THE d & f-BLOCK ELEMENTS

SOLVED SUBJECTIVE EXERCISE

Very Short Answer Type Questions (1 mark)

1. The E° (M^{2+}/M) value for copper is positive (+0.34 V). What is possibly the reason for this?

Ans. E° (M^{2+}/M) for any metal is related to the sum of the enthalpy change taking place in the following steps:

$$M(s) + \Delta_a H \longrightarrow M(g), \qquad (\Delta_a H = \text{Enthalpy of atomisation})$$

$$M(g) + \Delta_i H \longrightarrow M^{2+}(g), \qquad (\Delta_i H = \text{Ionisation enthalpy})$$

$$M^{2+}(g) + aq \longrightarrow M^{2+}(aq) + \Delta_{hyd} H \qquad (\Delta_{hyd} H = \text{Hydration enthalpy})$$

Copper has high enthalpy of atomisation and low enthalpy of hydration. So, E° (Cu^{2+}/Cu) is positive. The high energy to transform Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy.

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

Ans. Due to small size and high electronegativity, oxygen or fluorine can oxidise a metal to its highest oxidation state.

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

Ans. Cr^{2+} is a stronger reducing agent than Fe^{2+} because after the loss of one electron Cr^{2+} becomes Cr^{3+} which has more stable t_{2g}^{3} (half filled) configuration in a medium like water.

4. What is the effect of increasing pH on $K_2Cr_2O_7$ solution?

Ans. In aqueous solution, we have $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$. When pH < 4 (acidic medium), it exists as $Cr_2O_7^{2-}$ and the colour is orange. When pH > 7 (basic medium), it exists as CrO_4^{2-} and the colour is yellow.

5. Why is La $(OH)_3$ stronger base than Lu $(OH)_3$?

Ans. Due to lanthanoid contraction, the size of Lu^{3+} is smaller than that of La^{3+} ion. Because of small size of Lu^{3+} ion, the Lu—O bond is stronger than La—O bond. Hence, La $(OH)_3$ behaves as a stronger base.

6. For the first row transition metals the E° values are:

E°	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.

Ans. The E° (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.

7. Account for the following:

Cerium (atomic number = 58) forms tetra positive ion, Ce^{4+} in aqueous solution.

Ans. The electronic configuration of Ce (Z = 58) is $_{58}Ce = [Xe]4f^1\,5d^1\,6s^2$

Cerium can lose four electrons ($4f^1\,5d^1\,6s^2$) in aqueous solution to acquire stable configuration of rare gas xenon. Moreover due to small size and high charge, Ce^{4+} ion has high hydration energy.

8. Out of Ag_2SO_4, CuF_2, MgF_2 and CuCl, which compound will be coloured and why?

Ans. CuF_2

In CuF_2, Cu^{2+} ($3d^9$) has an unpaired electron.

9. In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, why is dil H_2SO_4 used instead of dil HCl?

Ans. Dil.H_2SO_4 is an oxidising agent and oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$.

Dil.HCl is a reducing agent and liberates chlorine on reacting with $KMnO_4$ solution.

Hence the part of the oxygen produced from $KMnO_4$ is used up by HCl.

10. How does ionic-covalent character of compounds of a transition metal vary within the range of its various oxidation states?

Ans. With increase in oxidation state, more and more of valence shell electrons are involved in bonding. The atomic core becomes less shielded resulting in the increased electronegativity of atoms. Because of this, ionic character of covalent bonds increases with the increase in oxidation state.

Short Answer Type Questions (2 mark)

11. How would you account for the following:

(i) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.

(ii) There is a greater range of oxidation states among the actinoids than among the lanthanoids.

Ans. (i) This due to filling of 4f orbitals which have poor shielding effect or due to lanthanoid contraction.

(ii) This is due to comparable energies of 5f, 6d and 7s orbital in actinoids.

12. What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

Ans. ***Lanthanoid contraction :*** The steady decrease in the atomic and ionic radii of lanthanoids with increase in atomic number is known as lanthanoid contraction.

Cause of lanthanoid contraction : As we move along the lanthanoid series, for every additional proton in the nucleus, the corresponding electron goes into 4f-subshell, there is poor shielding of one electron by another in this subshell due to the shapes of these f-orbitals. The imperfect shielding is not able to counterbalance the effect of the increased nuclear charge. Thus, the net result is decrease in size with increase in atomic number.

Consequences :

(i) 5d series elements have nearly same radii as that of 4d-series.

(ii) The basic strength of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

13. Complete the following chemical reaction equations :

(i) $CrO_7^{2-}(aq) + H_2S(g) + H^+(aq) \longrightarrow$

(i) $MnO_2(s) + KOH(aq) + O(2) \longrightarrow$

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

$H_2S \longrightarrow S + 2H^+ + 2e^-] \times 3$

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

(ii) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

14. Why the decrease in radii of transition elements is not as pronounced as those of representative elements?

Ans. On moving along a transition series, the nuclear charge increase which tends to decrease the atomic size but the addition of electron in the penultimate d-sub shell increases the screening effect which tends to neutralize the effect of the increased nuclear charge. Due to this reason, no pronounced change in the radii of transition elements is observed.

15. Why there is only a very small increase in ionization enthalpy of an element in a transition series as compared to s-and p-block elements in a period?

Ans. It is because, the effect of increased nuclear charge is balanced by shielding effect in transition series while it is not balanced in s and p-block elements in a period. The electron enters in (n-1) d orbital in transition elements while it enters in ns or np orbitals in s- and p-block elements with the increase in atomic number.

16. If the magnetic moment of a tripositive ion is 5.92 BM, what is the number of unpaired electrons present in the ion. (Element belongs to first series of transition elements)?

Ans. Magnetic moment, $\mu_B = \sqrt{n(n+2)}\,BM$

$\therefore\ 5.92 = \sqrt{n(n+2)}\,BM$

Squaring both sides, we have:

$35 = \sqrt{n(n+2)}$

Or $n^2 + 2n - 35 = 0$

Or $n = 5$ (unpaired electrons)

The trivalent ion is Fe^{3+} as there are five unpaired electrons in the configuration of Fe^{3+} $(1s^2, 2s^6, 3p^6, 3d^5)$

17. Why is chromium a hard metal whereas, mercury exists as liquid?

Ans. In chromium, there is half filled $(2d^5\ 4s^1)$ electronic configuration and interatomic bonding in the atoms is very strong as there are six unpaired electrons and this makes chromium a hard metal. However, in mercury, the outer electronic configuration is $5d^{10}6s^2$ and it contains no unpaired electrons and interatomic bonding is very weak and this makes mercury a liquid metal.

18. Phosphorus (at. No. =15) and vanadium (At. No. =23) exhibit variable oxidation state for different reasons. Explain this difference.

Ans. In excited state, electrons from 3s orbital get excited to empty 3d-orbitals in phosphorus to make five half filled orbitals and it shows +5 oxidation state in addition to +3 oxidation state. In vanadium, electrons form ns and (n –1) d orbitals can participate in bond formation and it shows variable oxidation states.

19. Explain as to why the E° values for the Mn^{3+}/ Mn couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.

Ans. The outer electronic configuration of Mn^{2+} is $3d^5$ whereas the outer electronic configuration of Mn^{3+} is $3d^4$. Thus, when Mn^{2+} (with half filled electronic configuration) is to be changed into Mn^{3+}, very large amount of ionization enthalpy is required and due to this reason, E° value for Mn^{3+}/Mn^{2+} couple is very highly positive than Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}. This also explains why +3 oxidation state of Mn has very little significance.

20. What is meant by 'disproportiopation' of an oxidation state? Give an example.

Ans. Those chemical reactions in which the same substance undergoes oxidation as well as reduction are called disproportionation reactions. During these reactions, a particular oxidation state becomes less stable in comparison to other oxidation states, one lower, one higher. For example, manganese (VI) becomes unstable as compared to manganese (VII) as well as manganese (IV) in acidic solution.

Short Answer Type Questions (3 mark)

21. Give reasons for the following:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The enthalpies of atomisation of the transition metals are high.

(iii) The transition metals generally form coloured compounds.

Ans. (i) ***Magnetic properties :*** Substances containing unpaired electrons are said to be paramagnetic. A diamagnetic substance is one in which all the electrons are paired. Except the ions of d° (Sc^{+3}, Ti^{+4}) or d^{10} (Cu^+, Zn^{+2}) configurations, all other simple ions of transition elements contain unpaired electrons in their (n – 1)d subshell and are, therefore, paramagnetic. The magnetic moments (μ) of the elements of first transition series can be calculated with the unpaired electrons (n) by the spin only formula.

$\mu = \sqrt{n(n+2)}$ B.M. (Bohr Magneton)

(ii) The transition elements exhibit high enthalpy of atomisation because they have large number of unpaired electrons in their atoms. Due to this they have stronger interatomic interaction and hence stronger bonding between atoms.

(iii) ***Colour :*** Most of the transition metal ions in solution as well as in solid states are coloured. This is due to the partial absorption of visible light. The absorbed light promotes the electron from one orbital to another orbital of the same d subshell. Since the electronic transition occurs within the d-orbitals of the transition metal ions, they are called d—d transitions. It is because of these d—d transitions occurring in a transition metal ion by absorption of visible light that they appear coloured.

22. Describe the preparation of potassium permanganate. How does the acidified permanganate react with (i) iron (II) ions (ii) SO_2 (iii) oxalic acid? Write the ionic equations for the reaction.

Ans. $\underset{\text{Chromite ore}}{4FeO.Cr_2O_3} + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Roasted}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

chemistry

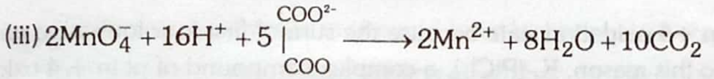
$2Na_2Cr_2O_4 + H_2SO_4 \longrightarrow Na_2CrO_7 + Na_2SO_4 + 2H_2O$

$Na_2Cr_2O_4 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

$K_2Cr_2O_7$ is separated by fractional crystallization.

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

(ii) $2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 4H^+ + 5SO_4^{2-}$



(iii) $2MnO_4^- + 16H^+ + 5\begin{array}{c}COO^{2-}\\|\\COO\end{array} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

23. Account for the following:

(i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidising.

(ii) Cobalt (III) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidised.

(iii) The d^1 configuration is very unstable in ions.

Ans. (i) E° value for Cr^{3+}/Cr^{2+} is negative (–0.41 V) while as E° value for Mn^{+3}/Mn^{2+} is positive (+1.57 V). Thus, Cr^{2+} ions can easily undergo oxidation to give Cr^{3+} ions and, therefore, act as strong reducing agent. On the other hand, Mn^{2+} can easily undergo reduction to give Mn^{2+} and hence act as oxidising agent.

(ii) Co (III) has greater tendency to form coordination complexes than Co (II). Thus, in the presence of ligands, Co (II) changes to Co (III), i.e., is easily oxidised.

(iii) The ions with d^1 configuration have the tendency to lose the only electron present in d-subshell to acquire stable d^0 configuration. Therefore, they are unstable and undergo oxidation or disproportionation.

24. Give reasons for the following:

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

(ii) $Fe^{3+}|Fe^{2+}$ redox couple has less positive electrode potential than $Mn^{3+}|Mn^{2+}$ couple.

(iii) Copper (I) has d^{10} configuration, while copper (II) has d^9 configuration, still copper (II) is more stable in aqueous solution than copper (I).

Ans. (i) Because Ce (IV) has extra stability due to empty f^0 orbital.

$Ce^{3+} \longrightarrow Ce^{4+} + e^-$

$[Xe]\ 4f^1\ 5d^0\ 6s^0$

(ii) In $Mn^{2+}\ d^5$ configuration leads to extra stability of half filled configuration, so $Mn^{3+}/Mn^{2+}(d^4)$ tends to get converted to stable d^5, configuration of Mn^{2+}, by accepting an electron so Mn^{+3}/Mn^{2+} redox couple has more positive potential than $Fe^{3+}(d^5)/Fe^{2+}(d^4)$ couple.

(iii) Due to more negative enthalpy of hydration of Cu^{2+}(aq) than Cu^+(aq) which compensates for second ionisation enthalpy of copper.

25. Explain:

(i) CrO_4^{2-} is a strong oxidizing agent while MnO_4^{2-} is not.

(ii) Z_r and H_f have identical sizes.

(iii) The lowest oxidation state of manganese is basic while the highest is acidic.

Ans. (i) Oxidation state of Cr in CrO_4^{2-} is 6+. This is its maximum oxidation state and it can only gain electrons. Oxidation state of Mn in MnO_4^{2-} is 6+. Mn can further loose electron to become 7+ which is its highest oxidation state.

(ii) This is due to lanthanoid contraction.

(iii) In its highest oxidation state manganese can only accept electrons and so is acidic in behaviour. Similarly in its lowest oxidation state, it can donate electrons and hence is basic.

26. The sum of first and second ionization energies and those of third and fourth ionization energies of nickel and platinum are:

$IE_1 + IE_2$ (MJ mol^{-1}) $IE_3 + IE_4$ (MJ mol^{-1})

Based on this information, write:

(a) The most common oxidation state for Ni and Pt and mention why they are common?

(b) Name the metal (Ni or Pt) which can easily form compounds in +4 oxidation state and why?

Ans. (a) + 2 oxidation state is most common for Ni the sum of first two ionization energies for Ni is lower than that of Pt, But +4 oxidation state is the most common for Pt as the sum of first four ionization energies for Pt is less than that of Ni.

(b) Platinum can easily form compounds in +4 oxidation state because the sum of first four ionization energies for Pt is lower than that of Ni and due to this reason, $K_2(PtCl_5)_6$ a complex compound of pt in + 4 oxidation state is well known whereas, the corresponding compound of nickel with + 4 oxidation state $K_2(NiCl_6)$ a complex compound of Pt in + 4 oxidation state is well known whereas, the corresponding compound of nickel with + 4 oxidation state $K_2(NiCl_6)$ is not known.

27. (a) Of the ions Ag^+, Co^{2+} and Ti^{4+}, which one will be coloured in aqueous solutions?

(Atomic numbers: Ag = 47, Co = 27, Ti = 22)

(b) If each one of the above ionic species is in turn placed in a magnetic field, how will it respond?

Ans. (a) A transition metal ion is coloured if it has unpaired electrons in the (n – 1)d sub shell. In case of above ions their electronic configurations are:

(i) $Ag^+[Kr]4d^{10}\,5s^0$ (ii) $Co^{2+}[Ar]3d^7\,4s^0$ (iii) $Ti^{4+}[Ar]3d^0\,4s^0$

Since only Co^{2+} has unpaired electrons in its configuration, it will be coloured in its aqueous solution.

(b) Since only in Co^{2+} ion, unpaired electrons are present, it will be attracted by external magnetic field and will show paramagnetic character whereas, the other ions Ag^+ and Ti^{4+} will be diamagnetic in nature.

28. (a) How poling process helps in the removal Cu_2O from copper?

(b) Why copper dissolves in dil. HNO_3 but remains ineffective in dil. HCl?

Ans. (a) Poling process involves green wood poles which produce carbon monoxide and hydrogen which reduce Cu_2O to Cu.

$Cu_2O + CO \rightarrow 2Cu + CO_2$ $\quad$ $Cu_2O + H_2 \rightarrow 2Cu + H_2O$

(b) Copper is less reactive than hydrogen as it has more reduction potential ($E^0_{Cu^{2+}}$ 0.34V) than hydrogen $E^0_{H^+/H_2} = 0V$ and it is unable to liberate H_2 from dilute acids. Copper dissolves in nitric acid as HNO_3 is a strong oxidizing agent.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O \text{ (Dilute)}$$

29. (a) Explain why a green solution of potassium manganate (VI), K_2MnO_4 turns purple and a brown solid is precipitated when CO_2 is bubbled into the solution.

(b) Ore of manganese (pyrolusite) on heating with KOH in the presence of air give dark green compound (A). The solution of (A) on treatment with H_2SO_4 gives purple coloured compound (B). Identify (A) and (B).

Ans. (a) CO_2 produce carbonic acid in aqueous solution which acts as a weak acid.

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

In the presence of H^+, MnO_4^{2-} undergo disproportionation to MnO^{4-} by oxidation and MnO_2 by reduction.

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

(+6) (+7) (+4)

(b) (i) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

Pyrolusite Potassium (a) Manganate

(ii) $\underset{(A)}{3K_2MnO_4} + 2H_2SO_4 \rightarrow \underset{(B)}{2KMnO_4} + MnO_2 + K_2SO_4 + 2H_2O$

30. (a) Why actinides have more tendency to form complexes than lanthanides?

(b) Among lanthanides, why are ions like Sm^{2+} are: Eu^{2+}, $[Xe]4f^7 5d^0$, Ce^{2+}, $[Xe]4f^1, 5d^1$ In Eu^{2+}, f-sub shell is half filled and d-sub shell is completely filled and is therefore more stable than Ce^{2+}.

Ans. (a) It is because–

(i) Actinides are smaller in size and have higher nuclear charge than lanthanides.

(ii) 5f-electrons have poor shielding effect than 4f- electrons in lanthanides.

(ii) Actinides have high charge density of M^{4+} ions.

(b) The most stable oxidation state of lanthanides is +3. Hence, an ion in +2 oxidation state tends to acquire +3 oxidation states by loss of electron and thus brings reduction of species. Similarly, those lanthanides ions which are in +4 oxidation state tend to acquire +3 oxidation state by gaining one electron and thus act as oxidizing agents

Sm^{2+} (At. No. 62) = $4f^6$ $5d^0$ $6s^0$
Eu^{2+} (At. No. 63) = $4f^7$ $5d^0$ $6s^0$
Yb^{2+} (At. No. 70) = $4f^{14}$ $5d^0$ $6s^0$
Ce^{4+} (At. No. 58) = $4f^0$ $5d^0$ $6s^0$

EXERCISE-1

PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

1. (a) Account for the following
(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
(ii) Zirconium and Hafnium exhibit similar properties.
(iii) Transition metals act as catalysts.
(b) Complete the following equations:
(i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$ (ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$

2. The elements of 3d transition series are given as:
Sc Ti V Cr Mn Fe Co Ni Cu Zn
Answer the following:
(i) Write the element which is not regarded as a transition element. Give reason.
(ii) Which element has the highest m.p ?
(iii) Write the element which can show an oxidation state of +1.
(iv) Which element is a strong oxidizing agent in +3 oxidation state and why ?

CBSE 2015

1. (i) E^0 value for the Mn^{3+}/Mn^{2+} couple is positive (+ 1.5 V) whereas that of Cr^{3+}/Cr^{2+} is negative (– 0.4 V). Why?
(ii) Transition metals form coloured compounds. Why?
(iii) Complete the following equation :
$2MnO^-_4 + 16\,H^+ + 5C_2O^{2-}_4 \rightarrow$

2. Why do transition elements show variable oxidation states? How is the variability in oxidation states of d-block different from that of the p-block elements?

CBSE 2014

1. (a) Compete the following equations:
(i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$
(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$
(b) Account for the following:
(i) Zn is not considered as transition element.
(ii) Transition metals form a large number of complexes.
(iii) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

2. (i) With reference to structural variability and chemical reactive write the differences between lanthanoids and actinoids.
(ii) Name a member of the lanthanoid series which is well known exhibit +4 oxidation state.
(iii) Complete the following equation:
$MnO_4^- + 8H^+ + 5e^- \longrightarrow$
(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why ? (Atomic numbers : Mn = 25, Cr = 24)

CBSE 2013

1. (i) Give reasons for the following.
(a) Mn^{3+} is a good oxidising agent.
(b) $E^0_{M^{2+}/M}$ values are not regular for first row transition metals (3d series).
(c) Although 'F' is more electronegative then 'O', the highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7.
(ii) Complete the following equations.
(a) $2CrO_4^{2-} + 2H^+ \longrightarrow$ (b) $KMnO_4 \xrightarrow{\text{Heat}}$

12 (II)

CBSE 2012

1. Complete the following chemical reaction equations.

(i) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow$ (ii) $MnO_4^- + NO_2^- + H^+ \longrightarrow$

2. How would you account for the following ?

(i) The $E^\circ_{M^{2+}/M}$ for copper is positive (0.34 V). Copper is the only metal in the first series of transition elements showing this behaviour.

(ii) The metallic radii of the third (5d) series of transition metals are nearly the same as those of the corresponding members of the second series (4d).

3. Explain the following observations

(i) Many of the transition elements are known to form interstitial compounds.

(ii) There is a general increase in density from titanium (Z = 22) to copper (Z = 39).

4. Explain each of the following observations :

(i) With the same d-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.

(ii) There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.

5. How would you account for the following Among lanthanoids, Ln (III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.

6. Explain the following observation

The members of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series.

CBSE 2011

1. Transition metals and their compounds generally exhibits a paramagnetic behaviour. Give reason.

2. Complete the following chemical equations

(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \longrightarrow$ (ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

3. State reasons for the following

(i) Cu(I) ion is not stable in an aqueous solution.

(ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3d-series of elements, the 4d and the 5d-series metals generally do not form stable cationic species.

4. Explain giving a suitable reason for each of the following.

(i) Transition metals and their compounds are generally found to be good catalysts.

(ii) Metal-metal bonding is more frequent for the 4d and 5d-series transition metals than that for the 3d-series.

5. What is meant by disproportion? Give two examples of disproportionation reactions in aqueous solution.

6. (i) Account for the following

(a) The transition metals and their compounds act as good catalysts.

(b) The lowest oxide of transition metal is basic, the highest is amphoteric/acid.

(c) A transition metal exhibits higher oxidation states in oxides and fluorides.

(ii) Describe the reactions involved in the preparation of $K_2Cr_2O_7$ from chromite ore.

7. What is meant by 'Lanthanoid contraction' ?

8. The chemistry of actinoids is not so smooth as that of lanthanoids. Give reason.

9. What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids ?

CBSE 2010

1. Explain the following observations.

(i) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.

(ii) Cu^+ ions is not known in aqueous solutions.

2. Account for the following

(i) The enthalpies of atomisation of the transition metals are high.

(ii) The lowest oxide of a transition metal is basic, the highest is amphoteric or acidic.

(iii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised.

3. (i) Complete the following chemical equations.

(a) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+(aq) \longrightarrow$

(b) $Cu^{2+}(aq) + I^-(aq) + H^+(aq) \longrightarrow$

(ii) 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^{2+} is a stronger reducing agent than Fe^{2+}.

4. (i) How does the acidified potassium permanganate solution react with

(a) iron (b) ions and (c) oxalic acid?

Write the ionic equations for the reactions.

(ii) Name the oxo metal anion of one of the transition metals in which the metal exhibits the oxidation state equal to the group number.

(iii) Account for the following

(a) Scandium (Z = 21) is regarded as a transition element but zinc (Z = 30) is not.

(b) E° (M^{2+}/M) value for copper is positive.

5. La^{3+} (Z = 57) and Lu^{3+} (Z = 71) do not show any colour in solutions.

6. Write the electronic configuration of Ce^{3+} ion, and calculate the magnetic moment of the basis of spin-only formula. (At. No. of Ce = 58)

CBSE 2009

1. Complete the following chemical reaction equations

(i) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \rightarrow$ (ii) $C_2O_4^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow$

2. How would you account for the following ?

(i) Many of the transition elements and their compounds can act as good catalyst.

(ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of corresponding members of the second series.

3. Give reasons for the following observations

(i) Of the d^4 species, Cr^{2+} is strongly reducing whereas manganese (III) is strongly oxidising.

(ii) The enthalpies of atomisation of the transition metal are quite high.

(iii) Interstitial compounds are well known for transition metals.

4. Describe the preparation of potassium dichromate from chromite ore with chemical equations involved. What is the effect of increasing pH on a solution of potassium dichromate.

5. (i) Describe the following characteristics of the first series of the transition metals and their trends in the series (Sc to Zn). (a) atomic radii (b) oxidation states (c) ionisation enthalpies

(ii) What is meant by disproportionating reaction? Give an example of disproportionation reaction in an aqueous solution.

6. What is lanthanoid contraction? List any two consequence of lanthanoid contraction.

EXERCISE-1

SOLUTION PREVIOUS YEARS BOARD PROBLEMS

D & F BLOCK

CBSE 2016

Sol.1 (a) (i) Ability of oxygen to form multiple bond .

(ii) Due to lanthanoid contraction.

(iii) Due to variable oxidation state/unpaired electrons

(b) (i) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

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

Sol.2 (i) Zn, because of not having partially filled d-orbital in its ground state or ionic state.

(ii) Cr

(iii) Cu

(iv) Mn, because Mn^{+2} has extra stability due to half filled d-orbital

CBSE 2015

Sol.1 (i) The large positive E^0 value for Mn^{3+} / Mn^{2+} shows that Mn^{2+} ($3d^5$ / half filled d orbital) is much more stable than Mn^{3+} Whereas Cr^{3+} ($t_{2g}^{\ 3}$) is more stable than Cr^{2+}

(ii) Due to d – d transition / due to presence of unpaired electrons in d – orbitals which absorb light in visible region

(iii) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

Sol.2 Due to comparable energies of ns & (n–1)d orbitals / due to presence of unpaired electrons in (n–1)d orbitals.

In transition elements, oxidation states differ from each other by unity whereas in case of p- block elements, the oxidation states differ by units of two / In transition elements, the higher oxidation states are more stable for heavier elements in a group. In p – block elements, the lower oxidation states are more stable for heavier members due to inert pair effect. **(Any one difference)**

CBSE 2014

Sol.1 (a) (i) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

(ii) $MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$

(b) (i) Zn, cannot be classified as transition elements because these have completely filled d-subshell. In their ground state as well as in their common oxidation state.

(ii) Due to high nuclear charge presence of vacant d-orbital and variable oxidation state it have great tendency to from complex.

(iii) Due to high sum of first two consquetive ($IP_1 + IP_2$).

Sol.2 (i) In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided.

(ii) Ce^{+4}

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

(iv) Mn^{+3} due to four unpaired electron in their 3d orbital.

CBSE 2013

Sol.1 (a) Mn^{3+}

(i) Mn → At. No. is 25

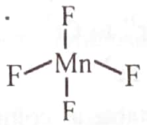
Mn $3d^5 4s^2$

Mn^{3+} is $3d^4 4s^0$

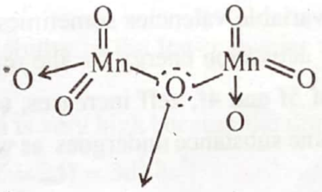
So it has tendency to accept one electron and undergo reduction because it will cause stable half filled configuration. Hence it can act as an oxidizing agent.

(ii) E° values are a function of many factors like electronic configuration of reactants and products. temperature, sizes of ions, hydration energy, sublimination and ionization energies etc so there is no uniform order expected as size also varies in an unexpected fashion.

(iii) This is because F can form only one bond and structure of MnF_4 is which is which is tetrahedral but



In Mn_2O_7 as 0 is present which can form 2σ bonds or 1σ and 1π bond so 0 can be present in between two Mn atoms giving it a structure.



Such budge cannot be formed by F

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

Chromate dichromate

(ii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

CBSE 2012

Sol.1 (i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

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

Sol.2 (ii) B'coz of high atomisation and low hydration enthalpy.

(iii) Poor shielding effect of 4f electrons known as L_n contraction.

Sol.3 (i) The compound in which small atoms like H,C,N etc. Occupy interstitial sites in the crystal lattice are calied interistitial compounds. These compunds are well known for transition metals because small atoms can easily occupy the positions in the voids present in the crystal lattices of transition metals.

(ii) Due to decrieasing atomic size mass per unit volume increase hence, density increases.

Sol.4 (i) It can be exaplained on the basis of E° values of Cr^{3+} / Cr^{2+} (−0.4 V) and Mn^{3+} / Mn^{2+} (+1.5 V). On the basis of these values, it is clear that Cr^{2+} has a great tendency to oxidise into Cr^{3+}, thus it acts as reducing agent.

$Cr^{2+} (aq) \rightarrow Cr^{3+} (aq) + e^-$

While Mn^{3+} has a great tendency to reduce into Mn^{2+} thus it acts as an oxidising agent

$Mn^{3+} (aq) + e^- \rightarrow Mn^{2+} (aq)$

(ii) Due to increasing nuclear charge this is compensenet sheilding effect.

Sol.5 This irregularity arises mainly from the extrastability of empty, halffilled or filled f subshell.

Sol.6 Actinoids show a large number of oxidation states because of small energy gap between 5f, 6d and 7s subshells.

CBSE 2011

Sol.1 Transition metal's have one or more unpaired electron. so, they are paramagnetic in nature.

Sol.2 (i) $8\,MnO_4^-(aq) + 3\,S_2O_3^{2-}(aq) + H_2O(l) \rightarrow 8\,MnO_2 + 6\,SO_4^{2-} + 2\,OH^-$

(ii) $Cr_2O_7^{2-}(aq) + 6\,Fe^{2+}(aq) + 14\,H^+(aq) \rightarrow 2\,Cr^{3+} + 6Fe^{3+} + 7H_2O$

Sol.3 (i) Cu^+ in aqueous solution undergoes disproportionation i.e.,

$$2\,Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

The E° value for this is favourable.

(ii) Cr^{2+} is stronger reducing agent than Fe^{2+}

Reason : $d^4 \rightarrow d^3$ occurs in case of Cr^{2+} to Cr^{3+}

But $d^6 \rightarrow d^5$ occurs in case of Fe^{2+} to Fe^{3+}

In a medium (like water) d^3 is more stable as compared to d^5.

Sol.4 (i) Many transition metals and their compounds are used as catalyst. Their activity is due to their ability to adopt multiple oxidation states and to form complexes.

Transition metals because of their variable valencies sometimes form unatable intermeatiate compounds and provide a new path with lower activation energy for the reaction.

(ii) due to poor sheilding effeact of 5f and 4f, zeff increases, so they form synergic bonding.

Sol.5 In a disproportionation reactions, Same substance undergoes as well as reduction resulting in the formation of two different products.

$$2\,Cu^+_{(eq)} \longrightarrow Cu^{2+} + Cu_{(s)}$$

Sol.6 (i)

(a) Many transition metals and their compounds are used as catalyst. Their activity is due to their ability to adopt multiple oxidation states and to form complexes.

Transition metals because of their variable valencies sometimes form unatable intermeatiate compounds and provide a new path with lower activation energy for the reaction.

(b) The lower oxides liberate hydsoxyl ion in eqouos solution while intarmediation librate both hydroxyl ion and H^+ ion in eqouos solution.

(c) Due to high electronegativity of oxygen and flearine.

(ii) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow Fe_2O_3 + 8NaCr2O4 + 8CO2$

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

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

Sol.7 The overall decrease in atomic and ionic radil from Lanthanum to Lutetium is a unique feature in the chemistry of the Lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements.

Sol.8 Lanthanodies show a number of other oxidation states also like Uranium and plutonium show +3, +4, +5 and +6, nepfunium shown +3, +4, +5 and +7. This is due to small energy difference, between 5f, 6d and 7s subshells of acfinoids.

Sol.9 Due to the poor shielding effect of 4f- electrons, the nucleus increases and hence, radius decreases.

(i) Baisc nature of oxides and hydrosides decreases.

(ii) Similarity in atomic radii

(iii) Separation of lanthanoids

CBSE 2010

Sol.1 (ii) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.

(iii) Cu^+ ion is not known in aqueous solutions.

Sol.2 (i) Strong interatomic interaction due to anpaired electrons. Greafer the number of unpaired electrons, stronger is the resultant bonding.

(ii) The lower oxides liberate hydsoxyl ion in eqouos solution while intarmediation librate both hydroxyl ion and H^+ ion in eqouos solution.

(iii) Cabalt (III) ion has oreater tendency to form complexes than cabalt (II) ion.

Sol.3 (a) (i)$Cr_2O_7^{2-}$ (aq) + 3 H_2S (g) + 8 H^+ (aq) → 2 Cr^{3+} (aq) + 7 H_2O (i) + 3S (s)

(ii)$2Cu^{2+}$ (aq) + 4 I^- (aq) → Cu_2 I_2 (s) + I_2(g)

(b) (i) This is due to the increasing stability of the lower species to which they are produced.

(ii)Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled 3d orbitals [$\because$ Mn (Z = 25) = $3d^5$ $4s^2$]

(iii) Since E° (Cr^{3+} / Cr^{2+}) is negative (-0.41V) whereas E° (Fe^{3+} / Fe^{2+}) is positive (+0.77 V). Thus Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. hence Cr^{2+} is stronger reducing agent thatn Fe^{2+}.

Sol.4 (i) (a) $16H^+ + 2MnO_4^- + 5Fe \longrightarrow 5Fe^{2+} + 2Mn^{2+} + 8H_2O$

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

(c) $2MnO_4^- + 5SO_2 + 7H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 14H^+$

(ii) $Cr_2O_7^{2-}, MnO_4^-$

(iii) (a) Zn have fullfilled d^{10} configuration in goo and state as well as common oxidation state.

(b) B'coz of high atomisation and low hydration enthalpy.

Sol.5 Because they have empty outer most shell.

Sol.6 Ce^{3+} = 4f'

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

$$\mu = \sqrt{1(1+2)} = 1.73 BM$$

CBSE 2009

Sol.1 (i) $2MnO_4^- (aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(\ell) + 10CO_2(g)$

(ii) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(\ell)$

Sol.2 (i) Transition element are good catalysts because they posess variable oxidation state and can from intermediated compounds with most of the reaction. Furthermore it is also attributed to the penultimate partially filled d-subshell possed by them.

e.g : Role of V_2O_5 in the manufacture of sulphuric acid by contact process.

$SO_2 + V_2O_5 \rightarrow V_2O_4 + SO_3$

$2V_2O_4 + O_2 \rightarrow 2V_2O_5$

(ii) This is due to the intervention of the 4f orbitals which must be filled before the 5d series of element begin. The filling of 4f before 5d orbitals results in regular decrease in atomic radii called Lanthanoid contraction.

Sol.3 (i) It can be exaplained on the basis of E° values of Cr^{3+} / Cr^{2+} (–0.4 V) and Mn^{3+} / Mn^{2+} (+1.5 V). On the basis of these values, it is clear that Cr^{2+} has a great tendency to oxidise into Cr^{3+}, thus it acts as reducing agent.

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(ii) Strong interatomic interaction due to anpaired electrons. Greafer the number of unpaired electrons, stronger is the resultant bonding.

(iii) The compound in which small atoms like H,C,N etc. Occupy interstitial sites in the crystal lattice are calied intersititial compounds. These compunds are well known for transition metals because small atoms can easily occupy the positions in the voids present in the crystal lattices of transition metals.

Sol.4 $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow Fe_2O_3 + 8NaCr2O4 + 8CO2$

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

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

Sol.5 (i) (a) In a given series, radii decrease with increasing atomic numbers.

(b) These elements exhibit variable oxidation states.

e.g. Cu shows two oxidation state (+1 and +2) and Mn shows oxidation states from +2 to +7.

(c) Due to an increase in nuclear charge which accompanies the filling of inner d-orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right.

(ii) In a disproportionation reactions, Same substance undergoes as well as reduction resulting in the formation of two different products.

$2\ Cu^+_{(eq)} \longrightarrow Cu^{2+} + Cu_{(s)}$

Sol.6 Due to the poor shielding effect of 4f- electrons, the nucleus increases and hence, radius decreases.

(i) Baisc nature of oxides and hydrosides decreases.

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