

Solution

D AND F BLOCK ELEMENTS

Class 12 - Chemistry

1. (d) K_2MnO_4
Explanation:
 K_2MnO_4
2. (c) Mn_2O_7
Explanation:
In Mn_2O_7 , each Mn is tetrahedrally surrounded by oxygen including Mn-O-Mn bridge.
3. (c) $\frac{2}{5}$
Explanation:
The following reaction takes place when $KMnO_4$ reacts with sulphide ions in acidic medium. 2 moles of $KMnO_4$ reacts with 5 moles of sulphide ions, so $\frac{2}{5}$ moles of $KMnO_4$ reacts with 1 mole of sulphide ions.
 $5S^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$
4. (a) Fe and Mg
Explanation:
Haemoglobin contains Fe and Chlorophyll contains Mg.
5. (a) $Cr_2O_7^{2-}$
Explanation:
Chromate ion (CrO_4^{2-}) changes to dichromate ion ($Cr_2O_7^{2-}$) on acidification.
 $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
6. (b) Cd^{2+}
Explanation:
The atomic number of Ag is 47 with an electronic configuration of $[Kr] 4d^{10} 5s^1$ whereas for Cd, the atomic number is 48 and electronic configuration is $[Kr] 4d^{10} 5s^2$. Ag^+ is isoelectronic with Cd^{2+} , since the electronic configuration of both of them is $[Kr] 4d^{10}$.
7. (a) 6
Explanation:
 $N_1V_1 = N_2V_2$
This equation can also be written as:
 $N_1 \times \text{no. of moles of 1} = N_2 \times \text{no. of moles of 2}$
As per the question, N_1 (n factor of $KMnO_4$) = 5 and N_2 (n factor of ferrous oxalate) = 3
Also no. of moles of 2 = 10
Substituting the values we get,
 $= 5 \times \text{no. of moles of 1} = 3 \times 10$
no. of moles of 1 = 6
Thus, **6 moles** of $KMnO_4$ are required in an acidic medium to oxidise 10 moles of ferric oxalate.

8. **(b) Tm**
Explanation:
 Tm (Thulium) is a lanthanoid series.
9. **(d) V^{3+} , V^{2+} , Fe^{3+}**
Explanation:
 V^{3+} , V^{2+} , Fe^{3+} ions exhibit specific colours.
 Electronic configuration of V^{2+} - $[Ar]3d^3$.
 Electronic configuration of V^{3+} - $[Ar]3d^2$.
 Electronic configuration of Fe^{3+} - $[Ar]3d^5$.
 Since these ions have partially filled d-subshells, they exhibit colour.
 Electronic configuration of Sc^{3+} - $[Ar]3d^0$
 Since d subshell is empty, it shows no colour.
 Electronic configuration of Ti^{4+} - $[Ar]3d^0$
 Since d subshell is empty, it shows no colour.
 Electronic configuration of Mn^{2+} $[Ar]3d^4$
 Since d subshell is partially filled, it shows colour.
 Electronic configuration of Ni^{4+} $[Ar]3d^8$
 Since d subshell is partially filled, it shows colour.
 Electronic configuration of Zn^{2+} - $[Ar]3d^{10}$
 Since d subshell is full, it shows no colour.
10. **(a) +3**
Explanation:
 +3 is most common and stable oxidation state
11. a. Transition metals form complex compounds due to small size, high ionic charge and availability of d-orbital.
 b. E^0 values for (Zn^{2+}/Zn) and (Mn^{2+}/Mn) are more negative than expected due to stable $3d^{10}$ configuration in Zn^{2+} and $3d^5$ configuration in Mn^{2+} .
 c. Actinoids show wide range of oxidation states due to comparable energies of 5f, 6d and 7s orbitals.
12. i. Silver has incompletely filled d-orbitals / d^9 configuration in +2 oxidation state.
 ii. Mn^{2+} and Zn^{2+} has stable half-filled and fully filled configurations / relatively less sublimation enthalpy of Mn and Zn.
 iii. Because of similar atomic radii.
13. Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidizing agent like KNO_3 . This produces dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.
 $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$
 $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$
 i. $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
 ii. $2KMnO_4 + 2H_2O + 5SO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$
 iii. $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$
14. i. Due to almost similar / comparable atomic radii.
 ii. Weak metallic bonding / no unpaired electrons / weak interatomic interaction.
 iii. The ability of oxygen to form multiple bonds with metals while F cannot.
15. a. Transition metal atoms have large number of unpaired electrons. More is the number of unpaired electron, more stronger is the metallic bonding and hence due to strong metallic bonding these elements have high enthalpy of atomization.
 b. Ce (IV) has extra stability due to noble gas configuration.

- c. E^0 value of $\text{Mn}^{3+} / \text{Mn}^{2+}$ is highly positive as d^4 in Mn^{3+} has tendency to get converted to stable d^5 configuration of Mn^{2+} by accepting an electron. While Fe^{3+} ($3d^5$) already has stable configuration so has less tendency to get converted Fe^{2+} .
- d. Due to high enthalpy of hydration of $\text{Cu}^{2+}(\text{aq})$ than $\text{Cu}^+(\text{aq})$ which compensates for second ionization enthalpy of copper. Cu^{2+} is more stable than Cu^+ .
- e. In the third transition series after lanthanum, there is lanthanoid contraction, due to ineffective shielding by intervening f-orbital electrons and hence second and third transition series elements have similar atomic radii.
16. a. i. MnO_4^{2-} ions disproportionate in acidic medium to give permanganate ions and manganese oxide.
- $$3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$$
- ii. Lanthanum sulphide if formed.
- $$2\text{La} + 3\text{S} \xrightarrow{\text{heat}} \text{La}_2\text{S}_3$$
- b. i. Copper has high enthalpy of atomisation and low enthalpy of hydration, thus the high energy is required to transform $\text{Cu}(\text{s})$ to $\text{Cu}^{2+}(\text{aq})$ which is not balanced by hydration enthalpy, therefore $E^0\left(\frac{M^{2+}}{M}\right)$ value for copper is positive (+0.34 V)
- ii. Cr^{2+} is reducing as its configuration changes from d^4 to d^3 , the latter having more stable half filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results an extra stable d^5 configuration.
- iii. This is due to the increasing stability of the species of lower oxidation state to which they are reduced.
17. i. Sc^{3+} does not have unpaired electron and has empty d-orbitals therefore, cannot undergo d-d transition hence its salts are white.
- ii. It is due to lanthanoid contraction, which is due to poor shielding effect of 5 d and 4f electrons effective nuclear charge increases, hence ionization energy of 5 d transition elements is more than that of 3d and 4d transition elements in respective groups.
18. a. Actinoids show wide range of oxidation states/most of them are radioactive elements therefore chemistry of actinoid is complicated as compare to lanthanoid.
- b. $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
- Oxidation state of Mn increases from +6 to +7 (oxidation) and decreases from +6 to +4 (reduction)/Mn undergoes increase and decrease in oxidation state simultaneously.
- c. Due to the presence of a greater number of unpaired electrons which leads to strong interatomic metal-metal bonding whereas Mn with a stable half-filled d^5 configuration has a weaker metallic bond.
19. i. **Electronic configuration:** In 1st transition series, 3d orbitals are progressively filled whereas in second transition series, 4d orbitals are progressively filled and in 3rd transition series 5d-orbitals are progressively filled.
- ii. **Oxidation states:** Elements show variable oxidation states in both the series. The highest oxidation state is equal to total number of 's' as well as 'd' orbitals. The number of oxidation states shown are less in 5d transition series than 4d series. In 3d series +2, +3 oxidation states are common and they form stable complexes in these oxidation states. In other series OsO_4 and PtF_6 are formed which are quite stable in higher oxidation state.
- iii. **Ionisation enthalpies:** The ionization enthalpy of 5d series is higher than 3d and 4d series due to lanthanoid contraction, effective nuclear charge increases.
- iv. **Atomic size:** The atomic size of 4d and 5d series do not differ appreciably due to lanthanoid contraction. The atomic radii of second and third series are larger than 3d series.