UNIT 8

d- and f- Block Elements

Points to Remember

Element having partially filled d-subshell in their elemental or common oxidation state.

Zn, Cd and Hg not considered as transition elements as not having partially filled d - subshell in their elemental or common oxidation state.

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

Outer Electronic Configurations of four d-block series elements.

First (3d) Transition Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

Second (4d) Transition Series										
	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

Third (5d) Transition Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

Fourth (6d) Transition Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

General Properties of the Transition Elements

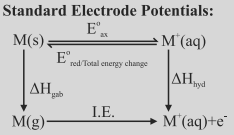
Atomic and Ionic Radii : In a given transition series, from left to right net nuclear charge as well as screening effect increase. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then screening effect counter balance nuclear
charge due to which atomic size becomes almost constant for next five elements of the series. Size of 4d and 5d series elements is almost same due to lanthanoid contraction.

Enthalpies of Atomisation: Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms.

Ionisation Enthalpies : ● In a series from left to right, ionization enthalpy increases due to increase in nuclear charge.

● The irregular trend in the first ionization enthalpy of the 3d metals, though of little chemical significance, considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

Standard Electrode Potentials:



Total energy change $E^{\circ}red. = \Delta Hsub + I.E. + \Delta H_{hyd}$. Thus, we can find the total energy change for a particular oxidation state of a metal in its aqueous solution.
The irregularity is due to irregular variation of ionisation energies and the sublimation energies of the atoms and the hydration energies of the divalent ions of the members of first transition series. Greater the value of negative electrode potential, greater will be the stability of M^{2+} state.

Oxidation States : Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are Sc(+3), Ti(+4), V(+5), Cr(+3,+6), Mn(+2,+7), Fe(+2,+3), Co(+2,+3), Ni(+2), Cu(+2), Zn(+2)

● The transition elements in their lower oxidation states (+2 and +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.

● Only Os and Ru show + 8 oxidation states in their compounds.

● Ni and Fe in $Ni(CO)_4$ and Fe $(CO)_5$ show zero oxidation state.

Magnetic Properties :

● When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moments associated with its spin angular momentum.

● The magnetic moment is determined by the number of unpaired electrons.

Magnetic moment $=\sqrt{n(n+2)}$ BM where, n=number of unpaired electron. If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

Formation of Complex Compounds

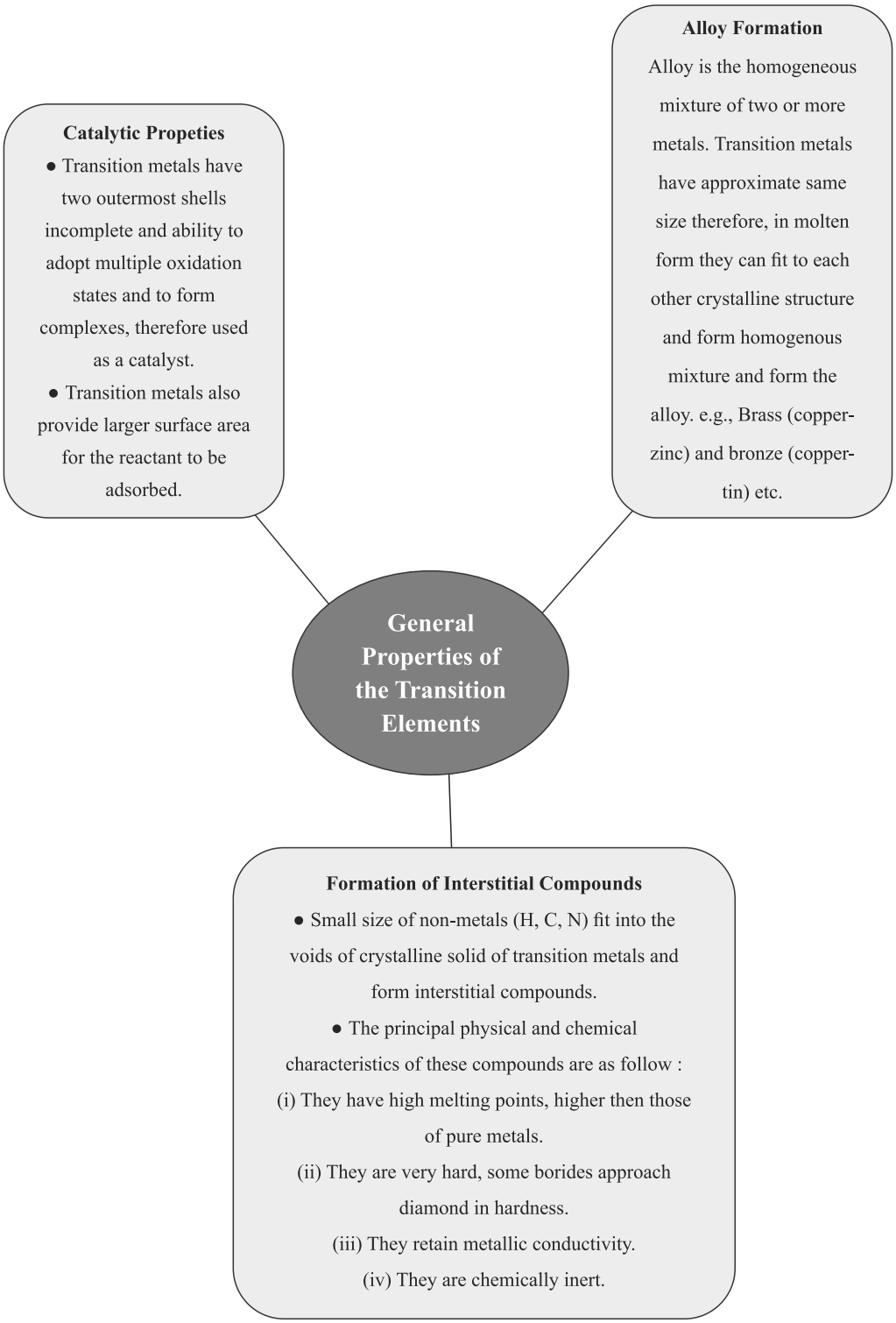
● Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of elements from ligands.

● They have vacant d-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

Formation of Coloured

● The d-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy d-orbitals is excited to a higher energy d-orbital, the energy of required wavelenght is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.

● In V_2O_5, V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.


Alloy Formation
Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogenous mixture and form the alloy. e.g., Brass (copper-zinc) and bronze (copper-tin) etc.
Catalytic Propeties
● Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.
● Transition metals also provide larger surface area for the reactant to be adsorbed.
General Properties of the Transition Elements
Formation of Interstitial Compounds
● Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.
● The principal physical and chemical characteristics of these compounds are as follow :
(i) They have high melting points, higher then those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

Some important Compounds of Transition Elements

Preparation

Ore- Ferrochrome or chromite ($FeO.Cr_2O_3$) or ($FeCr_2O_4$)

$4FeCr_2O_4+8Na_2CO_3+7O_2 \rightarrow 8Na_2CrO_4+2Fe_2O_3+8CO_2$

(yellow)

$2Na_2CrO_4+2H^+ \rightarrow Na_2Cr_2O_7+2Na^++H_2O$

(orange)

$Na_2Cr_2O_7+2KCl \rightarrow K_2Cr_2O_7+2NaCl$

Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

Propeties

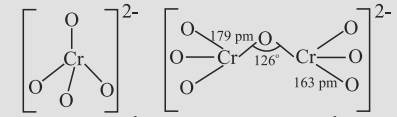
Sodium and potassium dichromates are strong oxidizing agents, thus, acidified, $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

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

$Cr_2O_7^{2-}+3H_2S+8H^+ \rightarrow 2Cr^{3+}+3S+7H_2O$

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

Potassium Dichromate ($K_2Cr_2O_7$)



chromate ion sp^3 dichromate ion sp^3

Uses

(a) $K_2Cr_2O_7$ is used as oxidizing agent in volumetric analysis.

(b) It is used in mordant dyes, leather industry, photography (for hardening of film).

(c) It is used in chromyl chloride test.

(d) It is used in cleaning glassware.

Preparation

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

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

(green)

Commercial preparation

$MnO_2 \xrightarrow[\text{with air on } KNO_3]{\text{Fused with KOH oxidised}} \underset{\text{Manganous ion}}{MnO_4^{2-}}$

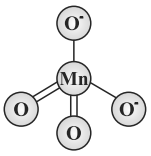
$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} \underset{\substack{\text{Permanganous ion}\\ \text{(purple)}}}{MnO_4^-}$

Uses

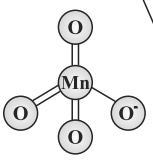
(a) In laboratory preparation of Cl_2.

(b) $KMnO_4$ is used as an oxidizing agent, disinfectant.

(c) In making Baeyer's reagent.



Tetrahendral manganate (green) ion



Tetrahendral permanganate (purple) ion

Potassium Permanganate $KMnO_4$

NOTE :

$K_2Cr_2O_7$ and $KMnO_4$ are coloured due to charge transfer complex formation.

PROPERTIES:

$KMnO_4$ acts as strong oxidizing agent.

(a) In presence of dilute H_2SO_4, $KMnO_4$ is reduces to manganous salt.

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

Acidic $KMnO_4$ solution oxidizes oxalates to CO_2, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

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

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

$NO_2^- \rightarrow NO_3^- + 2e^-$

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

To acidufy $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as oxidizing agent.

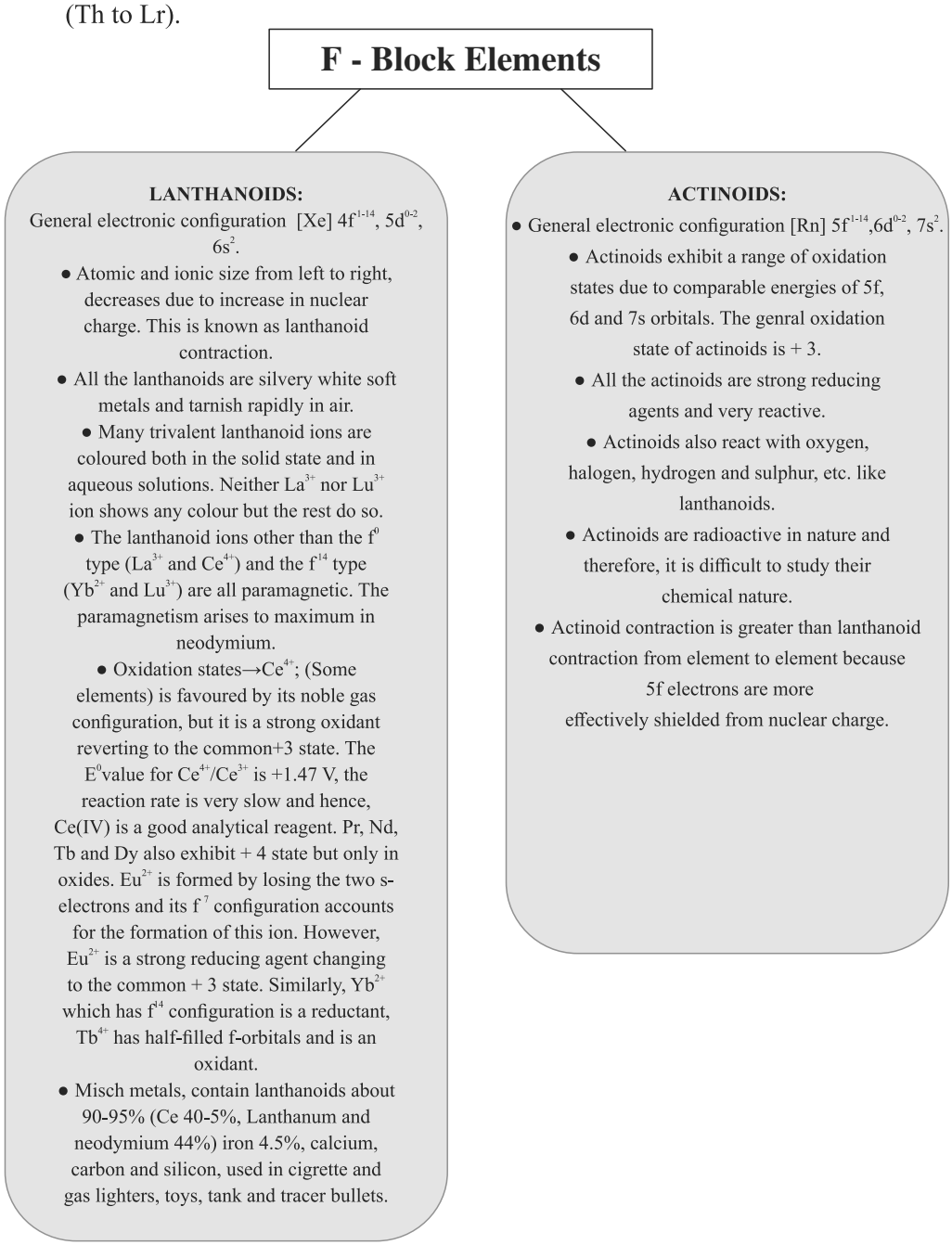
(b) in alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2.

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

Alkaline or neutral $KMnO_4$ solution oxidizes I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.

The Inner Transition Elements (f-Block)

The f-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).



OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. The characteristics of transition metals which is not responsible for formation of the complex ion is:
   (a) Presence of unpaired electron in d-subshell
   (b) Presence of paired electrons in d-subshells
   (c) Providing vacant d-orbitals
   (d) Having high charge/size ratio
2. The correct electronic configuration of copper atom is:
   (a) $3d^{10}4s^1$ (b) $3d^{10}4s^2$
   (c) $3d^9 4s^2$ (d) $3d^5 4s^2 4p^4$
3. Maximum number of unpaired electrons are in :
   (a) Cr (Z = 24) (b) Mn (Z = 25)
   (c) Fe^{2+} (Z = 26) (d) Co (Z = 27)
4. Manganese exhibits maximum oxidation state in:
   (a) K_2MnO_4 (b) $KMnO_4$
   (c) MnO_2 (d) Mn_3O_4
5. General electronic configuration of d-block elements is :
   (a) $(n-1)d^{1-10}\,ns^{0-2}$ (b) $(n-1)d^{1-10}\,ns^{1-2}$
   (c) $(n-1)d^{1-10}\,ns^0$ (d) $(n-1)d^{1-10}\,ns^1$
6. Electronic configuration of d-block element 'X' in +3 oxidation state in [Ar] $3d^5$, Atomic number of 'X' is :
   (a) 25 (b) 26
   (c) 27 (d) 24
7. $Cr_2O_7^{2-}$ dissolves in aqueous NaOH to give:
   (a) CrO_4^{2-} (b) $Cr(OH)_3$
   (c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$
8. The electronic configuration of gadolinium (At. No. 64) is:
   (a) $[Xe]\,4f^8\,5d^0\,6s^2$ (b) $[Xe]\,4f^7\,5d^1\,6s^2$
   (c) $[Xe]\,4f^3\,5d^5\,6s^2$ (d) $[Xe]\,4f^6\,5d^2\,6s^2$

9. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.

(a) Mn_2O_7 (b) MnO_2

(c) Mn_5O_4 (d) Mn_2O_3

10. Which of the following oxidation state is common for all lanthanoids?

(a) +2 (b) +3

(c) +4 (d) +5

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

(a) CO_2 is formed as the products

(b) Reaction is exothermic

(c) MnO_4^- catalysis the reaction

(d) Mn^{2+} acts as autocatalyst

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

(a) 2/5 (b) 3/5

(c) 4/5 (d) 1/5

13. Which of the following are amphoteric oxides?

(a) V_2O_5, Cr_2O_3

(b) Mn_2O_7, CrO_3

(c) CrO_3, V_2O_5

(d) V_2O_5, V_2O_4

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

(a) 2.87 B.M.

(b) 3.87 B.M.

(c) 3.47 B.M.

(d) 357 B.M.

15. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compound is coloured?

(a) $KMnO_4$ (b) $ZnSO_4$

(c) $TiCl_4$ (d) Cu_2Cl_2

16. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?

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

(c) Mn^{2+} ,Co^{2+} (d) Co^{2+},Cr^{3+}

17. Which of the following actionoids show oxidation states upto + 7?

(a) Am (b) Pu

(c) U (d) Th

18. Which of the following ions show highest spin only magnetic moment value?

(a) Ti^{3+} (b) Mn^{2+}

(c) Fe^{2+} (d) Co^{3+}

II FILL IN THE BLANKS

1. Hybridisation of Cr in Chromate ion is.....
2. Maximum oxidation state exhibited by Mn is.....
3. Electronic configuration of Cr is.....
4. Theoretical magnetic moment (spin - only) of Ti^{3+} ion is.....
5. The equivalent weight of $K_2Cr_2O_7$ in acidic medium is.....
6. Last element in the actinide series is.....
7. The general electronic configuration of d — block elements is.....
8. The colour of $KMnO_4$ is due to.....
9. Out of Sc^{2+} and Sc^{3+} ion, ... is paramagnetic in nature.
10. The oxidation state of Mn in K_2MnO_4 is .....

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both assertion and reason are True, and reason is the correct explanation of the assertion.
(b) Both assertion and reason are True, but reson is not the correct explanation of the assertion.
(c) Assertion is true, but reason is false.
(d) Assertion is false, reason is true.

1. **ASSERTION** : Sc does not show variable oxidation states.
   REASON : Sc has only one electron in the 3d subshell.
2. **ASSERTION :** Separation of Zr and Hf is difficult.
   REASON: Because Zr and Hf lie in the same period of the periodic table.
3. **ASSERTION :** Actinoids form relatively less stable complexes as compared to lanthanoids.
   REASON: Actinoids can utilise their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.
4. **ASSERTION :** Cu cannot liberate hydrogen from acids.
   REASON: Because it has positive electrode potential.
5. **ASSERTION :** The highest oxidation state of osmium is + 8.
   REASON: Osmium is a 5d element.
6. **ASSERTION :** Highest oxidation state is exhibited by transition metal lying in the middle of the series.
   REASON: The highest oxidation state exhibited corresponds to number of (n-1)d electrons.
7. **ASSERTION :** Fe^{3+} is more stable than Fe^{2+}
   REASON: Fe^{3+} has $3d^5$ configuration while Fe^{2+} has $3d^6$ configuration.
8. **ASSERTION :** Vanadium has the ability to exhibit a wide range of oxidation states.
   REASON: The standard potentials Vanadium are rather small, making a switch between oxidation states relatively easy.
9. **ASSERTION :** Transition metals like Fe, Cr and Mn form oxyions.
   REASON: Oxygen is highly electronegative and has a tendency to form multiple bonds.
10. **ASSERTION :** The highest oxidation states of the 3d metals depends only on electronic configuration of the metal.
    REASON: The number of electrons in the (n-1)d and ns subshells determine the oxidation states exhibited by the metal.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Which element in 3d series shows highest number of oxidation states?
2. Out of cuprous and cupric ions which is coloured?
3. Out of Zn and Cr which is having higher first ionisation enthalpy?
4. Give general Electronic configuration of actinoids.
5. Name the element of 3d series which does not exhibit variable oxidation state.

6. What is the equivalent mass of $KMnO_4$ in alkaline medium?
7. What is the maximum oxidation state shown by actinoids?
8. Out of $CuCl_2$ and Cu_2Cl_2 which is more stable?
9. What is the cause of similar size of Zr and Hf?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. Explain $CuSO_4.5H_2O$ is blue while $CuSO_4$ is colourless ?

Ans. Because water molecules act as ligands and results in crystal field splitting of d-orbitals of Cu^{2+} ion.

Q. 2. Which transition element 3d series exhibit highest oxidation state ?

Ans. Os

Q.3. In 3d series (Sc to Zn), the enthalpy of atomization of Zn is low. Why ?

Ans. Due to absence of unpaired electrons.

Q.4. Which element among 3d series exhibit only one oxidation state ?

Ans. Sc

Q.5. Why is the 3rd ionization energy of Mn (Z = 25) is unexpectedly high ?

Ans. Due to half-filled electronic configuration.

Q.6. Define alloy.

Ans. Alloys are homogeneous solid solutions of two or more metals.

Q.7. Transition metals show zero oxidation state with ligands like CO. Explain.

Ans. CO form synergic bonding with metal ion.

Q.8. Why HCl can not be used to acidify $KMnO_4$ solution ?

Ans. Because $KMnO_4$ oxidize HCl into Cl_2.

Q. 9. Name one ore of Mn and Cr.

Ans. Mn : MnO_2 Cr : $FeCr_2O_4$

Q.10. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their + 3 state ?

Ans. Mn^{2+} has half-filled electronic configuration (d^5).

Q.11. Why do transition elements show variable oxidation states ?

Ans. Due to presence of partially filled (n-1)d subshell in addition of ns subshell.

Q.12. Write any uses of pyrophoric alloy.

Ans. Making bullets, shells and ligher flints.

Q.13. Which is more basic - $La(OH)_3$ or $Lu(OH)_3$? Why ?

Ans. $La(OH)_3$, due to lanthanoid contraction, lower size, more covalent character, least basic.

Q.14. Find out number of Cr - O - Cr bond/bonds in $Cr_2O_7^{2-}$ ion.

Ans. 1

Q.15. Why is Ce^{4+} in aqueous solution a good oxidizing agent ?

Ans. Because Ce is most stable in Ce^{3+} state in aqueous solution.

Q.16. What is lanthanoid contraction ?

Ans. The regular steady decrease in the atomic or ionic radii of lanthanoids with increasing atomic number.

Q.17. Why is Cu (Z = 29) considered a transition metal ?

Ans. Due to its partially filled d-orbital in Cu^{2+} state.

Q.18. Arrange the given in increasing order of acidic character : CrO_3, CrO, Cr_2O_3.

Ans. $CrO_3 < CrO < Cr_2O_3$

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q. 1. Chromium is typical hard metal while mercury is a liquid. Explain why ?

Ans. Cr has five unpaired d-electrons. Hence metallic bonds are strong. In Hg, there is absence of 'unpaired electrons and size is larger.

Q.2. Why $KMnO_4$ is deep purple in colour?

Ans. $KMnO_4$ forms charge transfer complex.

Q.3. Most of the transition metals do not displace hydrogen from dilute acids, why ?

Ans. Due to their negative reduction potential.

Q.4. Explain why Cu^{+} is not stable in aqueous solution ?

Ans. Due to less negative $\Delta_{hyd}H$ of Cu^{+}/it cannot compensate 2nd ionization potential of Cu.

Q.5. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

Ans. Oxygen and fluoride have small size and high electronegativity. They can oxidise the metal.

Q.6. Write electronic configuration of Cu^{2+} and Co^{2+}.

Ans. $Cu^{2+} - [Ar]\, 3d^{9}\, 4s^{o}$ Co^{2+} - $[Ar]\, 3d^{7}$

Q.7. Briefly explain why electronic configuration of lanthanoids are not known with certainty ?

Ans. 4f/5d subshells are very close in energy. So electrons can jump from 4f to 5d or vice-versa.

Q.8. Why Zn, Cd, Hg are soft and have low melting point ?

Ans. Due to weak interatomic attraction/absence of unpaired electrons.

Q.9. Which of the following is/are transition element and why ? Zn, Cd, Ag, Fe, Ni

Ans. Fe, Ni, Ag

Q.10. What are interstitial compounds ? Give example.

Ans. When small atoms like C, H, B and N occupy interstitial site in crystal lattice of metals. Example : TiC.

Q.11. Why is first ionization enthalpy of 5d elements higher than those of 3d and 4d elements ?

Ans. Due to greater effective nuclear charge acting on outer most electrons because of poor shielding of 4*f* electrons.

Q.12. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% lanthanoid and 5% iron and traces of S, C, Ca and AI. Used in lighter flint, bullet tips etc.

Q.13. Write balanced chemical equations :

(a) $Cr_2O_7^{2-} + H^{+} + Fe^{2+} \rightarrow$

(b) $MnO_4^{-} + H^{+} + C_2O_4^{2-} \rightarrow$

Q.14. Out of Fe and Cu, which one would exhibit higher melting point ?

Ans. Fe, due to large number of unpaired d-electrons/more interatomic attraction.

Q.15. Sc does not exhibit variable oxidation state. Why ?

Ans. Due to noble gas electronic configuration in + 3 oxidation state no other oxidation state is stable.

Q.16. (a) Deduce the number of 3d electrons in the following ions : Cu^{2+}, Sc^{3+}

(b) Why do transition metals form alloy ?

(c) Why Zn^{2+} salts are white ?

Ans. (a) Cu^{+2} : 9 electrons : Sc^{3+} : 0 electron

(b) Transition metals have similar atomic radii.

(c) Absence of unpaired electron.

Q.17. (a) Why is separation of lanthanoid elements difficult ?

(b) Transition metal exhibit higher enthalpies of atomization. Explain.

(c) Why the transition metals have ability to form complexes?

Ans. (a) Due to lanthanide contraction, the size of these elements is nearly same.

(b) Transition metal contain large number of unpaired electrons, and they have strong interatomic attractions.

(c) Due to their small size and large nuclear charge.

Q.18. (a) Use Hund's rule to derive the electronic configuration of Ce^{3+} ions and calculate its magnetic moment.

(b) Is lanthanum a f-block element ?

Ans. (a) $Ce(58) = [Xe]\ 4f^1 5d^1\ 6s^2$; $Ce^{3+} = 4f^1$

$\mu = \sqrt{n(n+2)} = 1.73BM$

(b) No, it is a d-block element.

Q.19. Account for the following :

(a) Silver chloride dissolves in excess of NH_3.

(b) Cuprous chloride is diamagnetic while cupric chloride is paramagnetic.

(c) In CrO_4^{2-} ion, all the Cr-O bond length are equal.

Ans. (a) AgCl forms a soluble complex with NH_3. ($AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$)

(b) Cu^+ : $3d^{10}\ 4s^o$ - All electrons are paired. Cu^{2+} : $3d^9$ - Here, one unpaired electron is present.

(c) Due to resonance.

Q.20. The E^o values in respect of electrodes of Cr, Mn and Fe are : Cr^{3+}/Cr^{2+} = - 0.4 V Mn^{3+}/Mn^{2+} = + 1.5 V, Fe^{3+}/Fe^{2+} = + 0.8 V Compare the feasibilities of further oxidation of these ions.

Ans. Cr^{3+} is more stable than Cr^{2+}. Mn^{2+} is more stable than Mn^{3+}. Fe^{3+} is more stable than Fe^{2+}. Order of feasibility of + 2 oxidation state is : $Mn^{2+} > Fe^{2+} > Cr^{2+}$

Q.21. Write any four properties of interstitial compounds.

Ans. (a) They are chemically inert.

(b) They retain metallic conductivity.

(c) They have high melting point than their pure metals.

(d) These are harder and more corrosion resistant.

Q.22. Account for the following :

(a) All Scandium salts are white.

(b) The first ionization energy of the 5d series are higher than 3d and 4d transition elements in respective groups.

(c) Ce^{3+} can be easily oxidized to Ce^{4+}.

Ans. (a) Sc has only + 3 oxidation state, there is no unpaired electron.

(b) Due to lanthanoid contraction, effective nuclear charge increase.

(c) Due to attainment of noble gas electronic configuration.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (a) What is meant by disproportionation of an oxidation state ? Give one example.

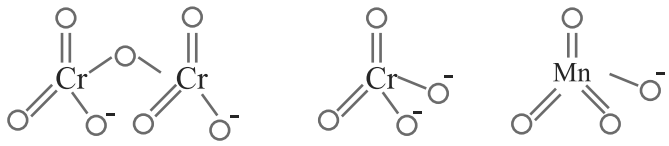
(b) Draw the structures of $Cr_2O_7^{2-}$, CrO_4^{2-}, MnO_4^-.

(c) What is the effect of lanthoid contraction beyond lanthanoid ?

Ans. (a) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.

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

(b)



(c) Size of respective 4d and 5d series elements becomes comparable (e.g., Zr and Hf).

2. On the basis of lanthanoid contraction, explain the following:

(i) Nature of bonding in La_2O_3 and Lu_2O_3.

(ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.

(iii) Stability of the complexes of lanthanoids.

(iv) Radii of 4d and 5d block elements.

(v) Trends in acidic character of lanthanoid oxides.

Ans. (i) As the size decreases covalent character increases. Therefore, La_2O_3 is more ionic and Lu_2O_3 is more covalent.

(ii) As the size decreases from La to Lu, stability of oxosalts also decreases.

(iii) Stability of complexes increases as the size of lanthanoids decreases.

(iv) Radii of 4d and 5d block elements will be almost same.

(v) Acidic character of Oxides increases from La to Lu.

3. (a) Answer the following questions:

(i) Which element of the first transition series has highest second ionisation enthalpy?

(ii) Which element of the first transition series has highest third ionisation enthalpy?

(iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Identify the metal and justify your answer.

(i) Carbonyl $M(CO)_5$

(ii) MO_3F

Ans. (a)

(i) Cu, because the electronic configuration of Cu is $3d^{10}4s^1$. So second electron needs to be removed from completely filled d-orbital.

(ii) Zn

(iii) Zn [Hint : No unpaired electron for metallic bonding]

(b) (i) $Fe(CO)_5$

(ii) MnO_3F [Hint : Mn shows + 7 oxidation state; d-electrons are not involved in bonding.]

4. (i) How would you account for the following?
   (a) The oxidising power of oxo-anions are in the order $VO^{2+} < Cr_2O_7^{2-} < MnO_4^-$
   (b) The third ionisation enthalpy of manganese (Z = 25) is exceptionally high.
   (c) Cr^{3+} is a stronger reducing agent than Fe^{2+}.

   (ii) Give reasons for the following:
   (a) Mn^{3+} is a good oxidising agent.
   (b) $E^o(M^{2+}/M)$ values are not regular for first row transition metals (3d-series).
   (c) Although 'F' is more electronegative than 'O' the highest Mn fluoride is MnF_4, where as the highest oxide is Mn_2O_7 reducing agent than Fe^{2+}.

Ans (i) (a) It is due to the fact that V in its lower oxidation state is less stable than Cr which in turn is less stable than Mn. Thus, MnO_4^- has a great tendency to get reduced and hence, behave as a good oxidising agent. Similary VO^{2+} has the least oxidising power.

(b) The third ionisation enthalpy of Mn is very high due to the fact that the third electron has to be removed from stable half-filled configuration, i.e., $3d^5$.

(c) Cr^{2+} is stronger reducing agent than Fe^{2+} because $d^4 \rightarrow d^3$ transition occurs in case of Cr^{2+} to Cr^{3+} while $d^6 \rightarrow d^5$ transition occurs in case of Fe^{2+} to Fe^{3+}. In a medium like water d^3 is more stable as compared to d^5.

(ii) (a) Mn^{3+} ($3d^4$) is a good electron acceptor as the resulting species is more stable ($3d^5$).

(b) The $E^o(M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionisation enthalpies ($\Delta_iH_1 + \Delta_iH_2$) and also the sublimation enthalpies which are relatively much less for Mn and V.

(c) Due to multiple bond formation ability of oxygen, Mn can form Mn_2O_7.

5. The elements of 3d-transition series are given as:

Sc , Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following :

(i) Name the element which shows maximum number of oxidation states. Give reason.

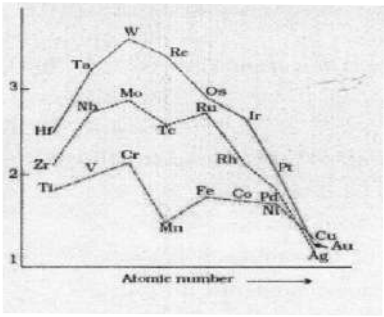
(ii) Which element has the highest melting point?

(iii) Name the element which shows only + 3 oxidation state?

(iv) Which element is a strong oxidizing agent in + 3 oxidation state and why?

Ans (I) Mn. It has maximum unpaired electrons.
(ii) Cr
(iii) Sc
(iv) Manganese. Mn^{3+} to Mn^{2+} results in the stable half filled (d^5) configuration.

6. On the basis of the figure given below, answer the following questions:



(i) Why Manganese has lower melting point than Chromium.

(ii) Why do transition metals of 3d series have lower melting points as compared to 4d series ?

(iii) In the third transition series, identify and name the metal with the highest melting point.

Ans. (i) Managnese is having lower m.p. as compared to Chromium, as it has highest number of unpaired electrons, strong interatomic metallic bonding, hence no delocalization of electrons.
(ii) Due to more frequent metal-metal bonding in compounds of heavy transition metals i.e. 4d and 5d series.
(iii) tungsten

CASE STUDY BASED QUESTIONS

1. Read the passage and answer the following questions.

Potassium dichromate is one of the crystalline inorganic chemical reagents. Hexavalent chromium compounds are harmful to health. $K_2Cr_2O_7$ is widely used in laboratories and industry as an oxidizing agent because it is not deliquescent. Potassium dichromate looks very bright and red-orange color. In this work different amount of acidic (HCl) and alkaline (NaOH) solutions were added to stoke solutions of K_2CrO_4 and $K_2Cr_2O_7$ to show the effect of pH values on their spectra.
The results of UV-Visible spectroscopy shows that, the changing of solution pH value when drops of HCI were added led to shift wavelength of K_2CrO_4 spectrum while no change has been occurred in $K_2Cr_2O_7$ spectrum. However, Changing pH values solution by adding drops of NaOH led to change in wavelength red shift for $K_2Cr_2O_7$ while no changes has been occurred in spectrum of K_2CrO_4.

Reference: Effect of the Acidic and Alkaline Solutions on K_2CrO_4 and $K_2Cr_2O_7$ by Ultraviolet and Visible Measurement Mohammad Radi Mohammad, Hasanain Saad Azeez* Al-Mustansiriyah Journal of Sience ISSN: 1814-635X (print), ISSN:2521-3520 (online) Volume 30, Issue 1, 2019, 221-224

(A) The hybridization of Cr in dichromate ion is :

(a) d^2sp^3 (b) sp^3

(c) dsp^2 (d) sp^3d

(B) Colour of potassium dichromate is :

(a) purple (b) green

(c) yellow (d) orange

(C) Chemical formula of ferrochrome is :

(a) $FeCrO_2$ (b) $FeO.Cr_2O_3$

(c) Fe_2CrO_4 (d) None of these

(D) On increasing pH of dichromate, it converts in :

(a) CrO_4^{2-} (b) $Cr_2O_4^{2-}$

(c) CrO_4^{-1} (d) CrO_3

2. Read the passage and answer the following questions.

Heavy rare earth elements crystallize into hexagonally close packed (h.c.p.) structures and share a common outer electronic configuration, differing only in the number of 4*f* electrons they have. These chemically inert 4f electrons set up localized magnetic moments, which are coupled via an indirect exchange interaction involving the conduction electrons. This leads to the formation of a wide variety of magnetic structures, the periodicities of which are often incommensurate with the underlying crystal lattice. Such incommensurate ordering is associated with a 'webbed' topology of the momentum space surface separating the occupied and unoccupied electron states (the Fermi surface). The shape of this surface—and hence the magnetic structure—for the heavy rare earth elements is known to depend on the ratio of the interplanar spacing c and the interatomic, intraplanar spacing a of the h.c.p. lattice. A theoretical understanding of this problem is, however, far from complete. Here, using gadolinium as a prototype for all the heavy rare earth elements, we generate a unified magnetic phase diagram, which unequivocally links the magnetic structures of the heavy rare earths to their lattice parameters. In addition to verifying the importance of the c/o ratio, we find that the atomic unit cell volume plays a separate, distinct role in determining the magnetic properties: we show that the trend from ferromagnetism to incommensurate ordering as atomic number increases is connected to the concomitant decrease in unit cell volume. This

volume decrease occurs because of the so-called lanthanide contraction, where the addition of electrons to the poorly shielding 4f orbitals leads to an increase in effective nuclear charge and, correspondingly, a decrease in ionic radii.

Reference:

Lanthanide contraction and magnetism in the heavy rare earth elements.

Hughes, I., Dane, M., Ernst, A. et al. Nature 446,650-653 (2007). https://doi.org/10.1038/nature05668

(A) Rare earth elements are also called :

(a) Actinoids (d) Lanthanoids

(c) Alkali metals (d) None of these

(B) Radioactive lanthanoids is :

(a) Pm (b) Ce

(c) Nd (d) Er

(C) Cause of lanthanoid contraction is :

(a) poor shielding of 5f orbitals (b) poor shielding of 4f orbitals

(c) poor shielding of 6f orbitals (d) All of these

(D) The common oxidation state of lanthanoides is :

(a) +4 (b) +3

(c) +2 (d) +1

3. **Read the passage given below and answer the following questions:**

The d block elements are the 40 elements contained in the four rows of ten columns (3-12) in the periodic table. As all the d block elements are metallic, the term d-block metals is synonymous. This set of d-block elements is also often identified as the transition metals, but sometimes the group 12 elements (zinc, cadmium, mercury) are excluded from the transition metals as the transition elements are defined as those with partly filled d or f shells in their compounds. Inclusion of the elements zinc, cadmium and mercury is necessary as some properties of the group 12 elements are appropriate logically to include with a discussion of transition metal chemistry.

The term transition element or transition metal appeared to derive from early studies of periodicity such as the Mendeleev periodic table of the elements. His horizontal table of the elements was an attempt to group the elements together so that the chemistry of elements might be explained and predicted. In this table there are eight groups labeled 1-VIII with each subdivided into A and B subgroups. Mendeleev recognized that certain properties of elements in. Group VIII are related to those of some of the elements in Group VII and those at the start of the next row Group I. In that sense, these elements might be described as possessing properties transitional from one row of the table to the next.

Reference: Winter, M. J. **d-Block Chemistry** *(Vol.* 27). Oxford University Press, USA.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement,
(d) Assertion is wrong statement but reason is correct statement.

(A) Assertion: Group 12 elements are not considered as transition metals.
Reason: Transition metals are those which have incompletely filled d sub-shell in their compounds.

(B) Assertion: All d block elements are metallic in nature.
Reason: The d —block elements belong to Group 3 -12 of the periodic table.

(C) Assertion: Nickel is a transition element that belongs to group 10 and period 4 of the modern periodic table.
Reason: Electronic configuration of nickel is [Ar] $3d^8 4s^2$

4. **Read the passage given below and answer the following questions:**

The transition metals when exposed to oxygen at low and intermediate temperatures form thin, protective oxide films of up to some thousands of Angstroms in thickness. Transition metal oxides lie between the extremes of ionic and covalent binary compounds formed by elements from the left or right side of the periodic table. They range from metallic to semiconducting and deviate by both large and small degrees from stoichiometry. Since d-electron bonding levels are involved, the cations exist in various valence states and hence give rise to a large number of oxides. The crystal structures are often classified by considering a cubic or hexagonal close-packed lattice of one set of ions with the other set of ions filling the octahedral or tetrahedral interstices. The actual oxide structures, however, generally show departures from such regular arrays due in part to distortions caused by packing of ions of different size and to ligand field effects. These distortions depend not only on the number of d-electrons but also on the valence and the position of the transition metal in a period or group.

Reference: Smeltzer, W.W., & Young, D. J. (1975). Oxidation properties of transition metals. Progress in Solid State Chemistry, 10,17-54.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement,
(d) Assertion is wrong statement but reason is correct statement

(A) Assertion: Cations of transition elements occur in various oxidation states
Reason: Transition metals are those which have incompletely filled d subshell in their compounds.

(B) Assertion: Crystal structure of oxides of transition metals often show defects.
Reason: Ligand field effect cause distortions in crystal structures.

(C) Assertion : Transition metals form protective oxide films.
Reason: Oxides of transition metals are always stoichiometric.

(D) Assertion: CrO crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by chromium ions
Reason: Transition metal oxide may be hexagonal close-packed lattice of oxide ions with metal ions filling the octahedral voids.

ANSWERS

I. MULTIPLE CHOICE TYPE QUESTIONS

1. b 2. a 3. b 4. b 5. b 6. b 7. a 8. b 9. a
10. b 11. d 12. a 13. a 14. b 15. a 16. d 17. b 18. b

II FILL IN THE BLANKS

1. sp^3 2. +7
3. $[Ar]3d^5 4s^1$ 4. 1.732
5. 49g 6. lawrencium
7. $(n-1)d^{1-10}\, ns^{1-2}$ 8. charge transfer complex
9. Sc^{2+} 10. 6

III ASSERTION REASON TYPE QUESTIONS

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

IV ONE WORD TYPE QUESTIONS

1. Mn 2. Cupric 3. Zn 4. $5f^{1-14}6d^{0-1}\,7s^2$ 5. Sc
6. 158g 7. 7 8. $CuCl_2$ 9. Lanthanoid Contraction

CASE STUDY BASED QUESTIONS

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

UNIT TEST-1

d- and f- block Elements

Time Allowed: 1 Hour **Maximum marks: 20**

1. Which element among 3d-transition elements, exhibit the highest oxidation state? 1
2. Name the transition element which has highest $E^{o}(M^{2+}/M)$ value 1
3. Calculate the magnetic moment of Cu^{2+} (Z = 29) on the basis of "spin-only" formula. 1
4. Name a transition element which does not exhibit variable oxidation state in 3d series. 1
5. Write the general electronic configuration of d-block elements. 1
6. Write balanced chemical equations for:
   (a) Oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium
   (b) Oxidation of Mn^{2+} by MnO_4^- in neutral or faintly alkaline medium. 2
7. Account for the following:
   (a) Copper shows its inability to liberate hydrogen gas from the dilute acids.
   (b) Scandium (Z = 21) does not exhibit variable oxidation states. 2
8. Explain lanthanoid contraction with its consequences. 2
9. Assign reasons for the following: 3
   (a) Majority of transition metals form complexes.
   (b) Ce^{3+} can be easily oxidised to Ce^{4+}.
   (c) Actinoids exhibits a variety of oxidation states.
10. Describe the preparation of potassium permanganate ($KMnO_4$), from MnO_2. Write the chemicalequations involved in the synthesis. 3
11. Explain giving reasons: 3
    (a) Zn, Cd and Hg are not considered as transition metals.
    (b) Elements in the middle of transition series have higher melting points.
    (c) The decrease in atomic size of transition elements in a series is very small.

UNIT TEST-2

d- and f- block Elements

Time Allowed: 1 Hour **Maximum marks: 20**

1. Explain- zinc is not regarded is transition element. 1
2. Name a lanthanoid well known to exhibit +4 oxidation state. 1
3. Out of Sc^{3+}, Co^{2+} and Cr^{3+} ions, which ion will be colourless in aqueous solutions? (Atomic no. : Co=27, Sc=21 and Cr=24) 1
4. Write general electronic configuration of lanthonoid series. 1
5. Why Zr(Z=40) and Hf(Z=72) shows similar properties? 1
6. Name the 3d element which: 2
   a) Does not exhibit variable oxidation state
   b) Exhibits highest oxidation state
   c) Has highest spin-only magnetic moment in +2 oxidation state
   d) Has highest $E^{o}(M^{2+}|M)$ value.
7. Write any two differences between lanthanoids and actinoids.
8. Explain disproportionation reaction giving one example of a compound/ion containing transition element. 2
9. Explain following in context of transition elements:
   a) High enthalpy of atomisation
   b) Catalytic activity
   c) Coloured complexes
10. Write balanced chemical equations for the following reactions: 3
    a) $MnO_4^- + S_2O_3^{2-} + H_2O \rightarrow$
    b) $Cr_2O_7^{2-} + Sn^{2+} + 4H^+ \rightarrow$
    c) $Fe^{2+} + MnO_4^- + 8H^+ \rightarrow$
11. When MnO_2 is fused with KOH and KNO_3 (oxidising agent) it gives a dark compound (A). Compound (A) disproportionates in acidic solution to give purple coloured compound (B). An alkaline solution of compound (B) oxidises KI to compound (C), whereas an acidified solution of compound (B) oxidises KI to (D). Identify A, B, C and D and write reactions involved. 3