Exercise 19

DETERMINATION OF MEAN ACTIVITY COEFFICIENTS AND THE THERMODYNAMIC SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALT

Topics: Interactions between ions, foundations of the theory of the conductivity of strong electrolytes. Ion activity and average electrolyte activity. The ionic strength of the solution. The Debye limiting law and the Debye-Hückel equation defining the relationship between the mean electrolyte activity coefficient and the ionic strength of the solution. Phase equilibrium law. Thermodynamic and approximate product of the solubility of sparingly soluble salt. Effect of non-participating ions and common-ion salt on solubility. Potentiometric titration.

Slightly soluble salts are mostly strong electrolytes, dissociating completely into ions when dissolved in a polar solvent. When the solution is saturated (with p and T = const), the salt remaining in the solid phase ($K_{\nu+} A_{\nu-}$) is in equilibrium with the corresponding cations (K_{z+}) and anions (A_{z-}) in the liquid phase:

$(K_{\nu+} A_{\nu-})_{\text{solid phase}} \rightleftarrows (\nu_+K^{z+} + \nu_-A^{z-})_{\text{liquid phase}}$ (1)

where the condition is fulfilled : $z_+\nu_+ = z_- \nu_-$ (z are charges, v are the coefficients of cations and anions). The equilibrium state in such a two-phase system, given the unit activity value for a pure solid ($a_{\text{salt}} / c^{\ominus} = 1$) is reflected by the thermodynamic solubility product ($K_{sp,,a}$). This quantity, using the molar system of ion activity, is described by the following expression::

$$K_{sp,a} = \left(\frac{a_{K^{z+}}}{c^{\ominus}}\right)^{v+} \left(\frac{a_{A^{z-}}}{c^{\ominus}}\right)^{v-} \qquad (2)$$

where a - molar activity of ions (cations and anions), $c^{\ominus} = 1M$ is the standard concentration.

Substituting the molar concentrations in equation (2) gives an approximate solubility product, simply called the solubility product:

$$K_{sp} = \left(\frac{c_{K^{z+}}}{c^{\ominus}}\right)^{v+} \left(\frac{c_{A^{z-}}}{c^{\ominus}}\right)^{v-} \qquad (3)$$

Bearing in mind that the activity of ions is defined as the product of their molar concentration (c) and molar activity coefficient (γ) and $a_i = \gamma_i c_i$, equation (2) can be written:

$$K_{L,a} = K_{L,c}\, \gamma_{K^{z+}}^{v_+}\, \gamma_{A^{z-}}^{v_-} \qquad (3a)$$

According to the above equations (2 and 3), both the thermodynamic solubility product ($K_{sp,a}$) and the approximate solubility product (K_{sp}) are dimensionless quantities. Since anions and cations are not independent components of the solution, the average electrolyte ion activity should be used ($a_{\pm}^{v} = a_{K^{z+}}^{v_+}\, a_{A^{z-}}^{v_-}$), as well as the average molar concentration ($c_{\pm}^{v} = c_{K^{z+}}^{v_+}\, c_{A^{z-}}^{v_-}$ and the mean electrolyte activity coefficient ($\gamma\pm^{v} = \gamma_{\pm}^{v} = \gamma_{K^{z+}}^{v_+}\, \gamma_{A^{z-}}^{v_-}$).
Of course $a_{\pm} = \gamma_{\pm}c_{\pm}$, and $v = v_+ + v_-$.

Equation (3a) can now be written:
$K_{sp,a} = K_{sp}\gamma\pm^{v}$ (4)
Assuming a low ionic strength of the solution ($I < 10^{-2}$), the average activity coefficient $\gamma_{\pm} \cong 1$ and then equation (4) takes the form:

$$K_{sp,a} \cong K_{sp} \qquad (5)$$

It is therefore obvious that the approximate solubility product K_{sp} reflects well enough the equilibrium state in the process of salt dissolution in a pure solvent. However, if the solution contains ions from the dissociation of other electrolytes, the description of the dissolution equilibrium of a given salt should be based on the thermodynamic solubility product, taking into account the value of the average molar activity coefficient described by equation (5).
Equation (5) can be rearranged to calculate K_{sp}:

$$\mathrm{K_{sp}} = \frac{\mathrm{K_{sp,a}}}{\gamma\pm^{\mathrm{v}}} \qquad (6)$$

To linearize equation (6), it needs to be logarithmically transformed:

$$\log \mathrm{K_{sp}} = \log \mathrm{K_{sp,a}} - \nu \log \gamma\pm \qquad (7)$$

Taking into account the reaction equation (1), the solubility product K_{sp} can be written as follows:

$$\mathrm{K_{sp}} = c_{K^{z+}}^{v_+} c_{A^{z-}}^{v_-} = c_{\pm}^{v} = (v_+ c_L)^{v_+} (v_- c_L)^{v_-} = c_L^{v}\left(v_+^{v_+} v_-^{v_-}\right) \qquad (8)$$

where: c_L is the molar concentration of salt in a saturated solution

The solubility of a sparingly soluble salt, i.e. its molar concentration in a saturated solution (c_L), is directly proportional to the value of the solubility product in a given solvent. The greater the solubility of the compound, the greater the value of K_{sp} and vice versa. From equation (8) the value of c_L can be calculated:

$$c_L = \left(\frac{K_{sp}}{v_+^{v_+} v_-^{v_-}}\right)^{\frac{1}{v}} \qquad (9)$$

Since in equation (8), from which expression (9) was derived, the reference concentration ($c^{\ominus}$), was formally omitted, therefore the numerical value of c_L calculated from expression (9) should be assigned the dimension [M]

It should be remembered that the solubility of salts is affected by the presence of other components in the solution. In the presence of salt ions, which do not have ions in common with salt ions ($K_{\nu+} A_{\nu-}$) there is an increase in interionic interactions, resulting in a decrease in ion activity coefficients. Since at T = const the thermodynamic product of solubility ($K_{sp,a}$) is a constant value (independent of the composition of the solution), a decrease in the value of $\gamma_\pm$ must entail an increase in the product of solubility K_{sp} and solubility c_L (see equations 4, 7, 8,). Thus, some increase in the solubility of the sparingly soluble salt is to be expected when a neutral salt is added to the solution. However, this effect is usually not very large.
On the other hand, the presence in the solution of an electrolyte having common ions with the salt ($K_{\nu+} A_{\nu-}$) shifts the reacti the solid phase, which results in a decrease in its solubility.
In order to determine the average molar activity coefficient of the electrolyte ($\gamma_\pm$) in solutions with an ionic strength (I_c) lower than 0.1, the Debye–Hückel equation can be used:

$$\log \gamma_\pm = \frac{-A|z_+ z_-|\sqrt{I_c}}{1+Bd\sqrt{I_c}} \qquad (10)$$

where:

$$I_c = \frac{1}{2}\sum_i \left(\frac{c_i}{c^{\ominus}}\right) z_i^2 \qquad (11)$$

A and B - constants depending on the permittivity of the solvent and temperature, d - effective diameter of ions (an empirical parameter determining the smallest distance to which dissimilar ions can approach), c_i - concentration of a given type of ions in the solution. It is important to remember that the calculation of I_c takes into account all types of ions present in the solution.

Methodology

Determination of the stoichiometric (end) point of titration by graphical method

By the stoichiometric point of the titration we mean the volume of the added titration solution (in this exercise it is $AgNO_3$) in which the number of moles of Ag^+ ions is equivalent to the initial number of moles of Cl^- ions in the tested solution. The graphic way of determining the stoichiometric point of titration (P.S.) is shown in Fig. 1. The tangents to the initial and final sections of the titration curve should be plotted, and then the middle of the section contained between these tangents should be determined. The projection of the point of intersection of this middle with the titration curve (E = f(V)) on the x-axis determines the number of cm^3 of the titration solution added, corresponding to the stoichiometric point.

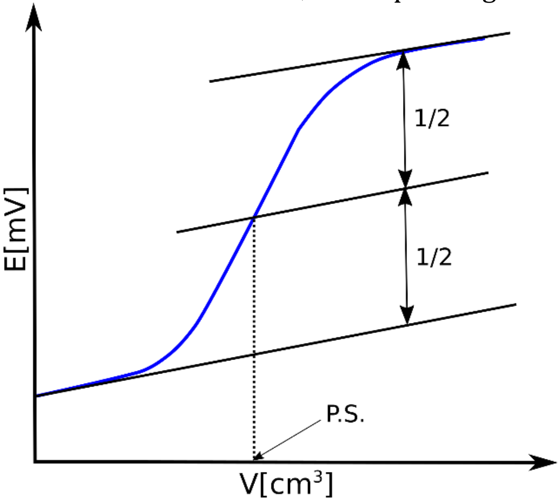

Fig. 1. Determination of the stoichiometric point of potentiometric titration.

Determination of the stoichiometric point by the "first derivative" method:

The "first derivative" method, which allows to determine the stoichiometric point of the titration, consists in determining the volume range of the titration reagent ($\Delta V_m = V_m - V_{m-1}$), in which there is the largest increase in the electromotive force of the tested cell (ΔE_m) in relation to the volume unit of the reagent titrating. The end point of the titration will be the arithmetic mean between the volumes V_m and V_{m-1}

Performing the exercise

The aim of the exercise is to determine the average molar activity coefficients ($\gamma\pm$) and the thermodynamic product of the solubility $K_{sp,a}$, of the sparingly soluble compound $PbCl_2$ by potentiometric titration, and to examine the effect of the neutral salt (KNO_3) on the solubility of this compound.

Preparation of solutions

- To 6 flasks, measure 10 cm^3 of a saturated solution of $PbCl_2$ in water or 10 cm^3 of saturated water solutions of $PbCl_2$ containing the addition of KNO_3 with concentrations: 0.05; 0.10; 0.20; 0.30; 0.40 M. Attention! The solutions should be taken without sediment from the bottom of the flask.
- Dilute the solutions to a volume of 50 cm^3.

Measurements:

- Thoroughly rinse the ion-selective chloride electrode and the reference electrode several times, changing distilled water approximately 5 times in a clean beaker each time, and gently agitating the electrodes vertically and horizontally. Then, dry the electrodes using blotting paper. The electrodes should be rinsed after each change of the test solution!

- Quantitatively transfer the test solution to a clean, dry beaker.
- Place the ion-selective chloride electrode and the reference electrode (e.g., a silver chloride electrode with an electrolyte junction) into the test solution.
- Connect the electrodes to the appropriate terminals of a high-input impedance digital voltmeter ($>10^{10}$ Ω) and plug in the voltmeter.
- Record the initial electromotive force (E) reading of the assembled cell. If the electrodes have been connected correctly, the reading should be positive. Record the result in Table 1.
- Each solution should be titrated twice.
  - In the first titration, add 0.5 cm^3 of the titrant solution. This step aims to estimate the position of the stoichiometric point of titration.
  - In the second titration, initially add 0.5 cm^3 of the solution, and near the endpoint determined in the first step, reduce the volume to 0.1 cm^3.

Titrating Process:

- Add successive volumes of the titrant solution, $AgNO_3$ with a concentration of 0.10 M, to the solution being titrated (sample solution).
- After adding each portion of the titrant solution, vigorously mix the contents of the beaker using a magnetic stirrer.
- Pause the stirring and wait for about 30 seconds to establish steady-state conditions (very important!).
- Read the electromotive force (EMF) value of the cell.
- Record the result in Table 1.
- Add the next portion of the titrant solution.
- Continue titration until a few points beyond the stoichiometric point are reached.
- Repeat the titration for each prepared solution.
- After completing the measurements, rinse the electrodes with distilled water, place the silver chloride reference electrode in a KNO_3 solution, and leave the ion-selective electrode dry in a stand

Calculations:

- Plot the relationship E = f(V) for each titration.
- Determine the stoichiometric point of titration using:
  - the graphical method
  - the first derivative method (Table 1)

Table 1. Results of Potentiometric Titration and Calculation of the Stoichiometric Point using the 'First Derivative' Method"

V $AgNO_3$[cm^3]	E[mV]	ΔV	ΔE	ΔE/ΔV
0				
0,1				
0,2				
…				

Stoichiometric Point of Titration (S.P.) is determined by the volume of titrant solution ($AgNO_3$) containing the amount of Ag^+ moles needed to react with the Cl^- ions present in the analyzed solution. Knowing the position of the stoichiometric point of titration for each of the studied solutions, conduct calculations and place the results in Table 2.

- Calculate the moles of chloride ions in the titrated solution.
- Determine the molar concentrations of Cl^- ions in the analyzed solution.
- Calculate the molar concentrations of lead ions in the analyzed solution.
- Determine the concentration of $PbCl_2$ in the titrated solution.

- Calculate the approximate solubility product constant, K_{sp}, using formula (8).
- Calculate the ionic strength of solution, I_c, using formula (11).
- Calculate the average activity coefficient, $\gamma_{\pm}$, using formula (10), with the effective average ion diameter expressed in [nm] (d = 0.3 [nm]). For this equation, the constants A and B (at $c^{\ominus} = 1$ M) are known to be A = 0.5092 and B = 3.287 [nm^{-1}], at 298 K.
- Plot the relation $\log K_{sp}$, = f($\log \gamma_{\pm}$).
- Use the least squares method to determine the parameters of equation (7).
- Using the fitting parameters for equation (7), calculate the thermodynamic solubility product constant ($K_{sp,a}$) for $PbCl_2$.
- Compare the obtained solubility product constant value for $PbCl_2$ in water with the literature value.

Table 2. Calculation results

c KNO_3	P.S. (V $AgNO_3$)	c Cl^-	c Pb^{2+}	c $PbCl_2$	K_{sp}	I_c	$-\log \gamma\pm$	$\gamma\pm$	$K_{L,a}$
0									
0,05									
0,10									
0,20									
0,30									
0,40									