When a few drops of a very dilute silver nitrate solution (c =0.01 mol/l) are added to a 1 molar solution of potassium halide solution (= KCl, KBr, KI), then there is an immediate precipitation of the corresponding silver halide (AgCl, AgBr, AgI), because the solubility product of these only very sparingly soluble salts is already exceeded even by these small amounts of added silver ions. Only that number of silver ions can remain free in these silver halide solutions, as are allowed to do so by the solubility product

$$K_L = c\,(Ag^+) - c\,(Hal\text{-}).$$

As hereby, in comparison with the initial concentration of the halide ions (c = 1 mol/l), only a minute quantity of these ions are bound, their concentration remains practically constant, despite the precipitation of the silver halide; c (Hal) so remains = 1 mol/l. The solubility product of the silver halides after precipitation therefore becomes:

$$K_L = c\,(Ag^+) \cdot 1$$

i.e. the solubility product is equal to the number of free silver ions.

When now a silver electrode is inserted in such a silver ion saturated potassium halide solution, this is practically a silver half-cell with a very strongly diluted silver ion concentration. On connecting this half-cell to another silver half-cell of known silver ion concentration (comparison cell) to a concentration series , then the voltage ΔE corresponding to the difference in silver ion concentration can be measured.

As the relationship between the difference in concentration and the voltage in a concentration series follows the Nernst equation, the solubility product, or the silver ion concentration, of each silver halide solution can be calculated from the appropriate measured voltage.

Objective

A silver half-cell with 0.01 molar silver nitrate solution (as comparison cell) and half-cells containing 1 molar KCl, Kbr and KI solutions, in which a few drops of silver nitrate are to be added to precipitate a small amount of the corresponding silver halides, are to be prepared as concentration series.

The voltages of these concentration series are to be measured and the solubility product of the corresponding silver halide is to be calculated.
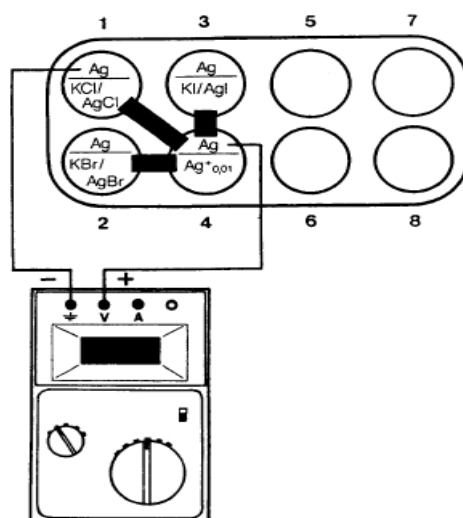

Fig. 1:

Equipment

From the Electrochemical Measurement Set:

1	Hand-held digital multimeter, LCD	07134-00
1	Connecting cord, 2 mm plug, 500 mm, red	07356-01
1	Connecting cord, 2 mm plug, 500 mm, blue	07356-04
1	Reducing plug, 4 mm/2 mm, pack of 2	11620-27
1	Measuring cell block	37682-00
1	Pipette with rubber bulb	64701-00
1	Crocodile clip, 2 mm socket, pack of 2	07275-00
5	Glass beaker, tall, 50 ml	36001-00
	Silver foil (for electrodes)	31839-04
	Emery cloth, 158 x 224 mm, pack of 2	01606-00
	Silver nitrate solution, c = 0.01 mol/l	
	Potassium chloride solution, c = 1 mol/l	
	Potassium bromide solution, c = 1 mol/l	
	Potassium iodide solution, c = 1 mol/l	
	Potassium nitrate solution, c = 1 mol/l	
	Filter paper strips	

Safety precautions

Potassium bromide and potassium chloride solutions of concentration c = 1.0 mol/l act as irritants. Potassium iodide solutions of concentration c = 1.0 mol/l are harmful if swallowed and may cause sensitization on skin contact.

Protect eyes and skin. Avoid contact of the chemicals with eyes and skin. Wear protective gloves and protective glasses!

Observe the detailed safety precautions described in the Appendix.

Set-up and procedure

As shown in Fig. 1, fill potassium chloride solution (c = 1 mol/l) into measuring cell 1, potassium bromide in cell 2 and potassium iodide in cell 3 (each of the same concentration). Fill 0.01 molar silver nitrate solution in cell 4. Use the pipette with rubber bulb to add 3 to 4 drops of 0.01 molar silver nitrate solution to each of the 3 halide solutions, and connect these measuring cells with measuring cell 4 using keys (filter paper strips wetted with potassium nitrate solution) as shown in Fig. 1.

Put covers on the 4 measuring cells, then connect an absolutely clean silver electrode to the voltage socket (positive pole connection) of the measuring instrument and insert it in measuring cell 4 (silver nitrate solution).

Connect a second absolutely clean silver electrode to the earthed socket (negative pole connection) of the measuring instrument. Insert this electrode first in measuring cell 1 (potassium chloride solution with

silver chloride precipitate) and measure the voltage between the half-cells 1 and 4. Remove the silver electrode from measuring cell 1, carefully clean it and then insert it in measuring cell 2 (potassium bromide solution with silver bromide precipitate).

Measure the voltage between the half-cells 2 and 4. Carry out this same procedure with half-cell 3 (potassium iodide solution with silver iodide precipitate).

Results

The voltage between the silver half-cell 4 and
Cell 1 (silver chloride) is approx. 0.427 V
Cell 2 (silver bromide) is approx. 0.580 V
Cell 3 (silver iodide) is approx. 0.805 V

Explanation

The increase in the voltage from the silver chloride solution over the silver bromide solution to the silver iodide solution indicates that the solubilities of the silver halides decrease in this succession. The Nernst equation can be now used to calculate the solubility products of the silver halides. The Nernst equation is (n = 1 for silver ions):

$$\Delta E = \frac{0.058 \text{ V} \cdot \lg c_1 \text{ (red)}}{c_2 \text{(ox)}}$$

or

$$(c_1 = 0.01 \text{ mol } \Delta E = 0.058 \text{ V} \cdot \lg 10\text{-}2 - 0.058 \text{ V} \cdot \lg c_2 \text{ (Ag}^+)$$

As was stated above, c_2 (Ag$^+$) = KL

We then have:

$$\Delta E = \text{-}2 \cdot 0.058 \text{ V} - 0.058 \text{ V} \cdot \lg K\text{L}$$

$$\lg K\text{L} = \frac{\Delta E + 2 \cdot 0.058}{0.058}$$

ΔE was measured in the experiment. When we enter this value in the equation above, we find the following solubility products KL for:

AgCl: 10-9.36
AgBr: 10-12
AgI: 10-15.88