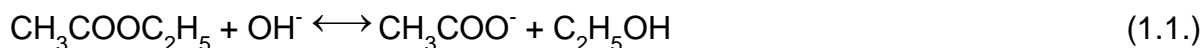# 1. Chemical kinetics

1.a. Saponification of ethyl acetate

Saponification of ethyl acetate is a reaction of second order kinetics. Reaction proceeds according to the equation:

$$CH_3COOC_2H_5 + OH^- \longleftrightarrow CH_3COO^- + C_2H_5OH \tag{1.1.}$$

The rate equation of the reaction is given by the relationship:

$$v = \frac{dx}{dt} = k(a-x) \cdot (b-x) \tag{1.2.}$$

where a and b are, respectively, initial concentrations of ethyl acetate and hydroxide. x is the extent of the reaction (in volume unit) that is equal to the acetic anion concentration or ethanol concentration at time t counted from the reaction begin. The mathematical solution of the velocity equation (1.2.) leads to the integral relationships

$$k = \frac{1}{(a-b)t}\ln\frac{(a-x)b}{(b-x)a} \qquad \text{and} \qquad \ln\frac{(a-x)b}{(b-x)a} = (a-b)kt \tag{1.3.}$$

The concentration of Na^+ ions remains constant and it is equal to the initial concentration of OH^- ions during the reaction. The initial concentration of the hydroxide has to be in excess with respect to the ethyl acetate concentration in order to avoid dividing by zero in eqn (1.3.) and to ensure reaction basic environment. Since the moving OH^- ions are replaced by less-moving acetate ions Ac^-, the reaction can be monitored by measuring the conductivity of the reaction mixture.

Concentration of the free acetate ions can be calculated according to relationship:

$$x = \frac{(\kappa_0 - \kappa)}{\lambda_{(OH^-)} - \lambda_{(Ac^-)}} \tag{1.4.}$$

where κ_0 is the specific conductivity of the hydroxide solution at reaction beginning, κ is the specific conductivity of the reaction mixture at time t. λ_{OH^-} and λ_{Ac^-} is the molar conductivity of OH^- and Ac^- ionts. The acetate and hydroxide anions are part of a strong electrolyte with Na^+ ions, so we can replace the molar conductivity λ_i by limiting molar conductivity λ_0^i (see values in **TABLE I**).

The dependence of the rate constant on temperatures is given by Arrhenius equation:

$$k = A \cdot \exp(-E_A / RT) \tag{1.5.}$$

where E_A is called the activation energy and A is the frequency factor. Both values can be obtained from the parameters of the regression line obtained using the linear form of the Arrhenius equation:

$$\ln(k) = \ln(A) - \frac{E_A}{R} \cdot \frac{1}{T} \tag{1.6.}$$

Frequency factor A is related to the activation entropy ΔS_A according to formula:

$$A = \frac{e \cdot k_b \cdot T}{h} \exp(\Delta S_A / R) = 5{,}664 \cdot 10^{10} \, T \cdot \exp(\Delta S_A / R) \qquad\qquad (1.7.)$$

where *e* is the basis of natural logarithm (*2.7182818*), *h* is the Planck constant (*6.6260755·10⁻³⁴ J s*), k_b means the Bolzman constant (*1.380658·10⁻²³ J K⁻¹*).

? TASK: Determine the rate constant of the saponification reaction of ethyl acetate with the hydroxide at three different temperatures. Monitor the concentration changes by measuring the specific conductivity of the reaction solution via automatic experimental data collection using PC. Calculate the activation energy, frequency factor, and activation entropy.

✂ LABORATORY AIDS AND CHEMICALS: conductivity meter connected to PC, conductivity vessel and probe, thermostatic bath, 2 volumetric flasks (*200 cm³* and *250 cm³*), glass weighing bottle with lid, volumetric pipette (*20 cm³*), grade pipette (*10 cm³*), ethyl acetate, *0,1 M NaOH*.

✚ Ethyl acetate is a volatile substance, so keep always the weighing bottle well closed. Take care to do weighting quickly and moving the substance into volumetric flask without delay.

▤ INSTRUCTIONS: Prepare the *250 cm³* of the *0,015 M NaOH* solution in volumetric flask. Then weigh about *0.2 g* of ethyl acetate (*16* drops, *±1 mg* accuracy) in the weighing bottle with lid and dilute it with water in the *200 cm³* volumetric flask.

1. **Preparation of experiment.** Switch the thermostatic bath on and check whether the medium circulate in the jacket of the reaction vessel. Set the first measuring temperature (close to 20.0 ° C). Close the volumetric flasks involving ethyl acetate and hydroxide by stopper and place the *Pb-* loads on the flask necks. Put the solutions into the thermostat bath and let them equilibrate.

2. **MEASUREMENT OF STARTING SPECIFIC CONDUCTIVITY ($t = 0$).** Pipette the same volumes of the *0.015 M NaOH* solution and water into dry beaker and mix. Use the part of the solution to rinsing of reaction vessel and conductivity probe. Put the rest of the solution into vessel and let it equilibrate. Measure specific conductivity κ_0 (the value is equal to the starting specific conductivity of the reaction mixture in subsequent experiment).

3. **CONDUCTIVITY MEASUREMENT OF REACTION MIXTURE.** Rinse the reaction vessel with water and make dry inside. Start the data collection with recording of each 3 seconds. Pipette 20ml of the 0.015 M NaOH into the reaction vessel, insert conductivity probe and let the solution equilibrate at measuring temperature. Take the basic solution of the ester from the thermostat, pipette 20 ml of ester solution directly into the measuring vessel with the hydroxide. Mix quickly but gently using conductivity probe. Record the specific conductivity for at least 30 min.

4. Repeat the measurement of the starting specific conductivity and the changes of the reaction conductivity at 30 and 40 °C by the same way as given above.

🖥 DATA ANALYSIS: Check the experimental data record of and identify the mixing moment (set t = 0sec). Find the specific conductivity at the at reaction beginning κ_0 by exponential extrapolation from measured data. Compare extrapolation value κ_0 with the experimental starting specific conductivity of the *NaOH* solution. It should be the same. In the calculations, pay the attention to use the correct units (S vs. mS, cm

vs. dm). Use the regression lines of the linear forms (1.3.) and (1.6.) to evaluate rate constants k, activation energy E_a and frequency factor A.

✍   **REPORT:** the weight of the ester droplets, the exact concentration of the ester and hydroxide solution, the concentrations of ester a and hydroxide b at the reaction beginning. **Table 1:** for each temperature: experimental and extrapolated specific conductivity at the reaction beginning κ_0, molar conductivities λ_{OH^-} and λ_{Ac^-}. **Table 2a,b,c:** for each temperature: reaction time t, specific conductivity κ, extend of the reaction x, value $\{[(a-x)b]/[(b-x)a]\}$ and $\ln\{[(a-x)b]/[(b-x)a]\}$. **Common graph 1:** for each reaction temperature: dependency of κ on t. **Common graph 2:** for each reaction temperature: dependency of $\ln\{[(a-x)b]/[(b-x)a]\}$ on t (including regression line). **Table 3:** temperature in Celsius and Kelvins, rate constants k calculated (1.3.) from slopes of the regression lines in Common graph 2, values $1/T$ and $\ln k$. **Graph 3:** dependence $\ln k$ on $1/T$ (including regression line). **Next:** value E_A, frequency factor A and activation entropy of the reaction ΔS_A calculated by use of eqn (1.7.).

TABLE I: Parameters that are used in the relationship $\lambda_0^i(T) = \lambda_0^i(291) \cdot (1 + \alpha \cdot (T - 291))$ for calculation of limiting molar conductivities of the selected ions at temperature T (in Kelvin).

Ion	$\lambda_0^i(291)$ / $S\ cm^2\ mol^{-1}$	$\alpha = d(\lambda_0^i(T))/dT$ / K^{-1}
OH^-	$1.670 \cdot 10^2$	$1.8 \cdot 10^{-2}$
Ac^-	$0.306 \cdot 10^2$	$2.4 \cdot 10^{-2}$