

28.5 STABILITY CONSTANT

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Learning outcomes

Candidates should be able to:

1. Define the stability constant, K_{stab} , of a complex as the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules)
2. Write an expression for K_{stab} of a complex ($[\text{H}_2\text{O}]$ should not be included)
3. Use K_{stab} expressions to perform calculations
4. Describe and explain ligand exchanges in terms of K_{stab} values and understand that a large K_{stab} is due to the formation of a stable complex ion

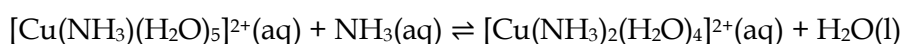
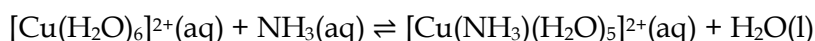
Initial assessment

1. Work with a partner to write a general set of rules to derive the expression for the equilibrium constant, K_c , for a reaction such as:
$$m A(\text{aq}) + n B(\text{aq}) \rightleftharpoons p C(\text{aq}) + q D(\text{aq})$$

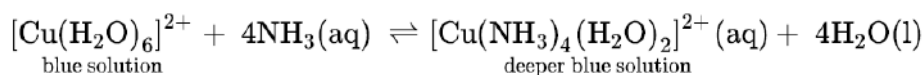
Introduction

Aqueous solutions of transition element ions are hydrated. They are complex ions with water molecules acting as ligands, forming dative (coordinate) bonds to the central metal ion.

Different ligands form complexes with different stabilities. For example, when we add concentrated aqueous ammonia to an aqueous solution of copper(II) sulfate, the ammonia ligands displace water ligands in a stepwise process.

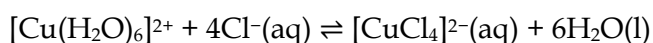


As we increase the concentration of ammonia, this process continues until four of the water molecules are replaced by ammonia molecules. The solution formed is a deep blue colour. The overall ligand substitution reaction is:



We can think of this exchange of ligands in terms of competing equilibria of the forward and backward reactions. The position of equilibrium lies in the direction of the more stable complex. In this case, the complex with ammonia as a ligand is more stable than the complex with just water as a ligand. If we dilute the complex with water, the position of equilibrium shifts to the left, and a complex with more water molecules as ligands forms.

The stability of the complex is expressed in terms of the equilibrium constants for ligand displacement. This is called the stability constant. Usually, an overall stability constant, K_{stab} , is given rather than the stepwise constants. The method for writing equilibrium expressions for stability constants is similar to the one we used for writing K_c . So, for the equilibrium:



The expression for the stability constant is:

$$K_{\text{stab}} = \frac{[\text{CuCl}_4]^{2-}(\text{aq})}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+} [\text{Cl}-(\text{aq})]^4}$$

Note:

- Water does not appear in the equilibrium expression because it is in such a large excess that its concentration is regarded as being constant
- The units for the stability constant are worked out in the same way as for the units of K_c . For example, in the above case:

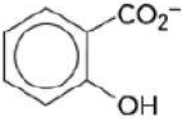
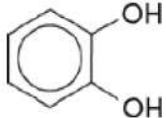
$$K_{\text{stab}} = \frac{[\text{CuCl}_4]^{2-}(\text{aq})}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+} [\text{Cl}-(\text{aq})]^4} \frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^4} = \text{dm}^{12} \text{mol}^{-4}$$

Stability constants are often given on a $\log_{10}$ scale. When expressed on a $\log_{10}$ scale, they have no units.

Stability constants can be used to compare the stability of any two ligands. The values quoted usually give

the stability of the complex relative to the aqueous ion, where the ligand is water.

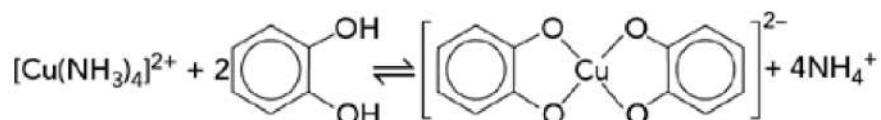
The following table gives some values of stability constants for various copper(II) complexes relative to their aqueous ions.

Ligand	$\log_{10} K_{\text{stab}}$
chloride, Cl^-	5.6
ammonia, NH_3	13.1
2-hydroxybenzoate 	16.9
1,2-dihydroxybenzene 	25.0

From the table, you can see that, in general, complexes with bidentate ions (2-hydroxybenzoate and 1,2-dihydroxybenzene) have higher stability constants than those with monodentate ligands.

We can use the values of the stability constants to predict the effect of adding different ligands to complex ions. For example, the addition of excess ammonia to the complex $[\text{CuCl}_4]^{2-}(\text{aq})$ should result in the formation of a dark blue solution of the ammonia complex. That is because the stability constant of the ammonia complex is higher than that of the chloride complex. The position of equilibrium is shifted to the right in the direction of the more stable complex.

Addition of excess 1,2-dihydroxybenzene to the dark blue ammonia complex results in the formation of a green complex with 1,2-dihydroxybenzene. This is because the stability constant with 1,2-dihydroxybenzene is much higher than that for ammonia. You can see from the Table that the log of K_{stab} for 1,2-dihydroxybenzene is 25.0, so the actual value of K_{stab} is 10 raised to the power 25, compared to the actual value for ammonia of 10 raised to the power of 13.1. This shows that the copper complex with 1,2-dihydroxybenzene is much more stable than the complex ion formed with ammonia. These values of K_{stab} predict that there will be hardly any of the copper complex with ammonia left in the equilibrium mixture shown in the equation below:



The stability constant, K_{stab} , of a complex is the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules)

The higher the value of the stability constant, the more stable the complex.

💡 Large K_{stab} means the equilibrium strongly favours formation of the complex, so the complex is thermodynamically more stable.

Larger K_{stab} $\Rightarrow$ more stable complex

Key points

K_{stab} measures the equilibrium tendency to form a complex.

Do not include $\text{H}_2\text{O}(\text{l})$ in the expression.

Larger $K_{\text{stab}} \rightarrow$ more stable complex $\rightarrow$ equilibrium favours its formation

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