Cambridge (CIE) A Level Chemistry

Your notes

Stability Constants, Kstab

Contents

Define & Write a Stability Constant for a Complex

- When transition element ions are in aqueous solutions, they will automatically become hydrated
  - Water molecules will surround the ion and act as **ligands** by forming dative covalent bonds to the central metal ion
- When there are other potential ligands present in the solution, there is a **competing equilibrium** in **ligand exchange** and the most stable complex will be formed
- For example, a Co(II) ion in solution will form a $[Co(H_2O)_6]^{2+}$ complex
- Adding ammonia results in the stepwise substitution of the water ligands by ammonia ligands until a stable complex of $[Co(NH_3)_4(H_2O)_2]^{2+}$ is formed

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

- For the substitution reaction above, there are **four** stepwise constants:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O \qquad K_1$$

$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O \qquad K_2$$

$$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O \qquad K_3$$

$$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O \qquad K_4$$

- These stepwise constants are summarised in the **overall stability constant**, K_{stab}
- The **stability constant** is the **equilibrium constant** for the formation of the complex ion in a solvent from its constituent ions or molecules

Expression of K_{stab}

- The expression for K_{stab} can be deduced in a similar way as the expression for the equilibrium constant (K_c)
- For example, the equilibrium expression for the substitution of water ligands by ammonia ligands in the Co(II) complex is:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2]^{2+}}{[Cu(H_2O)_6]^{2+}\ [NH_3]^4}$$

- The concentration of **water** is **not** included in the expression as the water is in **excess**
- Therefore, any water **produced** in the reaction is **negligible** compared to the water that is already present

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- The units of the K_{stab} can be deduced from the expression in a similar way to the units of K_c
- The stability constants can be used to **compare** the **stability** of ligands relative to the **aqueous metal ion** where the ligand is water
- The **larger** the K_{stab} value, the **more stable** the complex formed is

Calculations Involving Stability Constants

- If the concentrations of the transition element complex and the reacting ligands are known, the expression for the stability constant (K_{stab}) can be used to determine which complex is **more stable**
- The **greater** the value of K_{stab} the **more stable** the complex is

Worked Example

The addition of concentrated hydrochloric acid to copper(II) sulfate solution forms an aqueous solution containing $[CuCl_4]^{2-}$ and $[Cu(H_2O)_6]^{2+}$ complex ions. The overall ligand exchange involved is a series of stepwise reactions as successive ligands are replaced.

The second step in exchanging water ligands with chloride ligands is:

$$[Cu(H_2O)_5Cl]^+ (aq) + Cl^- (aq) \rightleftharpoons Cu(H_2O)_4Cl_2 (aq) + H_2O (l)$$

When a 0.15 mol dm^{-3} solution of $[Cu(H_2O)_5Cl]^+$ (aq) is mixed with 0.15 mol dm^{-3} hydrochloric acid, the equilibrium mixture of $Cu(H_2O)_4Cl_2$ (aq) was found to be 0.10 mol dm^{-3}.

1. Use this data to calculate K_{stab} for this step. Include the units for K_{stab}.
2. Use your answer to **(1)** to suggest the position of the equilibrium for this step. Explain your answer.

Answer 1

- **Step 1:** Calculate the equilibrium concentration of each ion:

	$[Cu(H_2O)_5Cl]^+$ (aq)	Cl^- (aq)	$Cu(H_2O)_4Cl_2$ (aq)
Initial concentration / mol dm^{-3}	0.15	0.15	0
Change in concentration	- 0.1.0	-0.10	+ 0.10
Equilibrium concentration / mol dm^{-3}	0.05	0.05	0.10

- **Step 2:** Write the K_{stab} expression for the reaction:

- K_{stab} = $\frac{[Cu(H_2O)_4Cl_2]}{[Cu(H_2O)_5Cl]^+ [Cl^-]}$
- **Step 3:** Substitute the equilibrium concentrations into the K_{stab} expression and evaluate:
  - K_{stab} = $\frac{[0.10]}{[0.05][0.0.5]}$
  - K_{stab} = 40
- **Step 4:** Determine the units:
  - K_{stab} = $\frac{[mol\ dm^{-3}]}{[mol\ dm^{-3}][mol\ dm^{-3}]}$
  - K_{stab} = $dm^3\ mol^{-1}$

Answer 2:

- The value of K_{stab} is 40 $dm^3\ mol^{-1}$
- This is a large value, which suggests:
  - The products are favoured
  - Therefore, the position of the equilibrium for this step is to the right / products

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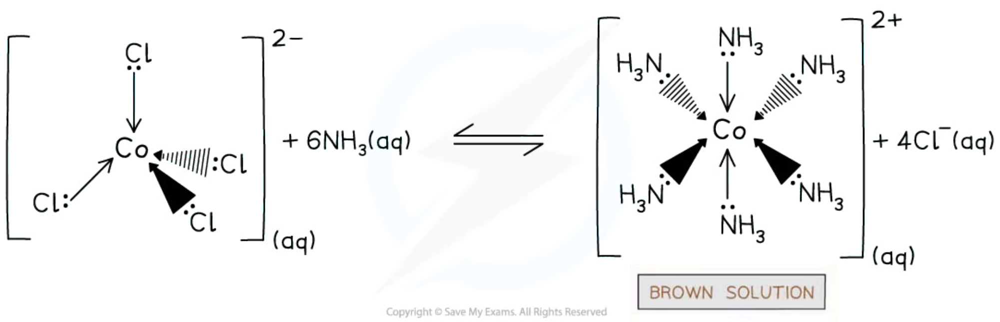
Effect of Ligand Exchange on Stability Constant

- The stability constants (K_{stab}) of ligands are often given on a $\log_{10}$ scale so that it becomes easier to compare them with each other
- Ligand exchange in a complex occurs to form a **more stable** complex with a larger K_{stab}
- The stability constants can be used to explain the substitution of ligands in a copper complex

Ligand substitution in a Co(II) complex

- When excess ammonia is added to the $[CoCl_4]^{2-}$ complex a **brown** solution is obtained

Ligand exchange of the $[CoCl_4]^{2-}$ complex by ammonia



The chloride ligands are substituted by the ammonia ligands to form the more stable ammonia complex

- The formation of the ammonia complex could be explained by comparing the stability of the chloride and ammonia ligands

Stability of chloride and ammonia ligands table

Ligand	Stability ($\log_{10} K_{stab}$)
Cl^-	5.6
NH_3	13.1

- The stability constant of the ammonia ligand is greater than that of the chloride ligands
- The brown ammonia complex is therefore **more stable**
- As a result, the position of the equilibrium is shifted **to the right**

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Worked Example

The numerical values for the stability constants, K_{stab}, of three silver(I) complexes are given.

Silver(I) complex	Numerical value of K_{stab}
$[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
$[Ag(CN)_2]^-$	5.3×10^{18}
$[Ag(NH_3)_2]^+$	1.6×10^{7}

An aqueous solution of Ag^+ is added to a solution containing equal concentrations of $S_2O_3^{2-}$ (aq), CN^- (aq) and NH_3 (aq). The mixture is left to reach equilibrium.

Deduce the relative concentrations of $[Ag(S_2O_3)_2]^{3-}$, $[Ag(CN)_2]^-$ and $[Ag(NH_3)_2]^+$ present in the equilibrium mixture. Explain your answer.

Answer

- The highest concentration will be $[Ag(CN)_2]^-$
  - This is because the K_{stab} value for $[Ag(CN)_2]^-$ is the largest value
    OR
  - $[Ag(CN)_2]^-$ is the most stable
- The lowest concentration will be $[Ag(NH_3)_2]^+$
  - This is because the K_{stab} value for $[Ag(NH_3)_2]^+$ is the smallest value
    OR
  - $[Ag(NH_3)_2]^+$ is the least stable
- An alternative explanation could be to state that higher K_{stab} values form a more stable complex