LIMITING MOLAR CONDUCTIVITY FOR WEAK AND STRONG ELECTROLYTES DETERMINATION

INTRODUCTION

An object of uniform cross-section has **electrical resistance** R proportional to its **resistivity** ρ and length l and inversely proportional to its cross-sectional area A.

$$R = \rho \cdot \frac{l}{A} \tag{1}$$

More generally, the geometric effects can be described by some factor k, which depends on the shape of the measuring object or, in the case of electrolytes, the shape of the conductivity measuring cell $R=\rho \cdot k$.
The coefficient ρ (Greek ‘rho’) is called **a specific resistance or a resistivity** and its SI unit is the ohms-meter [Ω·m]. The inverse of the specific resistance: ρ^{-1} is called **a specific conductance or conductivity**, σ (Greek: ‘sigma’) and the unity is Siemens per meter [$S \cdot m^{-1}$] :

$$\sigma = \frac{1}{\rho} \tag{2}$$

while the inverse of the resistance R is a conductance, G:

$$G = \frac{1}{R} \tag{3}$$

The **Siemens [S]** is the unit of conductance, while the **ohm [Ω]** (Ω = 1/S) is that of **resistance**.

The geometry of the measurement cell (conductivity cell) is expressed by a factor called constant cell k, calculated by the following equation:

$$k = \frac{l}{A} = \frac{\sigma}{G} \tag{4}$$

Where G is the measured value of conductance for electrolyte solution about known conductivity σ.
The unit of the conductivity is the **Siemens/cm [S/cm]** and **the constant** conductivity cell is the **1/cm.**

The **molar** or **equivalent conductivity** Λ of an electrolyte is defined as the conductivity of an electrolyte solution divided by the molar concentration of the electrolyte. Established by Kohlrausch, its physical meaning is an efficiency with which a charge is transferred by 1 mole of solute (or chemical equivalent).

$$\Lambda = \frac{\sigma}{c} \tag{5}$$

where c is the formal concentration in equivalents (‘moles of charge) per unit value ($mol \cdot dm^{-3}$).

According to **Kohlrausch's Law**, at infinite dilution of electrolyte interionic effects are negligible. The assumption of negligible ionic interactions at infinite dilute electrolytes makes the shares of ionic conductivities of particular ions additive.

$$\Lambda^{\infty} = \lambda_{+}^{\infty} + \lambda_{-}^{\infty} \tag{6}$$

Based on experimental data Kohlrausch (1900) proposed the non-linear law for strong electrolytes

$$\Lambda = \Lambda^{\infty} - K_{cf}\sqrt{c} \tag{7}$$

Where K_{cf} is Kohlrausch coefficient
Molar conductivity at infinite concentration Λ^{∞} (or limiting molar conductivity) can be determined by extrapolation of values of conductivities to zero concentration.

$$\Lambda^{\infty} = \lim_{c \to 0} \Lambda \tag{8}$$

The types and units of resistance and conductance are presented in Table 1.

Table 1. The units of the resistance and conductance parameters.

Name	Symbol		Unit SI
Electrical resistance	R		Ω
Electrical conductance	G		$S = \Omega^{-1}$
Resistivity	ρ	[rho]	$\Omega\cdot m$
Conductivity	σ	[sigma]	$Sm^{-1} = \Omega^{-1}\cdot m^{-1}$
Molar conductivity	Λ	[lambda]	$S\cdot m^{2}\cdot mol^{-1} = \Omega^{-1}\cdot m^{2}\cdot mol^{-1}$
Equivalent conductivity at infinite dilution	Λ^{∞}		$S\cdot m^{2}\cdot mol^{-1} = \Omega^{-1}\cdot m^{2}\cdot mol^{-1}$
Molar conductivity of an ion	λ		$S\cdot m^{2}\cdot mol^{-1} = \Omega^{-1}\cdot m^{2}\cdot mol^{-1}$
Molar conductivity of an ion at infinite dilution	λ^{∞}		$S\cdot m^{2}\cdot mol^{-1} = \Omega^{-1}\cdot m^{2}\cdot mol^{-1}$

The equivalent conductivity at infinite dilution, Λ^{∞} for weak electrolytes, can be calculated using equation (6). For example: Λ^{∞} for an acetic acid solution is calculated based on measured values of Λ^{∞} for HCl, NaCl, and NaAc

$$\Lambda^{\infty}(HAc) = \Lambda^{\infty}(HCl) + \Lambda^{\infty}(NaAc) - \Lambda^{\infty}(NaCl) \tag{9}$$

The degree of dissociation α and **dissociation constant**, K, for a 1:1 electrolyte, can be calculated from equation (10) and (11), respectively:

$$\alpha = \frac{\Lambda}{\Lambda^{\infty}} \tag{10}$$

and

$$K = \frac{\alpha^{2} c}{1 - \alpha} \tag{11}$$

EXERCISE PURPOSE

1. Determination of the influence of concentration of NaCl, CH_3COONa, HCl (strong electrolytes), and CH_3COOH (weak electrolyte) on molar conductivities.
2. Determination of the equivalent conductance Λ^∞ at infinite dilution for acetic acid.
3. Calculation of the dissociation degree α and the constant dissociation K for acetic acid.

APPARATUS

- Conductometer type N 5721
- Thermostat

LAB GLASS

- Beakers 100ml – 2 psc.
- Pipettes 10ml – 1 pc.
- Volumetric flasks 50ml – 6 pcs.
- Wash bottle

CHEMICALS

- Solutions: 0.1 M: NaCl, HCl, CH_3COONa, CH_3COOH

EXPERIMENT PROCEDURES

1. Conductivity measurements are carried out in the thermostatic cell at 25ºC.
2. Prepare appropriate concentrations of electrolytes and measure the specific conductance values of solutions (NaCl, HCl, CH_3COONa, and CH_3COOH) of known concentrations: 0.020, 0.015, 0.010, 0.005, 0.001, and 0.0005 mole·dm-3. It is advisable first to measure a solution 0.0005 M and then change it and refill the cell with the most concentrated solutions (**without washing between individual measurements**). Next, wash the experimental cell with distilled water and measure the conductance values of the other solutions chemical compounds starting with the most diluted one.

Before taking measurements, all lab glass should be thoroughly washed a distilled water.
Warning!
After the end, the electrode/dip cell should be immersed in the measuring cell filled with distilled water.
The conductometer is pre-integrated in the probe cell and adjusted in units of the specific conductivity [S/cm].

CALCULATIONS

1. Calculate the share of conductivity connected with the chemical compound itself - subtract the value of the specific conductivity of water from the measured specific conductivity of solutions.
$$\sigma_{XY} = \sigma_{solution} - \sigma_{H_2o}$$
2. Calculate the molar conductivities Λ for all electrolytes, based on equation (5).
3. Plot a graph Λ vs. $\sqrt{c}$ for all solutions of electrolytes.
4. From the above-obtained diagram determine values of Λ^∞ for NaCl, CH_3COONa and HCl by the extrapolation of Λ to the infinite dilution (values of the intercepts).
5. Calculate the value of Λ^∞ for CH_3COOH according to the Kohlrausch Law (equation (9).
6. Calculate the degree of dissociation α and dissociation constant K of CH_3COOH for each concentration.
7. Plot a graph K vs. $\sqrt{c}$ and c for CH_3COOH.

Template of the table and draft of the study

……………………………... *Faculty* ………………………………. *Field of study* *Full-time/ part-time studies*	………………………………………………. *Name and surname*	………………………………….... *Date:*
Group no.: ………………… *Team no.:* …………………	……...…………… *Exercise no.:*	……………………………………. *Instructor:*

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Nr grupy: ………………….. *Nr zespołu:* …………………..	……...…………… *Nr ćwiczenia:*	……………………………………. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia	1. Exercise title:
2. Cel ćwiczenia:	2. The aim of the exercise:
3. Wstęp teoretyczny:	3. Theoretical introduction:
4. Pomiary:	4. Results:
5. Obliczenia:	5. Calculations:
6. Wykresy:	6. Graphs:
7. Wnioski	7. Conclusions: