Exercise 10  DETERMINATION OF THE SOLUBILITY PRODUCT CONSTANT

Theory

Solubility is a physical property referring to the ability for a given substance, the solute to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium. The resulting solution is called a saturated solution. Solubility is commonly expressed as a concentration, either mass concentration (g of solute per kg of solvent, g per 100 ml of solvent), molarity, molality, mole fraction or other similar descriptions of concentration.

An oversaturated solution becomes a saturated solution by forming a solid to reduce the dissolved material. The crystals formed are called a precipitate. Often, however, a precipitate is formed when two clear solutions are mixed. For example, when a silver nitrate solution and sodium chloride solution are mixed, silver chloride crystals AgCl (a precipitate) are formed. Silver chloride is one of the few chloride that has a limited solubility. Formations of precipitates are considered between heterogeneous chemical equilibria phenomena. A saturated solution of a slightly soluble salt in contact with its undissolved salt involves an equilibrium like the one below:

\[ \text{AgX(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \]

where \( \text{X} = \text{Cl, Br, I} \)

The symbols (aq) indicate that these ions are surrounded by water molecules. These ions are in the solution. AgCl(s) is a precipitate (s – solid). One can express the equilibrium constant:

\[ K = \frac{a_{\text{Ag}^+} a_{\text{X}^-}}{a_{\text{AgX}}} \tag{1} \]

where \( a_{\text{Ag}^+} \) is activity of the silver cations in the solution
\( a_{\text{X}^-} \) is activity of the halogenide anions in the solution
\( a_{\text{AgCl}} \) is activity AgX in the solution

The activities of ions in solution are:

\[ a_{\text{Ag}^+} = \gamma_+ c_{\text{Ag}^+} \quad a_{\text{X}^-} = \gamma_- c_{\text{X}^-} \tag{2} \]

where \( \gamma_+ \) and \( \gamma_- \) are activity coefficients of cation and anion

According to the convention, the activity of any solid (s) is equal to 1, i.e. \( a_{\text{AgCl}} = 1 \)

Thus writing the equilibrium constant expression for heterogeneous equilibria, we ignore the concentrations of pure liquids (H\(_2\)O) and solids. So the equilibrium constant expression for the equilibria above is:

\[ K = K_{sp} = a_{\text{Ag}^+} a_{\text{X}^-} = \gamma_+ c_{\text{Ag}^+} \gamma_- c_{\text{X}^-} \tag{3} \]

This equilibrium constant \( K_{sp} \) is called a solubility-product constant. Even though AgX is
excluded from the equilibrium constant expression, some undissolved $\text{AgX (s)}$ must be present in order for the system to be in equilibrium. In general, the solubility product constant ($K_{\text{sp}}$) is the equilibrium constant for the equilibrium that exists between a solid ionic solute and its ions in a saturated aqueous solution. The rules for writing the solubility-product expression are the same as those for writing any other equilibrium constant expression:

The solubility product is equal to the product of the concentrations of the ions involved in the equilibrium, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

**Solubility and $K_{\text{sp}}$**

It is important to distinguish carefully between solubility and solubility product. The solubility of a substance is the quantity that dissolves to form a saturated solution. The molar solubility is the number of moles of the solute that dissolve in forming a liter of saturated solution of the solute. The solubility product constant is the equilibrium constant for the equilibrium between an ionic solid and its saturated solution. The solubility of a substance changes as the concentration of other solutes change. In contrast the solubility product for a given solute is constant at a specific temperature, and $K_{\text{sp}}$ values are tabulated in the chemistry handbooks.

Solubility products, $K_{\text{sp}}$, of salts are indirect indication of their solubilities expressed in mol dm$^{-3}$ (*called molar solubility*). However, the solubility products are more useful than molar solubility. The molar solubilities are affected when there are common ions present in the solution. We need to employ the solubility products to estimate the molar solubilities in these cases.

In studying solubility equilibria, it is important to be able to interconvert solubility and solubility product.

**Salt in pure water**

When a salt is dissolved in pure water, solubility products and molar solubilities are related. This is illustrated using $\text{AgX}$. The dissolution of $\text{AgX}$ in pure water follows the Eq.1: 1 molecule of $\text{AgX}$ dissociates into 1 $\text{Ag}^{+}$ and 1 $\text{Cl}^{-}$ ions, thus:

$$c_{\text{Ag}^{+}} = c_{\text{X}^{-}} = s_{0}$$

where $s_{0}$ is the molar solubility

Ionic activity coefficient is a function of the concentration (see Debye-Hückel limiting law below), and one can write:

$$\gamma_{+} = \gamma_{-} = \gamma_{\pm}$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient

According to the **Equation 4**, the solubility product constant is:

$$K_{\text{sp}} = \gamma_{\pm}^{2}s_{0}^{2}$$

(4)
The molar solubility of AgX is very low, and one can approximate $\gamma_{z} = 1$, what corresponds to pure water. Thus for the molar solubility of the salt in pure water one may write:

$$S_0 = \sqrt[3]{K_{sp}} \quad [\text{mol dm}^{-3}] \quad (5)$$

**Salt in a solution that contains a common ion**

The solubility of an ionic compound decreases in the presence of a common ion. A common ion is any ion in the solution that is common to the ionic compound being dissolved. For example, the chloride ion in a sodium chloride solution is common to the chloride in silver chloride. The presence of a common ion must be taken into account when determining the solubility of an ionic compound.

When you dissolve AgCl in a solution already containing NaCl (actually Na$^+$ and Cl$^-$ ions), the Cl$^-$ ions come from the ionization of both AgCl and NaCl. Thus, the concentration of Cl$^-$ differs from the concentration of Ag$^+$. Let $c$ is the concentration of NaCl, and $s_0$ is the solubility of AgCl. Then, the concentration of Ag$^+$ ions is $s_0$, but the concentration of Cl$^-$ is $s_0 + c$. The solubility product constant one can write as:

$$K_{sp} = s_0(s_0 + c)\gamma_\pm^2 \quad (6)$$

Because of low solubility of AgCl, the concentration of Cl$^-$ coming from AgCl ($s_0$) is much more lower than that from NaCl ($c$):

$$s_0 << c$$

so $s_0 + c = c$

and thus the Equation 6 is frequently used as:

$$K_{sp} = s_0 c \gamma_\pm^2 \quad (7)$$

The effect of the Cl$^-$ concentration on the solubility of AgCl is called the **common ion effect**.

**Salt in the solution of electrolyte without the common ion**

The solubility of an ionic compound increases when the ionic strength of the solution increases due to presence of other electrolyte from a substance containing no common ion with the salt. For example, silver chloride is dissolved in the solution of potassium nitrate (KNO$_3$). In this case, the solubility of salt is given by the **Equation 4**:

$$S_0 = \sqrt[3]{K_{sp}} \quad (8)$$

where the mean ionic activity coefficient $\gamma_{z} \neq 1$, because of the change in the ionic strength of solution. The mean ionic activity coefficient one can calculate using **Debye-Hückel limiting law**:

$$\log \gamma_\pm = -0.511 |z_+ z_-| \sqrt{I} \quad (9)$$

where $z_+$, $z_-$ are the charge numbers of cation and anion, respectively

$I$ is is the ionic strength of the solution.
The ionic strength of a solution \( I \) is a function of the concentration of all ions present in a solution:

\[
I = \frac{1}{2} \sum_{i}^{n} c_i z_i^2
\]

(10)

where \( c_i \) is the molar concentration of \( i \)-ion (in mol dm\(^{-3}\))

\( z_i \) is the charge number of that ion

\( \Sigma \) the sum is taken over all ions in the solution

Solubility product constants and solubility play an important role in analytical chemistry, chemical technology, but also in medicine and pharmacy. For example, the mineral found in teeth and bone is a salt formed from calcium phosphate. In dentistry, ionic and solubility products are important basic chemical phenomena supporting tooth mineralisation, demineralisation and stability.

**Task**

Determination of the solubility product constant either of AgCl, AgBr, or AgI.

Electromotoric force of a purpose-built electrochemical cell can be used for the determination of the solubility product constant. In our work we will determine the \( K_{sp} \) of silver halogenide salts. In this way we use the electrochemical cell built as shows Figure 1: two half-cells (with an electrode immersed to the electrolyte) are connected with a salt bridge to provide electrical contact between two half-cells with different electrolytes - to prevent the solutions from mixing. We use Ag (+) and Ag-AgX (-) electrode connected to the cell according to the diagram:

\[
\text{Ag} | \text{AgX} ; KX (c_2) || \text{AgNO}_3 (c_1) | \text{Ag}
\]

B

Ag electrode immersed in the solution of AgNO\(_3\) represents the positive terminal of the cell (right-hand side), and its potential depends on the activity of Ag\(^+\) ions according the Nernst equation:

\[
E_{Ag}^{\circ} = E_{Ag}^{\circ} + 2.303 \frac{RT}{zF} \log a_{Ag^{+}}
\]

(11)

The silver-silver halogenide electrode is a reference electrode (left-hand side), usually employed because of its potential dependence on the activity of chloride ions. However, in the cell according to the diagram (B) and keeping the experimental procedure described later, we use the sensitivity of Ag-AgX electrode for the activity of Ag\(^+\) ions resulting from low solubility of AgX. In this way, the electrochemical cell (A) represents a concentration cell where the two electrodes are the same material, the electrolytes on the two half-cells involve the same ions, but the electrolyte concentration differs between the two half-cells.

According to the Nernst equation, the electromotoric force for a concentration cell is given by:
\[
E = \frac{RT}{zF} \log \frac{a_1}{a_2}
\]

where \(a_1; a_2\) are activities of Ag\(^+\) ions in both solutions

Let us express the activities of Ag\(^+\) ions:
- Ag\(^+\) electrode (right-hand side) is immersed in the solution of AgNO\(_3\), thus
  \[
a_{AgNO_3} = c_{AgBO_x} \gamma_{AgNO_3}
\]
  \[\tag{13}\]
- Ag-AgCl electrode (left-hand side) is immersed in the KX solution saturated by AgX, so the activity \(a_2\) must be expressed using AgX solubility product constant:
  \[
  K_{sp} = a_{Ag^+} a_{X^-}
  \]
  where \(a_{X^-} = c_{X^-} \gamma_{KX}\)

thus:
  \[
a_2 = a_{Ag^+} = \frac{K_{sp}}{c_{KX} \gamma_{KX}}
\]
  \[\tag{14}\]

For the electromotoric force \((E)\) of the cell one can write:
\[
E = \frac{RT}{F} \ln \frac{c_{AgNO_3} \gamma_{AgNO_3} \gamma_{KCl} \gamma_{KCl}}{K_{sp}}
\]
\[\tag{15}\]

where \(\gamma_{AgNO_3}\) and \(\gamma_{KCl}\) may be approximated as the mean ionic activities \((\gamma_2)\) of solutions and calculated using the Debye – Hückel limiting law \textbf{Equation 9}.

In our experimental protocol (given below) we keep the concentrations of AgNO\(_3\) and KCl the same:
\[
c_{AgNO_3} = c_{KX} = c
\]

The ionic charge numbers of ions in both used electrolytes are equal either 1 or –1, thus:
\[
\gamma_{AgNO_3} = \gamma_{KX} = \gamma_{\pm}
\]

The \textbf{Equation 15} can be simplified to:
\[
E = \frac{RT}{F} \ln \frac{c^2 \gamma_{\pm}^2}{K_{sp}}
\]
\[\tag{16}\]
and rearranged into the form:
\[
\ln K_{sp} = 2 \ln c + 2 \ln \gamma_{\pm} + \frac{EF}{RT}
\]
\[\tag{17}\]
where \(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\)
\(F = 96 485 \text{ C mol}^{-1}\)
\[ T \] is thermodynamic temperature in K

**Equipment and chemicals**
- potentiometer – pH-meter
- electrochemical cell with Ag and Ag-AgCl electrodes (Figure 1)
- volumetric flasks (25 ml (2 pieces), 10 ml (9 pieces))
- pipettes, beakers

![Electrochemical cell](image.png)

**Fig. 1** Electrochemical cell

**Chemicals**
- AgNO\(_3\) solution at the concentration \( c = 0.025 \text{ mol dm}^{-3} \)
- KX (KCl, KBr, resp. KI)
- distilled water

**Procedure**

1. Prepare 25 ml of the solution KX (KCl, KBr resp. KI following the instruction of the teacher) at the molar concentration 0.025 mol dm\(^{-3}\). This is the stock solution.
2. Prepare 3 solutions, each of the volume 10 ml, with the concentration 0.0125, 0.00625 and 0.003125 mol dm\(^{-3}\), respectively, by dilution of the KX stock solution.
3. Prepare 3 solutions, each of the volume 10 ml, with the concentration 0.0125, 0.00625 and 0.003125 mol dm\(^{-3}\), respectively, by dilution of the AgNO\(_3\) solution.
4. Fill the (+) compartment of the electrochemical cell with the AgNO\(_3\) solution of the lowest concentration \( c = 0.003125 \text{ mol dm}^{-3} \) (V ~5 ml).
5. Fill the (-) compartment of the electrochemical cell with the KX solution of the same concentration (\( c=0.003125 \text{ mol dm}^{-3} \)) (V ~5 ml).
   Add few drops of AgNO\(_3\) solution with the same concentration as is the KX in the compartment (-). Mix the solution gently. Due to the reaction:
   \[
   \text{KNO}_3 + \text{AgCl} \rightarrow \text{KCl} + \text{AgNO}_3
   \]
a low soluble AgCl is formed and a turbidity of the solution is observed.
6. Measure the electromotoric force of the cell (\( E \)) in mV. Write its value down to the Table 1.
7. Drain both compartments of the cell, wash them with the distilled water.
8. Repeat the procedure for each prepared concentration i.e. 0.00625, 0.0125, and 0.025...
9 Finishing experiment, wash carefully both compartments of the cell with distilled water, and after, dip electrodes to distilled water in both compartments.

10 Do not forget to read the laboratory temperature, and write it down to the **Table 1**.

**Data treatment**

1. Calculate the ionic strength of prepared solutions \( I \) according to the **Equation 10**.
2. Calculate the mean activity coefficients of ions \( \gamma_{\pm} \) using Debye-Hückel limiting law **Equation 9**.
3. Calculate the solubility product constants \( K_{sp} \) for each measured \( E \) from **Table 1**.
4. Using the **Equation 17**.
5. Calculate the average value of \( K_{sp} \).
6. Calculate the standard deviation of \( K_{sp} \) according to the **Equation 18**:

\[
S_D = \sqrt{\frac{\sum_{i=1}^{n} (K_{spi} - K_{sp})^2}{n - 1}}
\]

where \( i = \) is from 1 to 4  
\( n = 4 \) is the number of values  

**Table 1** Experimental and calculated data

<table>
<thead>
<tr>
<th>No</th>
<th>( c_{AgNO_3} = c_{KX} ) (mol dm(^{-3}))</th>
<th>( E ) (V)</th>
<th>( I ) (mol dm(^{-3}))</th>
<th>( \gamma(\pm) )</th>
<th>( K_{sp} ) (mol(^2) dm(^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.003125</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td></td>
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<tr>
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</tr>
<tr>
<td>4</td>
<td>0.025</td>
<td></td>
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</tr>
</tbody>
</table>

**Report**

The report must include:
- Theory (solubility, solubility product constants)
- Equipments and chemicals
- Method and used procedure
- Tables of results and calculation
- In conclusions, compare the obtained \( K_{sp} \) with the tabulated \( K_{sp} \)

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