Some Solved Problems on Werner's Theory

Example-1. Given the following information,

Compound	Number of chloride ions precipitated
$PtCl_2 \cdot 4NH_3$	2
$PtCl_2 \cdot 3NH_3$	1
$PtCl_2 \cdot 2NH_3$	0

Write balanced equations for the reaction of theses compounds with silver nitrate.

Soln. The compound $PtCl_2 \cdot 4NH_3$ has two ionizable chlorines. It may be represented as $[Pt(NH_3)_4]Cl_2$ and its reaction with silver nitrate may be written as,

$$[Pt(NH_3)_4]Cl_2 + 2AgNO_3 \rightarrow [Pt(NH_3)_4](NO_3)_2 + 2AgCl$$

There is only one ionizable chlorine in $PtCl_2 \cdot 3NH_3$ compound. Its composition, $[Pt(NH_3)_3Cl]Cl$ indicates the presence of one chloride ion in the ionization sphere.

$$[Pt(NH_3)_3Cl]Cl + AgNO_3 \rightarrow [Pt(NH_3)_3Cl](NO_3) + AgCl$$

The fact that there are no ionizable chlorines in $PtCl_2 \cdot 2NH_3$ implies that there is no primary sphere in this complex. Accordingly, its composition is $[Pt(NH_3)_2Cl_2]$.

$$[Pt(NH_3)_2Cl_2] + AgNO_3 \rightarrow \text{No Reaction}$$

Example-2. A solution containing 2.674 g of $CoCl_3 \cdot 6NH_3$ was passed through a cation exchanger. The eluted solution gave 4.305 gram precipitate of silver chloride with silver nitrate solution. Determine the composition of the complex in accordance with Werner theory (Mass number of Ag = 108, Cl = 35.5; Molecular mass of $CoCl_3 \cdot 6NH_3$ = 267.4).

Soln. The passage of the solution of $CoCl_3 \cdot 6NH_3$ through the cation exchanger yields those chloride ions free which constitute the ionization sphere. These chloride ions react with silver nitrate, giving precipitates of silver chloride. The amount of silver chloride is indicative of the number of chloride ions in primary sphere. If three moles of silver chloride are obtained from one mole of $CoCl_3 \cdot 6NH_3$, then there are three chloride ions in ionization sphere. If two moles of silver chloride are obtained, there are two ionizable chlorines and if one mole of silver chloride is precipitated there is only one ionizable chlorine.

Mass of $CoCl_3 \cdot 6NH_3$ = 2.674 g

Molecular mass of $CoCl_3 \cdot 6NH_3$ = 267.4

Number of moles of $CoCl_3 \cdot 6NH_3$ = $\frac{2.674}{267.4} = 0.01$

Mass of silver chloride = 4.305 g

Molecular mass of silver chloride = 143.5

Number of moles of silver chloride = $\frac{4.305}{143.5} = 0.03$

Ratio between number of moles of $CoCl_3 \cdot 6NH_3$ to silver chloride = 1 : 3.

This means that there are three chloride ions in the ionization sphere of $CoCl_3 \cdot 6NH_3$. According to Werner theory, its composition may be represented as $[Co(NH_3)_6]Cl_3$. Its reaction with silver nitrate may be indicated as follows:

$$\underset{1\text{ mole}}{[Co(NH_3)_6]Cl_3} + 3AgNO_3 \longrightarrow [Co(NH_3)_6](NO_3)_3 + \underset{3\text{ moles}}{3AgCl}$$

Example-3. Using the following information, establish the correct structure of the complexes.

Compound	Molar conductivity	Cryoscopic measurements
$Co(NO_2)_3 \cdot KNO_2 \cdot 2NH_3$	2 charges	2 particles
$Co(NO_2)_3 \cdot 2KNO_2 \cdot NH_3$	4 charges	3 particles
$Co(NO_2)_3 \cdot 3KNO_2$	6 charges	4 particles

Soln. On the basis of molar conductivity and cryoscopic measurement data, the structure of—

$Co(NO_2)_3 \cdot KNO_2 \cdot 2NH_3$ is $K[Co(NH_3)_2(NO_2)_4]$

$Co(NO_2)_3 \cdot 2KNO_2 \cdot NH_3$ is $K_2[Co(NH_3)(NO_2)_5]$

$Co(NO_2)_3 \cdot 3KNO_2$ is $K_3[Co(NO_2)_6]$

Example-4. One mole of a pink solid (X), having empirical formula, $CoCl_3 \cdot 5NH_3 \cdot H_2O$ gives three moles of silver chloride on treatment with excess of silver nitrate solution. On heating, X loses a molecule of water to give a purple solid (Y) which has the same NH_3 : Cl : Co ratio. Deduce the structures of X and Y.

Soln. Since three moles of silver chloride are obtained from one mole X, it implies that all the three chlorines are a part of ionization sphere. The structure of X may, therefore, be represented as $[Co(NH_3)_5(H_2O)]Cl_3$.

$$\underset{1\text{ mole}}{[Co(NH_3)_5(H_2O)]Cl_3} + 3AgNO_3 \longrightarrow [Co(NH_3)_5(H_2O)](NO_3)_3 + \underset{3\text{ moles}}{3AgCl}$$

On heating, X loses a water molecules from the coordination sphere. In order to retain the coordination number, one of the chlorines from primary sphere enters the coordination sphere, to give purple colored Y.

$$\underset{\text{X (Pink)}}{[Co(NH_3)_5(H_2O)]Cl_3} \xrightarrow{\text{Heat}} \underset{\text{Y (Purple)}}{[Co(NH_3)_5Cl]Cl_2} + H_2O$$

X and Y have the same NH_3 : Cl : Co ratio.