Unit 8

The d- and f- Block Elements

I. Answer the following questions. Each question carries one mark

1**. Define transition elements**.
Ans. Transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states.

2**. What is the position of the d block elements in the periodic table?**

Ans. The d block elements are in the middle of s and p blocks, comprising the groups 3 to 12. They are the four rows of elements in the periods 4^{th} (3d series), 5^{th} (4d series), 6^{th} (5d series) and 7^{th} (6d series).

3. Zinc, cadmium and mercury of group 12 are not regarded as transition metals, Why ?
Ans. Zinc, cadmium and mercury of group 12 have full d^{10} configuration (d orbitals are completely filled) in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals

4. Why d- block elements are named as 'transition elements ' ?
Ans. The *d*–block elements occupies the middle of the periodic table and their properties are transitional between *s*– and *p*– block elements.

5**.Write the general electronic configuration of d block elements**.

Ans. [Noble gas] $(n-1)d^{1-10}ns^{1-2}$

6. **Write the general outer electronic configuration of d- block elements**. .
Ans. The general outer electronic configuration of d- block elements is $(n-1)d^{1-10}\ ns^{1-2}$

7. Write the general electronic configuration of f- block elements.
Ans. The general electronic configuration of f- block elements (Lanthanoids) is
$[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$
8**.Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.**
Ans. Cerium
9. The outer electronic configuration of Cr is $3d^5\ 4s^1$ instead of $3d^4 4s^2$, why?
Ans. Half filled ($3d^5$) orbitals are relatively more stable, hence one electron of 4s orbital jumps to 3d orbital.

10. The outer electronic configuration of Cu is $3d^{10}\ 4s^1$ instead of $3d^9 4s^2$, why?
Ans. Completely filled ($3d^{10}$) orbitals are relatively more stable, hence one electron of 4s orbital jumps to 3d orbital.

11. Account for high melting point and boiling points of transition metals.

Ans. The melting and boiling points of transition metals are high because of the involvement of greater number of electrons from (n-1)*d* orbitals in addition to the n*s* electrons in the inter atomic metallic bonding.

12.What is the trend in melting points of transition metals in a series?

Ans.The melting points of the transition metals in a series rise to a maximum at the middle of the series (i.e. Cr or Mo or W - element with d^5 configuration) and fall regularly as the atomic number increases.

13.Why do transition metals have higher enthalpies of atomization?

Ans. Involvement of a large number of unpaired electrons of d orbitals favour stronger inter atomic interactions resulting in stronger bonds between the atoms of a metal and higher enthalpies of atomization.

14.Name one 3d series elements, that do not show variable oxidation states.

Ans. Sc (+3)

15.Transition metals exhibit variable oxidation states in its compounds, why?

Ans. Transition metals exhibit variable oxidation states in its compounds due to the availability of both ns & (n – 1) d electrons for bond formation.

16**. Name 3d series metal which shows highest oxidation state**.

Ans. The highest oxidation state shown by 3d series transiNa

tion metals is +7 by Mn

17. **Name a metal in the 3d series of transition metals which exhibit +1 oxidation state most frequently**.

Ans. copper

18.What is the trend in oxidation state of transition metals ?

Ans. The oxidation state increases with increase in atomic number & reaches a maximum in the middle and then decreases.

19. **3d series transition metals exhibit +2 as the most common oxidation state (except Sc) why?**

Ans. The +2 oxidation state, which commonly occurs for nearly all the transition metals is due to the loss of their outer 4*s* electrons

20. Why transition metals and their compounds shows paramagnetic behavior ?

Ans. The transition metal ions are generally containing one or more unpaired electrons in them & hence their compounds are generally paramagnetic.

21. **Name an of alloys of transition metals with non transition metals.**

Ans. Brass (Cu & Zn) or Bronze (Cu & Sn)

22.What is the action of neutral or faintly alkaline permanganate solution on iodide ?

Ans. Alkaline permanganate solution oxidize iodide to iodate.

23. What happens when potassium permanganate is heated to 513 K ?

Ans. Potassium permanganate decomposes at 513K to potassium manganate, manganese dioxide and oxygen.

24. What is the principal oxidation state exhibited by the lanthanoids?
Ans. The principal oxidation state of lanthanoids is +3.

25.Write the spin-only formula used to calculate the magnetic moment of metal ions.
Ans. The magnetic moment is determined by using the spin only formula,

$\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM).

26. Why is Sc^{3+} (or Zn^{2+}) diamagnetic?

Ans. Sc^{3+}(Z=21) $3d^0$ no unpaired electron, n=0, μ=0.

(or Zn^{2+}(Z=30) $3d^{10}$ no unpaired electron, n=0, μ=0)

27. What is the most common oxidation state of lanthanoids and actionoids?
Ans. The most common oxidation state of lanthanoids and actionoids is +3.

28.What is Actinoid contraction?
Ans. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This is known as the actinoid contraction.

29.Actinoid contraction is more than lanthanoid contraction. Give reason.
Ans. The actinoid contraction is, more than lanthanoid contraction due to poor shielding by 5*f* electrons from nuclear charge.

30. Actionoids show larger number of oxidation states than lanthanoids. Why?
Ans. In actinoids 5f, 6d and 7s levels are of comparable energies ,hence electrons from these orbitals are available to lose or share.

31. Give one use of Mischmetall .

Ans. Mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

32. Why transition metals forms alloys readily?

Ans. Transition metals readily form alloys with other transition metals because of their similar radii

33. Give one use of transition metal alloy.

Ans.Ferrous alloys containing chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels.

II. Answer the following questions. Each question carries TWO marks.

34. Name two characteristic properties exhibited by d – block elements due to their partly filled d orbitals.

Ans. The characteristic properties exhibited by d – block elements due to their partly filled d orbitals are variable; (i) Oxidation states

(ii) Formation of coloured ions.

35. Name two typical metallic properties displayed by transition elements.

Ans.High tensile strength, ductility malleability, high thermal and electrical conductivity and metallic luster etc.

36. What are interstitial compounds? Give example.

Ans. Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of transition metals.

Example; TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc.

37. Give any two physical characteristics of interstitial compounds.

Ans.Two physical characteristics of interstitial compounds are:

(i) They have high melting points, higher than those of pure metals.

(ii) They are very hard and they retain metallic conductivity.

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

Ans. M (z= 27 , $3d^7\ 4s^2$) $\rightarrow$ M^{+2} ($3d^7\ 4s^0$) hence it has 3 unpaired electrons n= 3

$\mu = \sqrt{n(n+2)}$ $= \sqrt{3}(3+2) = 3.87$ BM

39. The second ionisation enthalpy is high for Cr and Cu , why?

Ans: The second ionisation enthalpy is unusually high values for Cr and Cu because when M^+ ion ionize to M^{+2} ion , the d^5 and d^{10} configurations of the M^+ ions (i.e Cr^+ or Cu^+) are disrupted, with considerable loss of exchange energy .

40. Why first ionisation enthalpy of Cr is lower than that of Zn ?

IE_1 of Cr is lower, because removal of an electron from Cr does not change the d ($3d^5\ 4s^1$ to $3d^5\ 4s^0$) configuration . Cr (z= 24 , $3d^5\ 4s^1$) $\rightarrow$ Cr^+ ($3d^5\ 4s^0$) ------ IE_1

IE_1 value for Zn is higher, because removal of electron from 4s level needs more energy.
Zn (z= 30 , $3d^{10}\ 4s^2$) $\rightarrow$ Zn^+ ($3d^{10}\ 4s^1$) ------ IE_1

$\therefore$ IE_1 (Zn) > IE_1 (Cr)

41.Give two characteristics of transition metal alloys.

. The alloys are hard and have high melting points.

42.What is the action of heat on potassium permanganate ? Give equation.

Ans. It decomposes at 513K to potassium manganate, manganese dioxide and oxygen.

$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

43. What is the action of neutral or faintly alkaline permanganate solution on iodide ?Give equation.

Ans. Alkaline permanganate solution oxidize iodide to iodate.

$I^- + 2MnO_4^- + H_2O \rightarrow IO_3^- + 2MnO_2 + 2OH^-$

44. Explain the oxidising action of acidified potassium dichromate on (iron(II) salts) Fe^{+2} ions and write the ionic equations for the reaction.

Ans. Acidified potassium dichromate oxidises iron(II) salts to iron(III).

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

45. The transition metals generally form coloured compounds, why?

Ans. The compounds of transition elements shows colour due to presence of unpaired electron & ability to undergo d-d transition.

When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region.

46. Give reason " transition metals and their many compounds acts as good catalysts".

Ans. Transition metals and their many compounds acts as good catalysts,it is due to (i) partially filled (n-1) d orbital (ii)variable oxidation state and provide a suitable surface for the reaction to take place.

47.Explain giving reason "transition metals form a large number of complex compounds".

Ans.Transition metals form a large number of complex compounds due to
(i) Small size & high charge density of the ions of transition metals.
(ii) presence of vacant d orbitals of suitable for bond formation.

48. What is the effect of increasing pH on a solution of potassium dichromate?

Ans.On increasing the pH of the solution Potassium dichromate (orange) becomes potassium chromate (yellow) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

49.What happens when H_2S is passed into potassium dichromate in acidic medium? Give the equation.

Ans. H_2S gets oxidized to sulphur

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$
$$3H_2S \rightarrow 6H^+ + 3S + 6e^-$$
$$Cr_2O_7^{-2} + 3H_2S + 8H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3S$$

50. What is 'disproportionation' of an oxidation state ? Give one example of disproportionation reaction in aqueous solution.

Ans. A particular oxidation state , which is relatively less stable compared to other oxidation states , under goes disproportion.

Manganese (VI) which is relatively less stable changes over to manganese (VII) and manganese (IV) in acid solution.

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

51. What is lanthanoid contraction? Write any one consequence of lanthanoid contraction.

Ans. Steady decrease in the size of lanthanides with increase in atomic number is known as lanthanoid contraction.

Due to lanthanoid contraction radii of members of 3rd transition series are very much similar to corresponding members of 2nd series.

52.Write any two consequences of lanthanoid contraction.

Ans. Two consequences of lanthanoid contrations are

(i) The radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. Ex. The almost identical radii of Zr (160 pm) and Hf (159 pm) & Nb (146pm) & Ta (146pm)

(ii) Difficulty in separation of lanthanoids due to similarity in chemical properties.

53. Name the two series of f-block.

Ans. The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium.

54. The chemistry of actionoids is more complicated than lanthanoids. Why?

Ans. The actinoids are radioactive elements having half lifes varying. Some members can be prepared only in nanogram quantities. These facts render their study more difficult.

55.Write two comparisons of variability in oxidation states of transition metals and non transition elements (p- block elements) ?

Ans. 1. In transition elements , variable oxidation state differ from each other by unity, whereas in case of non transition elements , oxidation state differ by units of two.(For example Fe exhibits o.s of +2 and +3 . similarly copper exhibits two o.s of +1 and +2 . on the other hand, Sn, Pb exhibit o.s of +2 and +4.)

2. In transition elements, higher o.s are more favoured in elements of higher atomic mass, whereas in p-block elements lower o.s are favoured by heavier members (due to inert pair effect, For example Mo(VI) and W(VI) are more stable than Cr(VI). On the other hand Pb(II) is more stable than Sn(II))

56. What happens when

(a) A lanthonoid reacts with dilute acids ?

(b) A lanthonoid reacts with water?

Ans.(a) When lanthonoid reacts with dilute acids , it liberates hydrogen gas.

(b)When lanthonoid reacts with water , it forms lanthanoid hydroxide and liberate hydrogen gas.

57. What is the gas liberated when

i) crystals of potassium permanganate is heated to 513K ?

ii) acidified potassium permanganate is treated with oxalate ion at 333K?

Ans. i) When crystals of potassium permanganate is heated to 513K Oxygen (O_2) gas is liberated .

ii) Acidified potassium permanganate when treated with oxalate ion at 333K liberates Carbon dioxide (CO_2) gas.

58. What is the composition of mischmetall? Give its one use.

Ans. The composition of mischmetall is lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.

Mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint

59. Show the interconversion of chromate and dichromate

The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

At pH less than 7: Chromate (yellow) on adding acid becomes dichromate (orange)

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

At pH more than 7 : Dichromate (orange) on adding base becomes Chromate (yellow)

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

60.How does the neutral or faintly alkalline potassium permanganate solution react with (a) Iodide (b) thiosulphite? Write the ionic equations for the reactions

In neutral or faintly alkaline solutions:

(a) The oxidation of iodide to iodate:

$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

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

III. Answer the following questions. Each question carries THREE marks

61.Name the metal of the 1st row transition series that

i) has highest value for magnetic moment

ii) has zero spin only magnetic moment in its +2 oxidation state.

iii) exhibit maximum number of oxidation states.

Ans. i) Chromium ii) Zinc iii) Manganese

62.Transition metals form a large number of complex compounds.Give reason.

Ans. Transition metals for complex compounds due to,

i) small sizes of metal cations

ii) their ionic charges and

iii) availability of d orbitals for bond formation.

63.Explain the trend in atomic size of 3d series of transition elements with reason.

Ans. With increase in atomic number in 3d series - atomic size decreases (Sc to Cr) , then remain almost constant (Cr to Cu) and increase slightly at the end (Cu to Zn).

Reason: In the beginning of the series the screening (or shielding effect) effect of a d electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases , hence atomic size radius decreases.

In the middle of the series, increase in nuclear charge and increase in screening effect balance each other. So atomic radii become almost constant.

Increase in atomic radii towards the end is due to the electro – electron repulsions causes the expansion of electron cloud.

64. Explain trend in Ionisation Enthalpies of 3d series of transition elements .

Ans.Ionisation enthalpy increase along each series of the transition elements from left to right. However many small variations, IE of Chromium is lower because removal of an electron from Chromium does not change in the d ($3d^5\ 4s^1$ to $3d^5\ 4s^0$) configuration. I.E value for Zn ($3d^{10}\ 4s^2$) is higher because an electron is removed from 4s level which needs more energy.

65. How is potassium dichromate prepared from iron chromite ore?

Ans.Potassium dichromate is manufactured from chromite ore ($FeCr_2O_4$).

(i) Chromite ore is fused ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air to get sodium chromate .

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

(ii) The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

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

Potassium dichromate prepared by treating the solution of sodium dichromate with potassium chloride.

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

Orange crystals of potassium dichromate crystallise out.

66. Describe the preparation of potassium permanganate from manganous dioxide.

Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

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

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

67.How does the acidified permanganate solution react with (a) iron(II) ions (b) oxalic acid and (c) hydrogen sulphide ? Write the ionic equations for the reactions

In acid solutions:

(a) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):

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

(b) Oxalate ion or oxalic acid is oxidised at 333 K:

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

(c) Hydrogen sulphide is oxidised, sulphur being precipitated:

$H_2S \longrightarrow 2H^+ + S^{2-}$

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