(Chapter 8)(The d and f Block Elements)

XII

Intext Questions

Question 8.1:

Silver atom has completely filled *d* orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Answer

Ag has a completely filled 4*d* orbital ($4d^{10}\,5s^1$) in its ground state. Now, silver displays two oxidation states (+1 and +2). In the +1 oxidation state, an electron is removed from the *s*-orboital. However, in the +2 oxidation state, an electron is removed from the *d*-orbital. Thus, the *d*-orbital now becomes incomplete ($4d^9$). Hence, it is a transition element.

Question 8.2:

In the series Sc (*Z* = 21) to Zn (*Z* = 30), the enthalpy of atomization of zinc is the lowest, i.e., 126 kJ mol^{-1}. Why?

Answer

The extent of metallic bonding an element undergoes decides the enthalpy of atomization. The more extensive the metallic bonding of an element, the more will be its enthalpy of atomization. In all transition metals (except Zn, electronic configuration: $3d^{10}\,4s^2$), there are some unpaired electrons that account for their stronger metallic bonding. Due to the absence of these unpaired electrons, the inter-atomic electronic bonding is the weakest in Zn and as a result, it has the least enthalpy of atomization.

Question 8.3:

Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?

Answer

Mn (Z = 25) = $3d^5\,4s^2$

Mn has the maximum number of unpaired electrons present in the *d*-subshell (5 electrons). Hence, Mn exhibits the largest number of oxidation states, ranging from +2 to +7.

Question 8.4:

The $E^{\theta}(M^{2+}/M)$ value for copper is positive (+0.34V). What is possibly the reason for this? (Hint: consider its high $\Delta_a H^{\theta}$ and low $\Delta_{hyd} H^{\theta}$)

Answer

The $E^{\theta}(M^{2+}/M)$ value of a metal depends on the energy changes involved in the following:

1. Sublimation: The energy required for converting one mole of an atom from the solid state to the gaseous state.

$$M_{(s)} \longrightarrow M_{(g)} \qquad \Delta_s H \text{(Sublimation energy)}$$

2. Ionization: The energy required to take out electrons from one mole of atoms in the gaseous state.

$$M_{(g)} \longrightarrow M^{2+}_{(g)} \qquad \Delta_i H \text{(Ionization energy)}$$

3. Hydration: The energy released when one mole of ions are hydrated.

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

Now, copper has a high energy of atomization and low hydration energy. Hence, the $E^{\theta}(M^{2+}/M)$ value for copper is positive.

Question 8.5:

How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

Answer

Ionization enthalpies are found to increase in the given series due to a continuous filling of the inner *d*-orbitals. The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as d^0, d^5, d^{10}. Since these states are exceptionally stable, their ionization enthalpies are very high.

In case of first ionization energy, Cr has low ionization energy. This is because after losing one electron, it attains the stable configuration ($3d^5$). On the other hand, Zn has exceptionally high first ionization energy as an electron has to be removed from stable and fully-filled orbitals ($3d^{10}\ 4s^2$).

Second ionization energies are higher than the first since it becomes difficult to remove an electron when an electron has already been taken out. Also, elements like Cr and Cu have exceptionally high second ionization energies as after losing the first electron, they have attained the stable configuration (Cr^+: $3d^5$ and Cu^+: $3d^{10}$). Hence, taking out one electron more from this stable configuration will require a lot of energy.

Question 8.6:

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

Answer

Both oxide and fluoride ions are highly electronegative and have a very small size. Due to these properties, they are able to oxidize the metal to its highest oxidation state.

Question 8.7:

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

Answer

The following reactions are involved when Cr^{2+} and Fe^{2+} act as reducing agents.

$Cr^{2+} \longrightarrow Cr^{3+}$ $Fe^{2+} \longrightarrow Fe^{3+}$

The $E^\circ_{Cr^{3+}/Cr^{2+}}$ value is −0.41 V and $E^\circ_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+} can be easily oxidized to Cr^{3+}, but Fe^{2+} does not get oxidized to Fe^{3+} easily. Therefore, Cr^{2+} is a better reducing agent that Fe^{3+}.

Question 8.8:

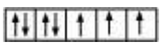
Calculate the 'spin only' magnetic moment of $M^{2+}_{(aq)}$ ion (Z = 27).

Answer

Z = 27

$\Rightarrow$ [Ar] $3d^7\ 4s^2$

$\therefore M^{2+}$ = [Ar] $3d^7$

$3d^7$ = 

i.e., 3 unpaired electrons

$\therefore n = 3$

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

$$\Rightarrow \sqrt{3(3+2)} = \mu$$

$$\Rightarrow \sqrt{15} = \mu$$

$\mu \approx 4$ BM

Question 8.9:

Explain why Cu^{+} ion is not stable in aqueous solutions?

Answer

In an aqueous medium, Cu^{2+} is more stable than Cu^{+}. This is because although energy is required to remove one electron from Cu^{+} to Cu^{2+}, high hydration energy of Cu2+ compensates for it. Therefore, Cu^{+} ion in an aqueous solution is unstable. It disproportionates to give Cu^{2+} and Cu.

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

Question 8.10:

Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Answer

In actinoids, 5*f* orbitals are filled. These 5*f* orbitals have a poorer shielding effect than 4*f* orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more that that experienced by lanthanoids. Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.