Difference Between Stepwise and Overall Stability Constants

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Key Difference - Stepwise vs Overall Stability Constants

The term stability constant refers to an equilibrium constant for the formation of a complex compound in a solution. It is a way of measuring the stability of these complexes of transition metal ions. As or all other equilibrium constants, stability constants are also temperature dependent. The definition for stability constant can be given as "the constant for an equilibrium existing between a transition metal ion surrounded by water ligands and, the complex formed when some transition metal ions undergo ligand substitution reactions". the symbol for stability constant is K_{stab}. Usually, the ligands are substituted one by one as a stepwise process. These steps are given stepwise stability constants. However, the stability constant for the overall process can also be given. It is the overall stability constant. The **key difference** between stepwise and overall stability constants is that **the values of stepwise stability constants are lower than the overall stability constant of the same reaction whereas the overall stability constant always have a higher value than each stepwise stability constant.**

What are Stepwise Stability Constants?

Stepwise stability constants are equilibrium constants given for each step of the process of ligand substitution. When a transition metal ion complex has water ligands surrounding the metal ion, the ligand substitution takes place as a stepwise process. There, only one water molecule is replaced by the ligand that is involved in the substitution. Let us consider an example to understand this process.

Ex: substitution of ammonia ligands.

The chemical formula of hexaaquacopper(II) ion is given as $[Cu(H_2O)_6]^{2+}$. The six water ligands can be replaced by ammonia ligands (NH_3).One water ligand is replaced by one ammonia ligand at a time.

$[Cu(H_2O)_6]^{2+} + NH_3 \leftrightarrow [Cu(NH_3)(H_2O)_5]^{2+}$ K1

$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \leftrightarrow [Cu(NH_3)_2(H_2O)_4]^{2+}$ K2

$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \leftrightarrow [Cu(NH_3)_3(H_2O)_3]^{2+}$ K3

$[Cu(NH_3)_3(H_2O)_3]^{2+} + \quad NH_3 \leftrightarrow \quad [Cu(NH_3)_4(H_2O)_2]^{2+} \quad K4$

$[Cu(NH_3)_4(H_2O)_2]^{2+} + \quad NH_3 \leftrightarrow \quad [Cu(NH_3)_5(H_2O)]^{2+} \quad K5$

$[Cu(NH_3)_5(H_2O)]^{2+} + \quad NH_3 \leftrightarrow \quad [Cu(NH_3)_6]^{2+} \qquad K6$

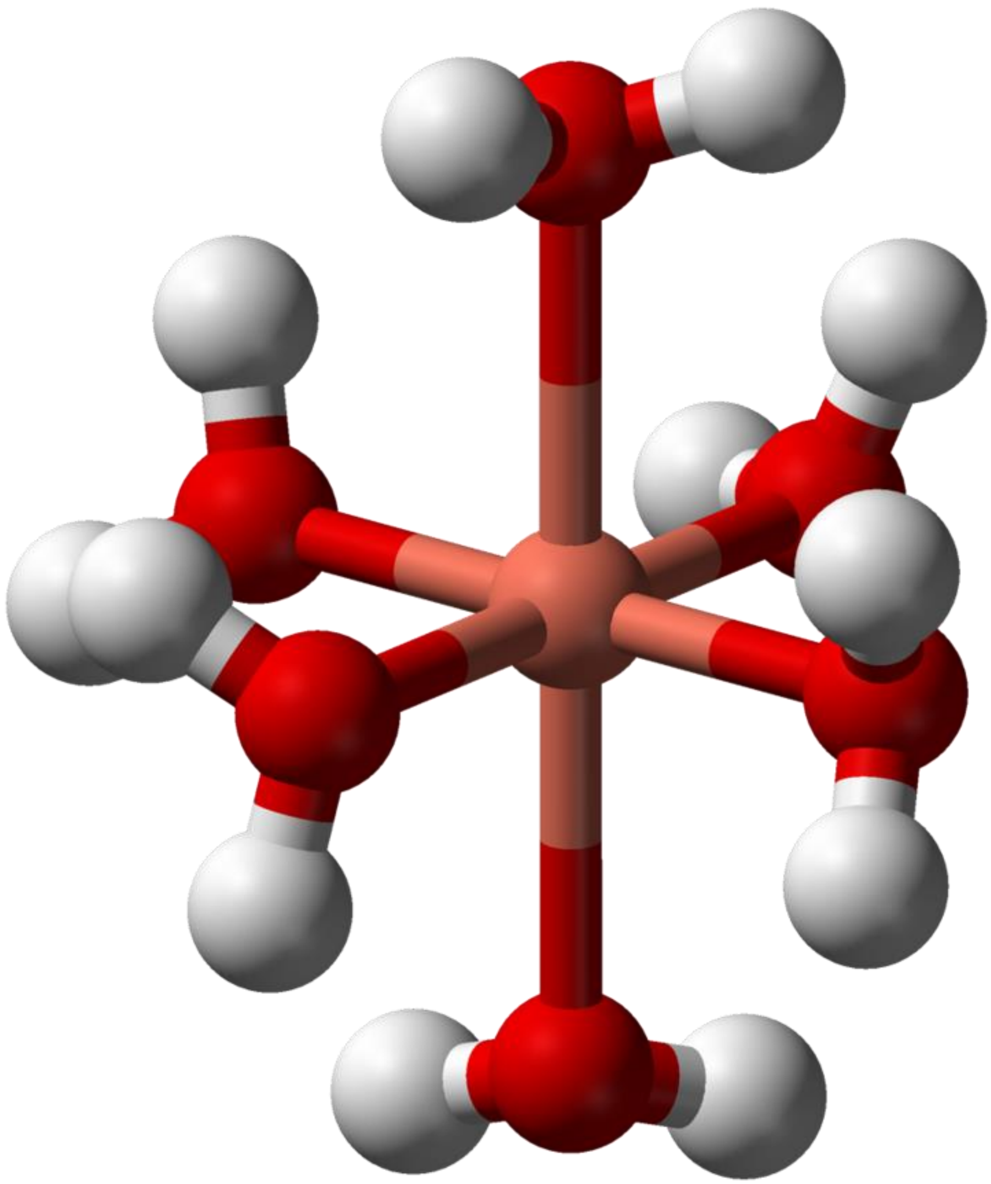

Figure 01: A 3D diagram of a hexaaquacopper(II) ion.

The stability constant for the first substitution is given as K1. For the second substitution, it is k2 and vice versa. For each equilibrium above, expressions can be derived as below.

For the first substitution, K1 $=\{[Cu(NH_3)(H_2O)_5]^{2+}\} / \{[Cu(H_2O)_6]^{2+}\} * \{NH_3\}$

In which, $\{[Cu(NH_3)(H_2O)_5]^{2+}\}$, $\{[Cu(H_2O)_6]^{2+}\}$ and $\{NH_3\}$ are concentrations of each chemical species inside the brackets.Expressions like above can be written for other stepwise stability constants as well (K2, K3, K4, K5 and K6).

What are Overall Stability Constants?

The overall stability constant is the equilibrium constant of the overall reaction. For the above reaction, the overall stability constant can be given as below.

$[Cu(H_2O)_6]^{2+}$ + $NH_3 \leftrightarrow$ $[Cu(NH_3)_6]^{2+}$

Hence, the overall stability constant is the equilibrium constant for the equilibrium between transition metal ion surrounded by water ligands and the transition metal ion surrounded by substituted ligands. Then the expression for overall stability constant can be derived as below.

Overall K_{stab} = $\{[Cu(NH_3)_6]^{2+}\} / \{[Cu(H_2O)_6]^{2+}\} * \{NH_3\}$

What is the Relationship Between Stepwise and Overall Stability Constants?

The overall stability constant can be obtained by multiplying all the stepwise stability constants together. For above example,

Overall K_{stab} = K1 * K2 * K3 * K4 * K5 * K6

What is the Difference Between Stepwise and Overall Stability Constants?

Stepwise vs Overall Stability Constants	
Stepwise stability constants are equilibrium constants given for each step of the process of ligand substitution.	The overall stability constant is the equilibrium constant of the overall reaction.
Nature	
The stepwise stability constants are given for steps of a substitution reaction that takes place in a transition metal ion	The overall stability constant is given for the whole substitution reaction that takes place in a transition metal ion

complex.	complex.
Value	
The values of stepwise stability constants are lower than the overall stability constant of the same reaction.	The overall stability constant always has a higher value than each stepwise stability constant.

Summary - Stepwise vs Overall Stability Constants

The stepwise stability constant and overall stability constant are equilibrium constants given for transition metal complexes in solutions. The difference between stepwise and overall stability constants is that the values of stepwise stability constants are lower than the overall stability constant of the same reaction whereas the overall stability constant always have a higher value than each stepwise stability constant.

Reference:

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Image Courtesy:

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