

Determination of the solubility product and enthalpy of dissolution of sparingly soluble salts by conductometry

Introduction

The electrical resistance is a property of the materials. The resistance R is constant for a given temperature, geometry and material. Therefore, the resistance of an object can be defined as the ratio of voltage to current, in accordance with Ohm's law:

$$R = U / I$$

Specific resistance, or resistivity, is the resistance in ohms offered by a unit volume (the circular-mil-foot or the centimeter cube) of a substance to the flow of electric current: resistivity of a 1 m long, object with a cross section area of 1 mm². In electrochemistry, it is more practical to use the reciprocal unit: the reciprocal of resistance is conductivity ($G = R^{-1}$, the unit is Siemens, 1 S = 1 Ω⁻¹).

By definition the specific conductivity (κ) of electrolyte solutions is the conductivity of a 1 cm³ liquid cube, measured between two parallel, 1cm² first-order electrodes in the distance of 1 cm. The material of the first-order electrode is usually an inert metal, e.g. often gold or platinum.

The specific conductivity is $\kappa = l R^{-1} A^{-1}$ where l is the distance between the surface of the two electrodes, so the unit of S m⁻¹, or S cm⁻¹. Specific conductivity depends on the quality of the electrolyte material, the concentration, and the temperature.

Molar specific conductivity (Λ_m) is the conductivity^d divided by the concentration of the electrolyte. The entire conductance is measured perpendicular to the electrode surface. As noted above,

$$\Lambda_m = \frac{\kappa 1000}{c} = \kappa V \quad (1)$$

where c is the solution concentration (mol dm⁻³) and V is the dilution. The conductance is closely related to the ions' mobility: if it is connected to the voltage measuring electrodes, the electrolyte ion migration starts. The migration speed depends on the magnitude of the electric field, so the migration rate of 1 V/cm relates to network power. The distance traveled by the ion in an electric field of 1 V/cm magnitude is the electric mobility of the ion (u). Since in a binary electrolyte, both the anions and cations contribute to the conductivity of the solution, the specific conductivity concentration dependence

$$\kappa = z c (u_a + u_c) / 1000$$

form can be written for diluted solutions of strong electrolytes. If the solution is highly diluted, the electrostatic interaction is not significant (does not occur) between the dissolved ions, and the solute completely dissociates, then the concentration of the solution can be calculated from the conductance:

$$c = \frac{\kappa 1000}{u_{c,0} + u_{a,0}} \quad (2)$$

where, $u_{c,0}$ and $u_{a,0}$ are the mobility of cations and anions in dilute solution.

The mobility of dissolved substances varies significantly with temperature. In aqueous solution 1°C temperature increase results about 2% rise (the temperature coefficient in case of cations is 1.94 %/°C, while 2.19%/°C for the anions). The solubility also varies with temperature, of course. Its quantitative description is given by the Clausius-Clapeyron equation:

$$\frac{d \ln c}{dT} = \frac{\Delta H}{RT^2}$$

where ΔH is the enthalpy of the dissolution, c is the solubility in the T temperature. If the solubility data of a sparingly soluble salt is available on multiple temperatures, using the Clausius-Clapeyron equation, the enthalpy of dissolution can be calculated. If T_1 and T_2 (given in Kelvin) are the two

temperatures, and the measured solubility of the salt is c_1 and c_2 , the dissolution of the enthalpy can be calculated from rearranging the following equation.

$$\ln \frac{c_1}{c_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3)$$

The work description

The solubility of sparingly soluble salts can be defined by the measured conductivity from their saturated solution. In this case, it is satisfied that, in a saturated solution only relatively a small number of ions are present. The conductivity of the solvent also contributes to the conductance, and since it's a highly diluted solution, it must be taken into account. Therefore the conductivity of the solvent should be subtracted from the conductivity of the solution.

The geometry of the electrodes differs from what is described for the measurements of the specific conductance determination. Therefore, the probe must be calibrated. The deviation of the measurement can be corrected with the application of a so-called cell constant. The cell constant (symbol C , and its unit is m^{-1} or cm^{-1}) expresses the relationship between a well-known solution (K_{ref}) and the conductance of the measured solution (G_{meas}).

$$C = \kappa_{ref}/G_{meas}$$

In addition, we have to consider that the pure solvent (eg, through auto dissociation) also contributes to the conductance. It is considered through the following equation:

$$\kappa_{corr} = (G_{solution} - G_{solvent})C$$

where κ_{corr} is the corrected value of the specific conductance with the solvent conductance, and C is the cell constant (not to be confused with the concentration, which is denoted by c).

Measurements description

The ultrathermostat is adjusted to 50 °C, and the conductivity meter is switched on Rinse the conductivity bell electrode into the double distilled water several times (4-5) Take two clean appropriate sized (approximately 100 ml) beakers fill with double distilled water same volume each and place one of them into the thermostat. Check their conductivity. While the apparatus heats up, prepare the precipitant of a sparingly soluble salt discussed with the instructor. Take the designated metal ion reagent and anion reagent 1 mol dm^{-3} concentration solutions to prepare the precipitate as follows: pipette 20 cm^3 solution containing the metal ion into a beaker and measure the appropriate amount of anion containing solution corresponding to stoichiometry. Pour them together, and then filter the resulting precipitate by vacuum filter. Wash the precipitate properly with conductivity water (double distilled water) and let the filter drain. Pour the conductivity water into a clean 100 cm^3 beaker and put the bell electrode and a thermometer into it, and measure the temperature and conductivity. Then sprinkle enough amount of the sparingly soluble salt into the glass beaker for the solution to be saturated and mix with a glass rod.

The same way prepare another beaker of water with precipitate and place into the thermostat. Rinse the conductivity electrode with water after the app. 20 °C saline solution, and keep it at room temperature for 2-3 minutes and record the measured values. The measurement can be regarded ready when the values do not change after three consecutive readings. Repeat the measurement in the thermostat, after equilibrating the saline solution (it takes about 30 minutes). Then carefully clean the electrode and measure the conductivity of water that is necessary for the correction in the calculation.

Finally, the conductivity of 0.01 M KCL solution should be measured so as to determine the cell constant value.

Calculate the cell constant value. Summarize the results of the measurements in the table:

T (K)	G_{meas} (S)	κ_{corr} (S)	c (mol dm^{-3})

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Calculate the enthalpy of dissolution, and prepare the conductivity - time diagrams. Calculate the solubility product for both temperatures.

Attachment

Table 1 Specific conductivity of KCl solutions at different temperatures.

Temperature (°C)	0.01 M	0.1 M	Temperature (°C)	0.01 M	0.1 M
	KCl solution			KCl solution	
	κ ($\Omega^{-1} \text{ cm}^{-1}$)			κ ($\Omega^{-1} \text{ cm}^{-1}$)	
18	0.001225	0.01119	25	0.001413	0.01288
19	0.001251	0.01143	26	0.001441	0.01313
20	0.001278	0.00167	27	0.001468	0.01337
21	0.001305	0.01191	28	0.001496	0.01362
22	0.001332	0.01215	29	0.001524	0.01387
23	0.001359	0.01239	30	0.001552	0.01412
24	0.001386	0.01264			

Table 2 Molar conductivity and diffusion coefficient of ions at 25 °C .

	λ $10^{-4} \text{ m}^2 \text{ S mol}^{-1}$	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$
Ag ⁺	61.9	1.648
1/3 Al ³⁺	61	0,541
1/2 Ba ²⁺	63.6	0,847
1/2 Ca ²⁺	59.47	0,792
1/2 Cd ²⁺	54	0,719
H ⁺	349.65	9,311
K ⁺	73.48	1,957
1/2 Mg ²⁺	53.0	0,706
1/2 Pb ²⁺	71	0,945
1/2 Hg ²⁺	68.6	0,913
1/2 Hg ²⁺	63.6	0,847
1/2 Fe ²⁺	54	0,179
1/3 Fe ³⁺	68	0,604
1/2 Zn ²⁺	52.8	0,703
	λ $10^{-4} \text{ m}^2 \text{ S mol}^{-1}$	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$
Br ⁻	78.1	2.080
Cl ⁻	76.31	2.032
ClO ₄ ⁻	67.3	1.792
CrO ₄ ²⁻	85	1.132
SCN ⁻	66	1.758
I ⁻	76.8	2.045
1/2 SO ₄ ²⁻	80.0	1.065
OH ⁻	198	5.273

formate-ion	54.6	1.454
Propionate-ion	35.8	0.953

	λ $10^{-4} \text{ m}^2 \text{ S mol}^{-1}$	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$
acetate-ion	40.9	1.089
monochlor-acetate-ion	42.2	1.124

