

## d & f BLOCK ELEMENTS

### 1 MARK QUESTIONS (1-20)

1. Zn, Cd & Hg are not treated as true transition elements. Why?
2. Cu & Ag are transition metals although they have completely filled d-orbitals. Why?
3. Why some d-block elements have irregular (exceptional) electronic configuration?
4. Atomic size does not change appreciably in a row of transition metals. Why?
5. Transition elements have variable oxidation states. Why?
6. Transition metals have high melting and boiling points. Why?
7. Transition metals have high enthalpy of atomization. Why?
8. Transition metals show catalytic properties .Why?
9. Transition metals and their salts are generally colored .Why?
10. Why transition metals form coordination compounds?
11. Why transition metals form alloys?
12. Transition metals form interstitial compounds. Why?

13. Zn, Cd & Hg have low boiling points and Hg is liquid. Why?
14. Transition metals and many of their compounds show paramagnetic behavior .Why?
15.  $d^1$  configuration is very unstable in ions .Why?
16.  $Cr^{2+}$  is strongly reducing while  $Mn^{3+}$  is strongly oxidizing. Why?
17. Cobalt(II) is stable in aqueous solution but in presence of complexing agents it gets oxidized. Why?
18.  $Mn^{2+}$  compounds are more stable than  $Fe^{2+}$  .Why?
19.  $Fe^{3+}$  is stable compared to  $Fe^{2+}$  .Why?
20. Transition metals exhibit highest oxidation states in oxides and fluorides. Why?

#### 2 Mark Questions (21-30)

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

For the first row transition metals the  $E^0$  values are:

$E^0$	V	Cr	Mn	Fe	Co	Ni	Cu
( $M^{2+}/M$ )	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.?

22. Why is the  $E^0$  value for the  $Mn^{3+}/Mn^{2+}$  couple much more positive than that for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$ ? Explain.?

23. In the series Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ), the enthalpy of atomization of zinc is the lowest. Why?

24. Explain why  $Cu^+$  ion is not stable in aqueous solutions?

25. Actinoid contractions are greater from element to element than lanthanoid contraction. Why?

26.  $K_2PtCl_6$  is well known compound and corresponding  $Ni^{4+}$  Salt is unknown . Whereas  $Ni^{2+}$  is more stable than  $Pt^{2+}$ .

27. Why  $\text{KMnO}_4$  is bright in colour ?
28.  $\text{CrO}$  is basic but  $\text{Cr}_2\text{O}_3$  is amphoteric?
29. In the titration of  $\text{Fe}^{2+}$  ions with  $\text{KMnO}_4$  in acidic medium, why dil.  $\text{H}_2\text{SO}_4$  is used and not dil  $\text{HCl}$ .
30.  $\text{K}_2\text{Cr}_2\text{O}_7$  is used as Primary Standard in volumetric analysis. Why?

3 MARKS QUESTIONS(31-40)

31. (a) Although  $\text{Cu}^+$  has configuration  $3d^{10} 4s^0$  (stable) and  $\text{Cu}^{2+}$  has configuration  $3d^9$  (unstable configuration) still  $\text{Cu}^{2+}$  compounds are more stable than  $\text{Cu}^+$ .
- (b) Titanium (IV) is more stable than Ti (III) or Ti (II).
32. The actinoids exhibit more number of oxidation states and give their common oxidation states.
33. (a) Give reason  $\text{CrO}_3$  is an acid anhydride.
- (b) Give the structure of  $\text{CrO}_5$ .
34. Why is  $\text{Cr}^{2+}$  reducing and  $\text{Mn}^{3+}$  oxidising when both have  $d^4$  configuration ?
35. (a) In  $\text{MnO}_4^-$  ion all the bonds formed between Mn and Oxygen are covalent. Give reason.
- (b) Beside + 3 oxidation state Terbium Tb also shows + 4 oxidation state. (Atomic no. = 65)
36. (a) Highest manganese fluoride is  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ .
- (b) Copper can not liberate  $\text{H}_2$  from dil acids :
- Note : Although only oxidising acids ( $\text{HNO}_3$  and hot conc.  $\text{H}_2\text{SO}_4$ ) react with Cu light.

37. A metal which is strongly attracted by a magnet is attacked slowly by the  $\text{HCl}$  liberating a gas and producing a blue solution. The addition of water to this solution causes it to turn pink, the metal is
38. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal ?
39. The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?
40. Why are  $\text{Mn}^{2+}$  compounds more stable than  $\text{Fe}^{2+}$  compounds towards oxidation to +3 state?

5 MARK QUESTIONS(41-45)

41. A wellknown orange crystalline compound (A) when burnt impart violet colour to flame. (A) on treating (B) and conc.  $\text{H}_2\text{SO}_4$  gives red gas (C) which gives red yellow solution (D) with alkaline water. (D) on treating with acetic acid and lead acetate gives yellow p. pt. (E). (B) sublimes on heating. Also on heating (B) with  $\text{NaOH}$  gas (F) is formed which gives white fumes with  $\text{HCl}$ . What are (A) to (F) ?

42. Give reasons for the following:

- (a) Among the lanthanoids, Ce(III) is easily oxidised to Ce(IV).
- (b)  $\text{Fe}^{3+} / \text{Fe}^{2+}$  redox couple has less positive electrode potential than  $\text{Mn}^{3+} / \text{Mn}^{2+}$  couple.
- (c) The second and third transition series elements have almost similar atomic radii.
- (d) Transition metals and many of their compounds show paramagnetic behaviour.
- (e)  $\text{KMnO}_4$  titration is not carried out using HCl as acid medium.

(iii) The transition metals generally form coloured compounds.

43. a) A Complex having scandium in +3 oxidation-state was found colorless why?

b) Show the splitting of d, orbitals of Ti in  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$

c)  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  is coloured why?

d) Differentiate between. Lanthanides and actinides w.r t.

- (i) Oxidation state
- (ii) electronic configuration

44. 1. Mixed oxide of iron and Chromium  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  is fused with Sodium Carbonate in the presence of air to form yellow compound (A). On acidification Compound (A) forms an orange coloured compound (B) which is an oxidizing agent

i) Identify A and B.

ii) Write balanced chemical equation for each

2. Among the lanthanoids, Ce(III) is easily oxidised to Ce(IV).

3.  $\text{Fe}^{3+} / \text{Fe}^{2+}$  redox couple has less positive electrode potential than  $\text{Mn}^{3+} / \text{Mn}^{2+}$  couple.

45. (I) Account for the following :

- (a) Zirconium & Hafnium exhibit almost similar properties
- (b) Zinc salts are white while  $\text{Cu}^{2+}$  salts are coloured
- (c) The transition elements have high enthalpies of atomization.
- (d) Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.
- (e)  $\text{Zn}^{2+}$  salts are white while  $\text{Cu}^{2+}$  salts are blue.

### D & f BLOCK ELEMENTS

#### ANSWERS

- 1. Because they have completely filled d-orbitals in their atomic as well as stable ionic state.
- 2.  $\text{Cu}^{2+}$  &  $\text{Ag}^{2+}$  have  $(n-1)d^9 4s^0$  configuration.
- 3. Due to very small energy difference between  $(n-1)d$  &  $ns$  sub-shell.
- 4. Along the rows nuclear charge increases but the penultimate d-sub shell has poor shielding effect so atomic and ionic size remain almost same.

5. Due to very small energy difference between  $(n-1)d$  &  $ns$  sub-shell electrons from both the sub-shell take part in bonding .
6. A large number of unpaired electrons take part in bonding so they have very strong metallic bonds and hence high m.pt & b.pt
7. A large number of unpaired electrons take part in bonding so they have very strong metallic bonds and hence high enthalpy of atomization
8. Because they have variable oxidation states and hence can form different intermediates. They also provide large surface area.
9. Because they have partially filled d-sub shell and hence d-d electron transition takes place when they absorb radiations from visible region and transmit complementary colors.
10. Because they have large number of vacant orbitals in  $(n-1)d$ ,  $ns$ ,  $np$  &  $ns$  sub shells so they can accept electron pairs from ligands
11. They have comparable atomic size and hence can be mixed uniformly.
12. Because small atoms like H, C, N etc can be entrapped in their metallic crystals.
13. They have full filled 3d-orbitals and no electrons from d-orbitals are taking part in metallic bonding so they have weak metallic bonding. Due to larger atomic size Hg is liquid.
14. Because they have unpaired electrons.
15. Because by losing one electron they get extra stability.
16.  $E^0$  value for  $Cr^{3+}/Cr^{2+}$  is negative but that of  $Mn^{3+}/Mn^{2+}$  is positive so  $Cr^{2+}$  can lose electron to form  $Cr^{3+}$  while  $Mn^{3+}$  accepts electron to form  $Mn^{2+}$ . In case of Cr  $d^4$  to  $d^3$  occurs for  $Cr^{2+}$  to  $Cr^{3+}$ .  $d^3$  is stable.
17. Oxidation state changes from +2 to +3 because in presence of ligands d-orbitals split up into  $t_{2g}$  and  $e_g$  having the stable configuration  $t_{2g}^6 e_g^0$ .
18.  $Mn^{2+}$  has half-filled d-orbitals i.e  $3d^5 4s^0$  configuration.
19. Due to half-filled configuration i.e  $3d^5 4s^0$  configuration.
20. Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.

2 Marks(21-30)

21. The  $E^0 (M^{2+}/M)$  values are not regular which can be explained from the irregular variation of ionisation enthalpies ( $\Delta_i H_1 + \Delta_i H_2$ ) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

22. 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.

23. 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.

24.  $Cu^+$  in aqueous solution undergoes disproportionation, i.e.,

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$  The  $E^0$  value for this is favorable.

25. The 5f electrons are more effectively shielded from nuclear charge. In other words the 5f electrons themselves provide poor shielding from element to element in the series.

26. The stability of the compounds depends upon sum of ionization enthalpies:

$$IE_1 + IE_2 < IE_1 + IE_2$$

in Ni                      in Pt

∴  $Ni^{2+}$  is stable than  $Pt^{2+}$ .

$$IE_1 + IE_2 + IE_3 + IE_4 < IE_1 + IE_2 + IE_3 + IE_4$$

in  $Pt^{4+}$

in  $Ni^{4+}$

∴  $Pt^{4+}$  is stable, ∴  $K_2PtCl_6$  is well known compound.

27. It is due to charge transfer. In  $MnO_4^-$  an electron is momentarily transferred from O to the metal, thus momentarily  $O^{2-}$  is changed to  $O^-$  and reducing the oxidation state of the metal from Mn (VII) to Mn (VI).

28.  $CrO$      $Cr_2O_3$

O. N.

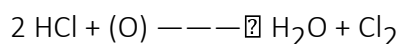
+ 2

+ 3

Higher the oxidation states higher the acidity. In lower oxidation state some of valence  $e^-$  of the metal atom are not involved in bonding, ∴ can donate  $e^-$  and behave as base. In higher oxidation state  $e^-$  are involved in bonding and are not available, rather it can accept  $e^-$  and behave as an acid.

29.  $KMnO_4$  produce  $Cl_2$   $KMnO_4$  in presence of dil. HCl acts as oxidising agent, Oxygen produced is used up partly for oxidation of HCl :

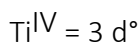
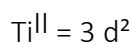
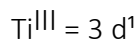
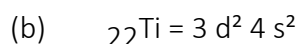




30.  $\text{K}_2\text{Cr}_2\text{O}_7$  is not much soluble in cold water. However, it is obtained in pure state and is not Hygroscopic in nature.

3 marks questions(31-40)

31.(a) It is due to much more (–) Hydration  $\text{H}^-$  of  $\text{Cu}^{2+}$  (aq) than  $\text{Cu}^+$ , which is more than compensates for the II ionization enthalpy of Cu.



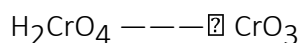
most stable configuration.

$\text{Ti}^{\text{IV}}$  is more stable than  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{II}}$ .

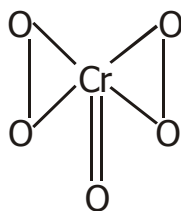
32. As the distance between the nucleus and 5 f orbitals (actinoids) is more than the distance between the nucleus and 4 f (lanthanoids) hence the hold of the nucleus on valence electrons decrease in actinoids. For this reason the actinoids exhibit more number of oxidation states in general.

Common O. N. exhibited are + 3 (similar to Lanthanoids) besides + 3 state, also show + 4, maximum oxidation state in middle of series i. e. Pu and Np. have an oxidation state upto + 7.

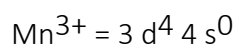
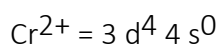
33. (a)  $\text{CrO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CrO}_4$  i. e.  $\text{CrO}_3$  is formed by loss of one  $\text{H}_2\text{O}$  molecule from chromic acid :



(b)

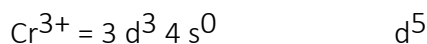
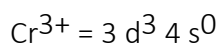
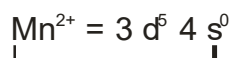


34.  $\text{Cr}^{2+}$  is reducing as its configuration changes from  $\text{d}^4$  to  $\text{d}^3$ , the  $\text{d}^3$  has half-filled  $t_{2g}$  level. On the other hand, the change from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  results in the half filled (d<sup>5</sup>) configuration which has extra stability.



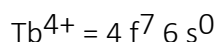
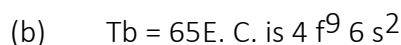
↓  
oxidation

↓  
reduction



have half-filled half-filled extra  
 $t_{2g}$  level. stable.

35. (a) In  $\text{MnO}_4^-$ , O. N. is + 7, but it is not possible to lose 7 electrons because very high energy is required to remove 7 electrons. Therefore it forms covalent bonds.



half-filled f-orbital  $\square$  stable.

after losing 4  $e^-$  it attains half-filled orbital.

36. (a) The ability of oxygen to form multiple bonds to metals, explain its superiority to show higher oxidation state with metal.

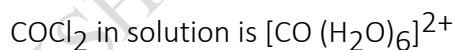
(b) Positive  $E^\circ$  value (+ 0.34 Volt) accounts for its inability to liberate  $\text{H}_2$  from acids. The high energy to transform  $\text{Cu (s)}$  to  $\text{Cu}^{2+} (\text{aq})$  is not balanced by its Hydration enthalpy.

Note : For (b) Consult Fig. 8.4 in NCERT

37. The metal is CO



blue solution



blue

pink

38. The following points justify that the given statement is true:-

(i) Ionization enthalpies of heavier transition elements are higher than the elements of 3d series.

Consequently, heavier transition elements are less reactive in comparison to 3d-elements.

(ii) Melting points of heavier transition elements are higher than 3d-elements.

(iii) Higher oxidation states of heavier transition elements are stable whereas lower oxidation states are stable in 3d-elements.



39. In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.
40. The electronic configuration of  $Mn^{2+}$  is  $[Ar] 3d^5$ , i.e. all five d-orbitals are singly occupied. Thus this is stable electronic configuration and further loss of electron requires high energy. On other hand side the electronic configuration of  $Fe^{2+}$  is  $[Ar] 3d^6$ , i.e. Loss of one electron requires low energy.

#### 5 MARK QUESTIONS(41-45)

- 41.(i)  $K_2Cr_2O_7 + 4 NH_4Cl + 3 H_2SO_4 \longrightarrow \square K_2SO_4 + 2 Cr_2O_2Cl_2 + 2 (NH_4)_2SO_4 + 3 H_2O$  (A) (B) Sublime Chromyl Chloride red gas(C)
- (ii)  $CrO_2Cl_2 + 4 NaOH \longrightarrow \square Na_2CrO_4 + 2 NaCl + 2 H_2O$   
(D) Yellow Soln.
- (iii)  $Na_2CrO_4 + (CH_3COO)_2 Pb \longrightarrow \square PbCrO_4 + 2 CH_3COONa$   
Yellow p. pt. (E)
42. (a) vacant (n-2) f subshell in Ce(IV).  
(b) extra stability of  $Fe^{3+}$  than  $Mn^{3+}$  ion (c) Due to lanthanoid contraction  
(d) they both will be reacting. (e) unpaired d –electrons and d-d transitions.
43. a) Due to absence of unpaired electron in d orbital  
b) Correct splitting of d orbitals in octahedral field into  $t_{2g}$  and  $e_g$  c) Due to presence of single electron  
d) lathanoid Actinoid  
(i) Shows common oxidation state of +3,+4,+5 It shows common oxidation state +3  
(ii) 4 f are filled 5f are filled
- 44.(1)  $A = Na_2CrO_4$  ;  $B = K_2Cr_2O_7$   
 $4FeCr_2O_4 + 8 NaCrO_4 + 7O_2 \longrightarrow 8 Na_2CrO_4 + 2 Fe_2O_3 + 8 CO_2$   
 $2Na_2CrO_4 + 2 H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$   
 . (2) vacant (n-2) f subshell in Ce(IV).  
 (3) extra stability of  $Fe^{3+}$  than  $Mn^{3+}$  ion
45. 1(a). Because of same size  
 (b). Because  $Zn^{+2}$  ion does not have unpaired electrons while  $Cu^{+2}$  have one unpaired electron  
 ©. Because of many unpaired electrons they have many metallic bonds  
 (d) In these oxoanions the oxygen atoms are directly bonded to the transition metal.  
 Since oxygen is highly electronegative, the oxoanions bring out the highest oxidation state of the metal.  
 (e)  $Zn^{2+}$  ion has all its orbitals completely filled whereas in  $Cu^{2+}$  ion there is one half-filled 3d-orbital. It therefore has a tendency to form coloured salts whereas  $Zn^{2+}$  has no such tendency. 1

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