

Determining the solubility products of silver halides

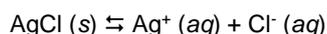
Aims of the experiment

- Getting to know the solubility product as a characteristic quantity of salts.
- Using the solubility product to determine concentrations of ions in solutions.
- Recognizing the correlation between the law of mass action and the solubility product.
- Applying the Nernst equation in combination with the solubility product.

Principles

Even only slightly soluble compounds dissolve to a certain extent in a solvent, e.g. water. An equilibrium then forms between the substance dissolved and its solid precipitate. A saturated solution is present when exactly as many ions dissolve as re-crystallize at the crystal surface.

The equilibrium can be described by the example of solid silver chloride and a saturated solution using the following formula:



Here, (s) stands for solid and (aq) for dissolved.

The law of mass action with the relevant equilibrium constant K is then:

$$K = \frac{c(\text{Ag}^+) \cdot c(\text{Cl}^-)}{c(\text{AgCl})}$$

Here, the concentration of the solid substance, in this case silver chloride, remains constant the whole time, which is why the concentration $c(\text{AgCl})$ can be included in the equilibrium constant:

$$K \cdot c(\text{AgCl}) = c(\text{Ag}^+) \cdot c(\text{Cl}^-) = K_{sp}$$

The constant K_{sp} is designated as solubility product constant. This in turn can be used to calculate the solubility. K_{sp} is thus a value for the maximum solubility of a substance in a solvent. If this maximum solubility is exceeded, ions will be precipitated and a saturated solution is formed. The smaller the solubility product, the less easily a substance is dissolved.

The solubility product can be determined experimentally by measuring potential differences and using the Nernst equation. A voltage measurement is set up between a measuring and a comparison half cell. In so doing, a defined silver ion concentration is provided in the comparison half cell (here: 0.1 mol/l). The halogen salt to be examined is provided in the measurement half cell. When silver ions are added drop by drop, the silver halide e.g. silver chloride is formed, which precipitates immediately. In addition to the precipitated silver chloride, there is a defined quantity of silver ions in the solution in accordance with the solubility product. Due to the differences in the concentrations of the silver ions in both half cells, a potential difference arises. The concentration of the silver ions in the silver chloride solution can be calculated from this potential difference. And from this the solubility product for silver chloride can be derived.



Fig. 1: Set-up of the experiment.

Risk assessment

During the test, the required protective equipment (protective goggles, gloves) must be worn, as some of the solutions used are corrosive.

Silver nitrate causes permanent black staining on the skin.

Silver nitrate	
   Danger	<p>Hazard statements</p> <p>H272: May intensify fire; oxidizer H314 Causes severe skin burns and eye damage.</p> <p>H410 Very toxic to aquatic life with long lasting effects.</p> <p>Precautionary statements</p> <p>P210 Protect from heat.</p> <p>P221 Take any precaution to avoid mixing with combustibles, heavy-metals compounds, acids and alkalis.</p> <p>P273 Avoid release to the environment. P280 Wear protective gloves / protective clothing / eye protection / face protection.</p> <p>P301+330+331 If swallowed: rinse mouth. Do not induce vomiting.</p> <p>P305+P351+ P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.</p> <p>P308+P310 IF exposed or concerned: Immediately call a POISON CENTER or doctor/physician.</p>
Potassium bromide	
 Warning	<p>Hazard statements</p> <p>H319 Causes serious eye irritation</p> <p>Precautionary statements</p> <p>P305+P351+P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing...</p>
Potassium nitrate	
 Warning	<p>Hazard statements</p> <p>H272 May intensify fire; oxidizer</p> <p>Precautionary statements</p> <p>P210 Keep away from heat, hot surfaces, sparks, open flames and other sources of ignition. No smoking.</p> <p>P221 Take any precaution to avoid mixing with combustibles/...</p>

Instruments and chemicals

1	Universal measuring instrument - Chemistry.	531 836
1	UIP-Sensor S	524 0621
4	Beaker Boro 3.3, 100 ml, tall	664 137
1	Measuring cylinder, 100 ml, with plastic base	665 754
1	Salt bridge, 90 x 90 mm, 20 mm Ø.....	667 455
1	Rubber stopper, solid, 16...21 mm Ø.....	667 255
1	Beaker Boro 3.3, 250 ml, squat.....	664 130
1	Plate electrodes silver, 55x40 mm, Set of 2 ..	664 421
1	Crocodile-clips, polished set of 6.....	501 861
1	Connecting leads, 19 A, 25 cm, pair.....	501 44
1	Electronic balance 440-3N, 200 g : 0.01 g	667 7977
1	Spoon-ended spatula, stainless steel.....	666 963
1	Saddle base	300 11
1	Stand rod 47 cm, 12 mm Ø	300 42
1	Boshead S.....	301 09
1	Universal clamp, 0...80 mm.....	666 555
1	Dropping pipette, 150 x 7 mm, Set 10.....	665 953
1	Rubber bulbs, 10 pcs	665 954
1	Funnel PP, 75 mm Ø.....	665 009
1	Silver nitrate solution, 0.1 mol/l, 250 ml.....	674 8800
1	Sodium chloride solution, 1 M, 500 ml.....	673 5740
1	Potassium bromide solution, 1 M, 250 ml.....	672 4930
1	Potassium iodide, 50 g	672 6620
1	Potassium nitrate, 100 g.....	672 6800

Set-up and preparation of the experiment

Set-up of equipment

- The equipment is set up as shown in Fig. 1.
- For this, attach support rod to the base.
- Using a double socket S, attach the universal clamp to the support rod.
- Clamp the salt bridge pipe into the universal clamp.
- The universal measuring instrument Chemistry (UMI C) is connected to power and the UIP sensor S to the interface of the UMI C.
- The experimental cables will be provided with beak-shaped clamps on one side and inserted on the other side into the voltage measurement inputs U of the UIP sensor S.

Preparation of the experiment

- For the experiment, in addition to three ready-made solutions (silver nitrate, sodium chloride, potassium bromide), two additional solutions (potassium iodide, potassium nitrate) are used, which must be initially prepared .
- In order to prepare the solutions, the weights must first be calculated.

- Solution of Potassium iodide

$$M(\text{KI}) = 166.0028 \text{ g/mol}$$

$$c(\text{KI}) = 1 \text{ mol/l}$$

$$V(\text{KI}) = 100 \text{ ml}$$

$$m(\text{KI}) = c(\text{KI}) \cdot M(\text{KI}) \cdot V(\text{KI})$$

$$m(\text{KI}) = 1 \text{ mol/l} \cdot 166.0028 \text{ g/mol} \cdot 0,1 \text{ l}$$

$$m(\text{KI}) = 16.6 \text{ g}$$

- Solution of potassium nitrate

For a saturated potassium nitrate solution, at a temperature of 20 °C 32 g potassium nitrate will be dissolved in 100 g water, so that a deposit remains. If necessary, add some more potassium nitrate.

- Use a funnel to fill the saturated potassium nitrate solution into the salt bridge. In so doing, ensure that the deposit is not transferred as well. Use a rubber stopper to close the salt bridge pipe.

- Each of the two silver plate electrodes is connected with a single beak-shaped clamp.
- The beakers are labelled with the designations of the individual solutions.

Performing the experiment

- Fill each of the beakers with 50 ml of silver nitrate, sodium chloride, potassium bromide and potassium iodide solutions, respectively.
- Switch on the universal measuring instrument Chemistry (UMI C).
- Immerse the silver plate electrodes into the silver nitrate solution and the sodium chloride solution. The electrodes in the silver nitrate solution here form the positive terminal (anode).
- Add 2 – 3 drops of the 0.1 mol/l silver chloride solution to the sodium chloride solution. Note observations.
- Now position the beakers with the two solutions such that one leg of the salt bridge pipe is respectively immersed into one of the solutions. As soon as a constant measurement value has appeared on the UMI C, note it down.
- Repeat this process for each salt solution in combination with silver nitrate. For this, wash off the salt bridge with water from time to time and dab dry. It does not need to be refilled.

Observation

When silver chloride is pipetted to each one of the halogen salt solutions, then turbidity occurs at the drop-in point.

Following immersion of the salt bridge, the UMI C shows potential differences for all the combinations of the various different salt solutions with the silver nitrate solution.

Evaluation

Calculation of the concentrations of silver ions in the halogen solutions

From the potential differences measured, using the Nernst equation, the concentration of silver ions in the halogen solutions can be calculated.

In this case, the Nernst equation is as follows:

$$\Delta E = \frac{R \cdot T}{n \cdot M \cdot F} \lg \frac{c_1(\text{Ag}^+)}{c_2(\text{Ag}^+)}$$

With:

c_1 : being the numeric value of the silver ion concentration in the comparison half element (higher concentration) in mol/l.

c_2 : being the numeric value of the silver ion concentration in the measurement half element (lower concentration) in mol/l.

For single value ions such as silver ($n = 1$), the following applies:

$$\frac{R \cdot T}{n \cdot M \cdot F} = 0,0059$$

Thus:

$$\Delta E = 0.059 \lg \frac{c_1(\text{Ag}^+)}{c_2(\text{Ag}^+)} = 0.059 \lg c_1(\text{Ag}^+) - 0.059 \lg c_2(\text{Ag}^+)$$

If, for the silver concentration c_1 , one now uses the initial concentration $c = 0.1$ mol/l, the formula can be reduced as follows.

$$\Delta E = -0.059 - 0.059 \cdot \lg c_2(\text{Ag}^+)$$

In this way, the potential change can be converted directly to a silver ion concentration.

Calculation of solubility product for silver chloride AgCl

When adding the silver nitrate solution drop by drop to the chloride solution, a turbidity is visible. Here, silver chloride precipitates. The concentrations of the silver ions and chloride ions are therefore high enough in combination that the solubility product is exceeded. It is therefore possible to calculate the concentration of the free silver ions from the solubility product.

In comparison to the chloride ions provided, the concentration of the silver ions is infinitesimal. Therefore the concentration of chloride can be regarded as constant. In the test it is $c = 1$ mol/l. Thus, the solubility product K_{sp} can be simplified to K_{sp}^* . The equation

$$K_{sp} = c(\text{Ag}^+) \cdot c(\text{Cl}^-)$$

becomes

$$K_{sp}^* = c(\text{Ag}^+).$$

In this way, the potential change can be converted directly into the solubility product K_{sp}^* .

$$\Delta E = -0.059 - 0.059 \cdot \lg K_{sp}^*$$

And

$$K_{sp}^* = 10^{-\frac{\Delta E + 0.059}{0.059}}$$

Analogously, the solubility products for silver bromide and silver iodide can be calculated.

Result

Table 1 shows the voltages obtained in the experiment for the various different salt solutions in combination with the silver nitrate solution.

Tab. 1: Results of the experiment: Measured potentials and calculated solubility product.

Salt	Potential ΔE	Solubility product K_{sp}
AgCl	0.509 V	$2.3 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$
AgBr	0.663 V	$5.8 \cdot 10^{-13} \text{ mol}^2/\text{l}^2$
AgI	0,870 V	$1.7 \cdot 10^{-16} \text{ mol}^2/\text{l}^2$

The solubility products of the difficult to dissolve silver salts, arrived at from the tests, can now be compared with literature values. Tab. 2 shows the literature values that coincide well with the measured values.

Tab. 2: Literature values of solubility products.

Salt	Solubility product
AgCl	$1.7 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$
AgBr	$5.0 \cdot 10^{-13} \text{ mol}^2/\text{l}^2$
AgI	$8.5 \cdot 10^{-17} \text{ mol}^2/\text{l}^2$

Cleaning and disposal

Silver nitrate in an aqueous solution is reduced to silver by the addition of iron filings or when heating with glucose. Subsequently, the solution can be disposed of in the drain. Potassium bromide and potassium iodide are disposed of in the waste material for inorganic salt solutions with heavy metals.

Potassium nitrate should be disposed of in separate waste material for nitrates. This must be kept alkaline in order to avoid the formation of hydrogen cyanide. Small quantities may also be disposed of in the drain. In this regard comply with the current and regional disposal information.