CHAPTER-7 d- and f- block elements

1. Why Zn, Cd and Hg are considered as transition element instead of full d-orbital?

a) Because they show similarities with other transition elements. In its native O.S it has partial filled-d-orbitals.

2. Why the atomic radii of elements of a particular series decreases upto midway and then remains constant, at the end it is increases?

a) Atomic radii decreases upto midway due to increase in the atomic number, nuclear charge increases, &

b) After midway due to increase in the number of electron in d- subshell the screening effect increases (Increased) and this neutralizes the effect of nuclear charge so the atomic radii remains constant.

c) At the end the d- and s- subshells are fully completed so their is strong inter electronic repulsion so size increases.

3. The atomic radii of 2nd transition series is more than 1st but 3rd series have ~~transition~~ atomic radii nearly same to that of 2nd?

a) Atomic radii increases from 1st transition series to 2nd due to the addition of one more shell.

b) Atomic radii of 3rd transition series is nearly same as 2nd due to the lanthanoid contraction.

Lanthanoid contraction - Filling of 4-f orbitals before 5d orbitals results in regular decrease in atomic radii which compensate the expected increase in atomic size with increasing atomic number.

Packing due to overlapping of unpaired electron of different metal atom.

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4. Enthalpy of atomization is higher at middle and then decreases. Why?

Ans Greater is the number of unpaired d-electrons, greater is the number of bonds and therefore greater is strength of these bonds and hence greater is the enthalpy of atomization.

5. Transition metals have very high melting and boiling point. Why?

Due to strong metallic bonds between atoms of these elements. Greater is the number of unpaired electron greater is the metallic bond so higher M.P and B.P.

6. Manganese and Technetium metals have abnormally low melting points.?

They have stable electronic configuration. As a result d-subshell's electrons are more tightly held by Mn/Tc atomic nucleus and this reduces delocalisation of electrons resulting weaker metallic bonding than in previous.

After attaining stable e⁻ configuration so half-filled orbitals, tendency to form metal-metal bonds decrease.

7. Transition elements show irregular trend in their ionization enthalpy?

4s > 3d, $E \propto \frac{1}{n^2}$, but after removal of one e⁻ energy of 4s < 3d so it becomes

Due to the fact that the removal of one electron alters the relative energies of 4s and 3d orbitals ∴ there is Reorganisation energy accompanying I.E (difficult to remove e⁻ from the 4s)

Electronic configuration

8. Why Cr and Cu have exceptionally high $I.E_2$ than those of other?

Ans After loss of one e⁻ both the elements acquire extra stability of half filled and completely filled orbitals so it becomes difficult to remove one electron from it.

9. Transition elements shows variable oxidation state? Due to participation of inner d and outer ns electrons. because the energies of ns and (n-1)d subshells are almost equal. As a result of which the electrons of (n-1)d and ns subshell both part in bond formation.

10. Ni (II) compounds are thermodynamically more stable than Pt (II) compounds. why?
Due to the fact that the sum of first two ionization enthalpy is less for nickel than for platinum, so Ni^{2+} is favourable than Pt^{2+}.

11. Pt (IV) compounds are thermodynamically more stable than Ni (IV) compounds. why?
Due to the fact that the sum of first four I.E is less for platinum than nickel., so Pt^{4+} is favourable as compared to nickel.

12. K_2PtCl_6 is a well known compound whereas corresponding nickel compound is not known.
Ans same as 11.

18. E° value of copper is positive. / E° Cu/Cu^{2+} for copper metal is positive unlike the remaining members of first transition series?
Due to the fact that the sum of sublimation enthalpy and ionization enthalpy to convert $Cu(s)$ to Cu^{2+} is so high that it is not balanced by its hydration enthalpy.

14. E° value of Mn and Zn are more negative as expected from the trend.
More negative values of E° for Mn and Zn are due to stability of half filled d-subshell in Mn^{2+} and completely filled ($3d^{10}$) in Zn^{2+}.

15. E° value of Ni is more negative than expected. Why?
Because of high enthalpy of hydration for the formation of an ion in solution.

- Cu and Zn do not show +3 oxidation state.

16. E° value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}?
~~Due to~~ much larger third ionization enthalpy of Mn (where the d-subshell stability is disturbed (d^5 to d^4) is mainly responsible for this)
Because Mn^{3+} has outer e.c of $3d^4$ and Mn^{2+} has outer e.c of $3d^5$. Thus the conversion of Mn^{3+} to Mn^{2+} will be favoured reaction since $3d^5$ is half filled stable configuration. Hence E° value of Mn^{3+}/Mn^{2+} couple is true)

17. Why does the first transition series element show irregularity in electrode potential?
Due to irregular variation of ionization enthalpy and sublimation enthalpies.

18. Cu (II) halides are known to exist except the iodide?
Because Cu^{2+} oxidises I^- to I_2.

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

white ppt

- Mn^{2+} and Co^{3+} – Strongest oxidising agents.
- Ti^{2+}, V^{2+} and Cr^{2+} – Strong reducing agent.

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

Cr^{2+} is a stronger reducing agent than Fe^{2+} because in case of Cr^{2+} to Cr^{3+} configuration changes from d^4 to d^3 but in case of Fe^{2+} to Fe^{3+} configuration changes from $d^6 \rightarrow d^5$. In a medium d^3 is more stable as compared to d^5.

- Paramagnetic character arises due to unpaired electrons which are attracted by field.

No of unpaired electron increases, so paramagnetism increases hence magnetic moment increases.

Unit of magnetic moment - BM (Bohr magnetons)

$$\mu = \sqrt{n(n+2)} \qquad n - \text{No of unpaired electrons}$$

20. Why d-block elements form coloured compounds in solution?

Because of d-d transition of e⁻, when in the presence of any reactant d-orbitals split into two sets of t_{2g} and e_g, when e⁻ transit in t_{2g} and e_g sets and emits energy of particular frequency which lies in the visible frequency region.

21. Why d-block elements form complex compounds?

a) Due to smaller size of metal ion.
b) High ionic charges
c) Availability of d-orbitals for bond formation.

22. Why are d-block elements good catalyst?

a) Due to the fact that they show multiple O.S.

b) Provide large surface area on which reactant may be adsorbed.

c) Their tendency to form reactive intermediate with suitable reactants.

28. Why Cu^+ ion is not stable in aqueous solution?

In aqueous solution Cu^+ undergoes disproportionate reaction

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

$\Delta_{hyd}H^\circ$ of Cu^{2+} is more negative than Cu^+

24. The highest oxidation state is exhibited in oxoanions of transition metal.

Oxygen forms multiple bond

Method of preparation of potassium dichromate

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

Chromite ore — (Yellow) (Sodium chromate)

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

(Orange) (Sodium dichromate)

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

(Orange) (Potassium dichromate)

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

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

~~e^- and thus function as Lewis~~

- Dichromate act as powerful oxidising agent in acidic medium.

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

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

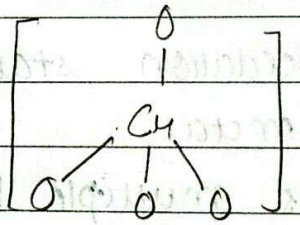
$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$$

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

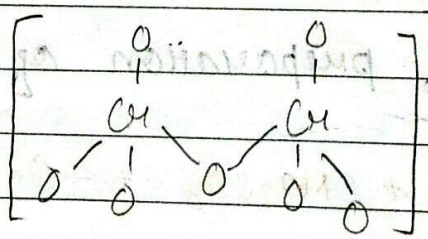
$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

Structure

i. Chromate ion



ii) Dichromate ion



Potassium permanganate

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

(dark green)

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

$$2Mn^{2+} + 5S_2O_8 + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

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

(Green) (Yellow)

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

$5S^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5S$

$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

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

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

$2MnO_4^- + 2H_2O + 3Mn^{2+} \longrightarrow 5MnO_2 + 4H^+$

25. HCl is not used to acidify $KMnO_4$ solution. Why?
Because $KMnO_4$ oxidises hydrochloric acid to chlorine which can bring errors in calculation.

26. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?
Because of relatively poor shielding by 5f electrons in actinoids in comparision with shielding of 4f electrons in lanthanoid.
Eu^{2+} is a strong reducing agent.
Eu^{2+} readily changes to common +3 O.S shown by the Lanthanoids by losing one more e^-. So, Eu^{2+} is regarded as a strong reducing agent.

27. Actinoids exhibit a large number of oxidation states than the corresponding members in lanthanoids. Lanthanoid show limited number of O.S because of large energy gap between 5d and 4f subshells. Actinoids exhibit large number of O.S because of small energy difference between 5f, 6d and 7s orbitals.

28. Which out of $Lu(OH)_3$ and $La(OH)_3$ is more basic and why?
$La(OH)_3$ is more basic than $Lu(OH)_3$.
Due to lanthanoid contraction, size of lanthanoid ion decreases so the covalent character between lanthanoid ion and OH^- ion increases from La^{3+} to Lu^{3+}
∴ basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

29. Ce(III) can be easily oxidized to Ce(IV).
Ce(III) has the electronic configuration: $4f^1 5d^0 6s^0$
It can easily oxidised because it can readily lose an electron to acquire ~~stable~~ stable $4f^0$ configuration and form Ce(IV)

30. Highest oxidation state of Mn with fluorine is +4 whereas with oxygen is +7.
Mn has highest O.S of +4 with fluorine and +7 with oxygen because of the ability of oxygen to form multiple bonds with metal ion, whereas fluorine being of small size and devoid of d-orbitals can't form multiple bonds.

• Alloy that contain some lanthanoid metal is Misch metal.

31. Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured ?

Sc^{3+} has a $3d^0$ configuration whereas Ti^{3+} has a $3d^1$ configuration. As there are no electrons in d-orbital for Sc^{3+} ion, there is no transition of electrons by absorption of energy and hence no emission in visible range imparting colour to Sc^{3+} ion.

32. Zn, Cd and Hg are soft metals.

Zn, Cd and Hg are soft metals because of their completely filled 3d, 4d and 5d orbitals respectively. Due to completely filled d-orbitals these metals are reluctant to form Zn-Zn, Cd-Cd and Hg-Hg bonds.

33. Write one similarity and difference between the chemistry of lanthanoids and that of actinoids.

Similarity -

1. Both involve the filling of f-orbital.
2. Both show contraction i.e lanthanoid contraction and actinoid contraction.

Difference

Lanthanoids	Actinoids
1. Except Pm (Promethium) all lanthanoids are non-radioactive.	1. Actinoids are radioactive.
2. Lanthanoids do not show wide range of O.S.	2. Actinoids shows the wide range of oxidation state.
3. Lanthanoids ions are generally coloured.	3. Actinoids ions are colourless.

34. The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic ?

As the oxidation state increases the size of ion goes on decreasing thus the covalent character increases as a result of this amphoteric and acidic strength increases. While in case of lower oxides of transition metals ionic size increases and thus basic character increases.

35. How is variability in oxidation states of transition metals different from that of the p-block elements ?

In p-block elements the differen in O.S is 2 and in transition elements the difference is 1.

36. Out of Cu^{+} and Cu^{2+}, which ion is unstable in aqueous solution and why ?

Cu^{+} is unstable in aq. solution because it undergoes disproportion reaction and has low hydration enthalpy.

37. Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali why?
In alkaline medium dichromate ions $Cr_2O_7^{2-}$ changes to chromate ion CrO_4^{2-}, which is yellow in colour due to which the colour changes when treated with an alkali.

38. Why is chemistry of actinoids complicated as compared to lanthanoids ~~?~~.
1. Actinoids show multiple O.S namely +5, +6 and +7 O.S respectively which permits the formation of higher O.S through the removal of the periphery electrons.
2. They are radioactive and have a strong propensity to form complex reactions because of its unstable isotopes, some actinoids are formed naturally by radioactive decay.

39. Account for the increasing Oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?
This is due to the increasing stability of the lower species to which they are reduced.

40. Following are the transition metal ions of 3d series: Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}
(A. number: Ti = 22, V = 23, Cr = 24, Mn = 25)

i) which ion is most stable in an aqueous solution and why?

ii) which ion is a strong oxidising agent and why?

iii) which ion is colourless and why?

i) Ti^{4+} is most stable in an aq. soln because of fully filled valence shell configuration.

ii) Mn^{3+} is the strong agent as it oxidises other species it will reduce itself by taking an electron and will stabilise its configuration to $3d^5$.

iii) Ti^{4+} is colourless due to absence of unpaired electrons.

41. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?

Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half filled t_{2g} level. On the other hand, the change from Mn^{2+} to Mn^{3+} results in half-filled configuration which has extra stability.

Actinoids show irregularities in their O.S ?

— Due to extra stability of empty, half filled and fully filled f-subshell.

Transition metal forms alloy?

- Because the atomic size of transition metal are very similar to each other. As the atomic size are similar, one metal can replace the other meta from its lattice and form a solid solution.

Mn_2O_3 is basic whereas Mn_2O_7 is acidic?

- In Mn_2O_3 magnese has +3 O.S, it has lone pairs of e^- which can be donated, hence it is basic in nature. Whereas in Mn_2O_7 magnese has +7 O.S Higher O.S are short of e^- and thus function as Lewis acids.

Ce^{4+} is a strong oxidising agent because Ce^{4+} oxidis others and itself gets reduced to the common and preferred +3 O.S of lanthanoid elements.