CHAPTER 8

The *d*- and *f*-Block Elements

ANSWERS

1. (i) **(c) :** $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$

Orange red fumes are due to CrO_2Cl_2.

(ii) **(b) :** $CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{yellow solution }(X)}{Na_2CrO_4} + 2NaCl + 2H_2O$

(iii) **(c) :** $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COO^-Na^+ + \underset{\text{yellow ppt }(Y)}{PbCrO_4}$

(iv) **(c) :** CrO_5 is formed in which the oxidation state of Cr is +6.

(v) **(a) :** CrO_5 decomposes on standing to Cr^{3+} ions and O_2.

2. Scandium.

3. Due to lanthanoid contraction Nb and Ta have nearly equal atomic and ionic radii. Moreover Nb and Ta have similar valence electrons, same charge/radius ratio and hence show similar properties.

4. It has completely filled *d*-orbital (d^{10}).

5. The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number across the series from lanthanum to lutetium is known as lanthanoid contraction.

6. Oxo-anion of chromium in which it shows +6 oxidation state equal to its group number is $Cr_2O_7^{2-}$ (dichromate ion).

7. **(c) :** $Gd(Z = 64) \rightarrow [Xe]4f^7 5d^1 6s^2$

$\therefore$ $Gd^{3+} \rightarrow [Xe]4f^7$.

8. **(c)**

9. **(a) :** Cu, Ag and Au are used in making coins and are called coinage metals.

10. **(b)**

11. **(d) :** $Eu(Z = 63) \rightarrow [Xe]\ 4f^7\ 5d^0\ 6s^2$

Eu^{2+} is stable due to half-filled configuration. Eu shows +3 oxidation state also, which is the most common oxidation state of lanthanoids.

12. **(b)**

OR

(d)

13. **(d)**

14. **(b)**

15. Zinc ($Z = 30$) has completely filled *d*-orbital ($3d^{10}$). These *d*-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak. This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

OR

Electronic configuration of *M* atom with $Z = 25$ is $[Ar]\ 3d^5\ 4s^2$.

$\therefore$ Electronic configuration of M^{2+} will be $[Ar]3d^5$, *i.e.*,

↑	↑	↑	↑	↑

Thus, it has five unpaired electrons.

$\therefore$ Spin only magnetic moment (μ) = $\sqrt{n(n+2)}$ B.M.

$\sqrt{5(5+2)} = \sqrt{35}$ B.M = 5.92 B.M.

16. Alloys are homogeneous solid solutions of metals and non-metals. Micshmetall is used to produce bullets, shell and lighter flint.

17. (a) Negative value of Zn^{2+} is due to fully filled ($3d^{10}$: Zn^{2+}) configuration.

(b) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali such as NaOH is added because on addition of an alkali, the concentration of H^+ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{yellow}}{2CrO_4^{2-}} + H_2O$$

18. **(b) :** $Co = [Ar]3d^7 4s^2$

$Co^{2+} = [Ar]3d^7$

i.e., there are three unpaired electrons ($n = 3$).

Hence, $\mu = \sqrt{n(n+2)}$ B.M. $= \sqrt{3(3+2)} = 3.87$ B.M.

19. Its electronic configuration is Nd : $[Xe]4f^4 5d^0 6s^2$. The possible oxidation state is +3 obtained by losing one 4*f* electron and two $6s^2$ electrons.

OR

$_{64}Gd^{3+}$: $[Xe]\ 4f^7$ has seven unpaired electrons. Magnetic moment, μ for seven unpaired electron ($n = 7$) is

$\mu = \sqrt{n(n+2)}$ BM $= \sqrt{7(7+2)} = \sqrt{63} = 7.93$ BM

20. Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

21. Lanthanoids resemble more closely with one another. Due to lanthanoid contraction the atomic radii of lanthanoids are almost similar and they show common +3 oxidation state. So, they are found in nature together and their physical properties are quite similar.

22. (i) Cr has higher melting and boiling point, due to unpaired electron in *d*-subshell and more *d-d* transition, it makes strong metal-metal bond.

(ii) Zinc, because oxidation potential of zinc is greater but that of tin is less than that of iron.

(iii) When Cr^{2+} oxidises to Cr^{3+}, its configuration becomes d^3, which is half filled t_{2g} with higher stability.

23. In acidic medium,

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

$$\text{Eq. mass} = \frac{158}{5} = 31.6$$

In neutral medium,

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

$$\text{Eq. mass} = \frac{158}{3} = 52.67$$

In alkaline medium,

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

$$\text{Eq. mass} = \frac{158}{1} = 158$$

24. (i) Transition metals form a large number of complex compounds due to following reasons :

– Variable oxidation states.

– Availability of *d*-orbitals for bond formation.

(ii) Lowest oxidation state compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas, the higher oxidation state of metal and compounds gets reduced to lower ones and hence are acidic in nature.

e.g., MnO is basic whereas Mn_2O_7 is acidic.

(iii) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

25. (i) Mn has half-filled *d*-subshell (d^5) and fully filled *s*-subshell (s^2) which results in stable configuration. Therefore, electrons are held tightly and this reduces delocalization of electrons which makes weak metal bond.

(ii) At the end of 3rd transition series, atomic size increases due to increase in electron-electron repulsion that causes the expansion of electron cloud.

26. (i) Ti^{4+} has stable inert gas configuration, the electronic configuration of Ti^{4+} is $[Ar]3d^04s^0$ and hence is most stable in aqueous solution.

On the other hand, V^{2+}, Mn^{3+}, Cr^{3+} have unstable electronic configuration and hence, are less stable.

(ii) Due to presence of highest oxidation state of Ti, it acts as the strongest oxidising agent among the given ions.

(iii) Due to absence of unpaired electron in Ti^{4+}, it is a colourless ion.

OR

(i) $Cr_2O^{2-}_{7(aq)} + 3H_2S_{(g)} + 8H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3S_{(s)}$

(ii) $2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(g)}$

(iii) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$

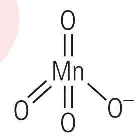
27. (a) The ground state electronic configuration for the given atoms would be

Atom with electronic configuration	Ground state electronic configuration	Stable oxidation state
$3d^2$	$3d^2\ 4s^2$	+4
$3d^5$	$3d^5\ 4s^1$, $3d^5\ 4s^2$	+2 and +7
$3d^7$	$3d^7\ 4s^2$	+2, +3
$3d^{10}$	$3d^{10}\ 4s^2$	+2

The maximum oxidation sate is given by the sum of 3*d* and 4*s* electrons upto Mn.

(b) (i) $Cr^{3+} = [Ar]\ 3d^3$ (ii) $Cu^+ = [Ar]\ 3d^{10}$

OR

(i) 

(ii) (a) It is used in analytical chemistry.

(b) It is used as an oxidant.

(c) It is used in bleaching of wool, cotton, silk and other textile fibres.

(iii) Potassium permanganate is strong oxidising agent, it oxidises HCl to give Cl_2 gas.

28. (a) Due to the ability of oxygen to form multiple bonds with metal.

(b) Scandium exhibits +3 oxidation state in its compounds. Electronic configuration of Sc in the ground state is $3d^1\ 4s^2$. So, Sc can easily lose $4s^2$ and $3d^1$ electron to give a stable $3d^0\ 4s^0$ configuration. Thus, it shows +3 oxidation state.

(c) (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4$

(ii) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.

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

29. (a) (i) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

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

(ii) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

(iii) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(b) (i) This is due to *d-d* transition. When visible (white) light falls on transition metal compounds, they absorb certain radiation of visible light for transition of electrons from lower *d* level to higher *d* level and transmit the remaining ones. The colour observed corresponds to complementary colour of the light absorbed.

(ii) Manganese has maximum number of unpaired electrons (5) in 3*d* subshell in addition to 2 electrons in the 4*s* subshell. It can use the 7 electrons for bonding purposes and shows the maximum oxidation states.

30. (a) The electronic configuration $4f^1 5d^1 6s^2$ corresponds to Ce(Z = 58).

It exhibits oxidation states + 3 and +4.

The electronic configuration $4f^7 5d^0 6s^2$ corresponds to Eu (Z = 63). It exhibits oxidation states +2 and +3.

(b) (i) The metal in the middle of the transition series contains greater number of unpaired electrons in (n −1)d and ns-orbitals.

(ii) As the atomic number increases each succeeding element contains one more electron in the 4*f*-orbital and one extra proton in the nucleus. The 4*f*-electrons are rather ineffective in screening the outer electrons from the charge of nucleus. As a result there is a gradual increase in the nuclear attraction for the outer electrons. Consequently, the atomic size gradually decreases. This is called lanthanoid contraction.