PG- I Semester

Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR

B. R. A. BIHAR UNIVERSITY

Dr. Priyanka

TOPIC:- METAL-LIGAND EQUILIBRIA IN SOLUTION.

Unit - 8 METAL-LIGAND EQUILIBRIA IN SOLUTION

INTRODUCTION

Generally complexes are designated as stable or unstable. The general meaning of stability is supposed to be related with the concept, whether a particular complex can be converted into other easily or not. As a matter of fact, this is kinetic aspect of stability; which deals with the rate of the reaction and its mechanism. The other aspect of stability is thermodynamic aspect. In which stability of a complex is related with the amount of energy released during its formation or the amount of energy required to break it.

In this unit we describe complex forming equilibria in solution and the various factors affecting it. We will also discuss the various factors affecting stability constants for the formation of complexes in solution. In the end of the unit we shall describe the method used for determining stability constants of the complexes formed in solution. Which involves quantitative characterisation of the complex-forming reaction in solution.

You may recall what you have already studied about the basic concept of chemical equilibria in solution.

OBJECTIVES

The main aim of this unit is to study the complex formation equilibria in solution. After going through this unit you should be able to:

- describe stepwise and overall formation constants;
- explain thermodynamic importance of stability constants;
- discuss factors affecting stability of complexes; and
- describe methods of determining stability constants for binary complexes in solution.

STEP-WISE AND OVERALL FORMATION CONSTANTS.

The term stability is a loose term, when the term stability is used without qualification, it means that the complex exists and under suitable conditions, it may be stored for a long time. The term can not be generalised for complexes. A complex may be quite stable to one reagent and may decompose readily in presence of another reagent.

In studying the formation of complexes in solution, two types of stability of complexes is found:

1. **Thermodynamic Stability**

   This is a measure of the extent of which the complex will form or will be transformed into another species under certain conditions, when the system has reached in equilibrium. When we are concerned with this type of stability, we deal with metal-ligand bond energies, stability constant etc.

2. **Kinetic Stability**

   This refers to the speed with which transformation leading to the attainment of equilibrium will occur. When we are interested in kinetic stability for complex ions in solutions, we deal with rates and mechanism of chemical reactions. These reactions may be substitution, isomerisation, recemisation and electron or group transfer reactions. In the kinetic sense, it is more proper to call the complexes inert or labile complex rather than stable or unstable complex. The complexes in which the ligands are rapidly replaced by others are called labile, while those in which substitution occurs slowly are called inert complexes.

Stepwise and Overall Formation Constants

According to J. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex MLn may be supposed to take place by the following n consecutive steps.

where M = central metal cation

L = monodentate ligand

n = maximum co-ordination number for the metal ion M for the ligand

$$M + L \leftrightarrows ML \quad K_1 = \frac{(ML)}{[M][L]}$$

$$ML \leftrightarrows ML_2 \quad K_2 = \frac{(ML_2)}{[ML][L]}$$

$$ML_2 \leftrightarrows ML_3 \quad K_3 = \frac{(ML_3)}{[ML_2][L]}$$

Thus $$ML_{n-1} + L \leftrightarrows ML_n \quad K_n = \frac{(ML_n)}{[ML_{n-1}][L]}$$

The equilibrium constants, K_1, K_2, K_3, ... K_n are called **stepwise stability constants.**

The formation of the complex MLn may also be expressed by the following steps and equilibrium constants.

$$M + L \xrightarrow{\beta_1} ML, \quad \beta = \frac{(ML)}{[M][L]}$$

$$M + 2L \xrightarrow{\beta_2} ML_2, \quad \beta_2 = \frac{(ML_2)}{[M][L]^2}$$

Thus $$M + nL \xrightarrow{\beta_n} MLn, \quad \beta_n = \frac{(MLn)}{[M][L]^n} \quad ....(8.1)$$

The equilibrium constants, β_1, β_2, β_3, ... β_n are called overall formation or **overall stability constant**s. βn is called as nth overall (or cumulative) formation constant or overall stability constants.

The higher the value of stability constant for a complex ion, the greater will be its stability. Alternatively 1/k values sometimes are called instability constant.

Stepwise and cumulative stability constants are also expressed as $\log_{10}K_1$, $\log_{10}K_2$............... $\log_{10}K_n$ and $\log_{10}\beta_n$ respectively.

Relationship or Interaction Between βn and K_1, K_2, K_3, K_n

K's and β's are related to one another consider for example, the expression for β_3 is:-

$$\beta_3 = \frac{(ML_3)}{[M][L]3}$$

On multiplying both numerator and denominator by [ML] [ML_2] and on rearranging we get:

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$= \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]}$$

$$= K_1 \times K_2 \times K_3$$

$$\text{Thus } \beta_n = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \ldots\ldots\ldots\ldots \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= K_1 \times K_2 \ldots\ldots\ldots K_n$$

$$\text{or } \beta_n = \sum_{n=1}^{n=n} K_n$$

From above relation, it is clear that the overall stability constant β_n is equal to the product of the successive (i.e. stepwise) stability constants, K_1, K_2, K_3, K_n. This in other words means that the value of stability constants for a given complex is actually made up of a number of stepwise stability constants.