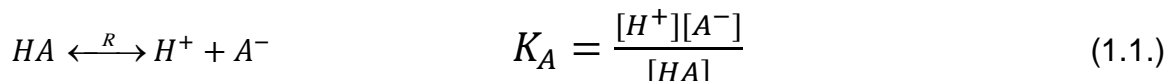


1. Acid-base equilibria

1.c. Determination of conductivity of strong and weak electrolyte



The solvated ions H^+ and A^- are occurred when a substance HA of analytical concentration c_{HA} is dissolved in water or other polar solvent. The thermodynamic equilibrium exists in the solution:



The degree of dissociation α determines whether the equilibrium is shifted in favour of the dissociated ions or original undissociated compound.

$$\alpha = \frac{(c_{HA} - [HA])}{c_{HA}} \quad (1.2.)$$

Rearranging of equation and apply of electroneutrality condition give (if we neglect solvent dissociation) following:

$$[HA] = c_{HA} \cdot (1 - \alpha) \quad \text{and} \quad [H^+] = [A^-] = c_{HA} \cdot \alpha \quad (1.3.)$$

The dissociation degree α is determined not only by the properties of the substance HA but also by the solvating ability of the solvent.

The dissociated solute HA increases the initial electrical conductivity of the solvent. Dissolved solute is called weak electrolyte in a given solvent (eg aqueous solutions of carboxylic acids, H_2S , H_3BO_3 , NH_3) if the dissociation degree is small or close to zero ($\alpha \rightarrow 0$). Dissolved solute HA is called a strong electrolyte if the dissociation degree is close $\alpha \cong 1$. For example, aqueous solutions of inorganic acids and bases (HCl , $NaOH$, ...) and ionic salts (KCl , $NaNO_3$, ...).

The concentration of dissociated ions in the solution has a significant effect on its total electrical conductance G (measured in Simens $1S = 1\Omega^{-1} = 1CV^{-1}s^{-1}$) that is the reciprocal quantity of electrical resistance R (unit Ω). Similarly to metal conductors, a specific resistance [Ωcm] can be detected for solutions, but it is preferred to monitor the specific conductivity of solutions [$S cm^{-1}$], which is as well the reciprocal value of specific resistance.

The specific conductivity κ of the solution is calculated from its conductivity G that is measured by conductivity probe with known resistance constant C [cm^{-1}] according to relationship:

$$\kappa = C \cdot G \quad (1.4.)$$

The geometric constant of conductivity probe C can be most easily determined by measuring the conductivity of solution G with known specific conductivity. Usually, the aqueous KCl solution is used as standard electrolyte.

Specific conductivity of $0,01 M KCl$ (i.e. $\kappa_{0,01M KCl}$ in [$S cm^{-1}$]) depending on temperature t (in $^{\circ}C$) can be found in tables or calculated using polynomial:

$$\kappa_{0,01M KCl} = a_1 + a_2 \cdot t + a_3 \cdot t^2$$

where: $a_1 = 7.728 \cdot 10^{-4}$, $a_2 = 2.345 \cdot 10^{-5}$, $a_3 = 7.816 \cdot 10^{-8}$. (1.5.)

Modern conductivity meters measure specific conductivity κ directly when properly calibrated to *KCl* standard solution.

A very important characteristic of the solutions is the molar conductivity, which is calculated from the specific conductivity according to the formula:

$$\lambda = \frac{\kappa}{c} \quad (1.6.)$$

where c is molar concentration of solute. The molar conductivity of the solute extrapolated to zero molarity (in the limit of zero concentration) is called the limiting molar conductivity:

$$\lambda_0 = \sum (v_i \cdot \lambda_0^i) \quad (1.7.)$$

where λ_0^i is a limiting molar conductivity of particular ion i presented in the solution (compare **TABLE I**), v_i is the number of ions to which the solute dissociates in the solution.

Assuming that the dissociated ions do not affect each other, we can calculate the dissociation degree for both strong and weak electrolytes:

$$\alpha = \frac{\kappa}{c \cdot \lambda_0} = \frac{\lambda}{\lambda_0} \quad (1.8.)$$

The dissociation constant of weak mono-acidic acids can be determined according to Ostwald's dilution law obtained by inserting eqn (1.8.) in (1.3.) and then into eqn (1.1.):

$$K_A = \frac{c \cdot \lambda^2}{\lambda_0 (\lambda_0 - \lambda)} \quad (1.9.)$$

The Ostwald dilution law can be arranged to a linearized formula

$$\frac{1}{\lambda} = \frac{c \cdot \lambda}{K_A (\lambda_0)^2} + \frac{1}{\lambda_0} \quad (1.10.)$$

that is appropriate for graphical determination of the dissociation constant K_a and the limiting molar conductivity of solute λ_0 .



TASK: Determine the dissociation degree of hydrochloric acid and acetic acid depending on their concentration in water at 25 °C. Decide whether they are strong or weak electrolyte. For both solutes, compare the experimentally measured λ_0 to the tabulated value. For acetic acid, calculate its dissociation constant K_A .



LABORATORY AIDS AND CHEMICALS: conductivity meter, conductivity vessel and probe, thermostatic bath, 14 volumetric flasks (50 ml), 1 volumetric pipette (25 ml), $5 \cdot 10^{-2} M$ hydrochloric acid, $5 \cdot 10^{-2} M$ acetic acid, 0.01M *KCl*, redistilled water to prepare aquatic solutions.



INSTRUCTIONS: We first check the conductivity of the redistilled water. Rinse thoroughly both the thermostatic measuring vessel and the conductivity probe with redistilled water. Measure the temperature and conductivity of the redistilled water. Conductivity should not be higher than 10 μS at 25 °C. Measure the conductivity of the standard solution of 0,01M *KCl* in the same way (including rinsing) if the geometric constant of probe C is not known.

During the previous measurement, prepare the hydrochloric and acetic acid solutions each in 7 different concentrations. Use 50 ml volumetric flasks, redistilled water (adjective "redistilled" will be omitted in further text), and stock solutions of both hydrochloric and acetic acid.

Use gradual dilution of stock solution with water in 1:1 ratio. Put the stock solution in the first flask. Prepare the second solution by taking the 25 ml from first solution and inserting in 50 ml volumetric flask. Add water up to marking and mix by gentle shaking. Prepare the third solution from the second solution by the same procedure as the second from the first solution. This is how we continue in a whole series. Do not forget to add water at the last solution up to 50 ml marking.

Rinse carefully the tempered vessel and the conductivity probe by water. Use a small part of HCL solution with the lowest concentration for definitive rinsing. Finally, let a sufficient amount of the solution in the thermostatic vessel for temperature equilibrating. Record the conductivity of the solution when the solution has a temperature of 25 °C and the conductivity value is stabilised (remains unchanged).

Subsequently, measure all prepared hydrochloric acid solutions. Proceed from the lowest concentrations to higher. Do the same way with acetic acid.



REPORT: Table 1: for each measured electrolytes: theoretical value λ_0 . **Table 2:** for each electrolyte: c , temperature t , κ , λ , α . **Common graph 1:** for both electrolyte: experimental dependence λ on c . **Common graph 2:** for both electrolyte: dependence α on c . **Table 3:** for weak acid: c , $1/\lambda$, $\lambda \cdot c$. **Graph 3:** for weak acid: dependence $1/\lambda$ on product $\lambda \cdot c$ (including regression line). **Next:** for weak acid: experimental value λ_0 and K_A calculated from intercept and slope of regression line.

TABLE I: Limiting molar conductivities of ions λ_0^i at 25 °C.

Ion	H^+	K^+	Na^+	OH^-	CH_3COO^-	CH_2ClCOO^-	Cl^-
$\lambda_0 [cm^2 Smol^{-1}]$	349.8	73.5	50.1	198.0	40.9	39.8	76.3