Determination of dissociation constant by conductometry

Theoretical background:

- Árpád Szűcs: *General Chemistry*, Ch. 7
- Árpád Szűcs, *Laboratory Practices in General Chemistry*, Ch. 13

Type of practice: Individual.

Purpose of practice: To learn how to use conductance measurement for the determination of a chemical property in solution.

1 Introduction

A group of electroanalytical procedures is based on conductance measurements. Each phenomenon can be studied if charged particles (ions) participate in the process. Because of their importance, the various methods based on conductance measurements belong to a separate branch of the broad field of analytical chemistry called conductometry.

1.1 Definitions

Electric conductance means the motion of charged particles (i.e., electric current, I) by potential difference (voltage, U). In case of electron conducting materials (such as metals), the moving charge is electron. Those materials in which charge is carried by ions are called ionic conductors (e.g., electrolytes, solution of electrolytes). The current is proportional to the voltage and their ratio is the conductance (G):

$$G = \frac{I}{U},$$

its SI unit is siemens (S).

Conductance is proportional to the cross section (A) of the conducting material (e.g., a simple wire) and inversely proportional to its length (ℓ):

$$G = \varkappa \frac{A}{\ell},$$

where the constant $\varkappa$ is the conductivity (or specific conductance). The numerical value of this conductivity is the conductance of a conductor having unit volume (e.g., $A = 1\,\mathrm{m}^2$ and $\ell = 1\,\mathrm{m}$).

In case of ionic conductors, conductance is measured in conductivity cells. In the simplest case, a conductivity cell consists of two parallel sheets of conducting material (electrodes) with equal surface area and known separation distance and of an ion conducting phase between the electrodes (see Fig. 1a). In this case, the geometry of the conductivity cell is directly the geometry of the ionic conductor, i.e., the length and cross section are easy to determine. The ratio of those two is the cell constant (c_{cell}), thus conductivity can be calculated as

$$\boxed{\varkappa} = G \cdot \frac{\ell}{A} \boxed{= G \cdot c_{\mathrm{cell}}}. \tag{1}$$

In practice, due to technical consideration, 2-, 3-, or 4-electrode cells (probes) often hosted in a bell-shaped (glass) cover are used (see Fig. 1b). The bell-shaped glass cover plays two different roles: (1) mechanically protects the electrodes and (2) determines the geometry of the electrolyte solution (only the solution inside the bell effects the measurement). The cell constant must be obtained from separate conductance measurements (calibration) by applying a solution with known conductivity. The cell constant can be manually programmed into many conductometers before the measurement, thus the meter displays conductivity directly (however, conductance is measured in each case).

Conductivity is independent of the conductor's geometry, however, it still depends on the number of the charged particles in the conductivity cell. Molar conductivity (Λ_{c}) is defined as the conductivity of an
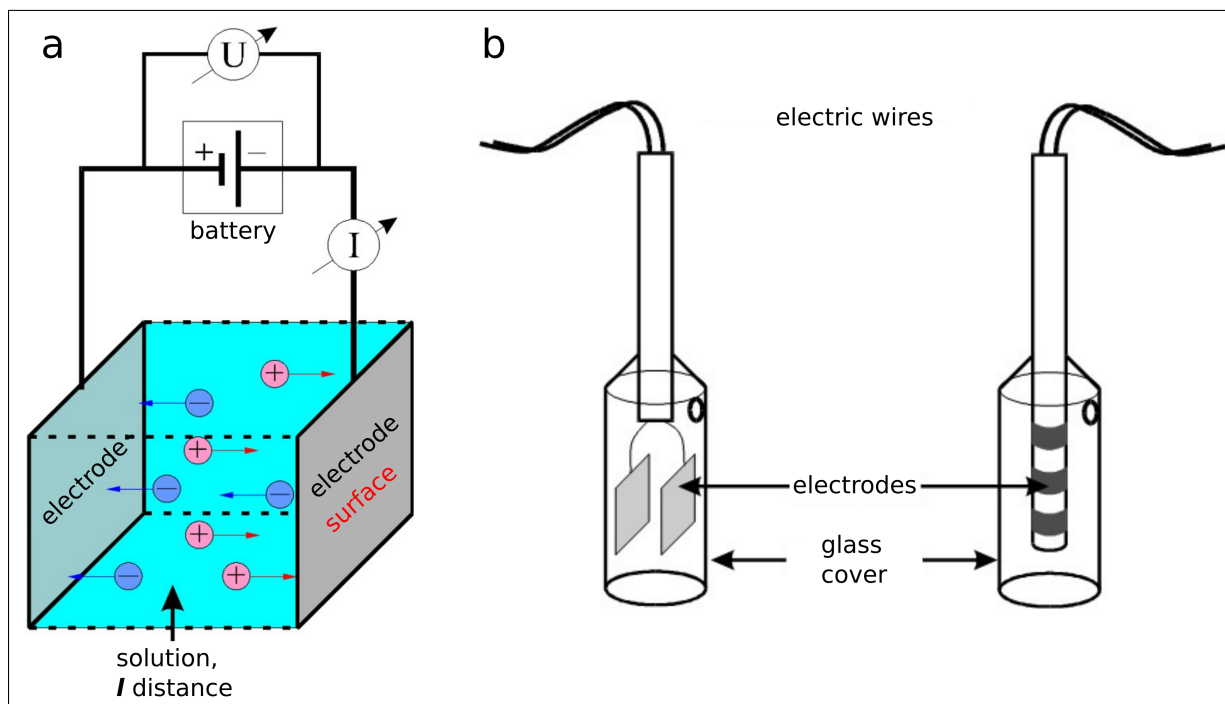
Figure 1: Conductivity cell (a) and the scheme of various probes (b).

electrolyte solution containing one mole dissolved substance. The numerical value of the molar conductivity is the conductance measured in a conductivity cell with such a volume which contains exactly one mole solute:

$$\Lambda_c = \frac{\varkappa}{c}, \tag{2}$$

where c is the (measured-in) analytical concentration of the electrolyte. Despite of the normalization to unit amount of substance, Λ_c still depends on the electrolyte concentration for both weak and strong electrolytes. Partly it is due to the change in electric mobilities with the concentration, and for weak electrolytes it is also due to the change in the degree of dissociation. In appropriately dilute solutions, where dissociation is complete and the motion of ions can be considered to be independent of each other (principally it should be an infinitely dilute solution), molar conductivity reaches a limiting value (Λ_0):

$$\Lambda_0 = \lim_{c \to 0} \Lambda_c \ .$$

Because of the complete dissociation, this physicochemcial property is characteristic for the electrolyte – solvent pair.

1.2 Connection between the dissociation of a weak electrolyte and its molar conductivity

Although the conductance of an electrolyte solution depends on various parameters, only the degree of dissociation shall be considered in an appropriately dilute solution of weak electrolytes. From that, dissociation constant of weak electrolytes can be determined by conductance measurements. Consider the dissociation of a weak acid

$$HA \rightleftharpoons H^+ + A^-, \quad K_d = \frac{[H^+] \cdot [A^-]}{[HA] \cdot c^\ominus},$$
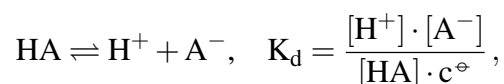
where $c^\ominus$ is the standard concentration. Having an analytical concentration $c = ([A^-] + [HA])$, the degree of dissociation (α) is written as

$$\alpha = \frac{[A^-]}{[A^-] + [HA]} = \frac{[A^-]}{c} = \frac{[H^+]}{c} \qquad \left(\Rightarrow 1 - \alpha = \frac{[HA]}{c} \right).$$

α is between 1 and 0, where 1 one means complete dissociation and 0 means complete lack of dissociation. Substituting equilibrium concentrations by α and by the analytical concentration, dissociation constant (K_d) is obtained as

$$K_d = \frac{\alpha^2 \cdot c}{(1 - \alpha) \cdot c^\ominus}. \tag{3}$$

Furthermore, the degree of dissociation, at dilute enough solutions, can also be expressed with molar conductivities:

$$\alpha = \frac{\Lambda_c}{\Lambda_0}.$$

After substituting this expression into Eq. (3) and rearranging it, we come to the final formula

$$\boxed{\frac{1}{\Lambda_c}} = \frac{1}{\Lambda_0} + \frac{\Lambda_c}{K_d \cdot \Lambda_0^2} \cdot \frac{c}{c^\ominus} \boxed{= \frac{1}{\Lambda_0} + \frac{1}{K_d \cdot \Lambda_0^2 \cdot c^\ominus} \cdot \varkappa}. \tag{4}$$

According to Eq. 4, the reciprocal of the molar conductivity linearly proportional to conductivity and from the intercept and the slope of the funtion Λ_0 and K_d can be determined (strictly in this order). That is, how we can determine dissociation constant of a weak electrolyte by conductometry.

2 Experimental

At the practice, water (purified by double distillation, ion exchange or reverse osmosis) will be titrated by the solution of a weak acid while conductance is measured in parallel.

The instructor *(1)* selects the weak acid to be investigated and *(2)* provides information about the volumes of the titrant. This must be planned in such a way that the square root of the titrant's volumes in the following steps have to be equally distributed between the minimum and maximum volumes. This ensures that sufficient amount of data points will cover each part of the investigated concentration range. The maximum titrant volume is $25\,\text{cm}^3$, while the minimum is given by the instructor in the range of 0,03–0,08 cm^3. The number of the titration points is also given by the instructor (20–30). *If not stated otherwise*, measurements must be done in 25 points and the first volume of the titrant is 0,05 cm^3. The calculated titration points must be approved by the instructor.

According to the selected weak acid, prepare the titrant solution with $100\,\text{cm}^3$ volume in a concentration given in Table 1. Because of the significant differences of concentrations of various titrants, see below for the appropriate preparation procedure:

– *Hydrogen sulfate*, as a salt, can be simply weigh in with the proper mass and dissolved in a beaker, poured into a volumetric flask, and filled.

– *Ascorbic acid* ($C_6H_8O_6$) solution is prepared in two steps. First, $100\,\text{cm}^3$ solution with $10\times$ larger concentration (0.05 M) is prepared by weighing-in. As a second step, $10.00\,\text{cm}^3$ of the just prepared stock solution is diluted to $100,0\,\text{cm}^3$ in a volumetric flask.

– *Phosphoric acid* and *salicylic acid* will be available at hand.

– *Glycolic acid*, *benzoic acid*, and *acetic acid* will be provided as stock solutions with approximately 0.01 M concentration. The tritrant must be prepared from the stock solutions by dilution.

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Table 1: List of available weak acids together with their concentrations as titrant solution.

	hydrogen sulfate	ascorbic acid	phosphoric acid	salicylic acid	glycolic- acid	benzoic- acid	acetic- acid
c_0/M	0.8	0.005	0.2	0.01	0.005	0.004	0.001

Once the titrant solution is prepared, switch on the conductometer and learn its use with the aid of the manual.

Measure $100,0\,cm^3$ pure water in a thin, tall, and dry beaker of $150\,cm^3$ volume by weighing-in (calculate the density of water at the temperature of the laboratory according to the Appendix). Place a clean and dry magnetic stirrer rod into the water and put the beaker on the stirrer. Place the already rinsed conductivity probe into the water and measure its conductance (G_0). *Note that as an industrial default of the instrument, cell constant is set to 1. Therefore, although conductivity is displayed, it is in fact conductance. After appropriate calibration, which will be performed by the end of the practice, such conductance will be transformed into conductivity with the determined cell constant.* Rinse and fill the burette with the titrant. Titrate the water with the titrant solution by adding the previously calculated volumes and register the conductance at the separate steps.

During the measurement, many predetermined points belong to relatively small volumes. Since adding portion of drops might be challenging, do not insist strictly to the calculated volumes, some hundredth cm^3 deviation will not cause any problem. The volume reading is easier and more precise at the instances when a drop just detached from the tip of the burette. In the lab note, always register the exact titrant volume added to the water, since those will be used for further evaluation. After adding the given titrant volume, turn on the stirrer to homogenize the solution. However, stirrer should be turned off and the solution steady during the conductance measurement.

Afterward, determine the conductance of the provided KCl solution (G_{KCl}) to obtain the cell constant.

The concentration of the weak acid solution used as titrant might not be analytically exact. Therefore, depending on the selected weak acid, the following procedure must be followed:

– *Hydrogen sulfate* and *ascorbic acid* solutions can be considered analytically exact, no further act is needed.

– For the other systems, concentration must be determined by acid−base titration. In the case of *phosphoric acid*, titrate $1\,cm^3$ in an Erlenmeyer flask with the provided 0.01 M NaOH solution. Add some water to the $1\,cm^3$ phosphoric acid to facilitate titration. For the rest of the systems, use $10\,cm^3$ instead and follow the same procedure. As indicator, use phenolphthalein in each case. *Phosphoric acid* behaves as diprotic acid under these conditions, while the other acids can be considered monoprotic.

At the end of the practice, thoroughly wash the equipment; the probe must be rinsed with pure water 5–6×, at least.

3 Evaluation

1. Calculate the cell constant with the aid of the Appendix and conductance measured in the KCl solution. If no conductivity data belonging to the lab temperature is found in the Appendix, interpolate.

2. Depending on the selected weak acid, calculate the concentration of the titrant solution on the appropriate way.

Table 2: Summary of measured and derived data.

$t_{lab}=\ldots\,^{\circ}C$, $c_{KCl}=\ldots M$, $G_{KCl}=\ldots S$, $c_{cell}=\ldots m^{-1}$, $c_0=\ldots M$, $G_0=\ldots S$

Added volume /cm^3	G /S	G_{corr} /S	c_{acid} /mol m^{-3}	$\varkappa$ /(S m^{-1})	Λ_c /(S m^2 mol^{-1})	$\dfrac{1}{\Lambda_c}$ /(S^{-1} m^{-2} mol)

3. Summarize the measured and calculated data according to Table 2. Obtain the not yet defined data as follows:

   – The measured conductance must be corrected by that of water, i.e., $G_{corr} = G - G_0$.
   – c_{acid} is the concentration of the weak acid solution at a given added titrant volume.

4. Plot $1/\Lambda_c - \varkappa$ function and determine Λ_0 and K_d together with their standard deviation (see Appendix: standard deviation of fitted parameters and its propagation). When deriving K_d, pay special attention to the effect of standard concentration appearing in the definition.

   Some deviation from a straight line can be observed when fitting the data points both at very low and relatively high concentrations. At low concentration, minor impurity can already cause such effect (e.g., HCO_3^- ions from by the dissolution of CO_2). At higher concentration, consider the change of equilibrium constant due to the varying ionic strength. If such effects are seen, fit the line through the middle of the data set only; as many points shall be used as possible.

5. Search the literature to compare the obtained dissociation constant with a tabulated value. Cite the literature accordingly.

Note:

1. Conductivity measurements must be performed with special care. Any charged impurity disturbs the system. Therefore, the purity of the equipment, solvents, and solutions is even more important than in other cases.

Questions

1. What is conductance and its SI unit?

2. What is conductivity and its SI unit?

3. What is cell constant for a conductivity cell with normal geometry?

4. How do you interpret the cell constant for a bell-shaped 3-electrode probe?

5. Define the molar conductivity and that for an infinitely dilute solution; provide the unit as well.

6. Define the dissociation constant. Give the expression between the degree of dissociation and molar conductivity.

7. Derive the expression between the dissociation constant of a weak electrolyte and the conductivity and molar conductivity of its solution.

8. Give the expression between the dissociation constant of a weak electrolyte and the conductivity and molar conductivity of its solution. Explain in 3–4 sentences how it is used in practice to obtain the dissociation constant.

9. How is the cell constant determined during the practice?

10. The conductance of a solution must be measured at 4 different added titrant volumes. The minimum added volume is $0.03\,cm^3$, its maximum is $10,00\,cm^3$. What are the two rest volumes if the square root of the volumes changes equidistantly.

11. The conductance of 0.01 M KCl solution is 1.23 mS at 24.3 °C. The conductivity of the same solution is $0.001386\,S\,cm^{-1}$ at 24.0 °C and $0.001413\,S\,cm^{-1}$ at 25.0 °C. Determine the cell constant.

12. $100.0\,cm^3$ water is titrated with 0.0049 M ascorbic acid solution. What is the analytical concentration of the weak acid at $12.73\,cm^3$ added titrant volume?

13. The conductance of 0.00017 M acetic acid solution is $153\,\mu S$ when applying a probe with $0.87\,cm^{-1}$ cell constant. The same probe measures $5.7\,\mu S$ for the conductance of water. Calculate the conductivity and molar conductivity of the solution.

14. The reciprocal of molar conductivity is plotted as a function conductivity for a data set. The slope of the fitted line is $35800\,S^{-2}\,m^{-1}\,mol$, while its intercept is $42.3\,S^{-1}\,m^{-2}\,mol$. Calculate the dissociation constant of the weak acid.