Complex formation equilibrium (Item No.: P3031001)

Curricular Relevance

Area of Expertise: Chemistry
Education Level: University
Topic: Inorganic Chemistry
Subtopic: Coordination Chemistry
Experiment: Complex formation equilibrium

Difficulty	Preparation Time	Execution Time	Recommended Group Size
Easy	10 Minutes	10 Minutes	2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

complex formation, chemical equilibrium, equilibrium constant

Overview

Short description

Principle

Many metals, in particular transition elements, can form complexes with charged or neutral ligands. Complex formation reactions are equilibrium reactions. The stability of these complexes is described by the complex formation constant.

Fig. 1: Experimental setup.

Safety instructions

Silver nitrate, cryst.
H272: May intensify fire; oxidizer
H314: Causes severe skin burns and eye damage
H410: Very toxic to aquatic life with long-lasting effects
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P221: Take any precaution to avoid mixing with combustibles.
P273: Avoid release to the environment.

Potassium bromide
H319: Causes serious eye irritation
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Ammonia solution, 25%
H314: Causes severe skin burns and eye damage.
H335: May cause respiratory irritation.
H400: Very toxic to aquatic life.
P273: Avoid release to the environment.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Equipment

Position No.	Material	Order No.	Quantity
1	Burette, lateral stopcock, Schellbach, 25 ml	36506-01	1
2	Burette clamp, roller mount., 2 pl.	37720-00	1
3	Retort stand, h = 750 mm	37694-00	1
4	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
5	Magnetic stirring bar 30 mm, cylindrical	46299-02	2
6	Graduated pipette 25 ml	36602-00	1
7	Volumetric pipette, 5 ml	36577-00	1
8	Volumetric pipette, 10 ml	36578-00	1
9	Volumetric pipette, 20 ml	36579-00	2
10	Pipettor	36592-00	1
11	Pipette dish	36589-00	1
12	Erlenmeyer wide neck,boro.,250ml	46152-00	5
13	Volumetric flask 100 ml, IGJ12/21	36548-00	4
14	Volumetric flask 250 ml, IGJ14/23	36550-00	3
15	Funnel, glass, top dia. 55 mm	34457-00	3
16	Weighing dishes, square shape, 84 x 84 x 24 mm, 25 pcs.	45019-25	1
17	Spoon, special steel	33398-00	1
18	Wash bottle, plastic, 500 ml	33931-00	1
19	Pasteur pipettes, 250 pcs	36590-00	1
20	Rubber caps, 10 pcs	39275-03	1
21	Silver nitrate, cryst. 15 g	30222-00	1
22	Potassium bromide, 100 g	30258-10	1
23	Ammonia solution, 25% 1000 ml	30933-70	1
24	Water, distilled 5 l	31246-81	1

Task

Determine the number of ligands of the silver amine complex with a precipitation titration from a silver salt solution.

Set-up and Procedure

Set up the experiment as shown in Fig. 1.

Prepare the solutions required for the experiment as follows:

- 0.01 molar silver nitrate solution: Weigh 0.425 g of silver nitrate in a 250 ml volumetric flask, dissolve it in approximately 100 ml of distilled water and fill up to the calibration mark with distilled water.
- 0.01 potassium bromide solution: Weigh 0.298 g of potassium bromide in a 250 ml volumetric flask, dissolve it in approximately 100 ml of distilled water, and fill up to the calibration mark with distilled water.
- 2 molar ammonia solution: Pipette 37.5 ml of 25 % molar ammonia solution into a 250 ml volumetric flask, dilute it with distilled water, and fill up to the calibration mark with distilled water.

Pipette 20 ml of the 0.01 M silver nitrate solution into each of the four 100 ml flasks, add 10, 15, 20 and 30 ml respectively of 2 molar ammonia solution and fill up to the calibration mark with distilled water.

Transfer each of these four solutions into a separate 250 ml Erlenmeyer flask and successively titrate each of them with 0.01 molar potassium bromide solution until the solution becomes slightly cloudy (compare it with pure water).

To calculate the equilibrium concentrations, take the total volume of the respective solution into account – including the potassium bromide solution used.

Theory and evaluation

Complexes are chemical compounds which consist of a central atom and a definite number of ligands. The central atom is normally a metal ion, transition metals in particular frequently form complexes. The ligands can be charged ions (anions) or neutral molecules. The formation of a complex can be perceived to be a Lewis acidbase reaction. The ligands, with their free pairs of electrons, represent the Lewis bases, while the central atom with its free orbitals functions as an acid. A complex is formed with atomic bonds between the ligands and the central atom, whereby the pairs of electrons only come from one partner, the ligand.

Complex formation can be described by the following equation:

$$\mathrm{M + nL} \rightleftharpoons [\mathrm{ML}_n]$$

where

n Number of ligands

For this experiment the complex formation reaction is

$$\mathrm{Ag}^+ + \mathrm{n\,NH_3} \rightleftharpoons [\mathrm{Ag(NH_3)}_n]^+ \quad (1)$$

in which the number of ligands is to be determined. The complex formation constant can be calculated according to the law of mass action:

$$K_c = \frac{c([\mathrm{Ag}^+(\mathrm{NH}_3)_n]^+)}{c(\mathrm{Ag}^+)\cdot c^n(\mathrm{NH}_3)} \quad (2)$$

Transformed to the logarithmic form, the following results:

$$\log c(\mathrm{Ag}^+) = -\mathrm{n}\cdot\log c(\mathrm{NH}_3) + \log\frac{c([\mathrm{Ag}(\mathrm{NH}_3)_n]^+)}{K_c} \quad (3)$$

Because ammonia is added in excess to the four silver nitrate solutions, the concentration of ammonia is much higher than the concentration of silver nitrate:

$$c(\mathrm{NH}_3) \gg c(\mathrm{AgNO}_3) \quad (4)$$

According to this we can assume that the concentration of the silver complex is nearly equal to the total concentration of silver ions in the solution and further, that the concentration of free ammonia after the complex formation reaction is nearly equal to the total concentration of ammonia:

$$[\mathrm{Ag}(\mathrm{NH}_3)_n]^+ \approx c(\mathrm{Ag}^+)_{\mathrm{total}} \quad (5)$$

$$c(\mathrm{Ag}^+)_{\mathrm{total}} = c(\mathrm{AgNO}_3) \quad (6)$$

$$c(\mathrm{NH}_3) \approx c(\mathrm{NH}_3)_{\mathrm{total}} \quad (7)$$

With equations (5), (6) and (7), equation (3) simplifies to

$$\log c(\mathrm{Ag}^+) = -n\cdot\log c(\mathrm{NH}_3)_{\mathrm{total}} + \frac{c(\mathrm{AgNO}_3)}{K_c} \quad (8)$$

After the complex formation reaction some of the silver ions remain in the solution as free silver ions (without ammonia ligands). The amount of these free silver ions can be determined by titration with potassium bromide solution. The titration is stopped when the solution begins to become cloudy (onset of precipitation, some solid silver bromide is formed). At this moment the maximum solubility of the silver bromide is reached. This is described by the solubility product:

$$K_S(\mathrm{AgBr}) = c(\mathrm{Ag}^+)\cdot c(\mathrm{Br}) \quad (9)$$

Combining (8) and (9), we obtain:

$$\log c(\mathrm{Br}^-) = n\cdot\log c(\mathrm{NH}_3)_{\mathrm{total}} + \log\frac{K_c\cdot K_s(\mathrm{AgBr})}{c(\mathrm{AgNO}_3)} \quad (10)$$

The concentration of silver nitrate is constant in the four solutions:

$$c(\mathrm{AgNO_3}) = \mathrm{const.}$$ (11)

So it follows:

$$\log \frac{K_c \cdot K_s(\mathrm{AgBr})}{\mathrm{const.}} = \mathrm{const.}$$ (12)

Combining equations (10) and (12), we obtain:

$$\log c(\mathrm{Br}) = n \cdot \log c(\mathrm{NH_3})_{\mathrm{total}} + \mathrm{const.}$$ (13)

This means that the number of ligands in the silver amine complex can be obtained from the slope of the plot log$c(\mathrm{Br^-})$ against $c(\mathrm{NH_3})$.

Data and results

Example for a measurement series (see Table 1):

The slope of the curve (Fig. 2) is 2.07, hence the co-ordination number for silver is 2.

Solution number	1	2	3	4
Volume of 0.01 M silver nitrate solution $V(\mathrm{AgNO_3})$	20 ml	20 ml	20 ml	20 ml
Volume of 2 M ammonia solution $V(\mathrm{NH_3})$	10 ml	15 ml	20 ml	30 ml
Number of moles of ammonia $n(\mathrm{NH_3}) = V(\mathrm{NH_3}) \cdot c_0\,(\mathrm{NH_3})$	0.02 mol	0.03 mol	0.04 mol	0.06 mol
Volume of added water $V\mathrm{H_2O}$	70 ml	65 ml	60 ml	50 ml
Volume of resulting solution V (solution)	100 ml	100 ml	100 ml	100 ml
Added volume of 0.01 M potassium bromide solution $V(\mathrm{KBr})$	1.30 ml	2.55 ml	4.20 ml	12.40 ml
Number of moles of added potassium bromide $n(\mathrm{KBr}) = V(\mathrm{KBr}) \cdot c(\mathrm{KBr})$	$1.3 \cdot 10^{-5}$ mol	$2.5 \cdot 10^{-5}$ mol	$4.2 \cdot 10^{-5}$ mol	$12.4 \cdot 10^{-5}$ mol
Total volume of the solution after titration $V(\mathrm{total}) = V(\mathrm{solution}) + V(\mathrm{KBr})$	101.30 ml	102.55 ml	104.20 ml	112.40 ml
Concentration of ammonia in the solution after titration $c(\mathrm{NH_3}) = n(\mathrm{NH_3})/V(\mathrm{total})$	0.1974 mol/l	0.2925 mol/l	0.3839 mol/l	0.5338 mol/l
$\log c(\mathrm{NH_{3;total}})$	- 0.7047	- 0.5339	- 0.4158	- 0.2726
Concentration of bromide ions in the solution after titration $c(\mathrm{Br^-}) = n(\mathrm{KBr}/V(\mathrm{total}))$	$1.2833 \cdot 10^{-4}$ mol/l	$2.4378 \cdot 10^{-4}$ mol/l	$4.0307 \cdot 10^{-4}$ mol/l	$11.0320 \cdot 10^{-4}$ mol/l
$\log c(\mathrm{Br^-})$	- 3.8917	- 3.6130	- 3.3946	- 2.9573

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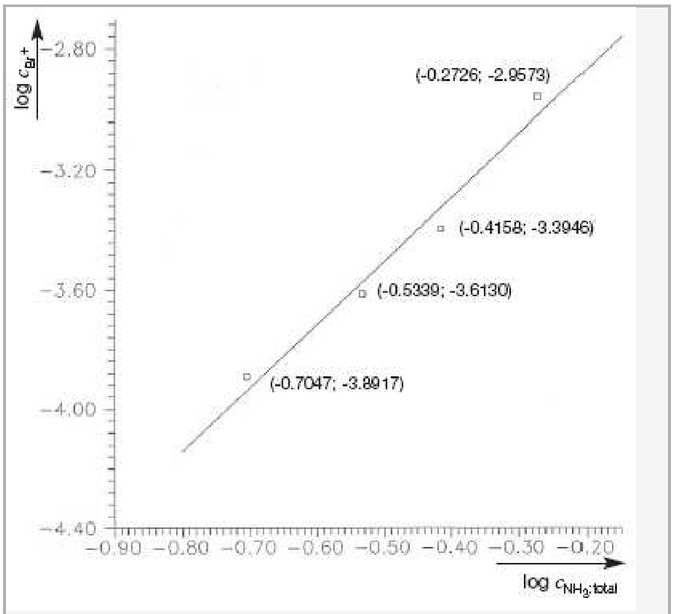

Fig. 2: Determination of the number of ligands bound in thecomplex.

If ammonia is added to a silver nitrate solution, therefore, the water molecules which are bound to the silver ion (aquo complex) are displaced by ammonia molecules and a silver diamine complex is formed:

$$[\mathrm{Ag}(H_2O)_2]^+ + 2\mathrm{NH_3} \rightleftharpoons [\mathrm{Ag}(\mathrm{NH_3})_2]^+ + 2\mathrm{H_2O}$$