sup>	0	0	0

The experimental data are mainly for hydrated ions in solution or in the solid state.

#### Formation of complexes :

In contrast to representative elements, the transition elements form a large number of coordination complexes. The transition metal ions bind to a number of anions or neutral molecules in these complexes. The common examples are [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup>, [Fe(CN)<sub>6</sub>]<sup>4-</sup>, [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, etc.

The great tendency of transition metal ions to form complexes is due to :

(i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.

#### Formation of Interstitial Compounds :

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.

They are generally non-stoichiometric and are neither typically ionic nor covalent. The common examples of interstitial compounds of transition metals are TiC, Mn<sub>4</sub>N, Fe<sub>3</sub>H, TiH<sub>2</sub> etc. It may be noted that these formula do not correspond to any normal oxidation state of the metal. Generally, the nonstoichiometric materials are obtained having the composition as TiH<sub>1.7</sub>, VH<sub>0.56</sub>, etc. Because of the nature of their composition, these compounds are referred to as **interstitial compounds**.

As a result of the filling up of the interstitial spaces, the transition metals become rigid and hard. These interstitial compounds have similar chemical properties as the parent metals but differ significantly in their physical properties particularly, density, hardness and conductivity. For example, steel and cast iron are hard because they form interstitial compounds with carbon.

The transition metals can easily accommodate the small non-metallic atoms because of void sites between the packed atoms of the crystalline metal. These spaces are present because of defects in their structures and existence of variable oxidation states.

The general characteristic physical and chemical properties of these compounds are :

- (i) They have high melting points which are higher than those of pure metals.
- (ii) They retain metallic conductivity i.e. of pure metals.
- (iii) They are very hard and some borides have hardness as that of diamond.
- (iv) They are chemically inert.

#### Catalytic properties

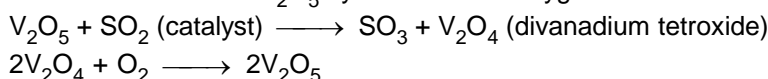
Many transition metals and their compounds act as good catalysts for various reactions. Of these, the use of Fe, Co, Ni, V, Cr, Mn, Pt, etc. are very common.

The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore increase the rate of the reaction.

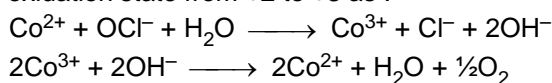
These reaction intermediates readily decompose yielding the products and regenerating the original substance. The transition metals form these reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

- (i) In some cases, the transition metal catalysts provide a suitable large surface area for the adsorption of the reactant. This increases the concentration of the reactants at the catalyst surface and also weakens the bonds in the reactant molecules. Consequently, the activation energy gets lowered.

For example, during the conversion of  $\text{SO}_2$  to  $\text{SO}_3$ ,  $\text{V}_2\text{O}_5$  is used as a catalyst. Solid  $\text{V}_2\text{O}_5$  adsorbs a molecule of  $\text{SO}_2$  on the surface to form  $\text{V}_2\text{O}_4$  and the oxygen is given to  $\text{SO}_2$  to form  $\text{SO}_3$ . The divanadium tetroxide is then converted to  $\text{V}_2\text{O}_5$  by reaction with oxygen :



- (ii) In some cases, the transition metal ions can change their oxidation states and become more effective as catalysts. For example, cobalt salts catalyse decomposition of bleaching powder as cobalt can easily change oxidation state from +2 to +3 as :



Iron (III) also catalyses the reaction between iodide and persulphate ions ( $\text{S}_2\text{O}_8^{2-}$ ).

### Alloy Formation :

Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed. Such alloys are hard, have high melting points and are more resistant to corrosion than parent metals.

For example, the most common known alloys are ferrous alloys. Chromium, manganese, vanadium, tungsten, molybdenum etc. are used to produce variety of steels and stainless steel. Alloys of transition metals with non-transition metals such as bronze (copper-tin), brass (copper-zinc) are also industrially important alloys.

## PREPARATIONS AND PROPERTIES OF SOME IMPORTANT d-BLOCK METAL COMPOUNDS

### [A] COMPOUNDS OF IRON :

#### Ferrous Sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Green vitriol)

It is commonly known as harakasis

#### Preparation

- (i) By iron scrap :
- $$\text{Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2 \uparrow$$
- (ii) From Kipp's waste :
- $$\begin{aligned} 3\text{FeS}_2 + 2\text{H}_2\text{O} + 11\text{O}_2 &\longrightarrow \text{FeSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4 \\ \text{Fe}_2(\text{SO}_4)_3 + \text{Fe} &\longrightarrow 3\text{FeSO}_4 \end{aligned}$$

#### Properties

(a) **Physical :** Hydrated ferrous sulphate is a green crystalline compound, effloresces on exposure to air. Anhydrous  $\text{FeSO}_4$  is colourless.

#### (b) Chemical :

- (i) On exposure to atmosphere, it turns brownish-yellow due to the formation of basic ferric sulphate.
- $$4\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe}(\text{OH}) \cdot \text{SO}_4 \text{ (basic ferric sulphate)}$$
- (ii) Aqueous solution is acidic due to hydrolysis.
- $$\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{H}^+$$
- (iii)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{140^\circ\text{C}} \text{FeSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{300^\circ\text{C}} 2\text{FeSO}_4 \xrightarrow[\text{Temp.}]{\text{High}} \text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + \text{SO}_3 \uparrow$
- (iv) It acts as reducing agent.
- $$\begin{aligned} \text{AuCl}_3 + 3\text{FeSO}_4 &\longrightarrow \text{Au} + \text{Fe}_2(\text{SO}_4)_3 + \text{FeCl}_3 \\ 6\text{Hg}_2\text{Cl}_2 + 6\text{FeSO}_4 &\longrightarrow 3\text{Hg}_2\text{Cl}_2 + 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{FeCl}_3 \end{aligned}$$

### Ferric Oxide, Fe<sub>2</sub>O<sub>3</sub> :

#### Preparation :

- (i)  $2\text{Fe}(\text{OH})_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$   
(ii)  $2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$

#### Properties :

(a) **Physical** : It is a deep red powder and is insoluble in water.

#### (b) Chemical :

- (i)  $6\text{Fe}_2\text{O}_3 \xrightarrow{1300^\circ\text{C}} 4\text{Fe}_3\text{O}_4 + \text{O}_2$   
(ii)  $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \longrightarrow 2\text{Fe} + 3\text{H}_2\text{O}$

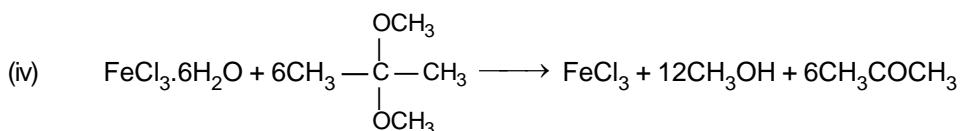
**Uses** : It is used as (i) a red pigment, (ii) an abrasive polishing powder and (iii) a catalyst.

### Ferric Chloride, FeCl<sub>3</sub> :

#### Preparation :

(a) Anhydrous FeCl<sub>3</sub> :

- (i)  $2\text{Fe} + 3\text{Cl}_2(\text{dry}) \xrightarrow{\Delta} 2\text{FeCl}_3$   
(iii)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{SOCl}_2 \longrightarrow \text{FeCl}_3 + 12\text{HCl} + 6\text{SO}_2$



(b) Hydrated FeCl<sub>3</sub> :

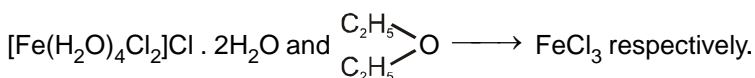
- (i)  $\text{Fe}(\text{OH})_3 + 3\text{HCl} \longrightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$   
(ii)  $2\text{Fe} + 4\text{HCl} + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3 + 2\text{H}_2 \uparrow$

All solutions of FeCl<sub>3</sub> obtained in above chemical reactions on crystallisation gives hydrated FeCl<sub>3</sub>·6H<sub>2</sub>O.

#### Properties

##### (a) Physical :

Anhydrous ferric chloride is dark black solid while hydrated salt, FeCl<sub>3</sub>·6H<sub>2</sub>O is yellowish-brown deliquescent crystalline solid. Both are soluble in water as well as in ether forming solvated species,



It is sublimed at 300°C giving a dimeric gas,  $\text{Cl}-\text{Fe}(\text{Cl})_2-\text{Fe}(\text{Cl})_2-\text{Cl}$ .

##### (b) Chemical :

(i) Action of heat :

- (a)  $2\text{FeCl}_3(\text{anhydrous}) \xrightarrow{\Delta} 2\text{FeCl}_2 + \text{Cl}_2$   
(b)  $2[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 6\text{HCl} + 9\text{H}_2\text{O}$   
(ii) As oxidising agent :  $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$   
 $2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$

[B]

### COMPOUNDS OF ZINC :

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

It is found in nature as zincite or red zinc ore.

#### Preparation :

- (i)  $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$  ; (ii)  $2\text{Zn}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{ZnO} + 4\text{NO}_2 + \text{O}_2$

#### Properties

##### (a) Physical :

It is a white powder which becomes yellow on heating due to change in the structure of lattice but again turns white on cooling. It is insoluble in water and sublimes at 400°C.

**(b) Chemical :**

- (i) It is amphoteric in nature.  

$$\text{ZnO} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O}$$

$$\text{ZnO} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$$
- (ii) 
$$\text{ZnO} + \text{H}_2 \xrightarrow[400^\circ\text{C}]{\Delta} \text{Zn} + \text{H}_2\text{O}$$

**[C] COMPOUNDS OF COPPER****Copper Sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Blue Vitriol)**

It is also called 'Nilathotha'.

**Preparation :**

- (i) 
$$\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$
- (ii) 
$$\text{Cu}(\text{OH})_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + 2\text{H}_2\text{O}$$

**Properties****(a) Physical :** It is a blue crystalline compound and is soluble in water.**(b) Chemical :**

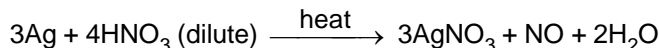
- (i) 
$$2\text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} + 2\text{KI} \longrightarrow \text{CuI}_2 + 2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$$

$$2\text{CuSO}_4 + 2\text{FeSO}_4 + 2\text{KI} \longrightarrow \text{CuI} + \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4$$
- (ii) 
$$\text{CuSO}_4 + \text{Fe} \longrightarrow \text{Cu} + \text{FeSO}_4$$

$$\text{CuSO}_4 + \text{Zn} \longrightarrow \text{Cu} + \text{ZnSO}_4$$
- (iii) 
$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow[\text{effloresces}]{\text{air}} \text{CuSO}_4 \cdot 4\text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} \text{CuSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{250^\circ\text{C}} \text{CuSO}_4 \xrightarrow{750^\circ\text{C}} \text{CuO} + \text{SO}_2 +$$

 $\text{O}_2$ **[D] COMPOUNDS OF SILVER :****Silver Nitrate,  $\text{AgNO}_3$  (Lunar caustic) :****Preparation :**

It is prepared by heating silver with dilute nitric acid. The solution is concentrated and cooled when the crystals of silver nitrate separate out.

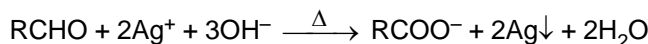
**Properties****(a) Physical :**It is a colourless crystalline compound, soluble in water and alcohol. It melts at  $212^\circ\text{C}$ .**(b) Chemical :**

- (i) It possesses powerful corrosive action on organic tissues, which it turns black especially in presence of light. The blackening is due to finely divided metallic silver, reduced by organic tissue. It is, therefore, stored in coloured bottles.
- (ii) On heating above its melting point, it decomposes to silver nitrite and oxygen.  

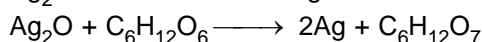
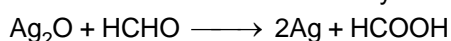
$$2\text{AgNO}_3 \longrightarrow 2\text{AgNO}_2 + \text{O}_2$$
 When heated red hot, it gives metallic silver  

$$2\text{AgNO}_3 \longrightarrow 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$$
- (iii) The ammonical solution of  $\text{AgNO}_3$  react with acetylene to form a white precipitate.  

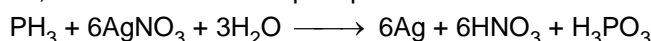
$$2\text{AgNO}_3 + 2\text{NH}_4\text{OH} + \text{C}_2\text{H}_2 \longrightarrow \text{Ag}_2\text{C}_2 \downarrow (\text{silver acetylide}) + 2\text{NH}_4\text{NO}_3 + 2\text{H}_2\text{O}$$
- (vi) Ammonical silver nitrate is called Tollen's reagent and is used to identify reducing sugars and aldehydes.



It is known as "silver mirror" test of aldehydes and reducing sugars.



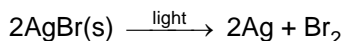
- (vii) Phosphine, arsine and stibine all precipitate silver from silver nitrate solution



### Photography :

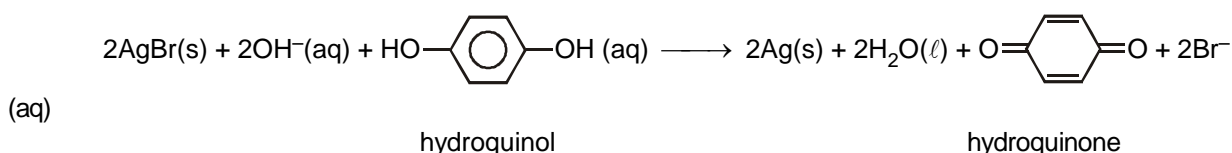
A photographic film consists of a light sensitive emulsion of fine particles (grains) of silver salts in gelatine spread on a clear celluloid strip or a glass plate. The grain size is very important to photographers, as this affects the quality of the pictures produced. AgBr is mainly used as the light sensitive material. Some AgI is used in 'fast' emulsions.

The film is placed in a camera. When the photograph is exposed, light from the subject enters the camera and is focussed by the lens to give a sharp image on the film. The light starts a photochemical reaction by exciting a halide ion, which loses an electron. The electron moves in a conduction band to the surface of the grain, where it reduces a  $\text{Ag}^+$  ion to metallic silver.

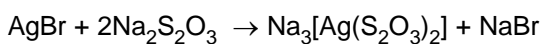


In modern photography only a short exposure of perhaps 1/100th of a second is used. In this short time, only a few atoms of silver (perhaps 10–50) are produced in each grain exposed to light. Parts of the film which have been exposed to the bright parts of the subject contain a lot of grains with some silver. Parts exposed to paler parts of the subject contains a few grains with some silver, whilst parts not exposed contain none. Thus the film contains a latent image of the subject. However, the number of silver atoms produced is so small that the image is not visible to the eye.

Next the film is placed a developer solution. This is a mild reducing agent, usually containing quinol. Its purpose is to reduce more silver halide to Ag metal. Ag is deposited mainly where there are already some Ag atoms. Thus the developing process intensifies the latent image on the film so it becomes visible. The correct conditions for processing must be used to obtain an image of the required blackness.



If the film was brought out into daylight at this stage, the unexposed parts of the emulsion would turn black and thus destroy the picture. To prevent this happening any unchanged silver halides are removed by placing the film in a fixer solution. A solution of sodium thiosulphate is used as fixer. It forms a soluble complex with silver halides.



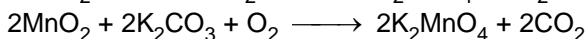
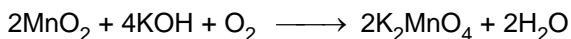
After fixing, the film can safely be brought out into daylight. Parts blackened by silver represent the light parts of the original picture. This is therefore a negative.

To obtain an image with light and dark the right way round, a print must be made. Light is passed through the negative onto a piece of paper coated with AgBr emulsion. This is then developed and fixed in the same way as before.

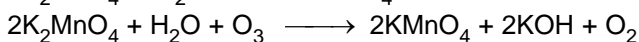
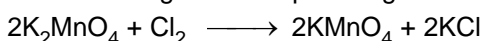
### [E] POTASSIUM PERMANGANATE ( $\text{KMnO}_4$ ) :

#### Preparation

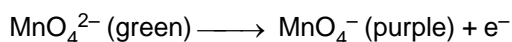
This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or  $\text{K}_2\text{CO}_3$  in presence of atmospheric oxygen or any other oxidising agent such as  $\text{KNO}_3$ . The fused mass turns green with the formation of potassium manganate,  $\text{K}_2\text{MnO}_4$ .



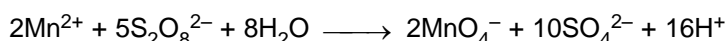
The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.



Commercially it is prepared by fusion of  $\text{MnO}_2$  with KOH followed by electrolytic oxidation of manganate.



In the laboratory, a manganese(II) ion salt is oxidised by peroxodisulphate to permanganate



## Properties

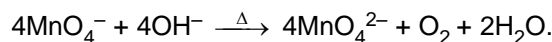
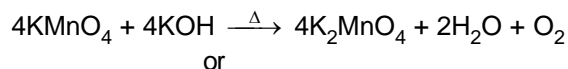
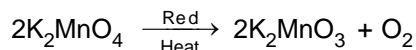
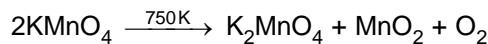
### (a) Physical :

It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

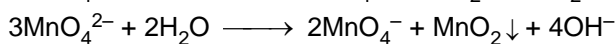
### (b) Chemical :

(i) Effect of heating

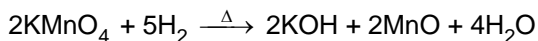
When heated alone or with an alkali, it decomposes evolving oxygen.



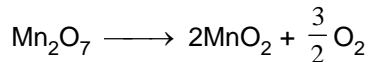
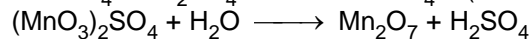
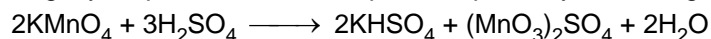
$\text{MnO}_4^{2-}$  in dilute alkaline, water and acidic solutions is unstable and disproportionates to give  $\text{MnO}_4^-$  and  $\text{MnO}_2$



On heating in current of  $\text{H}_2$ , solid  $\text{KMnO}_4$  gives  $\text{MnO}$



(ii) On treatment with concentrated  $\text{H}_2\text{SO}_4$  ( $\text{KMnO}_4$  is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.



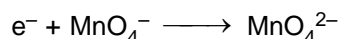
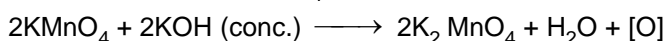
(iii) Potassium permanganate is a powerful oxidising agent.

Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.

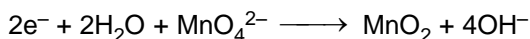
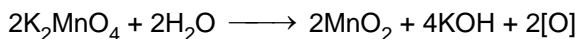
A mixture of sulphur, charcoal and  $\text{KMnO}_4$  forms an explosive powder. A mixture of oxalic acid and  $\text{KMnO}_4$  catches fire spontaneously after a few seconds. The same thing happens when glycerine is poured over powdered  $\text{KMnO}_4$ .

### In alkaline & neutral medium :

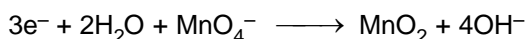
In strongly alkaline medium  $\text{KMnO}_4$  is reduced to manganate.



However if solution is dilute then  $\text{K}_2\text{MnO}_4$  is converted into  $\text{MnO}_2$  which appears as a brownish precipitate.

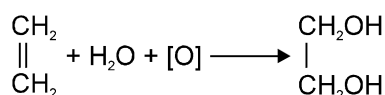


This type of behaviour is shown by  $\text{KMnO}_4$  itself in neutral medium



In alkaline or neutral medium  $\text{KMnO}_4$  shows following oxidising properties.

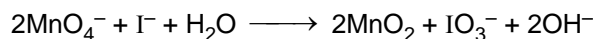
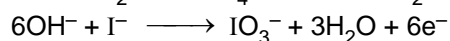
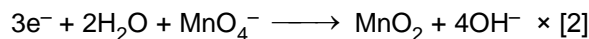
(a) It oxidises ethene to glycol.



In alkaline medium  $\text{KMnO}_4$  solution is also known as Bayer's reagent (1% alkaline  $\text{KMnO}_4$  solution).

(b) It oxidises iodide into iodate.



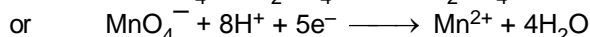
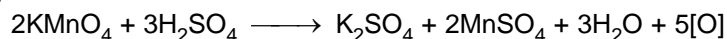


(c) In neutral/ faintly alkaline solution thiosulphate is quantitatively oxidised to sulphate.



**In acidic medium (in presence of dilute  $H_2SO_4$ ) :**

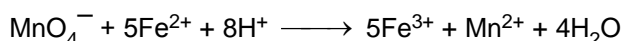
Manganous sulphate is formed. The solution becomes colourless.



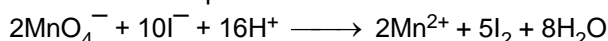
This medium is used in quantitative (volumetric) estimations. The equivalent mass of  $KMnO_4$  in acidic medium

$$\text{is} = \frac{\text{Molecular mass}}{5}.$$

(a) Ferrous salts are oxidised to ferric salts.



(b) Iodine is evolved from potassium iodide.



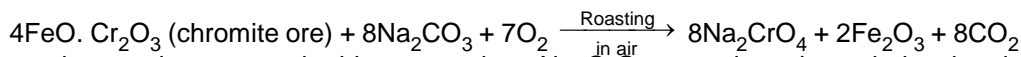
(c)  $H_2S$  is oxidised to sulphur :



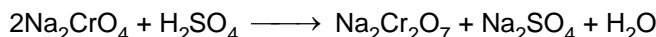
## [F] POTASSIUM DICHROMATE ( $K_2Cr_2O_7$ ) :

### Preparation :

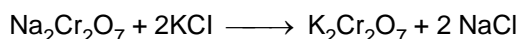
The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace



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



The solution is concentrated when less soluble  $Na_2SO_4$  crystallises out. The solution is further concentrated when crystals of  $Na_2Cr_2O_7$  are obtained. Hot saturated solution of  $Na_2Cr_2O_7$  is then treated with  $KCl$  when orange red crystals of  $K_2Cr_2O_7$  are obtained on crystallisation.



$K_2Cr_2O_7$  is preferred over  $Na_2Cr_2O_7$  as a primary standard in volumetric estimation because  $Na_2Cr_2O_7$  is hygroscopic in nature but  $K_2Cr_2O_7$  is not.

### Properties

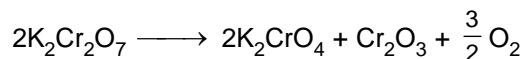
#### (a) Physical :

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at  $398^\circ C$ .

#### (b) Chemical :

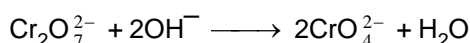
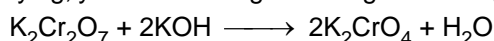
(i) Effect of heating :

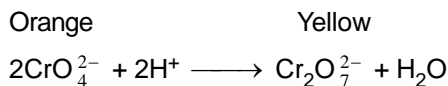
On heating strongly, it decomposes liberating oxygen.



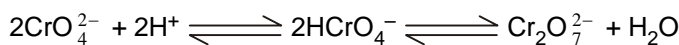
On heating with alkalis, it is converted to chromate, i.e., the colour changes from orange to yellow.

On acidifying, yellow colour again changes to orange.

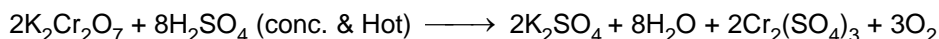
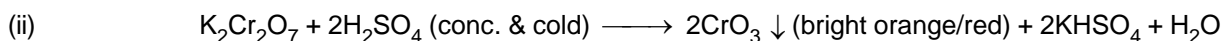




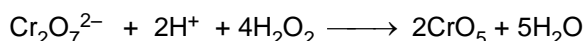
Thus  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  exist in equilibrium and are interconvertible by altering the pH of solution.



In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.



(iii) Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution reacts with  $\text{H}_2\text{O}_2$  to give a deep blue solution due to the formation of  $\text{CrO}_5$ .



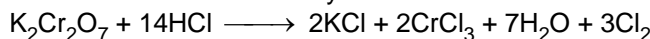
Blue colour in aqueous solution fades away slowly due to the decomposition of  $\text{CrO}_5$  to  $\text{Cr}^{3+}$  ions and oxygen.

In less acidic solution  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{O}_2$  give salt which is violet coloured and diamagnetic due to the formation of  $[\text{CrO}(\text{O}_2)(\text{OH})]^-$ .

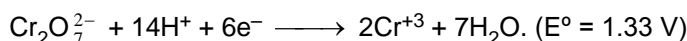
In alkaline medium with 30%  $\text{H}_2\text{O}_2$ , a red-brown  $\text{K}_3\text{CrO}_8$  (diperoxo) is formed. It is tetra peroxospecies  $[\text{Cr}(\text{O}_2)_4]^{3-}$  and thus the Cr is in +V oxidation state.

In ammoniacal solution a dark red-brown compound,  $(\text{NH}_3)_3\text{CrO}_4$  - diperoxo compound with Cr(IV) is formed.

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

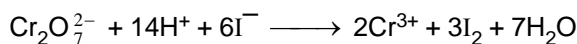
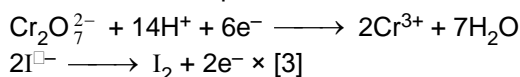


(v) It acts as a powerful oxidising agent in acidic medium (dilute  $\text{H}_2\text{SO}_4$ )

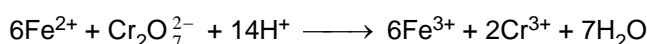


The oxidation state of Cr changes from +6 to +3.

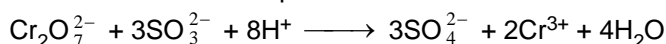
(a) Iodine is liberated from potassium iodide :



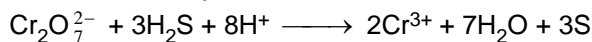
(b) Ferrous salts are oxidised to ferric salts :



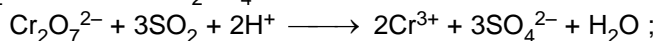
(c) Sulphites are oxidised to sulphates :



(d)  $\text{H}_2\text{S}$  is oxidised to sulphur :



(e)  $\text{SO}_2$  is oxidised to  $\text{H}_2\text{SO}_4$  :



# EXERCISE # 1

## PART - I : OBJECTIVE QUESTIONS

\* Marked Questions are having more than one correct option.

### Section (A) : Electronic configuration, atomic size and ionic size, density, melting and boiling points.

- A-1.** The transition elements have a general electronic configuration :  
(A)  $ns^2 np^6 nd^{1-10}$  (B)  $(n-1) d^{1-10} ns^{0-2} np^{0-6}$   
(C)  $(n-1) d^{1-10} ns^{1-2}$  (D) none.
- A-2.** Which of the following is a correct statements -  
(A) Iron is an element of third transition series (B) Iron is a f-block element  
(C) Iron is an element of first transition series (D) None of these
- A-3.** The atomic volumes of the transition elements are low compared with elements in neighboring group 1 and 2 because :  
(A) the nuclear charge is poorly screened and so attracts all the electrons more strongly.  
(B) the extra electrons added occupy inner orbitals.  
(C) (A) and (B) both.  
(D) none.
- A-4.** The metallic bond strength in first transition series increases from -  
(A) Sc to Mn (B) Sc to Cr (C) Cr to Zn (D) Sc to Cu
- A-5.** The wrong statement regarding transition metals among the following is :  
(A) 4s electrons penetrate towards the nucleus more than 3d electrons  
(B) atomic radii of transition metals increase rapidly with increase in atomic number because of poor shielding of nuclear attraction by  $(n-1)d$  electrons  
(C) second and third transition series elements have nearly the same size  
(D) their densities are higher and densities of the 5d series elements are higher than those of 4d series elements.
- A-6.\*** The melting point of Zn is lower as compared to those of the other elements of 3d series because :  
(A) the d-orbitals are completely filled.  
(B) the d-orbitals are partially filled.  
(C) d-electrons do not participate in metallic bonding.  
(D) size of Zn atom is smaller

### Section (B) : Ionization enthalpy and oxidation state.

- B-1.** First IE of 5d series elements are higher than those of 3d and 4d series elements. This is due to :  
(A) bigger size of atoms of 5d-series elements than 3d-series elements.  
(B) greater effective nuclear charge is experienced by valence electrons because of the weak shielding of the nucleus by 4f-electrons in 5d series.  
(C) (A) and (B) both.  
(D) None of these.
- B-2.** Transition elements show variable oxidation states because they lose electrons from the following orbitals -  
(A) ns and np (B)  $(n-1) d$  and ns (C)  $(n-1) d$  (D) ns
- B-3.** The highest oxidation state achieved by a transition metal is given by -  
(A) ns electrons (B)  $(n-1) d$  electrons (C)  $(n+1) d$  electrons (D) ns +  $(n-1) d$  electrons

- B-4.** The pair in which both the elements generally shows only one oxidation state is -  
 (A) Sc and Zn (B) Zn and Cu (C) Cu and Ag (D) Zn and Au
- B-5.** Which of the following statements is correct ?  
 (A) The lesser number of oxidation states in 3d-series in the beginning of the series is due to the presence of too few electrons to loose or share  
 (B) The lesser number of oxidation states in 3d-series towards the end of the series is due to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands  
 (C) (A) and (B) both  
 (D) None is correct
- B-6.** Ionisation energies of Ni and Pt in  $\text{kJ mol}^{-1}$  are given below.
- |    |                                 |                                 |
|----|---------------------------------|---------------------------------|
|    | $(\text{IE})_1 + (\text{IE})_2$ | $(\text{IE})_3 + (\text{IE})_4$ |
| Ni | 2.49                            | 8.80                            |
| Pt | 2.60                            | 6.70                            |
- So, (select the correct statement)  
 (A) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)  
 (B) platinum (IV) compounds tend to be more stable than nickel (IV)  
 (C) (A) & (B) both  
 (D) none is correct
- B-7.** Maximum oxidation state is shown by :  
 (A) Os (B) Mn (C) Cr (D) Co
- B-8.\*** The less stable oxidation states of Cr are :  
 (A)  $\text{Cr}^{2+}$  (B)  $\text{Cr}^{3+}$  (C)  $\text{Cr}^{4+}$  (D)  $\text{Cr}^{6+}$

### Section (C) : Electrode potential and chemical reactivity.

- C-1.** Which of the following statement is false ?  
 (A) Of the  $d^4$  species, manganese (III) is strongly reducing while  $\text{Cr}^{2+}$  is strongly oxidising.  
 (B) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.  
 (C) The  $d^1$  configuration is very unstable in ions.  
 (D) None of these
- C-2.\*** Which of the following statements are correct ?  
 (A) Transition elements exhibit higher enthalpies of atomization as they have stronger interatomic interaction  
 (B)  $\text{IE}_2$  of  ${}_{23}\text{V} < {}_{24}\text{Cr} > {}_{25}\text{Mn}$  and  ${}_{28}\text{Ni} < {}_{29}\text{Cu} > {}_{30}\text{Zn}$   
 (C) Ni(II) compounds are more stable than Pt(II) where as Pt(IV) compounds are more stable than nickel (IV)  
 (D) The elements which gives the greatest number of oxidation states does not occur in or near the middle of the series

### Section (D) : Magnetic properties, formation of coloured ions

- D-1.** Titanium shows magnetic moment of 1.73 B.M. in its compounds. What is the oxidation number of Ti in the compound ?  
 (A) + 1 (B) + 4 (C) + 3 (D) + 2
- D-2.** Which of the following has the maximum number of unpaired d-electron?  
 (A)  $\text{Zn}^{2+}$  (B)  $\text{Fe}^{2+}$  (C)  $\text{Ni}^{2+}$  (D)  $\text{Cu}^{2+}$
- D-3.** The highest magnetic moment is shown by the transition metal ion with the outermost electronic configuration is :  
 (A)  $3d^5$  (B)  $3d^2$  (C)  $3d^7$  (D)  $3d^9$
- D-4.** Which of the following has maximum magnetic moment -  
 (A)  $\text{V}^{3+}$  (B)  $\text{Cr}^{3+}$  (C)  $\text{Fe}^{3+}$  (D)  $\text{Co}^{3+}$

- D-5.** The ion pair of the following in which both the ions have unpaired electron -  
 (A)  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$  (B)  $\text{Sc}^{3+}$ ,  $\text{Cr}^{3+}$  (C)  $\text{Cu}^+$ ,  $\text{Fe}^{3+}$  (D)  $\text{Mn}^{2+}$ ,  $\text{Cu}^+$
- D-6.**  $\text{Ti}^{+2}$  and  $\text{Ni}^{+2}$  contain -  
 (A) Equal number of paired electrons (B) Equal number of unpaired electrons  
 (C) Different number of 2p electrons (D) Different number of 3p electrons
- D-7.** Which of the following is diamagnetic -  
 (A)  $\text{Zn}^{2+}$  (B)  $\text{Ni}^{2+}$  (C)  $\text{Co}^{2+}$  (D)  $\text{Cu}^{2+}$
- D-8.** A metal ion from the first transition series has a magnetic moment (calculated) of 3.87 B.M. How many unpaired electrons are expected to be present in the ion?  
 (A) 1 (B) 2 (C) 3 (D) 4
- D-9.** Magnetic moment of  $\text{Cr}^{+2}$  ( $Z=24$ ),  $\text{Mn}^{+2}$  ( $Z=25$ ) and  $\text{Fe}^{+2}$  ( $Z=26$ ) are x,y,z. They are in order :  
 (A)  $x < y < z$  (B)  $x > y > z$  (C)  $z < x = y$  (D)  $x = z < y$
- D-10.** The magnetic moment of  ${}_{25}\text{Mn}$  in ionic state is  $\sqrt{15}$  B.M, then Mn is in :  
 (A) +2 state (B) +3 state (C) +4 state (D) +5 state
- D-11.** Which of the following group of ions is paramagnetic in nature :  
 (A)  $\text{Cu}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Sc}^{3+}$  (B)  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  (C)  $\text{Cr}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Sc}^{3+}$  (D)  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ti}^{4+}$
- D-12.** The reason for the formation of complex compounds by transition metal is -  
 (A) Availability of empty d-orbitals (B) Completely filled d-orbitals  
 (C) Paramagnetism (D) Bigger size
- D-13.** Which of the following is not a characteristic property of transition metal -  
 (A) High enthalpy of atomisation (B) Formation of interstitial compounds  
 (C) Diamagnetism (D) Variable oxidation state
- D-14.** The colour of transition metal ions is attributed to :  
 (A) exceptionally small size of cations (B) absorption of ultraviolet rays  
 (C) incomplete  $(n-1)$  d - subshell (D) absorption of infrared radiations
- D-15.** Which one of the ionic species will impart colour to an aqueous solution ?  
 (A)  $\text{Ti}^{4+}$  (B)  $\text{Cu}^+$  (C)  $\text{Zn}^{2+}$  (D)  $\text{Cr}^{3+}$
- D-16.**  $\text{MnO}_4^-$  is of intense pink colour, though Mn is in (+7) oxidation state. It is due to :  
 (A) oxygen gives colour to it  
 (B) charge transfer when Mn gives its electron to oxygen  
 (C) charge transfer when oxygen gives its electron to Mn making it Mn(+VI) hence coloured  
 (D) none is correct
- D-17.** Transition metals ions form interstitial compounds because -  
 (A) Interstices are available in their crystal lattice  
 (B) They have empty d-orbitals  
 (C) They have high value of ionic potential  
 (D) They show variable oxidation states
- D-18.** Transition elements act as catalyst because -  
 (A) Their melting points are higher (B) Their I.P. values are higher  
 (C) They have high density (D) They can show variable oxidation states
- D-19.** The yellow colour of chromates changes to orange on acidification due to formation of :  
 (A)  $\text{Cr}^{3+}$  (B)  $\text{Cr}_2\text{O}_3$  (C)  $\text{Cr}_2\text{O}_7^{2-}$  (D)  $\text{CrO}_4^-$

- D-20.**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour because  
 (A) It contains water of crystallization (B)  $\text{SO}_4^{2-}$  ions absorb red light  
 (C)  $\text{Cu}^{2+}$  ions absorb red light  
 (D)  $\text{Cu}^{2+}$  ions absorb all colours except red from the white light
- D-21.\*** Which of the following ions give(s) coloured aqueous solution?  
 (A)  $\text{Ni}^{2+}$  (B)  $\text{Fe}^{2+}$  (C)  $\text{Cu}^{2+}$  (D)  $\text{Cu}^+$

### Section (E) : Catalytic properties, formation of interstitial compounds, alloy formation.

- E-1.** The catalytic activity of the transition metals and their compounds is ascribed to :  
 (A) their chemical reactivity. (B) their magnetic behaviour.  
 (C) their filled d-orbitals.  
 (D) their ability to adopt multiple oxidation state and their complexing ability.
- E-2.** Cementite is :  
 (A) interstitial compound of iron and carbon (B) an alloy of Fe and Cr  
 (C) a compound resembling cement (D) an ore of iron
- E-3.** Which forms interstitial compounds?  
 (A) Fe (B) Co (C) Ni (D) All
- E-4.** Which of the following ions in solution undergoes disproportionation -  
 (A)  $\text{Fe}^{+2}$  (B)  $\text{Cr}^{+3}$  (C)  $\text{Cu}^+$  (D)  $\text{Zn}^{+2}$
- E-5.\*** Which of the following statement is/are correct ?  
 (A) Transition metals and their many compounds act as good catalyst.  
 (B) The enthalpies of atomisation of the transition metals are high.  
 (C) The transition metals generally form interstitial compounds with small atoms like C, B, H etc.  
 (D) All transition metal compounds are not paramagnetic.
- E-6.** If  $n$  is the number of unpaired electron, the magnetic moment (In B.M.) of transition metal/ion is given by -  
 (A)  $\sqrt{n(n+2)}$  (B)  $\sqrt{2n(n+1)}$  (C)  $\sqrt{n(n-2)}$  (D)  $\sqrt{2n(n-1)}$

### Section (F) : Important d-block metal compounds.

- F-1.**  $\text{KMnO}_4$  is the oxo salt of :  
 (A)  $\text{MnO}_2$  (B)  $\text{Mn}_2\text{O}_7$  (C)  $\text{MnO}_3$  (D)  $\text{Mn}_2\text{O}_3$
- F-2.** When  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is added to  $\text{FeCl}_3$ , the complex compound formed is :  
 (A)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$  (B)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (C)  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$  (D)  $\text{K}_2\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
- F-3.** A compound is yellow when hot and white when cold. The compound is :  
 (A)  $\text{Al}_2\text{O}_3$  (B)  $\text{PbO}$  (C)  $\text{CaO}$  (D)  $\text{ZnO}$
- F-4.** On heating  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ , the compound obtained is :  
 (A)  $\text{ZnCl}_2$  (B)  $\text{Zn}(\text{OH})\text{Cl}$  (C)  $\text{Zn}(\text{OH})_2$  (D)  $\text{Zn}$
- Sol.**  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{Zn}(\text{OH})\text{Cl} + \text{HCl} + \text{H}_2\text{O}$ .
- F-5.** The reaction,  $2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$  is called -  
 (A) Reduction (B) Oxidation (C) Displacement (D) disproportionation
- F-6.** When copper is placed in the atmosphere for sufficient time, a green crust is formed on its surface. The composition of the green crust is :  
 (A)  $\text{Cu}(\text{OH})_2$  (B)  $\text{CuO}$  (C)  $\text{CuCO}_3$  (D)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- F-7.** The solubility of silver bromide in hypo solution (excess) is due to the formation of :  
 (A)  $\text{Ag}_2\text{SO}_3$  (B)  $\text{Ag}_2\text{S}_2\text{O}_3$  (C)  $[\text{Ag}(\text{S}_2\text{O}_3)]^-$  (D)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$



- F-8.** In dilute alkaline solution,  $\text{MnO}_4^-$  changes to :  
 (A)  $\text{MnO}_4^{2-}$  (B)  $\text{MnO}_2$  (C)  $\text{Mn}_2\text{O}_3$  (D)  $\text{MnO}$
- F-9.**  $\text{CuSO}_4$  solution + lime is called :  
 (A) Lucas reagent (B) Barfoed's reagent (C) Fehling solution A (D) Bordeaux mixture
- F-10.** Water soluble salt among  $\text{AgNO}_3$ ,  $\text{AgF}$  &  $\text{AgClO}_4$  are -  
 (A)  $\text{AgF}$ ,  $\text{AgNO}_3$  (B)  $\text{AgF}$  (C)  $\text{AgF}$ ,  $\text{AgNO}_3$ ,  $\text{AgClO}_4$  (D) None of these
- F-11.**  $\text{CrO}_3$  is a/an.....  
 (A) Acidic oxide (B) Basic oxide (C) Neutral oxide (D) Amphoteric
- F-12.** The developer used in photography is an alkaline solution of :  
 (A) hydroquinone (B) glycerol (C) phenol (D) picric acid
- F-13.** When acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  is shaken with aqueous solution of  $\text{FeSO}_4$ , then :  
 (A)  $\text{Cr}_2\text{O}_7^{2-}$  ion is reduced to  $\text{Cr}^{3+}$  ions (B)  $\text{Cr}_2\text{O}_7^{2-}$  ion is converted to  $\text{CrO}_4^{2-}$  ions  
 (C)  $\text{Cr}_2\text{O}_7^{2-}$  ion is reduced to Cr (D)  $\text{Cr}_2\text{O}_7^{2-}$  ion is converted to  $\text{CrO}_3$
- F-14.**  $\text{FeCl}_3$  dissolves in :  
 (A) water (B) ether (C) ammonia (D) (A) and (B) both
- F-15.** Which of the following compounds is used as the starting material for the preparation of potassium dichromate?  
 (A)  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  (chrome alum) (B)  $\text{PbCrO}_4$  (chrome yellow)  
 (C)  $\text{FeCr}_2\text{O}_4$  (chromite) (D)  $\text{PbCrO}_4 \cdot \text{PbO}$  (chrome red)
- F-16.**  $\text{CrO}_3$  dissolves in aqueous  $\text{NaOH}$  to give :  
 (A)  $\text{CrO}_4^{2-}$  (B)  $\text{Cr}(\text{OH})_3$  (C)  $\text{Cr}_2\text{O}_7^{2-}$  (D)  $\text{Cr}(\text{OH})_2$
- F-17.** The equilibrium  
 $\text{Cr}_2\text{O}_7^{2-} \rightleftharpoons 2\text{CrO}_4^{2-}$  is shifted to right in -  
 (A) An acidic medium (B) A basic medium (C) A neutral medium (D) It does not exist
- F-18.** When the same amount of Zn is treated with excess of  $\text{H}_2\text{SO}_4$  and excess of  $\text{NaOH}$  separately, the ratio of the volume of hydrogen evolved is -  
 (A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) 9 : 4
- F-19.** The final products obtained for the following reaction is :  
 $\text{KMnO}_4$  (excess) +  $\text{H}_2\text{SO}_4$  (concentrated and cold)  $\longrightarrow$   
 (A)  $\text{Mn}_2\text{O}_7$  (B)  $\text{MnO}$  (C)  $\text{Mn}_3\text{O}_4$  (D)  $\text{MnO}_3^+$
- F-20.** When  $\text{AgNO}_3$  (aq) reacts with excess of iodine, we get :  
 (A)  $\text{AgIO}_3$  (B)  $\text{HIO}_3$  (C)  $\text{AgO}$  (D)  $\text{HI}$
- F-21.** The compound that gets oxidised even on exposure to atmosphere is :  
 (A)  $\text{Co}_2(\text{SO}_4)_3$  (B)  $\text{NiSO}_4$  (C)  $\text{KMnO}_4$  (D)  $\text{FeSO}_4$
- F-22.\*** Select correct statement (s).  
 (A)  $\text{PH}_3$  reduces  $\text{AgNO}_3$  to metallic Ag.  
 (B) Organic tissues turn  $\text{AgNO}_3$  black by reducing it to Ag.  
 (C)  $\text{AgCN}$  is soluble in  $\text{KCN}$ .  
 (D) Zr and Ta have almost similar size due to lanthanide contraction.
- F-23.** Ferric chloride exists as -  
 (A)  $\text{FeCl}_3$  (B)  $\text{Fe}_2\text{Cl}_6$  (C)  $(\text{FeCl}_3)_3$  (D) Both 2 and 3
- F-24.** Which of the following compounds is most likely to contain non-metal atoms in the interstices of a metals lattice?  
 (A)  $\text{Fe}_3\text{O}_4$  (B)  $\text{TiN}$  (C)  $\text{MnO}_2$  (D)  $\text{CoF}_2$

## PART - II : MISCELLANEOUS QUESTIONS

### COMPREHENSION

Read the following comprehension carefully and answer the questions :

#### Comprehension # 1

Transition metals usually form coloured complexes and d – d transitions ( $t_{2g} \longleftrightarrow e_g$ ) are responsible for colour as the energy difference between  $t_{2g}$  and  $e_g$  lies in visible region. But all the coloured ions are not due to d–d transition but charge transfer bands also play important roles. Charge transfer bands may be of two types.

(i) ligand to metal (CTLM) (ii) metal to ligand (CTML).

Charge transfer transition always produces intense colour as compared to d-d transition.

- Select the incorrect statement :  
 (A) d-block metal ions are usually coloured.  
 (B) Colour of the most of d-block metal ions is generally due to d-d transition.  
 (C) All the complexes of  $Cu^+$  are colourless on account of diamagnetic nature i.e.  $d^{10}$  configuration.  
 (D)  $CrO_3$  is bright orange due to CTLM.
- $MnO_4^-$  is dark purple coloured although Mn is in (+ VII) oxidation state with  $3d^0$  configuration :  
 (A) due to d-d transition. (B) due to CTML spectra.  
 (C) due to CTLM spectra (D) none of these.
- Select the correct statement.  
 (A) In CTML, no net reduction-oxidation takes place because of the short life time of excited state.  
 (B)  $Cu_2O$  is a red coloured salt.  
 (C) Vermilion ( $HgS$ ) is a red coloured compound.  
 (D) All of these.

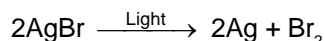
#### Comprehension # 2

(i) A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).  
 (ii) The solution of (B) in boiling water on acidification with dilute  $H_2SO_4$  gives a pink coloured compound (C) and brown colour compound (D).  
 (iii) The aqueous solution of (A) on treatment with  $NaOH$  and  $Br_2$ -water gives the compound (D).  
 (iv) A solution of (D) in concentrated  $HNO_3$  on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour as that of (C).  
 (v) A solution of (A) on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in concentrated  $HNO_3$  and concentrated  $HCl$ .

- Which of the following is true for compound (C) ?  
 (A) It oxidises ammonia to nitrogen dioxide in neutral medium.  
 (B) It's pink colour is due to d-d transition.  
 (C) It can be oxidised by ozone.  
 (D) It is obtained by alkaline fusion of pyrolusite followed by electrolytic oxidation.
- The oxidation state of central metal ions of (A), (B) and (C) compounds are respectively :  
 (A) +II, + VI and + VII (B) +II, + VI and + VI (C) +II, + VII and + VII (D) +VI, + VII and + VII
- Consider the following statements ;  
 (I) anions of both (B) and (C) are diamagnetic and have tetrahedral geometry.  
 (II) anions of both (B) and (C) are paramagnetic and have tetrahedral geometry.  
 (III) anion of (B) is paramagnetic and that of (C) is diamagnetic but both have tetrahedral geometry.  
 (IV) green coloured compound (B) in a neutral or acidic medium disproportionates to give (C) and (D).  
 of these select the correct one from the codes given :  
 (A) I and III only (B) II and III only (C) II and IV only (D) III and IV only

### Comprehension # 3

Photography is based on the nature of silver halides. Except AgF, the silver halides are photosensitive. These undergo decomposition in light and turn black due to formation of free silver.



The photographic plates or films are prepared in a dark and dust free room by applying a light sensitive mixture called emulsion which is prepared by adding 20 per cent aqueous solution of silver nitrate to ammonium bromide solution containing gelatin.

When such a film is exposed, the emulsion gets affected. Since different parts of the body reflect light of varied intensity, the film or plate is affected proportionately. An actual but inverted image of the object is thus formed on the film or plate which is not visible to the eye. It is, therefore, called the latent image.

When this exposed film or plate is dipped in a developer which contains a reducing agent, the parts affected most during exposure are reduced to maximum. The image becomes visible. It is called a negative. The remaining sensitive emulsion on the negative is removed by dissolving it in hypo solution (fixer). Finally, a positive of the negative already prepared is made on silver bromide paper.

7. The compound formed on the unexposed photographic film or plate is :  
(A) silver nitrate. (B) ammonium bromide.  
(C) diamminesilver bromide. (D) silver bromide.
8. The exposed part of the film or plate after developing contains :  
(A) silver metal (B) silver oxide (C) silver bromide (D) silver nitrate.
9. The solution of the developer consists :  
(A) alkaline solution of pyrogallol (B) alkaline solution of quinol  
(C) either (A) or (B) (D) neither (A) nor (B).
10. Silver halides are used in photography because these compounds :  
(A) are insoluble in water  
(B) are affected by light  
(C) are soluble in ammonia solution  
(D) easily stick on the surface of photographic plate or film
11. Silver bromide dissolves in hypo solution forming :  
(A)  $\text{Ag}_2\text{S}_2\text{O}_3$  (B)  $\text{Ag}_2\text{S}$  (C)  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$  (D)  $\text{NaAgS}_2\text{O}_3$ .

### MATCH THE COLUMN

12. Match the reactions in **Column I** with nature of the reactions/type of the products in **Column II**.
- | <b>Column I</b>  | <b>Column II</b>   |
|--|--|
| (A) $\text{FeSO}_4 \xrightarrow{\Delta}$   | (p) One of the products is coloured due to charge transfer |
| (B) $\text{Mn}^{2+} + \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \longrightarrow$                                | (q) One of the products is in + VI oxidation state         |
| (C) $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow$<br>(saturated solution) | (r) Redox reaction   |
| (D) $\text{N}_2\text{H}_4 + \text{CuSO}_4 \longrightarrow$   | (s) One of the products is acidic oxide                    |
13. Match the reactions listed in column(I) with the characteristic(s) of the products/type of reactions listed in column(II).
- | <b>Column - I</b>  | <b>Column - II</b>   |
|--|--|
| (A) $\text{MnO}_4^{2-} + \text{CO}_2 \longrightarrow$              | (p) Two pungent smelling gases are liberated.                                    |
| (B) $\text{CrO}_4^{2-} + \text{H}^+ \longrightarrow$               | (q) Show disproportionation reaction.  |
| (C) $\text{FeSO}_4 \xrightarrow{\Delta}$                           | (r) Dimeric bridged tetrahedral metal ion.                                       |
| (D) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta}$ | (s) One of the products has central metal in its highest stable oxidation state. |

14. Match the reactions in **Column I** with nature of the reactions/type of the products in **Column II**.
- | Column I   | Column II                                     |
|--|---|
| (A) $\text{AgNO}_3(\text{aq}) + \text{I}_2 (\text{excess}) + \text{H}_2\text{O} \longrightarrow$ | (p) Disproportionation                        |
| (B) $\text{K}_2\text{MnO}_4(\text{aq}) + \text{CO}_2(\text{g}) \longrightarrow$                  | (q) Comproportionation                        |
| (C) $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{C} \xrightarrow{\Delta}$                           | (r) Redox                                     |
| (D) $\text{CuCl}_2(\text{aq}) + \text{Cu}(\text{s}) \longrightarrow$                             | (s) One of the products is insoluble in water |

## ASSERTION / REASONING

### DIRECTIONS :

Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

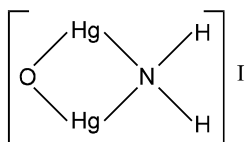
- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.  
 (E) Statement-1 and Statement-2 both are False.
15. **Statement-1** : The order of atomic radii of Cu, Ag and Au is  $\text{Cu} < \text{Ag} \approx \text{Au}$ .  
**Statement-2** : The atomic radii of 4d series elements are larger than those of 3d series elements but generally the radii of 4d and 5d series elements are almost identical.
16. **Statement-1** : 4d & 5d series elements have nearly same atomic radius.  
**Statement-2** : Lanthanoid contraction.
17. **Statement-1** : The value of enthalpy of atomisation is maximum at about the middle of each series.  
**Statement-2** : There is one unpaired electron per d-orbital and this results in stronger interatomic interaction.
18. **Statement-1** : The spin only magnetic moment of  $\text{Sc}^{3+}$  is 1.73 B.M.  
**Statement-2** : The spin only magnetic moment of an ion is equal to  $\sqrt{n(n+2)}$  ; where n is the number of unpaired electrons in the ion.
19. **Statement-1** : The highest manganese fluoride is  $\text{MnF}_4$  and the highest oxide is  $\text{Mn}_2\text{O}_7$  .  
**Statement-2** : In  $\text{Mn}_2\text{O}_7$ , each Mn is tetrahedrally surrounded by O's including Mn–O–Mn bridge.
20. **Statement-1** : The lowest oxide of a transition metal (say, chromium, atomic number 24) is basic where as the highest oxide is usually acidic.  
**Statement-2** :  $\text{Cr}_2\text{O}_3$  is amphoteric in nature.
21. **Statement-1** : In acid solution permanganate is reduced to  $\text{Mn}^{2+}$  by an excess of reducing agent.  
**Statement-2** :  $\text{MnO}_4^-$  reduced in  $\text{Mn}^{2+}$  in acidic medium and the product in the presence of an excess of permanganate is  $\text{MnO}_2$  .
22. **Statement-1** : Hydrochloric acid is not used to acidify a  $\text{KMnO}_4$  solution in volumetric analysis of  $\text{Fe}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  because.  
**Statement-2** : Part of the oxygen produced from  $\text{KMnO}_4$  and HCl is used up in oxidising HCl to  $\text{Cl}_2$  .
23. **Statement-1** : Potassium dichromates gives deep red vapours with concentrated  $\text{H}_2\text{SO}_4$  and sodium chloride.  
**Statement-2** : The reaction of sodium chloride with solid  $\text{K}_2\text{Cr}_2\text{O}_7$  and concentrated  $\text{H}_2\text{SO}_4$  produces chromyl chloride.
24. **Statement-1** : Solution of  $\text{Na}_2\text{CrO}_4$  in water is intensely coloured.  
**Statement-2** : Oxidation state of Cr in  $\text{Na}_2\text{CrO}_4$  is (+VI).

25. **Statement-1** : Reaction of thionyl chloride with hydrated ferric chloride yields anhydrous ferric chloride.  
**Statement-2** : Water of crystallisation present with ferric chloride reacts with thionyl chloride to liberate HCl and SO<sub>2</sub> gases.
26. **Statement-1** : Hydroquinone is used as a developer for developing black and white photographic film.  
**Statement-2** : Hydroquinone reduces silver bromide to black silver particles and an inverted image of the object is produced on a celluloid film.
27. **Statement-1** : Silver nitrate is reduced to silver by the hydrides of 15th group elements (except NH<sub>3</sub>) because  
**Statement-2** : They act as strong reducing agents.
28. **Statement-1** :  $\text{Ag}_2\text{S} + 4\text{KCN} \xrightleftharpoons{\text{O}_2} 2\text{K}[\text{Ag}(\text{CN})_2] + \text{K}_2\text{S}$   
**Statement-2** : The reaction is carried out in presence of air or O<sub>2</sub> so that K<sub>2</sub>S is oxidised to K<sub>2</sub>SO<sub>4</sub> thereby shifting the equilibrium in forward direction.
29. **Statement-1** : CuSO<sub>4</sub>·5H<sub>2</sub>O on heating to 250°C loses all the five H<sub>2</sub>O molecules and becomes anhydrous.  
**Statement-2** : All the five H<sub>2</sub>O molecules are co-ordinated to the central Cu<sup>2+</sup> ion.
30. **Statement-1** : CrO<sub>3</sub> is an acid anhydride.  
**Statement-2** : CrO<sub>3</sub> is obtained as bright orange crystals by the reaction of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with cold concentrated H<sub>2</sub>SO<sub>4</sub>
31. **Statement-1** : Solid potassium dichromate gives greenish yellow vapours with concentrated H<sub>2</sub>SO<sub>4</sub> and solid ammonium chloride.  
**Statement-2** : The reaction of ammonium chloride with solid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> produces chromyl chloride.
32. **Statement-1** : The free gaseous chromium atom has six unpaired electrons  
**Statement-2** : Half filled orbital has greater stability than fully filled
33. **Statement-1** : K<sub>2</sub>CrO<sub>4</sub> has yellow colour due to charge transfer.  
**Statement-2** : CrO<sub>4</sub><sup>2-</sup> ion is tetrahedral in shape.
34. **Statement-1** : The green manganate is paramagnetic but the purple permanganate is diamagnetic in nature.  
**Statement-2** : MnO<sub>4</sub><sup>2-</sup> contains one unpaired electron while in MnO<sub>4</sub><sup>-</sup> all electrons are paired.
35. **Statement-1** : Copper metal is turned green when exposed to atmospheric CO<sub>2</sub> and moisture.  
**Statement-2** : Copper gets covered with a green layer of basic copper carbonate.
36. **Statement-1** : Ammoniacal silver nitrate converts glucose to gluconic acid and metallic silver is precipitated.  
**Statement-2** : Glucose acts as a weak reducing agent.

## TRUE / FALSE

37. S<sub>1</sub> : Interstitial compounds have high melting points, higher than those of pure metals.  
S<sub>2</sub> : Permanganate titrations in presence of hydrochloric acid are unsatisfactory.  
S<sub>3</sub> : KMnO<sub>4</sub> does not act as an oxidising agent in strong alkaline medium.  
S<sub>4</sub> : KMnO<sub>4</sub> on heating in a current of H<sub>2</sub> gives MnO.  
(A) T T F T (B) T F F T (C) T F T T (D) F F T F
38. S<sub>1</sub> : Mn<sup>2+</sup> compounds are more stable than Fe<sup>2+</sup> towards oxidation to their +3 state.  
S<sub>2</sub> : Titanium and copper both in the first series of transition metals exhibits +1 oxidation state most frequently.  
S<sub>3</sub> : Cu<sup>+</sup> ion is stable in aqueous solutions.  
S<sub>4</sub> : The E<sup>0</sup> value for the Mn<sup>3+</sup> / Mn<sup>2+</sup> couple is much more positive than that for Cr<sup>3+</sup> / Cr<sup>2+</sup> or Fe<sup>3+</sup> / Fe<sup>2+</sup>.  
(A) T T F T (B) T F F T (C) T F T T (D) F F T F

39. **S<sub>1</sub>** : Covalent and ionic radii of Nb and Ta are almost the same.  
**S<sub>2</sub>** : Ionisation energies of transition elements decrease with increase in atomic number in a given group.  
**S<sub>3</sub>** : Iodide of Millon's base is believed to have the structure.



**S<sub>4</sub>** : Yellow colour of  $\text{CrO}_4^{2-}$  is due to d-d transition.

- (A) T T F T (B) T F F T (C) T F T F (D) F F T F

40. **S<sub>1</sub>** : Acidic dichromate solutions on treatment with  $\text{H}_2\text{O}_2$  gives deep blue  $\text{CrO}(\text{O}_2)_2$ .  
**S<sub>2</sub>** : A deep red liquid,  $\text{CrO}_2\text{Cl}_2$  is formed by the reaction of chromium(III) oxide with HCl in presence of conc.  $\text{H}_2\text{SO}_4$ .  
**S<sub>3</sub>** :  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating yields green chromium(III) oxide and nitrogen gas.  
**S<sub>4</sub>** :  $\text{K}_2\text{Cr}_2\text{O}_7$  on heating with charcoal produces  $\text{K}_2\text{CO}_3$ .  
and arrange in the order of true/false.

- (A) T T T T (B) T F T T (C) T F T F (D) F F T T

41. **S<sub>1</sub>** :  $\text{Mn}^{II}$  ions in solution is oxidised to  $\text{MnO}_4^-$  by  $\text{PbO}_2$  or  $\text{NaBiO}_3$ .  
**S<sub>2</sub>** :  $\text{MnO}_4^{2-}$  ions in neutral, acid or slightly basic solutions readily disproportionate.  
**S<sub>3</sub>** :  $\text{KMnO}_4$  gives MnO on heating in current of hydrogen.  
and arrange in the order of true/false.

- (A) T T T (B) T F T (C) T F F (D) F T F.

## FILL IN THE BLANKS

42. Paramagnetism arises from the presence of \_\_\_\_\_.
43. The solubility of  $\text{Cu}(\text{OH})_2$  in ammonia is due to the formation of a complex of the formula \_\_\_\_\_.
44.  $\text{Cu}^+$  in aqueous solution undergoes \_\_\_\_\_ (disproportionation/comproportionation)
45. Pot. permanganate in neutral medium oxidises thiosulphate to \_\_\_\_\_ (sulphate / dithionate).
46. Permanent magnets are made of an alloy known as \_\_\_\_\_.
47. On adding alkali, the dichromate solution changes to \_\_\_\_\_.
48. Potassium iodide is oxidised by  $\text{KMnO}_4$  to \_\_\_\_\_ in acidic medium.
49.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[\text{strong}]{\Delta}$  \_\_\_\_\_ +  $\text{Cu}_2\text{Cl}_2$  +  $\text{HCl}$  +  $\text{Cl}_2$  +  $\text{H}_2\text{O}$
50. The ammonical silver nitrate reacts with acetylene to give \_\_\_\_\_.
51. Anhydrous ferrous sulphate on strong heating decomposes to give \_\_\_\_\_ and \_\_\_\_\_ gases.
52.  $\text{CuO} \xrightarrow[1100-1200^\circ\text{C}]{\Delta}$  \_\_\_\_\_ +  $\text{O}_2$
53. Green  $\text{K}_2\text{MnO}_4$  disproportionates in a neutral or acidic medium to give \_\_\_\_\_ and \_\_\_\_\_.



## EXERCISE # 2

### PART - I : MIXED OBJECTIVE

#### Single choice type

- In a transition series, as the atomic number increases, paramagnetism -  
(A) Increases gradually  
(B) Decreases gradually  
(C) First increases to a maximum and then decreases  
(D) First decreases to a minimum and then increases
- The magnetic moment of a transition metal ion is found to be 3.87 B.M. The number of unpaired electrons present in it is -  
(A) 2 (B) 3 (C) 4 (D) 5
- Which of the following transition metal has the highest melting point -  
(A) Cr (B) Mo (C) W (D) Hg
- Ionic character of halides of metals (3d-transition series) decreases in the order -  
(A) M-I > M-Br > M-Cl > M-F (B) M-Cl > M-Br > M-I > M-F  
(C) M-Br > M-Cl > M-F > M-I (D) M-F > M-Cl > M-Br > M-I
- Which of the following group of transition metals is called coinage metals -  
(A) Cu, Ag, Au (B) Ru, Rh, Pd (C) Fe, Co, Ni (D) Os, Ir, Pt
- The correct ground state electronic configuration of chromium atom ( $Z = 24$ ) is :  
(A)  $[\text{Ar}] 4d^5 4s^1$  (B)  $[\text{Ar}] 3d^4 4s^2$  (C)  $[\text{Ar}]3d^6 4s^0$  (D)  $[\text{Ar}] 3d^5 4s^1$
- Transition metals :  
(A) exhibit only diamagnetism (B) undergo inert pair effect  
(C) do not form alloys (D) show variable oxidation states
- The radii (metallic) of Fe, Co and Ni are nearly same.  
This is due to :  
(A) lanthanide contraction  
(B) the fact that successive addition of d-electrons screen the outer electrons (4s) from the inward pull of the nucleus.  
(C) increase in radii due to increase in 'n' is compensated by decrease in radii due to increase in effective nuclear charge (Z).  
(D) atomic radii do not remain constant but decrease in a normal gradation.
- Atoms of the transition elements are smaller than those of the s-block elements, because :  
(A) there is increase in the nuclear charge along the period.  
(B) orbital electrons are added to the penultimate d-subshell rather than to the outer shell of the atom.  
(C) the shielding effect of d-electrons is small.  
(D) All of these
- Which of the following factor may be regarded as the main cause of Lanthanide contraction ?  
(A) Poor shielding of 4 f-electrons in compare to other electrons in the sub-shell.  
(B) Effective shielding of one of the 4 f-electrons by another in the sub-shell.  
(C) Poorer shielding of 5 d electron by 4 f- electrons.  
(D) Greater shielding of 5 d electron by 4 f- electron.
- Which of the following transition metal ions has the lowest density ?  
(A) Copper (B) Nickel (C) Scandium (D) Zinc

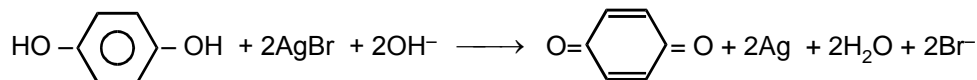
12. Brown's catalyst is -  
 (A) Pt/PtO (B) Pd/BaSO<sub>4</sub> (C) Nickel boride (D) None
13. A mixture of TiO<sub>2</sub> and BaSO<sub>4</sub> is called -  
 (A) Titanox (B) Lithopone (C) White pigment (D) None
14. Which of the following contains the maximum number of unpaired electrons -  
 (A) TiCl<sub>3</sub> (B) MnCl<sub>2</sub> (C) FeSO<sub>4</sub> (D) CuSO<sub>4</sub>
15. CuSO<sub>4</sub> solution + lime is called -  
 (A) Luca's reagent (B) Barfoed's reagent (C) Fehling solution A (D) Bordeaux mixture
16. Lunar caustic is -  
 (A) NaOH (B) KOH (C) Ba(OH)<sub>2</sub> (D) AgNO<sub>3</sub>
17. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is preferred to Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for use in volumetric analysis as a primary standard because -  
 (A) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is hygroscopic while K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is not  
 (B) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is hygroscopic while Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is not  
 (C) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is pure while Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is impure  
 (D) None of these
18. Of the ions Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cr<sup>3+</sup> (atomic number Zn = 30, Ni = 28, Cr = 24) :  
 (A) only Zn<sup>2+</sup> is colourless and Ni<sup>2+</sup> and Cr<sup>3+</sup> are coloured.  
 (B) all three are colourless.  
 (C) all three are coloured.  
 (D) only Ni<sup>2+</sup> is coloured and Zn<sup>2+</sup> and Cr<sup>3+</sup> are colourless.
19. Among the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other, in:  
 (A) Zn<sup>2+</sup>, Zn<sup>3+</sup> (B) Cu<sup>+</sup>, Cu<sup>2+</sup> (C) Cr<sup>2+</sup>, Cr<sup>3+</sup> (D) V<sup>2+</sup>, VO<sup>2+</sup>
20. VO<sub>2</sub> is an amphoteric oxide and in acidic medium it forms :  
 (A) VO<sup>2+</sup> (B) VO<sub>2</sub><sup>+</sup> (C) V<sup>3+</sup> (D) VO<sub>2</sub><sup>2+</sup>
21. Match the compounds of column X with oxidation state of column Y.
- |     | Column X  |    |     |    | Column Y |   |    |     |    |
|-----|---|----|-----|----|----------|---|----|-----|----|
| I   | [Cr(H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub> |    |     |    | 5        |   |    |     |    |
| II  | CrO <sub>5</sub>                                    |    |     |    | 4        |   |    |     |    |
| III | K <sub>3</sub> CrO <sub>8</sub>                     |    |     |    | 6        |   |    |     |    |
| IV  | (NH <sub>3</sub> ) <sub>3</sub> CrO <sub>4</sub>    |    |     |    | 3        |   |    |     |    |
|     | I   | II | III | IV |          | I | II | III | IV |
| (A) | 3   | 6  | 5   | 4  | (B)      | 3 | 4  | 5   | 6  |
| (C) | 4   | 5  | 6   | 3  | (D)      | 6 | 5  | 4   | 3  |
22. Which of the following transition element shows the highest oxidation state :  
 (A) Mn (B) Fe (C) V (D) Cr
23. Standard reduction electrode potential of Zn<sup>2+</sup> / Zn is – 0.76 V. This means :  
 (A) ZnO is reduced to Zn by H<sub>2</sub>  
 (B) Zn can't liberates H<sub>2</sub> with concentrated acids  
 (C) Zn is generally the anode in an electrochemical cell  
 (D) Zn is generally the cathode in an electrochemical cell
24. E<sup>o</sup> values for the couples Cr<sup>3+</sup>/Cr<sup>2+</sup> and Mn<sup>3+</sup>/Mn<sup>2+</sup> are – 0.41 and + 1.51 volts respectively. Considering these values select the correct option from the following statements.  
 (A) Cr<sup>2+</sup> acts as a reducing agent and Mn<sup>2+</sup> acts as an oxidising agent in their aqueous solutions.  
 (B) Cr<sup>2+</sup> (aq.) is more stable than Cr<sup>3+</sup> (aq.).  
 (C) Mn<sup>3+</sup> (aq.) is more stable than Mn<sup>2+</sup> (aq.).  
 (D) None of these.

25. Which one of the following shows highest magnetic moment ?  
 (A)  $V^{3+}$  (B)  $Cr^{3+}$  (C)  $Fe^{3+}$  (D)  $Co^{3+}$
26. Amongst the following the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by:  
 (A)  $MnSO_4 \cdot 4H_2O$  (B)  $CuSO_4 \cdot 5H_2O$  (C)  $FeSO_4 \cdot 6H_2O$  (D)  $NiSO_4 \cdot 6H_2O$
27. Baeyer's reagent is-  
 (A)  $KMnO_4 + H_2SO_4$  (B)  $KMnO_4 + KOH$  (C)  $K_2Cr_2O_7 + H_2SO_4$  (D)  $K_2Cr_2O_7 + KOH$
28. Lanthanoid contraction implies -  
 (A) Decrease in density (B) Decrease in mass  
 (C) Decrease in ionic radii (D) Decrease in radioactivity
29. The lanthanide contraction is responsible for the fact that -  
 (A) Zr and Y have about the same radius (B) Zr and Nb have similar oxidation state  
 (C) Zr and Hf have about the same radius (D) Zr and Zn have the same oxidation state
30. The basic character of the transition metal monoxide follows the order -  
 (A)  $VO > CrO > TiO > FeO$  (B)  $CrO > VO > FeO > TiO$   
 (C)  $TiO > FeO > VO > CrO$  (D)  $TiO > VO > CrO > FeO$
31. Lanthanide contraction is due to increase in -  
 (A) Shielding by 4f electrons (B) Atomic number  
 (C) Effective nuclear charge (D) size of 4 f-orbital
32. When  $MnO_2$  is fused with  $KOH$ , a coloured compound is formed, the product and its colour is -  
 (A)  $K_2MnO_4$ , green (B)  $KMnO_4$ , purple (C)  $Mn_2O_3$ , brown (D)  $Mn_3O_4$ , black
33. Which one of the transition metal ions is coloured in aqueous solution ?  
 (A)  $Cu^+$  (B)  $Zn^{2+}$  (C)  $Sc^{3+}$  (D)  $V^{4+}$
34. Compound that is both paramagnetic and coloured is :  
 (A)  $K_2Cr_2O_7$  (B)  $(NH_4)_2[TiCl_6]$  (C)  $VOSO_4$  (D)  $K_3[Cu(CN)_4]$
35. Which of the following compounds is expected to be coloured ?  
 (A)  $Ag_2SO_4$  (B)  $CuF_2$  (C)  $MgF_2$  (D)  $CuCl$
36. Most transition metals :  
 I : form sets of compounds which display different oxidation states of the metal.  
 II : form coloured ions in solution.  
 III : burn vigorously in oxygen.  
 IV : form complex compound.  
 of these :  
 (A) I, II, III are correct (B) II, III, IV are correct (C) I, II are correct (D) all are correct.
37. The aqueous solution of the following salts will be coloured in the case of :  
 (A)  $Zn(NO_3)_2$  (B)  $LiNO_3$  (C)  $Co(NO_3)_2$  (D) Potash alum
38. Which one of the following characteristics of the transition metals is associated with their catalytic activity ?  
 (A) Colour of hydrated ions. (B) Variable oxidation states.  
 (C) High enthalpy of atomization. (D) Paramagnetic behaviour.
39. German silver is an alloy of copper and :  
 (A) Zn + Ni (B) Al + Ag (C) Zn + Ag (D) Sn + Zn
40. Ferric sulphate on heating gives :  
 (A)  $SO_2$  and  $SO_3$  (B)  $SO_2$  only (C)  $SO_3$  only (D) S

41. Anhydrous ferric chloride is prepared by :  
 (A) dissolving ferric hydroxide in dilute HCl. (B) dissolving ferric hydroxide in concentrated HCl.  
 (C) by passing dry  $\text{Cl}_2$  gas over heated scrap iron. (D) by dissolving iron (III) oxide in concentrated HCl.
42. At  $300^\circ\text{C}$ ,  $\text{FeCl}_3$  :  
 (A) decomposes into  $\text{FeCl}_2$  and  $\text{Cl}_2$  (B) decomposes into Fe and  $\text{Cl}_2$   
 (C) sublimes to give liquid  $\text{FeCl}_3$  (D) sublimes to give gaseous dimer  $(\text{FeCl}_3)_2$
43. Iron is rendered passive by treatment with concentrated :  
 (A) HCl (B)  $\text{H}_2\text{SO}_4$  (C)  $\text{H}_3\text{PO}_4$  (D)  $\text{HNO}_3$
44. Lucas reagent is :  
 (A) Anhydrous  $\text{ZnCl}_2 + \text{HCl}$  (conc.) (B)  $\text{MnO}_2 + \text{H}_2\text{O}$   
 (C)  $\text{H}_2\text{SO}_4 + \text{HCl}$  (D)  $\text{NO} + \text{H}_2\text{O}$
45. Which one of the following dissolves in hot concentrated NaOH ?  
 (A) Fe (B) Zn (C) Cu (D) Ag
46. The compound used for gravimetric estimation of Cu(II) is :  
 (A)  $\text{Cu}_2(\text{SCN})_2$  (B)  $\text{Cu}_2\text{O}$  (C)  $\text{Cu}_2\text{I}_2$  (D)  $\text{Cu}_2\text{CO}_3$
47. In the reaction,  $2\text{CuCl}_2 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{A} + \text{H}_2\text{SO}_4 + 2\text{HCl}$  ; A is  
 (A)  $\text{Cu}_2\text{Cl}_2$  (B) Cu (C)  $\text{CuSO}_4$  (D) CuS
48. Sodium thiosulphate is used in photography because of its :  
 (A) oxidising behaviour (B) reducing behaviour  
 (C) complexing behaviour (D) photochemical behaviour
49.  $\text{MnO}_4^{2-}$  (1 mole) in neutral aqueous medium disproportionates to :  
 (A)  $2/3$  mole of  $\text{MnO}_4^-$  and  $1/3$  mole of  $\text{MnO}_2$  (B)  $1/3$  mole of  $\text{MnO}_4^-$  and  $2/3$  mole of  $\text{MnO}_2$   
 (C)  $1/3$  mole of  $\text{Mn}_2\text{O}_7$  and  $1/3$  mole of  $\text{MnO}_2$  (D)  $2/3$  mole of  $\text{Mn}_2\text{O}_7$  and  $1/3$  mole of  $\text{MnO}_2$
50. When  $\text{H}_2\text{O}_2$  is added to an acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  :  
 (A) solution turns green due to formation of  $\text{Cr}_2\text{O}_3$  (B) solution turns yellow due to formation of  $\text{K}_2\text{CrO}_4$   
 (C) a blue coloured compound  $\text{CrO}(\text{O}_2)_2$  is formed (D) solution gives green ppt of  $\text{Cr}(\text{OH})_3$
51. The number of moles of  $\text{KMnO}_4$  that will be needed to react with one mole of sulphite ion in acidic medium is  
 (A)  $2/5$  (B)  $3/5$  (C)  $4/5$  (D) 1
52. Ammonium dichromate is used in some fire works. The green coloured powder blown in the air is  
 (A)  $\text{CrO}_3$  (B)  $\text{Cr}_2\text{O}_3$  (C) Cr (D)  $\text{CrO}(\text{O}_2)$
53. The number of moles of  $\text{KMnO}_4$  that will be needed to react completely with one mole of ferrous oxalate in acidic solution is :  
 (A)  $3/5$  (B)  $2/5$  (C)  $4/5$  (D) 1
54. Which of the following compounds is diamagnetic -  
 (A)  $\text{ZnCl}_2$  (B)  $\text{CrCl}_3$  (C)  $\text{CuSO}_4$  (D)  $\text{NiCl}_4^{2-}$
55. The complex  $[\text{CoF}_6]^{3-}$  should have a spin only magnetic moment is -  
 (A)  $\sqrt{3}$  B.M. (B)  $2\sqrt{5}$  B.M. (C)  $\sqrt{24}$  B.M. (D) 6 B.M.
56. The highest oxidation state is exhibited by the transition metals with configuration -  
 (A)  $(n-1)d^3ns^2$  (B)  $(n-1)d^5ns^1$  (C)  $(n-1)d^5ns^2$  (D)  $(n-1)d^8ns^2$
57. The common oxidation state of the elements of lanthanide series is -  
 (A) + 2 (B) + 3 (C) + 4 (D) + 1

### More than one choice type

58. In photography, quinol is used as developer according to following reaction.



Which of the following describe(s) the role of quinol in this reaction ?

- (A) It acts as an acid. (B) It acts as a weak base.  
(C) It acts as an oxidising agent. (D) It acts as a reducing agent.
59. Which of the following statement (s) is/are correct ?  
(A)  $\text{S}_2\text{O}_8^{2-}$  oxidise  $\text{Ag}^+$  in presence of pyridine and give red colour compound.  
(B)  $\text{MnO}_4^{2-}$  disproportionates to yield  $\text{MnO}_4^-$  and  $\text{MnO}_2$  in presence of  $\text{H}^+$  ions.  
(C) In  $\text{Cr}_2\text{O}_7^{2-}$  each Cr is linked to four oxygen atoms.  
(D)  $\text{Ti}^{2+}$  is purple while  $\text{Ti}^{4+}$  is colourless.
60. Following reaction(s) is/are involved in the iodometric estimation.  
(A)  $\text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + \text{I}^- \longrightarrow 2\text{Cr}^{3+} + \text{I}_2$ ;  $\text{I}_2 + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$   
(B)  $\text{MnO}_4^- + \text{H}^+ + \text{I}^- \longrightarrow \text{Mn}^{2+} + \text{I}_2$ ;  $\text{I}_2 + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$   
(C)  $\text{MnO}_4^- + \text{OH}^- + \text{I}^- \longrightarrow \text{MnO}_2 + \text{I}_2$ ;  $\text{I}_2 + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$   
(D)  $\text{Cr}_2\text{O}_7^{2-} + \text{OH}^- + \text{I}^- \longrightarrow 2\text{Cr}^{3+} + \text{I}_2$ ;  $\text{I}_2 + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$
61. The colour of the transition metal ions is/are due to :  
(A) d-d transition of electrons in presence of ligands  
(B) charge transfer from ligand to metal ion.  
(C) change in the geometry  
(D) polarisation of anion by cation
62. Which of the following statement(s) is/are not correct ?  
(A) The blue colour of aqueous  $\text{CuCl}_2$  is due to  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$   
(B) The yellow colour of aqueous  $\text{CuCl}_2$  is due to  $[\text{CuCl}_4]^{2-}$   
(C) The green colour of aqueous  $\text{CuCl}_2$  is due to the presence of both  $[\text{Cu}(\text{H}_2\text{O})_4]^+$  and  $[\text{CuCl}_4]^{2-}$   
(D) The blue colour of aqueous  $\text{CuCl}_2$  is due to  $[\text{CuCl}_4]^{2-}$
63. Select correct statement (s).  
(A)  $\text{MnO}_4^-$  is intense pink colour due to d-d transition of electron.  
(B) Cu(I) is diamagnetic while Cu(II) is paramagnetic.  
(C)  $\text{CrO}_3$  is amphoteric oxide.  
(D)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  both are coloured in aqueous solution.
64. Correct statements about transition metals are that they :  
(A) form complex (B) show variable oxidation states  
(C) show magnetic properties (D) do not form coloured compounds
65. Transition elements have greater tendency to form complexes because they have :  
(A) vacant d-orbitals (B) small size  
(C) higher nuclear charge (D) variable oxidation states
66. Which of the following statements are correct when a mixture of  $\text{NaCl}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  is gently warmed with conc.  $\text{H}_2\text{SO}_4$  ?  
(A) Deep red vapours are liberated  
(B) Deep red vapours dissolve in  $\text{NaOH}$  (aq.) forming a yellow solution.  
(C) Greenish yellow gas is liberated  
(D) Deep red vapours dissolve in water forming yellow solution

67. Which of the following reaction(s) is/are incorrect for silver nitrate ?  
 (A)  $6\text{AgNO}_3 + 3\text{I}_2$  (excess) +  $3\text{H}_2\text{O} \longrightarrow \text{AgIO}_3 + 5\text{AgI} + 6\text{HNO}_3$   
 (B)  $\text{AgNO}_3$  (excess) +  $2\text{KCN} \longrightarrow \text{K}[\text{Ag}(\text{CN})_2] + \text{KNO}_3$   
 (C)  $2\text{AgNO}_3 + 4\text{Na}_2\text{S}_2\text{O}_3$  (excess)  $\longrightarrow 2\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + 2\text{NaNO}_3$   
 (D)  $\text{PH}_3 + 6\text{AgNO}_3 + 3\text{H}_2\text{O} \longrightarrow 6\text{Ag} + 6\text{HNO}_3 + \text{H}_3\text{PO}_3$
68. Which of the following reaction(s) is/are used for the preparation of anhydrous  $\text{FeCl}_3$  ?  
 (A)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{SOCl}_2 \longrightarrow \text{FeCl}_3 + 12\text{HCl} + 6\text{SO}_2$   
 (B)  $\text{Fe}(\text{OH})_3 \downarrow + 3\text{HCl} \longrightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$   
 (C)  $2\text{Fe} + 4\text{HCl}$  (aq.) +  $\text{Cl}_2 \longrightarrow 2\text{FeCl}_3 + 2\text{H}_2$   
 (D)  $2\text{Fe} + 3\text{Cl}_2$  (dry)  $\longrightarrow 2\text{FeCl}_3$
69. Which of the following is/are false ?  
 (A)  $\text{Na}_2\text{Cr}_2\text{O}_7$  is used as a primary standard in volumetric analysis.  
 (B) Potassium permanganate in excess on treatment with conc.  $\text{H}_2\text{SO}_4$  forms manganese heptoxide  
 (C) Phosphine, arsine and stibine all precipitates silver from silver nitrate  
 (D) From kipp's apparatus waste ferric sulphate and ferrous sulphate mixture is obtained when air or oxygen is passed for longer time.
70. Which of the following chemical reaction(s) is/are involved in developing of photographic plate ?  
 (A)  $\text{C}_6\text{H}_4(\text{OH})_2 + 2\text{AgBr} \longrightarrow 2\text{Ag} + \text{C}_6\text{H}_4\text{O}_2 + 2\text{HBr}$       (B)  $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$   
 (C)  $2\text{AgNO}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3 + 2\text{NaNO}_3$       (D)  $\text{AgNO}_3 + \text{KCN} \longrightarrow \text{AgCN} + \text{KNO}_3$
71. Pyrolusite is  $\text{MnO}_2$  used to prepare  $\text{KMnO}_4$ . Steps are :  

$$\text{MnO}_2 \xrightarrow{\text{I}} \text{MnO}_4^{2-} \xrightarrow{\text{II}} \text{MnO}_4^-$$
  
 Steps I and II are respectively :  
 (A) fuse with  $\text{KOH}$  / air, electrolytic oxidation  
 (B) fuse with  $\text{KOH}$  /  $\text{KNO}_3$ , electrolytic oxidation  
 (C) fuse with concentrated  $\text{HNO}_3$  / air, electrolytic reduction  
 (D) dissolve in  $\text{H}_2\text{O}$ , oxidation
72. Which are correct statements ?  
 (A) In less acidic solution  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{O}_2$  gives violet coloured diamagnetic  $[\text{Cr}(\text{O}_2)(\text{OH})]^-$  ion.  
 (B) In alkaline  $\text{H}_2\text{O}_2$ ,  $\text{K}_2\text{CrO}_8$  (with tetraperoxo species  $[\text{Cr}(\text{O}_2)_4]^{3-}$ ) is formed with  $\text{K}_2\text{Cr}_2\text{O}_7$ .  
 (C) In ammonical solution of  $\text{H}_2\text{O}_2$ ,  $(\text{NH}_3)_3\text{CrO}_4$  is formed with  $\text{K}_2\text{Cr}_2\text{O}_7$ .  
 (D)  $\text{CrO}_4^{2-}$  changes to  $\text{Cr}_2\text{O}_7^{2-}$  by oxidation.
73. When  $\text{CO}_2$  is passed into aqueous :  
 (A)  $\text{Na}_2\text{CrO}_4$  solution, its yellow colour changes to orange.  
 (B)  $\text{K}_2\text{MnO}_4$  solution, it disproportionates to  $\text{KMnO}_4$  and  $\text{MnO}_2$   
 (C)  $\text{Na}_2\text{Cr}_2\text{O}_7$  solution, its orange colour changes to green  
 (D)  $\text{KMnO}_4$  solution, its pink colour changes to green.

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## PART - II : SUBJECTIVE QUESTIONS

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- What is the general electronic configuration of transition elements.
- Write the electronic configurations of the following ions.  
 (i)  $\text{Mn}^{2+}$  (ii)  $\text{Fe}^{3+}$  (iii)  $\text{Ni}^{2+}$  (iv)  $\text{Cr}^{3+}$
- Name the d-block elements which do not have partially filled d-orbitals in their atoms or in their simple ions.
- What is meant by the 'lanthanide contraction'? Mention one important fact that can be considered as a consequence of the lanthanide contraction.



5. Name the (i) lightest and the (ii) heaviest elements (in terms of density) among the transition elements.
6. Which element among d-block elements has (i) the lowest melting point and (ii) the highest melting point
7. Why zinc has lowest melting point in 3d series ?
8. Why are ionization energies of 5d - elements greater than those of 3d - elements ?
9.  $K_2PtCl_6$  is a well known compound whereas corresponding Ni compound is not known. Explain.
10. Why do transition elements show variable oxidation state ?
11. What is the most common oxidation state of first transition series?
12. What is meant by disproportionation of an oxidation state ? Give an example.
13. Name the three factors which determine the stability of a particular oxidation state in solution.
14. Explain as to why the  $E^\ominus$  value for the  $Mn^{3+} / Mn^{2+}$  couple is much more positive than that for  $Cr^{3+} / Cr^{2+}$  or  $Fe^{3+} / Fe^{2+}$ .
15. Most of transition metals can displace hydrogen from dilute acids. Why ?
16.

Element	Cr	Mn	Fe
$E^\ominus (M^{2+}/M)$	– 0.90 V	– 1.18 V	– 0.4 V
$E^\ominus (M^{3+}/M^{2+})$	– 0.41 V	+ 1.57 V	+ 0.8 V

Use this data to comment upon

  - (i) The stability of  $Fe^{3+}$  and  $Mn^{2+}$  in acid solutions.
  - (ii) The ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.
17. Which of the following ions would form (i) coloured and (ii) colourless complexes in water ?  
 $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ti^{3+}$ ,  $Ti^{4+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$
18. Why  $Ti^{4+}$  complexes are diamagnetic ?
19. A substance is found to have a magnetic moment of 3.9 BM. How many unpaired electrons does it contain?
20. Why do Mn(II) show maximum paramagnetic character amongst the bivalent ions of the 1<sup>st</sup> transition series?
21. Explain giving Statement-2.  
(a) Transition metals and many of their compounds show paramagnetic behaviour.  
(b) The enthalpies of atomisation of the transition metals are high.  
(c) The transition metals generally form coloured compounds.
22. Explain why transition metals and their many compounds act as good catalyst.
23. A transition metal forms alloys with other transition elements. Explain.
24. Describe the general characteristics of transition elements with special reference to the following :  
(i) catalytic behaviour. (ii) complex formation. (iii) interstitial compounds.
25. What happens when  $CuSO_4$  solution is treated with  
(i) excess of ammonia solution and (ii) KI solution ?

26. What happens when silver nitrate solution is added to  $\text{Na}_2\text{S}_2\text{O}_3$  solution and then content is allowed to keep for a longer period?
27. What reaction will take place if a silver coin is put in dilute  $\text{HNO}_3$  ?
28. Which type of reaction  $\text{MnO}_4^{2-}$  shows with acid, dilute-alkali or water.
29. Why  $\text{KMnO}_4$  is stored in dark bottle and what happens to its acidic solution ?
30. Why does  $\text{AgNO}_3$  produce a black stain on the skin ?
31. Why is  $\text{AgBr}$  used in photography ?
32. Why it is not advisable to dissolve  $\text{KMnO}_4$  in cold and concentrated  $\text{H}_2\text{SO}_4$  ?
33. What happens when :
- Green vitriol is strongly heated.
  - $\text{FeSO}_4$  reacts with potassium ferricyanide.
  - $\text{Fe}_2\text{O}_3$  is fused with soda ash.
  - Salts of iron (III) reacts with  $\text{NH}_4\text{SCN}$ .
  - Zinc oxide and cobalt oxide is fused.
  - Malachite is made to react with dilute  $\text{H}_2\text{SO}_4$ .
  - Copper sulphate is exposed to air for longer period.
  - Lunar caustic is made to react with sodium hydroxide and then product is dried.
  - Silver nitrate reacts with excess iodine.
  - Potassium dichromate reacts with cold and concentrated  $\text{H}_2\text{SO}_4$ .
34. Complete and balance the following reactions :
- (a)  $\text{FeSO}_4 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow$
- (b)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{CH}_3 - \overset{\text{OCH}_3}{\underset{\text{OCH}_3}{\text{C}}} - \text{CH}_3 \longrightarrow$
- (c)  $\text{Cu}(\text{OH})_2 + \text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4 \longrightarrow$
- (d)  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[\text{strong}]{\Delta}$
- (e)  $\text{AgNO}_3 (\text{excess}) + \text{I}_2 + \text{H}_2\text{O} \longrightarrow$
- (f)  $\text{KMnO}_4 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow$
- (g)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + \text{SO}_2 + \text{H}_2\text{O} \xrightarrow{\text{Temp} < 70^\circ\text{C}}$
35.  $\text{CrO}(\text{O}_2)_2$  is stable in pyridine. Explain ?
36. Write the formula of the compound formed by  $\text{K}_2\text{Cr}_2\text{O}_7$  in alkaline solution with 30%  $\text{H}_2\text{O}_2$  :
37. Between  $\text{Na}^+$  and  $\text{Ag}^+$ , which is stronger Lewis acid and why?
38. Why the highest oxidation state of a metal is exhibited in its oxide or fluoride only?
39. 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  $3d^4$ ?
40. Why are  $\text{Mn}^{2+}$  compounds more stable than  $\text{Fe}^{2+}$  towards oxidation to their +3 state?
41. How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

42. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
43. The  $E^{\circ}$  ( $M^{2+}/M$ ) value for copper is positive (+0.34V). What is possibly the Statement-2 for this?
44. Why is the  $E^{\circ}$  value for the  $Mn^{3+}/Mn^{2+}$  couple much more positive than that for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$ ? Explain.
45. Which is a stronger reducing agent  $Cr^{2+}$  or  $Fe^{2+}$  and why?
46. Explain why  $Cu^{+}$  ion is not stable in aqueous solutions?
47. The aqueous solution of  $FeCl_3$  is acidic. Why?
48. Ferric iodide is very unstable but ferric chloride is not.
49. Copper dissolves in dilute nitric acid but not in dilute HCl. Why?
50. Blue colour of  $CuSO_4$  solution is discharged slowly when an iron rod is dipped into it. Why?
51. Copper (I) salts are not known in aqueous solutions.
52. Calculate the number of unpaired electrons in the following gaseous ions:  $Mn^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$  and  $Ti^{3+}$ . Which one of these is the most stable in aqueous solution?
53. Mercurous ion is written as  $Hg_2^{2+}$  whereas cuprous ion is written as  $Cu^{+}$ . Explain.
54. Copper sulphate dissolves in  $NH_4OH$  solution but  $FeSO_4$  does not.
55. An aqueous solution of inorganic compound (X) gives following reactions.  
 (i) With an aqueous solution of barium chloride a precipitate insoluble in dilute HCl is obtained.  
 (ii) Addition of excess of KI gives a brown precipitate which turns white on addition of excess of hypo solution.  
 (iii) With an aqueous solution of  $K_4[Fe(CN)_6]$ , a brown coloured precipitate is obtained.  
 Identify (X) and give equations for the reaction for (i), (ii) and (iii) observations.
56.  $H_2S$  gas is passed through an acidic solution of  $K_2Cr_2O_7$ . The solution turns milky, why?
57. What happens when (i) a small amount of  $KMnO_4$  is added to concentrated  $H_2SO_4$  (ii) an excess amount of  $KMnO_4$  is added to concentrated  $H_2SO_4$  solution.
58. A hydrated metallic salt (A), light green in colour, on careful heating gives a white anhydrous residue (B), (B) is soluble in water and its aqueous solution gives a dark blue precipitate (C) with potassium hexacyanidoferrate(III). (B) on strong heating gives a brown residue (D) and a mixture of two gases (E) and (F). The gaseous mixture when passed through acidified potassium dichromate, produces green colour solution and when passed through lead acetate solution gave a white precipitate. Out of two gases (E) can act as both reducing as well as oxidising agent.  
 (a) Identify (A), (B), (C), (D), (E) and (F) and give the reactions involved.  
 (b) Explain why salt (A) becomes white on heating.
59. A white substance (A) reacts with dilute  $H_2SO_4$  to produce a colourless suffocating gas (B) and a colourless solution (C). The reaction of gas (B) with potassium iodate and starch solution produces a blue colour solution. Aqueous solution of (A) gives a white precipitate with  $BaCl_2$  solution which is soluble in dilute HCl. Addition of aqueous  $NH_3$  or NaOH to (C) produces first a precipitate which dissolves in excess of the respective reagent to produce a clear solution. Similarly addition of excess of potassium ferrocyanide to (C) produces a precipitate (D) which also dissolves in aqueous NaOH giving a clear solution. Identify (A), (B), (C) and (D). Write the equations of the reactions involved.
60. Write the balanced chemical equation for the following reaction :-  
 Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate
61. Complete and / balance the following equation :  
 $Ag_2S + CuCl_2 + Hg \dots\dots\dots + \dots\dots\dots + S + 2Ag$

## EXERCISE # 3

### PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)

\* Marked Questions are having more than one correct option.

1. Amongst the following identify the species with an atom in +6 oxidation state. [JEE 2000, 3/35]  
 (A)  $\text{MnO}_4^-$  (B)  $\text{Cr}(\text{CN})_6^{3-}$  (C)  $\text{NiF}_6^{2-}$  (D)  $\text{CrO}_2\text{Cl}_2$
2. Write the balanced chemical equations for developing photographic films. [JEE 2000, 2/100]
3. In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry, the equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is :  
 (A) (molecular weight)/2, (molar mass)/2 (B) (molecular weight)/6  
 (C) (molecular weight)/3 (D) same as molecular weight [JEE 2001, 3/35]
4. Anhydrous ferric chloride is prepared by : [JEE 2002, 3/150]  
 (A) heating hydrated ferric chloride at a high temperature in a stream of air.  
 (B) heating metallic iron in a stream of dry chlorine.  
 (C) reaction of metallic iron with hydrochloric acid.  
 (D) reaction of metallic iron with nitric acid.
5. When  $\text{MnO}_2$  is fused with  $\text{KOH}$ , a coloured compound is formed. The product and its colour is : [JEE 2003, 3/144]  
 (A)  $\text{K}_2\text{MnO}_4$ , green (B)  $\text{Mn}_2\text{O}_3$ , brown (C)  $\text{Mn}_2\text{O}_4$ , black (D)  $\text{KMnO}_4$ , purple
6. The product of oxidation of  $\text{I}^-$  with  $\text{MnO}_4^-$  in alkaline medium is : [JEE 2004, 3/144]  
 (A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}^-$  (D)  $\text{IO}_4^-$
7. The pair of compounds having metals in their highest oxidation state is : [JEE 2004, 3/144]  
 (A)  $\text{MnO}_2$ ,  $\text{FeCl}_3$  (B)  $[\text{MnO}_4]^-$ ,  $\text{CrO}_2\text{Cl}_2$   
 (C)  $[\text{Fe}(\text{CN})_6]^{2-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  (D)  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$ .
8. Which of the following pair of compounds is expected to exhibit same colour in aqueous solution ? [JEE 2005, 3/84]  
 (A)  $\text{FeCl}_3$ ,  $\text{CuCl}_2$  (B)  $\text{VOCl}_2$ ,  $\text{CuCl}_2$  (C)  $\text{VOCl}_2$ ,  $\text{FeCl}_2$  (D)  $\text{FeCl}_2$ ,  $\text{MnCl}_2$
9. Give equations and describe the process for the developing of black and white photographic film. When sodium thiosulphate solution is treated with acidic solution turns milky white. Give the half reaction of the above described process. [JEE 2005, 4/60]
10.  $\text{MCl}_4 \xrightarrow{\text{Zn}}$  (B) purple colour compound  
 (A)  
 Colourless liquid at room temperature, transition metal  
 ↓ moist Air  
 White fumes (C)

Identify (A), (B) and  $\text{MCl}_4$ . Also explain colour difference between  $\text{MCl}_4$  and (A). [JEE 2005, 4/60]

11. Match the reactions in Column I with nature of the reactions/type of the products in Column II.

[JEE 2007, 6/162]

Column I	Column II
(A) $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) Redox reaction
(B) $CrO_4^{2-} + H^+ \rightarrow$	(q) One of the products has trigonal planar structure
(C) $MnO_4^- + NO_2^- + H^+ \rightarrow$	(r) Dimeric bridged tetrahedral metal ion
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s) Disproportionation

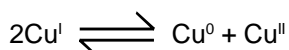
12. Among the following, the coloured compound is :

[JEE 2008, 3/163]

(A) CuCl	(B) $K_3[Cu(CN)_4]$	(C) $CuF_2$	(D) $[Cu(CH_3CN)_4]BF_4$
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13. The oxidation number of Mn in the product of alkaline oxidative fusion of  $MnO_2$  is. [JEE 2009, 4/160]

14. The equilibrium [JEE 2011]



in aqueous medium at 25°C shifts towards the left in the presence of

(A) $NO_3^-$	(B) $Cl^-$	(C) $SCN^-$	(D) $CN^-$
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## PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)

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Marked Questions are having more than one correct option.

- Number of electrons transferred in each case when  $KMnO_4$  acts as an oxidising agent to give  $MnO_2$ ,  $Mn^{2+}$ ,  $Mn(OH)_3$  and  $MnO_4^{2-}$  are respectively : [AIEEE 2002]  
(1) 3,5,4 and 1      (2) 4,3,1 and 5      (3) 1,3,4 and 5      (4) 5,4,3 and 1
- Which of the following ions has the maximum magnetic moment? [AIEEE 2002]  
(1)  $Mn^{2+}$       (2)  $Fe^{2+}$       (3)  $Ti^{2+}$       (4)  $Cr^{2+}$ .
- Most common oxidation state for Ce (Cerium) are : [AIEEE 2002]  
(1) +3, +4      (2) +2, +3      (3) +2, +4      (4) +3, +5
- What would happen when a solution of potassium chromate is treated with an excess of dilute  $HNO_3$  ? [AIEEE 2003]  
(1)  $Cr_2O_7^{2-}$  and  $H_2O$  are formed      (2)  $CrO_4^{2-}$  is reduced to +3 state of Cr  
(3)  $CrO_4^{2-}$  is oxidised to +7 state of Cr      (4)  $Cr^{3+}$  and  $Cr_2O_7^{2-}$  are formed
- Which one of the following nitrates will leave behind a metal on strong heating ? [AIEEE 2003]  
(1) Copper nitrate      (2) Manganese nitrate      (3) Silver nitrate      (4) Ferric nitrate
- The atomic numbers of V, Cr, Mn and Fe are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionization enthalpy ? [AIEEE 2003]  
(1) Cr      (2) Mn      (3) Fe      (4) V
- Which of the following group of transition metals is called coinage metals ? [AIEEE 2003]  
(1) Cu, Ag, Au      (2) Ru, Rh, Pb      (3) Fe, Co, Ni      (4) Os, Ir, Pt
- The number of d-electrons retained in  $Fe^{2+}$  (At. no. Fe = 26) ions are : [AIEEE 2003]  
(1) 3      (2) 4      (3) 5      (4) 6

9. Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in the alkaline solutions but not in acidic solutions. What is the Statement-2 for it? **[AIEEE 2003]**  
 (1) In acidic solutions hydration protects copper ions  
 (2) In acidic solutions protons co-ordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available.  
 (3) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali  
 (4) Copper hydroxide is an amphoteric substance.
10. The radius of  $\text{La}^{3+}$  (Atomic number of La = 57) is  $1.06\text{\AA}$ . Which one of the following given values will be closest to the radius of  $\text{Lu}^{3+}$  (Atomic number of Lu = 71)? **[AIEEE 2003]**  
 (1)  $1.60\text{\AA}$  (2)  $1.40\text{\AA}$  (3)  $1.06\text{\AA}$  (4)  $0.85\text{\AA}$
11. Cerium ( $Z = 58$ ) is an important member of the lanthanoids. Which of the following statement about cerium is incorrect? **[AIEEE 2004]**  
 (1) The common oxidation state of cerium are +3 and +4.  
 (2) The +3 oxidation state of cerium is more stable than +4 oxidation state.  
 (3) The +4 oxidation state of cerium is not known in solution.  
 (4) Cerium (IV) acts as an oxidizing agent.
12. The lanthanoid contraction is responsible for the fact that **[AIEEE 2005]**  
 (1) Zr and Y have about the same radius (2) Zr and Nb have similar oxidation state  
 (3) Zr and Hf have about the same radius (4) Zr and Zn have same oxidation state.
13. Which of the following factors may be regarded as the main cause of lanthanoid contraction? **[AIEEE 2005]**  
 (1) Greater shielding of 5d electrons by 4f electrons  
 (2) Poorer shielding of 5d electron by 4f electrons  
 (3) Effective shielding of one of 4f electrons by another in the sub-shell  
 (4) Poor shielding of one of 4f electron by another in the sub-shell.
14. The "spin-only" magnetic moment [in units of Bohr magneton, ( $\mu_B$ )] of  $\text{Ni}^{2+}$  in aqueous solution would be (atomic number of Ni = 28) **[AIEEE 2006]**  
 (1) 2.84 (2) 4.90 (3) 0 (4) 1.73
15. Lanthanoid contraction is caused due to : **[AIEEE 2006]**  
 (1) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge  
 (2) the appreciable shielding on outer electrons by 5f electrons from the nuclear charge  
 (3) the same effective nuclear charge from Ce to Lu  
 (4) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
16. Identify the incorrect statement among the following. **[AIEEE 2007, 3/120]**  
 (1) The chemistry of various lanthanoids is very similar.  
 (2) 4f and 5f orbitals are equally shielded.  
 (3) d-block elements show irregular and erratic chemical properties among themselves.  
 (4) La and Lu have partially filled d orbitals and no other partially filled orbitals.
17. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because **[AIEEE 2007, 3/120]**  
 (1) The actinoids are more reactive than the lanthanoids.  
 (2) The 5f orbitals extend farther from the nucleus than the 4f orbitals.  
 (3) The 5f orbitals are more buried than the 4f orbitals  
 (4) There is a similarity between 4f and 5f orbitals in their angular part of the wave function
18. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main Statement-2 being **[AIEEE 2008, 3/105]**  
 (1) lesser energy difference between 5f and 6d than between 4f and 5d orbitals  
 (2) more energy difference between 5f and 6d than between 4f and 5d orbitals  
 (3) more reactive nature of the actinoids than the lanthanoids  
 (4) 4f orbitals more diffused than the 5f orbitals



19. In context with the transition elements, which of the following statements is incorrect ? [AIEEE 2009, 4/144]
- (1) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
  - (2) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
  - (3) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
  - (4) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.
20. Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statement is incorrect ? [AIEEE 2009, 4/144]
- (1) The ionic sizes of Ln (III) decrease in general with increasing atomic number.
  - (2) Ln (III) compounds are generally colourless.
  - (3) Ln (III) hydroxides are mainly basic in character
  - (4) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
21. The correct order of  $E_{M^{2+}/M}^\circ$  values with negative sign for the four successive elements Cr, Mn, Fe and Co is [AIEEE 2010, 4/144]
- (1) Mn > Cr > Fe > Co
  - (2) Cr > Fe > Mn > Co
  - (3) Fe > Mn > Cr > Co
  - (4) Cr > Mn > Fe > Co
22. In context of the lanthanoids, which of the following statements is not correct ? [AIEEE 2011, 4/120]
- (1) There is gradual decrease in the radii of the members with increasing atomic number in the series
  - (2) All the members exhibit +3 oxidation state.
  - (3) Because of similar properties the separation of lanthanoids is not easy
  - (4) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series
23. The outer electron configuration of Gd (Atomic N : 64) is : [AIEEE 2011, 4/144]
- (1)  $af^3 5d^5 6s^2$
  - (2)  $4f^3 5d^0 6s^2$
  - (3)  $4f^4 5d^4 6s^2$
  - (4)  $af^7 5d^1 6s^2$
24. Iron exhibits + 2 and + 3 oxidation states. Which of the following statements about iron is incorrect ? [AIEEE 2012, 4/120]
- (1) Ferrous oxide is more basic in nature than the ferric oxide.
  - (2) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
  - (3) Ferrous compounds are less volatile than the corresponding ferric compounds.
  - (4) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.
25. Which of the following arrangement does **not** represent the correct order of the property stated against it? [JEE Mains 2013]
- (1)  $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$  : paramagnetic behaviour
  - (2)  $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$  : ionic size
  - (3)  $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$  : stability in aqueous solution
  - (4)  $Sc < Ti < Cr < Mn$  : number of oxidation states

## EXERCISE # 4

### NCERT QUESTIONS

- Write down the electronic configuration of :  
(i)  $\text{Cr}^{3+}$       (ii)  $\text{Pm}^{3+}$       (iii)  $\text{Cu}^+$       (iv)  $\text{Ce}^{4+}$       (v)  $\text{Co}^{2+}$   
(vi)  $\text{Lu}^{2+}$       (vii)  $\text{Mn}^{2+}$       (viii)  $\text{Th}^{4+}$
- Why are  $\text{Mn}^{2+}$  compounds more stable than  $\text{Fe}^{2+}$  towards oxidation to their + 3 state?
- Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?
- To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.
- 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  $3d^4$ ?
- 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.
- 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?
- In what way is the electronic configuration of the transition elements different from that of the non transition elements?
- Explain giving reasons :  
(i) Transition metals and many of their compounds show paramagnetic behaviour.  
(ii) The enthalpies of atomisation of the transition metals are high.  
(iii) The transition metals generally form coloured compounds.  
(iv) Transition metals and their many compounds act as good catalyst.
- What are interstitial compounds? Why are such compounds well known for transition metals?
- How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.
- Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?
- Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with :  
(i) iodide      (ii) iron(II) solution and      (iii)  $\text{H}_2\text{S}$
- Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with  
(i) iron(II) ions      (ii)  $\text{SO}_2$  and      (iii) oxalic acid?  
Write the ionic equations for the reactions.
- For  $\text{M}^{2+}/\text{M}$  and  $\text{M}^{3+}/\text{M}^{2+}$  systems the  $E^\ominus$  values for some metals are as follows :  

$\text{Cr}^{2+}/\text{Cr}$	- 0.9V	$\text{Cr}^3+/\text{Cr}^{2+}$	- 0.4 V
$\text{Mn}^{2+}/\text{Mn}$	- 1.2V	$\text{Mn}^{3+}/\text{Mn}^{2+}$	+1.5 V
$\text{Fe}^{2+}/\text{Fe}$	- 0.4V	$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.8 V

  
Use this data to comment upon :  
(i) the stability of  $\text{Fe}^{3+}$  in acid solution as compared to that of  $\text{Cr}^{3+}$  or  $\text{Mn}^{3+}$  and  
(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

16. Predict which of the following will be coloured in aqueous solution?  $Ti^{3+}$ ,  $V^{3+}$ ,  $Cu^+$ ,  $Sc^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$  and  $Co^{2+}$ . Give reasons for each.
17. Compare the stability of +2 oxidation state for the elements of the first transition series.
18. 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 oxidised.
  - The  $d^1$  configuration is very unstable in ions.
19. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
20. Calculate the number of unpaired electrons in the following gaseous ions :  $Mn^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$  and  $Ti^{3+}$ . Which one of these is the most stable in aqueous solution?
21. Give examples and suggest reasons for the following features of the transition metal chemistry :
- The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
  - A transition metal exhibits highest oxidation state in oxides and fluorides.
  - The highest oxidation state is exhibited in oxoanions of a metal.
22. Indicate the steps in the preparation of :
- $K_2Cr_2O_7$  from chromite ore.
  - $KMnO_4$  from pyrolusite ore.
23. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.
24. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points :
- electronic configurations
  - oxidation states
  - ionisation enthalpies and
  - atomic sizes.
25. Write down the number of 3d electrons in each of the following ions :  $Ti^{2+}$ ,  $V^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ . Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).
26. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.
27. What can be inferred from the magnetic moment values of the following complex species ?

Example	Magnetic Moment (BM)
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3
$K_2[MnCl_4]$	5.9

# ANSWERS

## EXERCISE # 1

### PART - I

- |           |              |           |           |           |            |              |
|-----------|--------------|-----------|-----------|-----------|------------|--------------|
| A-1. (C)  | A-2. (C)     | A-3. (C)  | A-4. (B)  | A-5. (B)  | A-6.* (AC) | B-1. (B)     |
| B-2. (B)  | B-3. (D)     | B-4. (A)  | B-5. (C)  | B-6. (C)  | B-7. (A)   | B-8.* (ACD)  |
| C-1. (A)  | C-2.* (ABC)  | D-1. (C)  | D-2. (B)  | D-3. (A)  | D-4. (C)   | D-5. (A)     |
| D-6. (B)  | D-7. (A)     | D-8. (C)  | D-9. (D)  | D-10. (C) | D-11. (B)  | D-12. (A)    |
| D-13. (C) | D-14. (C)    | D-15. (D) | D-16. (C) | D-17. (A) | D-18. (D)  | D-19. (C)    |
| D-20. (C) | D-21.* (ABC) | E-1. (D)  | E-2. (A)  | E-3. (D)  | E-4. (C)   | E-5.* (ABCD) |
| E-6. (A)  | F-1. (B)     | F-2. (B)  | F-3. (D)  | F-4. (B)  | F-5. (D)   | F-6. (D)     |
| F-7. (D)  | F-8. (B)     | F-9. (D)  | F-10. (C) | F-11. (A) | F-12. (A)  | F-13. (A)    |
| F-14. (D) | F-15. (C)    | F-16. (A) | F-17. (B) | F-18. (A) | F-19. (A)  | F-20. (B)    |
| F-21. (D) | F-22.* (ABC) | F-23. (B) | F-24. (B) |           |            |              |

### PART - II

- |   |   |                        |  |         |         |         |
|---|---|------------------------|--|---------|---------|---------|
| 1. (C)  | 2. (C)  | 3. (D)                 | 4. (D)   | 5. (A)  | 6. (D)  | 7. (D)  |
| 8. (A)  | 9. (C)  | 10. (B)                | 11. (C)  |         |         |         |
| 12. (A → q, r, s) ; (B → p, q, r) ; (C → p, q, s) ; (D → q, r)  |   |                        |  |         |         |         |
| 13. (A) - q, s ; (B) - r, s ; (C) - p, s ; (D) - p, s           |   |                        |  |         |         |         |
| 14. (A → p, r, s) ; (B → p, r, s) ; (C → r, s) : (D → q, r, s). |   |                        |  |         |         |         |
| 15. (A)   | 16. (A)   | 17. (A)                | 18. (D)  | 19. (B) | 20. (B) | 21. (B) |
| 22. (A)   | 23. (A)   | 24. (B)                | 25. (A)  | 26. (A) | 27. (A) | 28. (A) |
| 29. (C)   | 30. (B)   | 31. (D)                | 32. (C)  | 33. (B) | 34. (A) | 35. (A) |
| 36. (A)   | 37. (A)   | 38. (B)                | 39. (C)  | 40. (B) | 41. (A) |         |
| 42. unpaired electron(s).                                       | 43. [Cu(NH <sub>3</sub> ) <sub>4</sub> ](OH) <sub>2</sub> . | 44. disproportionation |  |         |         |         |
| 45. sulphate  | 46. Alnico  | 47. Chromate           | 48. Iodine   | 49. CuO |         |         |
| 50. Silver acetylide (Ag <sub>2</sub> C <sub>2</sub> )          | 51. SO <sub>2</sub> , SO <sub>3</sub> .                     | 52. Cu <sub>2</sub> O  | 53. MnO <sub>4</sub> <sup>-</sup> , MnO <sub>2</sub> , |         |         |         |

## EXERCISE # 2

### PART - I

- |           |           |            |          |           |         |          |
|-----------|-----------|------------|----------|-----------|---------|----------|
| 1. (C)    | 2. (B)    | 3. (C)     | 4. (D)   | 5. (A)    | 6. (D)  | 7. (D)   |
| 8. (B)    | 9. (D)    | 10. (A)    | 11. (C)  | 12. (C)   | 13. (A) | 14. (B)  |
| 15. (D)   | 16. (D)   | 17. (A)    | 18. (A)  | 19. (A)   | 20. (A) | 21. (A)  |
| 22. (A)   | 23. (C)   | 24. (A)    | 25. (C)  | 26. (B)   | 27. (B) | 28. (C)  |
| 29. (C)   | 30. (D)   | 31. (C)    | 32. (A)  | 33. (D)   | 34. (C) | 35. (B)  |
| 36. (C)   | 37. (C)   | 38. (B)    | 39. (A)  | 40. (C)   | 41. (C) | 42. (D)  |
| 43. (D)   | 44. (A)   | 45. (B)    | 46. (A)  | 47. (A)   | 48. (C) | 49. (A)  |
| 50. (C)   | 51. (A)   | 52. (B)    | 53. (A)  | 54. (A)   | 55. (C) | 56. (C)  |
| 57. (B)   | 58. (AD)  | 59. (ABCD) | 60. (AB) | 61. (ABD) | 62. (D) | 63. (B)  |
| 64. (ABC) | 65. (ABC) | 66. (ABD)  | 67. (AB) | 68. (AD)  | 69. (A) | 70. (AB) |
| 71. (AB)  | 72. (ABC) | 73. (AB)   |          |           |         |          |

### PART - II

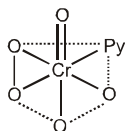
1.  $(n-1)d^{1-10} ns^{1-2}$  (palladium is exception) ; [Kr]<sup>36</sup> 4d<sup>10</sup> 5s<sup>0</sup>.
2. (i) [Ar] 3d<sup>5</sup> 4s<sup>0</sup> (ii) [Ar] 3d<sup>5</sup> 4s<sup>0</sup> (iii) [Ar] 3d<sup>8</sup> 4s<sup>0</sup> (iv) [Ar] 3d<sup>3</sup> 4s<sup>0</sup>
3. Zn, Cd and Hg have  $(n-1)d^{10} ns^2$  electron configuration in their atoms and  $(n-1)d^{10} ns^0$  electron configuration in their most stable simple ions i.e. M<sup>2+</sup>. So they do not have partially filled d-orbitals in their atoms or in their simple ions.
4. Lanthanide contraction phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction**. This essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii and have very similar physical and chemical properties.

5. (i) Sc (ii) Os or Ir
6. (i) As Hg has weakest interatomic interaction on account of no unpaired electrons,  $(n-1)d^{10}ns^2$  available for bonding.  
(ii) As W has highest interatomic interaction on account of more number of unpaired electrons,  $(n-1)d^5ns^1$  available for bonding.
7. In case of zinc, no electrons from 3d-orbitals are involved in the formation of metallic bonds.
8. In the 5d series, after lanthanum ( $Z = 57$ ), there is lanthanide contraction. As a result, in each group the atomic size of 5d element is small and its nuclear charge is large. Hence the ionisation energies of 5d elements are large than 3d elements.
9. This is because  $Pt^{4+}$  is more stable than  $Ni^{4+}$  as the sum of four ionisation energies of Pt is less than those of Ni.
10. The energies of  $(n-1)d$  orbitals and  $ns$  orbitals are very close. Hence, electrons from both can participate in bonding.
11. + 2
12. When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher. It is said to undergo disproportionation, e.g.,  $3Mn^{VI}O_4^{2-} + 4H^+ \longrightarrow 2Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$   
Mn (VI) is unstable relative to Mn (VII) and Mn (IV).
13. (i) enthalpy of sublimation (ii) ionisation energy (iii) enthalpy of hydration
14. Much larger third ionisation energy of Mn (change from  $3d^5$  to  $3d^4$ ) is responsible for this. This also explains why the +3 state of Mn is of little importance.
15. Because most of the transition metals have negative oxidation potential and lie above hydrogen in electrochemical series.
16. (i) The comparatively high value for Mn shows that  $Mn^{2+}(d^5)$  is particularly stable, whereas comparatively low value for Fe shows the extra stability of  $Fe^{3+}(d^5)$ .  
(ii) The order of getting oxidised is  $Mn > Cr > Fe$ .
17. (i)  $Ti^{3+}(3d^1)$ ,  $Cu^{2+}(3d^9)$  and  $Mn^{2+}(3d^5)$  have unpaired electron(s). Thus they are coloured due to d-d transition of electron according to CFT.  
(ii)  $Zn^{2+}(3d^{10})$ ,  $Ti^{4+}(3d^0)$  and  $Cd^{2+}(4d^{10})$  do not have unpaired electron(s). Thus they do not undergo d-d transition of electron according to CFT and, therefore, are colourless.
18. Electronic configuration of  ${}_{22}Ti^{4+}$  is  $[Ar]^{18}3d^04s^0$ . So all electrons are paired and thus its all complexes are diamagnetic.
19.  $\mu_B(3.9) = , n = 3$
20.  $Mn^{2+}$  has maximum number of unpaired electrons i.e.  $3d^5$ .
21. (a) As metal ions generally contain one or more unpaired electrons in them & hence their complexes are generally paramagnetic  
(b) Because of having larger no of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between the atoms.  
(c) May be attributed to the presence of unpaired electrons (d-d transition in most of the compounds)
22. The transition metals form reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction. These reaction intermediates readily decompose yielding the products and regenerating the original substance.

23. Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed.
24. (i) The transition metals form reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction. These reaction intermediates readily decompose yielding the products and regenerating the original substance.  
(ii) The transition elements form a large number of coordination complexes. The transition metal ions bind to a number of anions or neutral molecules in these complexes. The great tendency of transition metal ions to form complexes is due to (i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.  
(iii) Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.  
As a result of the filling up of the interstitial spaces, the transition metals become rigid and hard. These interstitial compounds have similar chemical properties as the parent metals but differ significantly in their physical properties particularly, density, hardness and conductivity.
25. (i)  $\text{CuSO}_4 + 4\text{NH}_4\text{OH} \longrightarrow [\text{Cu}(\text{NH}_3)_4] \text{SO}_4$  (blue colour complex) +  $4\text{H}_2\text{O}$   
(ii)  $\text{CuSO}_4 + 2\text{KI} \longrightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4$   
 $2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2$  (white) +  $\text{I}_2$  (violet vapour)
26. White precipitate of  $\text{Ag}_2\text{S}_2\text{O}_3$  is obtained which turns yellow, brown and finally black on keeping.  
 $2\text{AgNO}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3 \downarrow$  (white) +  $2\text{NaNO}_3$   
 $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{Ag}_2\text{S} \downarrow$  (black) +  $\text{H}_2\text{SO}_4$
27.  $3\text{Ag} + 4\text{HNO}_3 \longrightarrow 3\text{AgNO}_3 + \text{NO} + 2\text{H}_2\text{O}$
28. It is unstable in acidic medium and disproportionates.  
 $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$   
 $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 4\text{OH}^-$
29.  $\text{MnO}_4^-$  solutions are intrinsically unstable in acidic solutions and decompose slowly. This decomposition is catalysed by sun light. This is the Statement-2 for which  $\text{KMnO}_4$  solution is kept in dark bottles.  
 $4\text{MnO}_4^- + 4\text{H}^+ \xrightarrow{h\nu} 4\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O}$
30. In presence of organic matter (skin) and light,  $\text{AgNO}_3$  decomposes to produce a black stain of metallic silver.  
 $2\text{AgNO}_3 \longrightarrow 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$
31. Out of all silver halides,  $\text{AgBr}$  is most sensitive to light and under goes photo reduction to metallic silver instantaneously on exposure to light.  
 $2\text{AgBr} \longrightarrow 2\text{Ag} + \text{Br}_2$   
Unexposed  $\text{AgBr}$  can be dissolved out in hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution.  
 $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$
32. Because explosive  $\text{Mn}_2\text{O}_7$  is formed.  
 $2\text{KMnO}_4 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Mn}_2\text{O}_7 + 2\text{KHSO}_4 + \text{H}_2\text{O}$   
 $2\text{Mn}_2\text{O}_7 \longrightarrow 4\text{MnO}_2 + 3\text{O}_2$



33. (a)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow[-7\text{H}_2\text{O}]{300^\circ\text{C}} \text{FeSO}_4 \xrightarrow[\text{tempt}]{\text{high}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$   
 (b)  $3\text{FeSO}_4 + 2\text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 + 3\text{K}_2\text{SO}_4$   
 (c)  $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaFeO}_2 + \text{CO}_2$   
 (d)  $\text{Fe}(\text{III}) + 3\text{NH}_4\text{SCN} \longrightarrow [\text{Fe}(\text{SCN})_3] + 3\text{NH}_4^+$   
 (e)  $\text{ZnO} + \text{CoO} \longrightarrow \text{CoZnO}_2$  (Rinmann's green)  
 (f)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{CuSO}_4 + 3\text{H}_2\text{O} + \text{CO}_2 \uparrow$   
 (g)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow[\text{effloresces}]{\text{air}} \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$   
 (h)  $2\text{AgNO}_3 + 2\text{NaOH} \longrightarrow \text{Ag}_2\text{O} \downarrow (\text{black}) + 2\text{NaNO}_3 + \text{H}_2\text{O}$   
 (i)  $5\text{AgNO}_3 + 3\text{I}_2 (\text{excess}) + \text{H}_2\text{O} \longrightarrow \text{HIO}_3 + 5\text{AgI} \downarrow (\text{yellow}) + 5\text{HNO}_3$   
 (j)  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 (\text{conc \& cold}) \longrightarrow 2\text{CrO}_3 (\text{red}) + 2\text{KHSO}_4 + \text{H}_2\text{O}$
34. (a)  $4\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe}(\text{OH}) \cdot \text{SO}_4$
- (b)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{CH}_3 - \overset{\text{OCH}_3}{\underset{\text{OCH}_3}{\text{C}}} - \text{CH}_3 \longrightarrow \text{FeCl}_3 + 12\text{CH}_3\text{OH} + 6\text{CH}_3\text{COCH}_3$
- (c)  $\text{Cu}(\text{OH})_2 + 2\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  (Switzer reagent) +  $4\text{H}_2\text{O}$
- (d)  $3\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[\text{strong}]{\Delta} \text{CuO} + \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{Cl}_2 + \text{H}_2\text{O}$
- $3\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[\text{प्रबल}]{\Delta} \text{CuO} + \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{Cl}_2 + \text{H}_2\text{O}$
- (e)  $6\text{AgNO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} \longrightarrow \text{AgIO}_3 + 5\text{AgI} + 6\text{HNO}_3$   
 (f)  $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$   
 (g)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2 + 23\text{H}_2\text{O} \xrightarrow{\text{Tempt} < 70^\circ\text{C}} \text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
35. It forms adducts with pyridine  $\text{CrO}(\text{O}_2)_2$ .



36.  $\text{K}_3\text{CrO}_8$ .
37.  $\text{Ag}^+$  is a stronger Lewis acid as it has pseudo inert gas configuration (high polarising power due to less screening effect of inner d-electrons) whereas  $\text{Na}^+$  is a weaker acid as it has inert gas configuration (less polarising power).
38. Because of small size and high electronegativity of oxygen and fluorine, they can oxidise the metal to its highest oxidation state.
39. Stable oxidation states :  
 Vanadium =  $3d^3$  : (+2), +3, +4 and +5  
 Chromium =  $3d^5$  : +3, +4, +6  
 Manganese =  $3d^5$  : +2, +4, +6, +7  
 Cobalt =  $3d^8$  : +2, +3 (In complex)  
 In ground state for  $3d^4$  configuration no one metal occur.
40. It is because  $\text{Mn}^{2+}$  has  $3d^5$  configuration which has extra stability.

41. In transition elements the oxidation states vary from +1 to any highest oxidation state by one. For example, for manganese it may vary as +2, +3, +4, +5, +6, +7. In the non-transition elements the variation is selective, always differing by 2, e.g. +2, +4 or +3, +5 or +4, +6 etc.
42. Copper, because with +1 oxidation state an extra stable configuration,  $3d^{10}$  results.
43. Consider its high  $\Delta_a H^0$  and low  $\Delta_{hyd} H^0$
44. Much larger third ionisation energy of Mn (where the required change is  $d^5$  to  $d^4$ ) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.
45.  $Cr^{2+}$  is stronger reducing agent than  $Fe^{2+}$ .  
Change from  $d^4$  to  $d^3$  occurs in case of  $Cr^{2+}$  to  $Cr^{3+}$  but from  $d^6$  to  $d^5$  occurs in case of  $Fe^{2+}$  to  $Fe^{3+}$ . In a medium (like water)  $d^3$  is more stable as compared to  $d^5$  according to CFSE (CFSE for octahedral splitting in case of  $d^3$  is  $-1.2 \Delta_o$  while for  $d^5$  is 0).
46.  $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$   
The  $E^\circ$  value for this is favourable.
47.  $FeCl_3$  hydrolyses in water to form acidic solution.  

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$
or 
$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$
48.  $I^-$  ion is a stronger reducing agent in comparison to  $Cl^-$  ion.  $Fe^{3+}$  is easily reduced by iodide ion.  

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$
49. Copper has less standard oxidation potential ( $E_{op}^\circ$ ) than H and thus cannot liberate  $H_2$  from acids. However, it dissolves in nitric acid because  $HNO_3$  is strong oxidant.  

$$3Cu + 8HNO_3 \text{ (dilute)} \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$
50. Iron has more  $E_{op}^\circ$  than Cu and thus liberated  $Cu^{2+}$  ions from solution to discharge blue colour.  

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$
51.  $Cu(I)$  salts undergo disproportionation in aqueous solution.  

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$
52. The electron configuration of  $Mn^{3+}$  is  $[Ar]^{18} 3d^4$  so  $n = 4$ ; The electron configuration of  $Cr^{3+}$  is  $[Ar]^{18} 3d^3$  so  $n = 3$ ; The electron configuration of  $V^{3+}$  is  $[Ar]^{18} 3d^2$  so  $n = 2$ ; The electron configuration of  $Ti^{3+}$  is  $[Ar]^{18} 3d^1$  so  $n = 1$ .  $Cr^{3+}$  is most stable in aqueous solution because it has half filled  $t_{2g}^3$  energy level of 3d orbitals in octahedral crystal field splitting and according to crystal field theory (CFT) it has highest value of CFSE i.e.  $-1.2 \Delta_o$ .
53.  $Hg^+$  has  $[Xe] 4f^{14} 5d^{10} 6s^1$  configuration and thus  $Hg^+$  ion should be paramagnetic due to one unpaired electron but  $Hg^+$  ions show diamagnetic nature and for this it exists as  $Hg_2^{2+}$  by sharing of one electron each. Cuprous ions are diamagnetic with  $[Ar] 3d^{10}$  configuration and so written as  $Cu^+$ .
54. Copper sulphate dissolves in the ammonium hydroxide due to formation of a copper complex. Ferrous sulphate reacts with  $NH_4OH$  to form insoluble  $Fe(OH)_2$ . It does not form any complex with  $NH_4OH$ .  

$$CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$
Deep blue solution  

$$FeSO_4 + 2NH_4OH \longrightarrow Fe(OH)_2 + (NH_4)_2SO_4$$
Insoluble
55.  $X = CuSO_4$

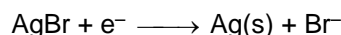
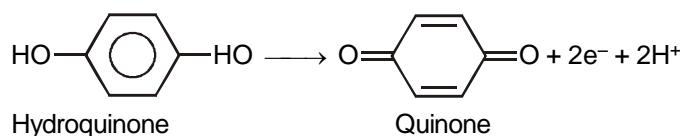
56.  $\text{H}_2\text{S}$  is oxidised to colloidal sulphur (milky) by  $\text{K}_2\text{Cr}_2\text{O}_7$ .  
 $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{S} \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{S}$  Colloidal (milky)
57. (i)  $\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}^+ + \text{MnO}_3^+$  (green) (हरा) +  $3\text{HSO}_4^- + \text{H}_3\text{O}^+$   
 $2\text{MnO}_3^+ + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{MnO}_3 + \text{CO}_2 + \frac{1}{2}\text{O}_2 + 2\text{Na}^+$
- (ii)  $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + (\text{MnO}_3)_2\text{SO}_4 + 2\text{H}_2\text{O}$   
 $(\text{MnO}_3)_2\text{SO}_4 + \text{H}_2\text{O} \longrightarrow \text{Mn}_2\text{O}_7 + \text{H}_2\text{SO}_4$
58. (a)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (green)  $\longrightarrow \text{FeSO}_4 + 7\text{H}_2\text{O}$   
 (A) (B)  
 $\text{Fe}^{2+}(\text{aq}) + [\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + [\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$   
 (B)  
 $4\text{Fe}^{3+}(\text{aq}) + 3[\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \downarrow$  (Turnbull's blue-(C))  
 $2\text{FeSO}_4 \xrightarrow[\text{strong}]{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + \text{SO}_3 \uparrow$   
 (B) (D) (E) (F)  
 $3\text{SO}_2 + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \longrightarrow 2\text{Cr}^{3+}$  (green solution) +  $3\text{SO}_4^{2-} + \text{H}_2\text{O}$   
 (E)  
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$   
 $\text{Pb}^{2+} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4 \downarrow$  (white)
- (b) According to CFT there is no d-d transition of electrons in absence of ligands in anhydrous ferrous sulphate.
59.  $\text{ZnSO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{SO}_2 \downarrow + \text{H}_2\text{O}$   
 (A) (C) (B)  
 $5\text{SO}_2 + 2\text{IO}_3^- + 4\text{H}_2\text{O} \longrightarrow \text{I}_2 + 5\text{SO}_4^{2-} + 8\text{H}^+$   
 $\text{I}_2 + \text{starch solution} \longrightarrow \text{blue colour solution.}$   
 $\text{SO}_3^{2-} + \text{Ba}^{2+} \longrightarrow \text{BaSO}_3 \downarrow$  (white)  
 $\text{BaSO}_3 + 2\text{H}^+ \longrightarrow \text{Ba}^{2+} + \text{SO}_2 + \text{H}_2\text{O}$   
 $\text{Zn}^{2+} + 2\text{OH}^- \longrightarrow \text{Zn}(\text{OH})_2 \downarrow$  (white)  
 $\text{Zn}(\text{OH})_2 + 2\text{OH}^- \longrightarrow [\text{Zn}(\text{OH})_4]^{2-}$   
 $\text{Zn}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} \longrightarrow \text{Zn}(\text{OH})_2 \downarrow + 2\text{NH}_4^+$   
 $\text{Zn}(\text{OH})_2 \downarrow + 4\text{NH}_3 \longrightarrow [\text{Zn}(\text{NH}_3)_4]^{2+} + 2\text{OH}^-$   
 $3\text{Zn}^{2+} + 2\text{K}^+ + 2[\text{Fe}(\text{CN})_6]^{4-} \longrightarrow \text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \downarrow$   
 $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 + 12\text{OH}^- \longrightarrow 2[\text{Fe}(\text{CN})_6]^{4-} + 3[\text{Zn}(\text{OH})_4]^{2-} + 2\text{K}^+$
60.  $2\text{KMnO}_4 + 2\text{NH}_3 \longrightarrow 2\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O} + \text{N}_2$
61.  $\text{Ag}_2\text{S} + 2\text{CuCl}_2 + 2\text{Hg} \longrightarrow \text{Hg}_2\text{Cl}_2 + 2\text{CuCl} + \text{S} + 2\text{Ag}$ .

## EXERCISE # 3

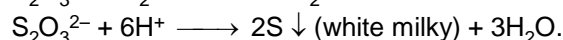
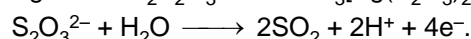
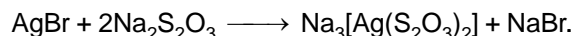
### PART - I

1. (D)  
 2.  $\text{C}_6\text{H}_4(\text{OH})_2 + 2\text{AgBr} \longrightarrow 2\text{Ag} + \text{C}_6\text{H}_4\text{O}_2 + 2\text{HBr}$ .  
 $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$ .
3. (B)    4. (B)    5. (A)    6. (A)    7. (B)    8. (B)

9. Developer is usually a weak reducing agent like potassium ferrous oxalate, an alkaline solution of pyrogallol or an alkaline solution of quinol.  
In the process of development of the photographic film, the exposed/activated AgBr grains are preferentially reduced by one of the reducing agent described above.

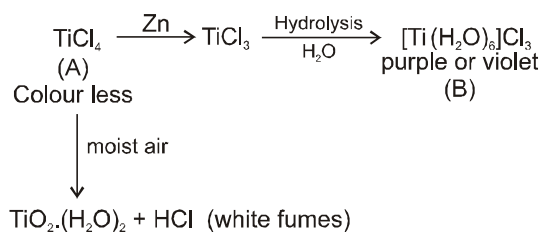


The photographic film is then fixed by washing with hypo solution to remove the unreduced AgBr grains from the film.



10. (A) is  $\text{TiCl}_4$  as it has no unpaired electron and is liquid at room temperature on account of covalent character because of high polarising power of  $\text{Ti}^{+4}$ .  $\text{TiCl}_4$  being covalent gets hydrolysed forming  $\text{TiO}_2(\text{H}_2\text{O})_2$  and HCl (B) which fumes in air.

In  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  complex Ti(III) has one unpaired electron ( $3d^1$ ) which gives violet / purple colour due to d-d transition.



11. A – p, s ; B – r ; C – p, q ; D – p.  
12. (C) 13. 6 14. (BCD)

## PART - II

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

## EXERCISE # 4

- Silver ( $Z = 47$ ) can exhibit +2 oxidation state wherein it will have incompletely filled d-orbitals (4d), hence a transition element.
- 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.
- Manganese ( $Z = 25$ ), as its atom has the maximum number of unpaired electrons.
- Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3d-configurations (e.g.,  $d^0$ ,  $d^5$ ,  $d^{10}$  are exceptionally stable).
- Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.
- $\text{Cu}^+$  in aqueous solution undergoes disproportionation, i.e.,  
 $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu(s)}$   
The  $E^\ominus$  value for this is favourable.