

Program Bachelor of Science., Third year subject chemistry  
Semester 6 paper code CHC 109, Paper title Inorganic chemistry.

Myself, Mrs Deepa Audi Assistant professor from Dhempe College of Arts and Science will be presenting for the module. Stability, constant instability, constant, and relationship between free energy change an overall formation constant from the Unit 3 titled Reaction kinetics and mechanism.

The outline of this module are stability of complexes, instability, constant, overall formation, constant, and thermodynamic aspects of stability.

The learning outcomes of this module are to elaborate the terms stability, constant instability, constant, an overall formation, constants. To derive the relationship between overall formation constant and free energy change.

Let us consider the formation of a complex with the formula  $ML_n$ . Metal M reacts with N number of ligands L and the reaction proceeds via equilibrium reaction to form the complex  $ML_n$ , where n is the coordination number of the metal M in the complex.

The stability refers to the extent of association between the metal and the ligand, and so, in other words, stability also refers to the extent to which the complex is being formed from the metal and ligands.

So stability is a measure of the strength of the metal ligand bond.

Let us consider the formation of Tetra amine cupric ion. Cupric ion reacts with four ammonia ligands.

The equilibrium reaction forming Tetra amine cupric ion

Applying the laws of mass action to this equilibrium reaction, we can write the equilibrium constant K, which is a ratio of the molar concentration of tetramine cupric ion to the product of the molar concentration of cupric ion and four ammonia ligands.

This equilibrium constant is termed as this stability constant or the formation constant cause it is a measure of the complex formation reaction. Now let us consider the dissociation of the same complex giving the metal ion and four ammonia ligands so tetramine cupric ion undergoes dissociation giving cupric ion and four ammonia ligands.

Applying the laws of mass action, we can write an equilibrium constant K which is a ratio of the product of the molar concentration of cupric ion and four ammonia ligands to the molar concentration of Tetra amine cupric ion.

In this case, the equilibrium constant is called as the instability constant or the dissociation constant because it is being written for a complex dissociation reaction, so it is a measure of the complex instability, so it is also termed as the instability constant. The instability constant is related to the stability constant by the relation .

The instability constant is the reciprocal of stability constant, so smaller the value of the instability or the dissociation constant, greater is the stability of the complex because if the instability constant has a smaller value, It indicates the complex has not undergone dissociation to a large extent.

In this slide, 2 examples have been cited, one is tetrammine cupric ion and the 2nd is hexamine cobalt ion. The first complex has dissociation constant value of  $10^{-12}$  and the second hexamine cobalt (III) ion has a dissociation constant of  $6.2 \times 10^{-36}$ , which is a lower value. So the cobalt complex is much more stable than the copper complex.

Now let us write an equilibrium reaction for the complex formation of  $ML_n$ , which proceeds via equilibrium reaction between metal M and n number of ligands L.

A complex formation reaction constant can be written as indicated by  $\beta_n$ , which is a ratio of the molar concentration of complex  $ML_n$  and the product of the molar concentration of the metal M and n number of ligands L. In this case, the stability constant is termed as overall formation constant because the entire complex is being indicated to be formed in a single step.

We know that the coordination number of metal in complexes ranges from as low as one to as high as eight and even 12. Now the complex formation can be written in a single step in which the metal reacts with n number of ligands molecule, forming the final complex. So the overall formation reaction constant can be returned for each of these reactions in which it is a ratio of the molar concentration of the product complex to the product of the molar concentration of the metal M and n number of ligands L.

So it has been written for coordination numbers right from 1 to 6.

Let us take one example, the last example, which indicates that metal M reacts with six ligand molecule. The reaction proceeds via equilibrium one forming the product, complex  $ML_6$ , writing the overall formation constant  $\beta$  for this particular reaction. It is a ratio of the molar concentration of complex  $ML_6$  to the product of molar concentration of metal M and six ligands. So in general also we can write it for a complex  $ML_n$ , which is written as  $\beta_n$  which is the ratio of molar concentration of the complex  $ML_n$  to the product of the molar concentration of metal M and n number of ligands L.  $\beta_n$  is the nth overall formation or stability constant. Since the value of the formation constant gives a measure to which or the extent to which the complex formation has taken place, so the formation constant is also a measure of this stability constant. Now we need to relate this formation constant to the other thermodynamic variables of this system. When the complex formation is being taking place. So we shall discuss the relationship between the free energy change, and overall formation constant. The standard free energy change as indicated by  $\Delta G$  is related to the overall formation constant  $\beta$  by the relation  $\Delta G$  is equal to minus 2.303 RT log to the base 10 beta where R is the gas constant, T is the absolute temperature and beta is the overall formation constant.  $\Delta G$  is the standard free energy change.

Now, this standard free energy change is related to the other thermodynamic variables of this system, which are the standard enthalpy change and standard entropy change by the equation to, which is  $\Delta G$  is equal to  $\Delta H - T \Delta S$ . Now the left hand side terms in equation one and two are same and that is this standard free energy change.

So the right hand side terms also should be equated. That is written in the form of equation 3, which is minus 2.303 RT log to the base 10 beta equal to  $\Delta H - T \Delta S$ .

The main aim is to relate the overall formation constant beta to the thermodynamic variables of this system. So on the left hand side we should have minimum variables. So in order to remove the variable

temperature from the left hand side term, we need to divide the right hand side and left hand side terms by the temperature and it takes the form of equation 4 and slightly rearranging it so as to remove the negative sign from the left hand side.

$\beta$  is the overall formation constant. The equation four is  $2.303 RT \log_{10} \beta$  is equal to  $\Delta S^\circ - \Delta H^\circ / T$ . So the overall formation constant has been related to the standard entropy change and is standard enthalpy change. So we can conclude that the overall formation constant  $\beta$  is enhanced by negative enthalpy change. An positive entropy change. Because  $\beta$  is equated to  $\Delta S^\circ$  and negative of  $\Delta H^\circ / T$ . So the complex formation is enhanced or favored by negative enthalpy change. That is, it is favored by exothermic reaction, wherein large amount of energy will be liberated, making enthalpy change negative. And it is also favored by positive entropy change reactions in which a lot of independent particles are produced on the product side, thereby giving positive entropy change.

These are the references.

Thank you.