Determining the Characteristics of Sodium Benzoate (E211) Production Using Mathematical Method

Anita Kovač Kralj*

Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, Maribor, Slovenia

Abstract: The productivity of a particular product is highly effective if we know the chemical kinetics. Determining chemical kinetics requires a fundamental knowledge of reactants' declining concentrations or the formation of product concentration. Concentration can be determined by double-linear extrapolation, using the conductivity measurement of strong electrolytes. This method is based on two linear sloped-lines from which the linear constants from different diagrams can be read:

The first diagram represents linear time dependence regarding difference in conductivity

2) The second diagram represents linear difference in conductivity dependence regarding concentration.

Determining the characteristics of sodium benzoate (E211) production by using double-linear extrapolation provides fast results for chemical kinetics.

Sodium benzoate ($NaC_6H_5CO_2$) is a preservative. It is produced by the neutralization of benzoic acid ($C_7H_6O_2$) with sodium hydroxide (NaOH) in a stirred batch reactor under different room temperatures:

$$NaOH + C_7H_6O_2 \leftrightarrow NaC_6H_5CO_2 + H_2O$$
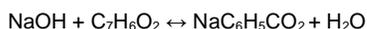
The kinetic parameters and characteristics of sodium benzoate production (activation energy, reaction rate constant, rate order) were determined.

Keywords: Sodium benzoate synthesis, strong electrolyte, strong electrolyte, linear extrapolation, conductivity.

1. INTRODUCTION

Changes in concentration, depending on time, are basic for chemical kinetics. Eldridge and Piret [1] obtained the pseudo-first-order reaction rate constant using a batch reactor. In order to determine the acetic anhydride concentration, samples from the reactor were withdrawn into tarred flasks containing 15-20 times the quantity of saturated aniline-water required to react with the sample. Since the anhydride rapidly acetylates the aniline, thus producing acetanilide and acetic acid, the samples were then titrated to determine the concentration of acetic acid. In another study, Shatyski and Hanesian [2] determined the kinetics of the above reaction by using temperature-time data obtained under adiabatic conditions in a batch reactor. The use of in-situ FTIR spectroscopy for following the hydrolysis of acetic anhydride reaction has already been demonstrated [3]. The analysis of the batch reactor data showed that the hydrolysis of acetic anhydride is a pseudo-first order reaction. The rate constants were calculated from the batch data using both integral and differential methods of analyses.

Sodium benzoate is produced by the neutralization of benzoic acid with sodium hydroxide. It is

bacteriostatic and fungistatic under acidic conditions. Sodium benzoate is declared on a product label as E211. Benzoic acid is a more effective preservative; whilst sodium benzoate is more commonly used as a food additive because benzoic acid does not dissolve well in water. The International Programme on Chemical Safety found no adverse effects in humans at doses of 647–825 mg/kg of body weight per day [4].

The knowledge of the chemical reaction kinetic in complex chemical systems is essential for the accurate and reliable design of reactors. It has a significant impact on the equipment needed in chemical production plants [5-9].

The problem of an accurate design of chemical reactors is not only economical, it is directly related to safety issues and hazard assessment. Simplified or inaccurate design of a chemical reactor can lead to disastrous consequences. Without knowledge of chemical kinetic the chemical process can accelerate significantly and it can lead to runaway reaction and possible explosion of a reactor [10-12].

The main problem in the modelling of complex kinetics is the huge amount of data needed to describe accurately the chemical processes. These data are not always available, and, even if they are known and accurate, in order to find important physical characteristics of a system extensive computational

*Address corresponding to this author at the Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, Maribor, Slovenia; Tel: +386 02 2294454; Fax: +386 02 2527 774
E-mail: anita.kovac@uni-mb.si

resources are required to perform numerical integration of a system of equations [13-15].

This paper studies the determination of chemical kinetics regarding the production of sodium benzoate from benzoic acid ($C_7H_6O_2$) and sodium hydroxide (NaOH), by using the double-linear extrapolation method.

2.   THE   DOUBLE-LINEAR   EXTRAPOLATION METHOD

The double-linear extrapolation method is an alternative method for determining concentration by measuring the conductivity of a strong electrolyte. This double-linear extrapolation method is a very simple method over two stages, each stage of the method looks for different constants from the sloped-lines in each diagram (Figure **1**):

2.1. First Step - Determining the Conductivity Constant

The basis of the first step is a diagram which represents the linear time dependence regarding the difference in conductivity. The conductivity constant, s_κ, can be read from the sloped-line, which is constant for each reaction. So, with a known value for the conductivity constant s_κ, any difference in conductivity ($\Delta\kappa$) at a specific time (t) can be determined:

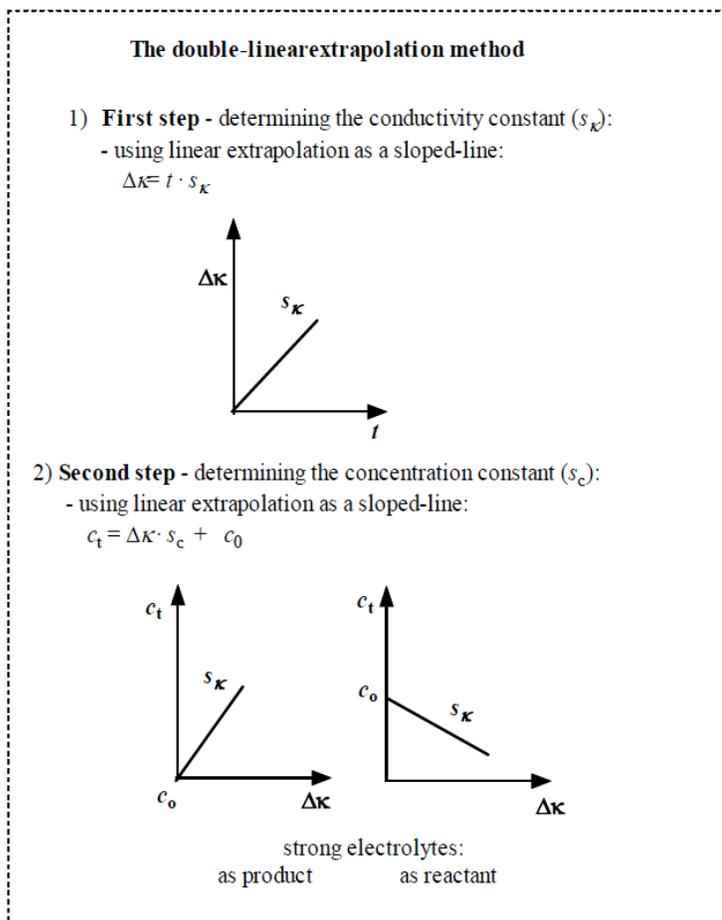$$\Delta\kappa = t \cdot s_\kappa \qquad (2.1)$$

$$\Delta\kappa = \kappa_0 - \kappa_t \qquad (2.2)$$

The conductivity constant (s_κ) can be determined graphically by using linear extrapolation as a sloped-line (eq. 2.1). The difference in conductivity ($\Delta\kappa$; eq. 2.2) can be determined by subtracting the initial conductivity (κ_0) of the conductivity, at different times (κ_t).

2.2. Second Step - Determining the Concentration Constant

The basis of the second step is a diagram which represents the linear difference in conductivity, depending on the concentration. The concentration constant s_c, can be read from the sloped-line, which is constant for each reaction. So, with a known value for

Figure 1: The double-linear extrapolation method.

concentration constant s_c, concentration (c) at a specific difference in conductivity ($\Delta\kappa$) can be determined:

$$c_t = \Delta\kappa \cdot s_c + c_0 \tag{2.3}$$

Concentration constant (s_c) can be determined graphically by using linear extrapolation as a sloped-line (eq. 2.3). c_0 is the known initial concentration.

Concentration constant (s_c) can be calculated by using equation 2.4 from a known concentration, depending on time and conductivity. This is sufficient for some data.

$$s_c = -(c_0 - c_t)/(\kappa_0 - \kappa_t) \tag{2.4}$$

Concentration can be determined by various methods: by titration for strong electrolytes (as shown in Chapter 3) etc. The theories of strong electrolytes and double-linear extrapolation methods would produce similar values for concentration, since they are based on similar mathematical connections - both are linear dependent.

Each reaction has specifically characteristic double-linear constants, which can be determined by using double mathematical linear extrapolation. Conductivity for a specific reaction has a specific characterization, therefore, certain linear constants can be determined, which are constant during a specific reaction. Once we know both the conductivity and concentration constants, which can be calculated after only a few known parameters (eq. 2.1 and 2.4) and can further calculate the desired concentration (eq. 2.3).

The accuracy of this method was tested by using the theory of strong electrolytes (ch. 3)

3. DETERMINING THE CONCENTRATION BY USING THE THEORY OF STRONG ELECTROLYTES

Strong electrolytes are substances that are almost fully ionized in solution, and include ionic solids and strong acids. As a result of their complete ionization, the concentration of ions within a solution is proportional to the concentration of the added strong electrolyte [5].

In an extensive series of measurements during the nineteenth century, Friedrich Kohlrausch showed that, at low concentrations, the molar conductivities of strong electrolytes vary linearly with the square root of the concentration:

$$\Lambda_m = \Lambda_m^\circ - K\sqrt{c} \tag{3.1}$$

where Λ_m introduces the molar conductivity in siemens metre-squared per mole (S m^2 mol^{-1}), which is defined as:

$$\Lambda_m = \frac{\kappa}{c} \tag{3.2}$$

where c is the molar concentration of the added electrolyte, and κ is the conductivity in siemens per meter (S m^{-1}).

Equation 3.1 is called Kohlrausch's Law. The constant Λ_m° is the limiting molar conductivity, the molar conductivity within the limit of zero concentration. The Λ_m° for sodium hydroxide at a temperature of around 25°C is [5]:

$$\Lambda_m^\circ = 5.01 + 19.91 = 24.92 \text{ mS m}^2 \text{ mol}^{-1} = 2492 \text{ mS dm}^2 \text{ mol}^{-1} \tag{3.3}$$

Kohlrausch's constant can be calculated by known values for initial concentration (c_0) and initial conductivity (κ_0), using equation 3.1 and 3.2:

$$K = \frac{\Lambda_m^\circ}{c_0^{0.5}} - \frac{\kappa_0}{c_0^{1.5}} \tag{3.4}$$

The essence of the strong electrolytes theory is that you can determine the concentration of the reactant or product. The reaction was observed by the concentration calculation. The two basic equations 3.1 and 3.2 were used:

$$\Lambda_m^\circ - K\sqrt{c} = \frac{\kappa}{c} \tag{3.5}$$

The concentration can be expressed as a cubic equation:

$$c^3 - \frac{\Lambda_m^{\circ 2} c^2}{K^2} + \frac{\Lambda_m^\circ 2\kappa c}{K^2} - \frac{\kappa^2}{K^2} = 0 \tag{3.6}$$

or in general:

$$ax^3 + bx^2 + cx + d = 0 \tag{3.7}$$

The concentration was expressed for equation 3.5 using for the numerical method:

$$c = \frac{\kappa + c^{1.5} K}{\Lambda_m^\circ} \tag{3.8}$$

The concentration was calculated by using a numerical method (for example successive substitution; addition A). The initial concentration (zc) and the allowed differences between the initial and target values (EPS) are needed.

The determination of concentration change by using a numerical method is very long-term, so it is only used

at the beginning in order to determine the conductivity and concentration constants when using the double-linear extrapolation method (chapter 2.), which is faster and sufficiently precise.

The simplified chemical kinetics, which includes the excesses of other components, is described in Chapter 4.

4. REACTION RATE

For a constant-volume batch reactor [3], the rate at which reactant A' appears (sodium hydroxide (NaOH)), r_A, is given by:

$$-r_A = \frac{dc_A}{dt} \tag{4.1}$$

where r_A can be expressed as:

$$-r_A = k \cdot c_A^n \cdot c_B^m \tag{4.2}$$

where k is the reaction rate constant, n and m are the reaction orders with respect to species A (sodium hydroxide) and B (benzoic acid ($C_7H_6O_2$)), respectively. The first benzoic acid is in excess, and c_B remains essentially unchanged during the course of the reaction:

$$-r_A = k' \cdot c_A^n \tag{4.3}$$

where k' is a pseudo rate constant

$$k' = k \cdot c_B^m \approx k \cdot c_{B0} \tag{4.4}$$

The second sodium hydroxide is in excess, and c_A remains essentially unchanged during the course of the reaction:

$$-r_B = k'' \cdot c_B^m \tag{4.5}$$

where k'' is a pseudo rate constant

$$k'' = k \cdot c_A^n \approx k \cdot c_{A0} \tag{4.6}$$

The reaction order and rate constant can be determined by the integral method of analysis. In this method, the rate expression is guessed and the differential equation used to model the batch system is integrated. If the assumed order is correct, the appropriate plot (determined from the integration) of concentration-time data should be linear.

For the first-order case where $-r_A = k\,c_A$, integration of equation 4.1 yields:

$$k \cdot t = \ln \frac{c_{A0}}{c_A} \tag{4.7}$$

where c_A is the current sodium hydroxide concentration and c_{A0} is the initial sodium hydroxide concentration. Benzoic acid, c_B, is in excess.

For the first-order case where, c_A, sodium hydroxide is in excess:

$$k \cdot t = \ln \frac{c_{B0}}{c_B} \tag{4.8}$$

where c_B is the benzoic acid concentration, and c_{B0} is the initial benzoic acid concentration.

For the second-order case where $-r_A = k\,c_A^2$, integration of equation 4.1 yields:

$$\frac{1}{c_A} = \frac{1}{c_{A0}} + k \cdot t \tag{4.9}$$

For the second-order case where, c_A, sodium hydroxide is in excess:

$$\frac{1}{c_B} = \frac{1}{c_{B0}} + k \cdot t \tag{4.10}$$

The specific reaction rate k, is a function of the reaction temperature, and is given by the Arrhenius equation:

$$k = k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \tag{4.11}$$

where k_0 is the pre-exponential factor, E_a is the activation energy for the reaction, and T is the absolute temperature.

This paper presents the chemical kinetic and characteristics determination of sodium benzoate, by using the double-linear extrapolation method.

5. CASE STUDY - SODIUM BENZOATE SYNTHESIS

Simplified chemical kinetics regarding the synthesis of E211, performed using different excesses of components - benzoic acid (chapter 5.1) and sodium hydroxide (chapter 5.2).

5.1. Benzoic Acid is in Excess

A schematic diagram of the laboratory apparatus is shown in Figure **2**. A batch reactor with a stirrer was used in the experiment. Sodium hydroxide (0.2850 g) was dissolved in water (0.1 L) and heated in a reactor at a temperature of 18.5 °C. 61.45 % surplus of benzoic acid (1.4035 g dissolved in 0.5 L of water) was added:

$$NaOH + C_7H_6O_2 \leftrightarrow NaC_6H_5CO_2 + H_2O \tag{R1}$$
$$\quad A \qquad\qquad B \qquad\qquad\quad C \qquad\qquad D$$
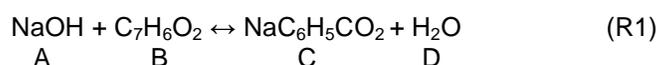
5.1.1. Determining the Concentration by Using the Theory of Strong Electrolytes

Both substance were mixed and the conductivity (κ_t) depending on time, t (Table **1**) was measured.

Firstly, the conductivity of the sodium hydroxide (κ_0) was 4.098 mS/dm.

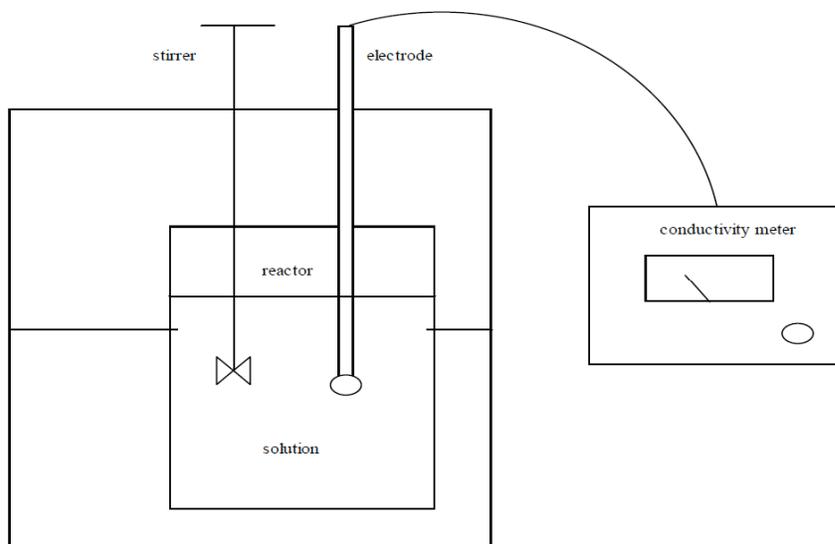The initial sodium hydroxide concentration c_{A0}, was 0.01187 mol/L. The molar conductivity at infinite

Figure 2: The apparatus – stirred batch reactor.

Table 1:   The Experimental Data and Calculation at *T* = 18.5ºC

t/min	κ_t /(mS/dm)	$\Delta\kappa_t$/(mS/dm)	c_A /(mol/L) giving by strong el. theory	c_A /(mol/L) giving by double l. e. method
0.00	4.098	0.000	0.0118700	0.011870
0.58	4.084	0.014	0.0118644	0.011864
0.70	4.080	0.018	0.0118628	0.011863
0.86	4.077	0.021	0.0118616	0.011862
1.06	4.071	0.027	0.0118592	0.011859
1.30	4.065	0.033	0.0118568	0.011857
1.50	4.060	0.038	0.0118548	0.011855
1.73	4.056	0.042	0.0118532	0.011853
1.88	4.051	0.047	0.0118512	0.011851
2.08	4.047	0.051	0.0118496	0.011850
2.23	4.045	0.053	0.0118488	0.011849
2.41	4.041	0.057	0.0118472	0.011847
2.56	4.036	0.062	0.0118452	0.011845
2.73	4.034	0.062	0.0118444	0.011844
3.00	4.030	0.064	0.0118428	0.011843
3.20	4.027	0.068	0.0118416	0.011842
3.58	4.020	0.071	0.0118388	0.011839
4.00	4.010	0.078	0.0118348	0.011835
4.65	4.007	0.088	0.0118336	0.011834
5.18	4.000	0.098	0.0118308	0.011831
5.86	3.995	0.103	0.0118288	0.011829

dilution (Λ_m^o) of the sodium hydroxide was 2492 mS dm^2 mol^{-1} [5] at a temperature around 25°C. Kohlrausch's constant can be calculated by known values for initial concentration (c_{A0}) and initial conductivity (κ_0), using equation 3.4, and was 19 704.16 mS dm^2/((mol L^{-1})$^{1/2}$ mol). Further concentration was calculated by using the numerical method (eq. 3.8, Table **2**). The concentration depending on time ($c_t = c_A$) was calculated by using equation 3.8 (Table **1**).

Table 2: Concentration Data were Giving by the Numerical Method

t/min	c_A /(mol/L)
0.70	0.0118627
0.86	0.0118615
1.30	0.0118567

Figure **3** illustrates the plotted sodium hydroxide concentration c_A, as a function of time at a temperature of 18.5°C.

5.1.2. First Step - Determining the Conductivity Constant

The basis of the first step is the diagram which represents the measured time (t), depending on the difference in conductivity ($\Delta\kappa$; Table **1**, eq. 5.1, Figure **4**). Therefore, conductivity is measured as a function of time.

$$\Delta\kappa = \kappa_0 - \kappa_t = 4.098 - \kappa_t \tag{5.1}$$

The conductivity constant, s_κ, can be read from the sloped-line, being 0.0231 (eq. 2.1), which is constant for each reaction. So, with a known value for

conductivity constant s_κ, any difference in conductivity ($\Delta\kappa$) at any specific time (t) can be determined:

$$\Delta\kappa = t \cdot s_\kappa = t \cdot 0.0231 \tag{5.2}$$

5.1.3. Second Step - Determining the Concentration Constant

The basis of the second step is the diagram which represents the linear difference in conductivity, depending on the concentration (Figure **5**, Table **1**). The concentration constant of conductivity (s_c) for this reaction was 0.0004 (eq. 2.4, Table **1**). The same value was also obtained from the sloped-line (Figure **5**):

$$c_t = \Delta\kappa \cdot s_c + c_0 = c_t = \Delta\kappa \cdot 0.0004 + 0.0119 \tag{5.3}$$

Once both the conductivity and concentration constants are known, which can be calculated after only a few known parameters (eq. 5.1 – 5.3), the desired concentration can be further calculated (Table **1**).

The slope is negative, because the reactant concentration (NaOH) is decreasing. The parameters are graphically defined, producing the ideal line. c_0 as the known initial concentration is 0.01187.

The theories of the strong electrolytes and double-linear extrapolation methods would give similar values for concentration, since they are both based on similar mathematical connections - both are linear dependent.

5.1.4. Determination of Chemical Kinetics

The basis of chemical kinetics, equation 4.1, is incorporated within the first order (eq. 4.7). The plot of $\ln(c_{A0}/c_A)$ as a function of time is quite linear (Figure **6**). The slope of the curve represents the rate constant, k
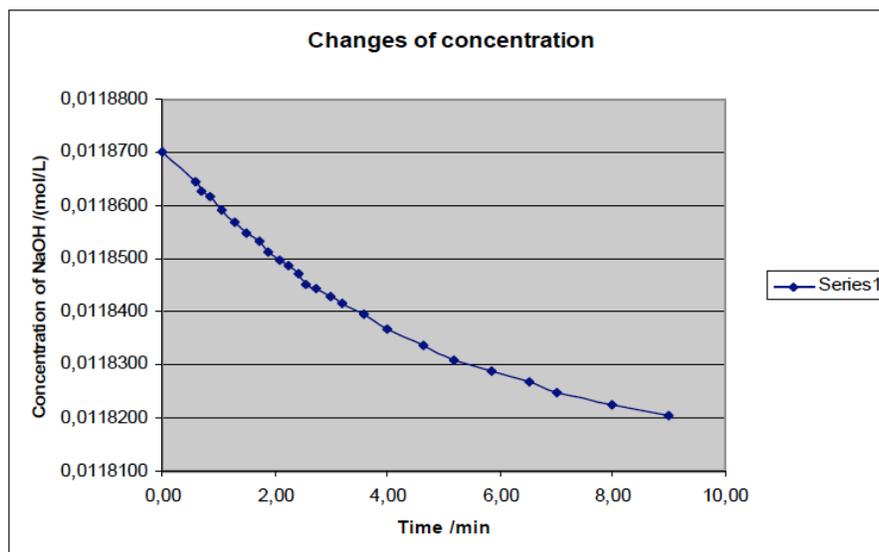
Figure 3: Concentration of sodium hydroxide c_A, as a function of time at 18.5°C.
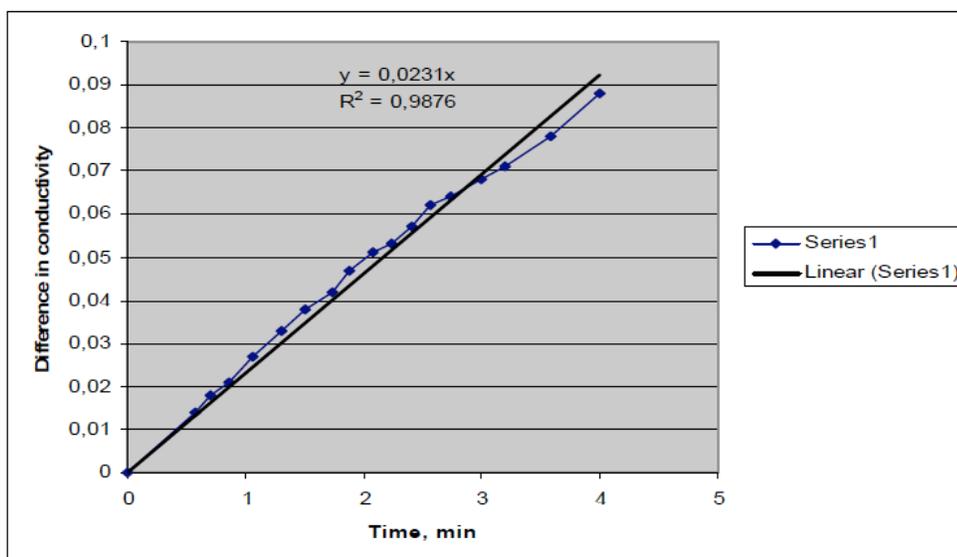
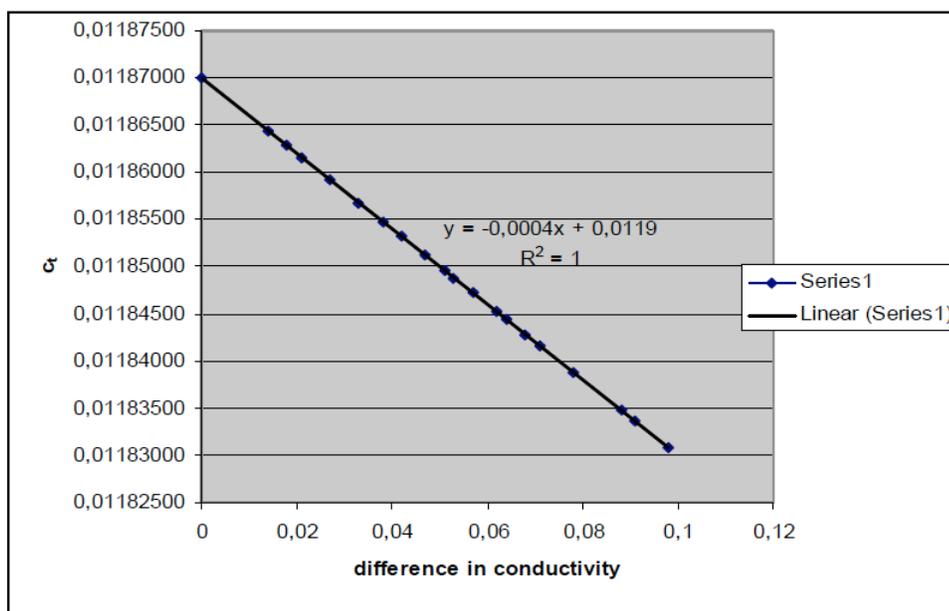**Figure 4:** Difference in conductivity as a function of time.

Figure 5: Concentration as a function of difference in conductivity.

(eq. 4.7). The rate constant was found to be 0. 0008 min^{-1} at 18.5 $^{\circ}$C.

As Figure **7** illustrates, the plot of ($1/c_A$) as a function of time is linear, which suggests that the rate law is second order with respect to sodium hydroxide concentration, under given reactive conditions for excess benzoic acid. The sloped-line represents the rate constant *k*. The rate constant was found to be 0.0671 L/(mol min^{-1}) at 18.5 $^{\circ}$C (eq. 4.9). The data shows the reaction was second order under all the temperatures studied (Table **3**).

The experiment at temperatures 16.7 $^{\circ}$C and 17.2 $^{\circ}$C was repeated using the same procedure.

5.2. Sodium Hydroxide is in Excess

5.2.1. Determining the Concentration by Using the Theory of Strong Electrolytes

The same experimental procedure took place for an excess concentration of sodium hydroxide. Benzoic acid (1.4046) was dissolved in water (0.5 L) and heated in a reactor at a temperature of 18.5 °C. 52.74 % surplus of sodium hydroxide was added (0.7034 g dissolved in 0.1 L of water).

Both substances were mixed and the conductivity (κ_t) measured, depending on time, *t* (Table **4**). Firstly, the conductivity of the sodium hydroxide (κ_0) was 31.161 mS/dm. The initial sodium hydroxide
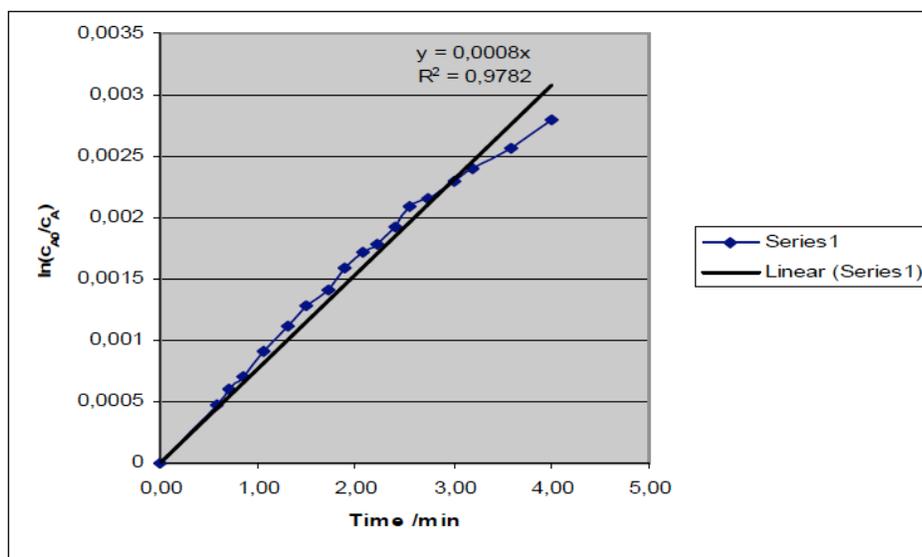
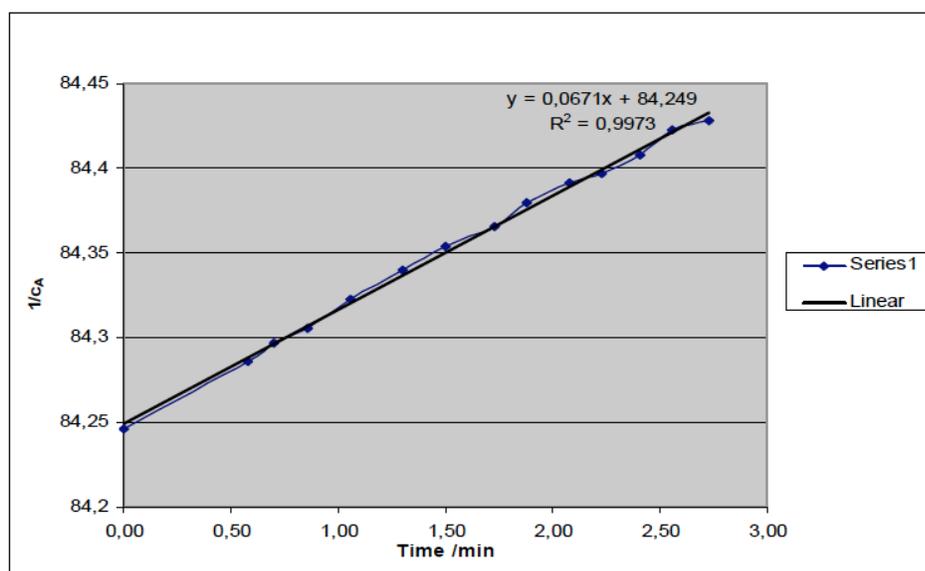**Figure 6:** The plot of $\ln(c_{A0}/c_A)$ as a function of time at 18.5 °C.

Figure 7: The plot of $(1/c_A)$ as a function of time at 18.5 °C.

Table 3:   The Reaction Rate Constant, *k*

	First order		Second order	
T/°C	k min^{-1}	R^2	k L/(mol min^{-1})	R^2
16.7	0.0002	0.9682	0.0224	0.9869
17.2	0.0007	0.9829	0.0651	0.9864
18.5	0.0008	0.9782	0.0671	0.9973

concentration, c_{A0}, was 0.0293 mol/L. The initial benzoic acid, c_{B0}, was 0.01917 mol/L. The molar conductivity at an infinite dilution (Λ_m^o) of sodium hydroxide was 2492 mS dm^2 mol^{-1} [5] at a temperature of around 25°C. Kohlrausch's constant can be calculated by known values for initial concentration (c_{A0}) and initial conductivity (κ_0), using equation 3.4 and was 8 345.29 mS dm^2/((mol L^{-1})$^{1/2}$ mol). Further concentration was calculated by using the numerical method (eq. 3.8). The concentration depending on time ($c_t = c_A$) was calculated by using equation 3.8 (Table **4**).

The reacted sodium hydroxide $c_{A(reacted)}$, can be calculated (Table **4**) by using equation (5.4):

$$c_{A(reacted)} = c_{Ao} - c_A \qquad (5.4)$$

The non-reactive benzoic acid is:

$$c_{B(non-reacted)} = c_B = c_{B0} - c_{A(reacted)} \qquad (5.5)$$

Figure **8** illustrates the plot of benzoic acid concentration (c_B) as a function of time at a temperature of 18.5 ºC.

5.2.2. First Step - Determining the Conductivity Constant

The basis of the first step is the diagram which represents the measured time (t), depending on the difference in conductivity ($\Delta\kappa$; Table **4**, eq. 5.6, Figure

9). Therefore, conductivity is measured as a function of time.

$$\Delta\kappa = \kappa_0 - \kappa_t = 31.161 - \kappa_t \qquad (5.6)$$

Conductivity constant, s_κ, can be read from the sloped-line, being 0.1146 (eq. 2.1), which is constant for each reaction. So, with a known value for the conductivity constant s_κ, the difference in conductivity ($\Delta\kappa$) at a specific time (t) can be determined:

$$\Delta\kappa = t \cdot s_\kappa = t \cdot 1146 \qquad (5.7)$$

### 5.2.3. Second Step - Determining the Concentration Constant

The basis of the second step is the diagram which represents the linear difference in conductivity, depending on concentration (Figure **10**, Table **1**). The concentration constant of conductivity (s_c) for this

Table 4: The Experimental Data and Calculation at T = 18.5 ºC.

t/min	κ_t/(mS/m)	C_A /(mol/L) giving by strong el. theory	C_A /(mol/L) giving by double l. e. method	$C_{A(reacted)}$ /(mol/L)	C_B /(mol/L)
0.00	31.161	0.0293000	0.029300	0.0000000	0.01917000
0.60	31.140	0.0292916	0.029292	0.0000084	0.01916160
0.73	31.130	0.0292876	0.029288	0.0000124	0.01915760
0.96	31.090	0.0292716	0.029272	0.0000284	0.01914160
1.11	31.060	0.0292596	0.029260	0.0000404	0.01912960
1.26	31.030	0.0292476	0.029260	0.0000524	0.01911760
1.41	31.010	0.0292396	0.029248	0.0000604	0.01910960
1.68	30.960	0.0292196	0.029240	0.0000804	0.01908960
1.90	30.920	0.0292036	0.029220	0.0000964	0.01907360
2.08	30.890	0.0291916	0.029204	0.0001084	0.01906160
2.25	30.870	0.0291836	0.029192	0.0001164	0.01905360
2.58	30.820	0.0291636	0.029184	0.0001364	0.01903360
2.81	30.790	0.0291516	0.029164	0.0001484	0.01902160
3.00	30.760	0.0291396	0.029152	0.0001604	0.01900960
3.46	30.700	0.0291156	0.029140	0.0001844	0.01898560
3.91	30.650	0.0290956	0.029116	0.0002044	0.01896560
4.45	30.590	0.0290716	0.029096	0.0002284	0.01894160
4.85	30.550	0.0290556	0.029072	0.0002444	0.01892560
5.25	30.520	0.0290436	0.029056	0.0002564	0.01891360
5.63	30.480	0.0290276	0.029044	0.0002724	0.01889760
6.13	30.450	0.0290156	0.029028	0.0002844	0.01888560
6.73	30.400	0.0289956	0.029016	0.0003044	0.01886560
7.13	30.370	0.0289836	0.028996	0.0003164	0.01885360
7.75	30.340	0.0289716	0.028984	0.0003284	0.01884160
9.21	30.260	0.0289396	0.028972	0.0003604	0.01880960
10.26	30.220	0.0289236	0.028940	0.0003764	0.01879360
12.41	30.130	0.0288876	0.028924	0.0004124	0.01875760
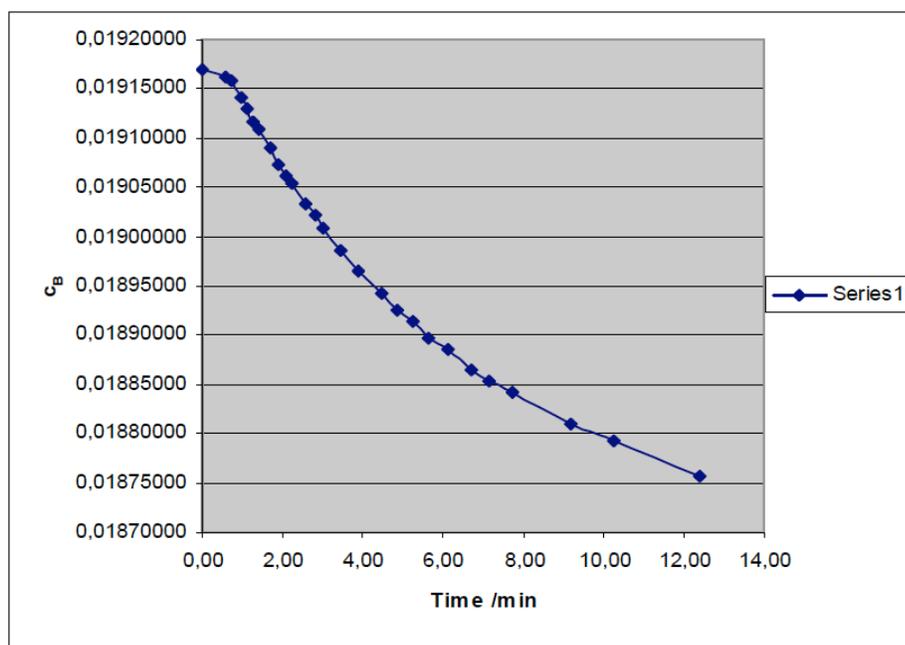
Figure 8: Concentration of benzoic acid, c_B, as a function of time at 18.5 ºC.
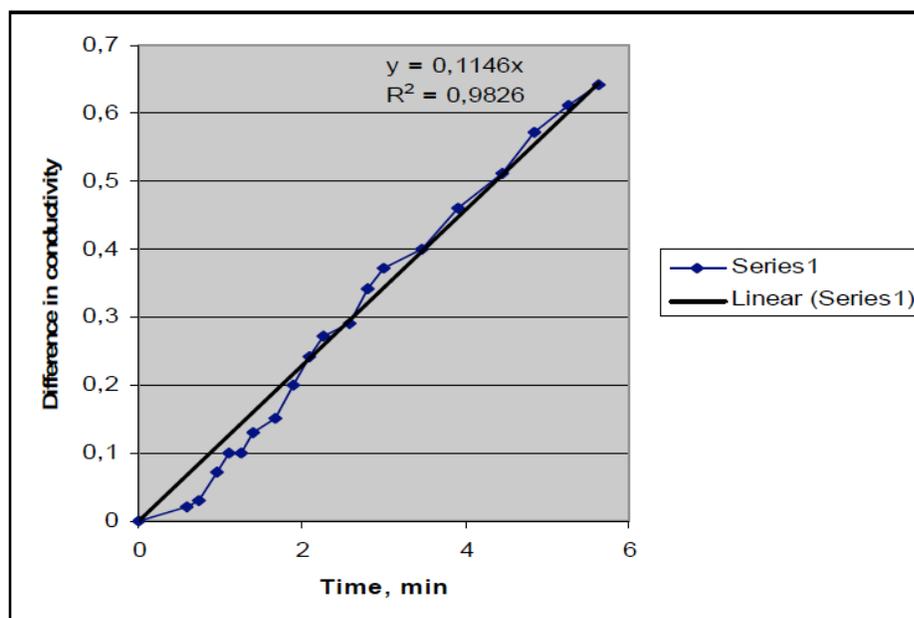
Figure 9: Difference in conductivity as a function of time.

reaction was 0.0004 (eq. 2.4, Table **4**). The same value was also obtained from the sloped-line (Figure **11**):

$$c_t = \Delta \kappa \cdot s_c + c_0 = c_t = \Delta \kappa \cdot 0.0004 + 0.0293 \qquad (5.8)$$

Once both the conductivity and concentration constants are known, which can be calculated after only a few known parameters (eq. 5.06 – 5.8) the desired concentration can be further calculated (Table **4**).

The slope is negative, because the reactant concentration (NaOH) is decreasing. The parameters are graphically defined, producing the ideal line. c_0, as the known initial concentration, is 0.0293.

The values for constant concentration are the same (0.0004), regardless of the excess component.

5.2.4. Determination of Chemical Kinetics

The basis of chemical kinetics, equation 4.1, is incorporated within the first order (eq. 4.7). The plot of $\ln(c_{B0}/c_B)$ as a function of time is quite linear (Figure **11**; eq. 4.8). As Figure **12** illustrates, the plot of $(1/c_B)$ as a function of time is linear, which suggests that the rate
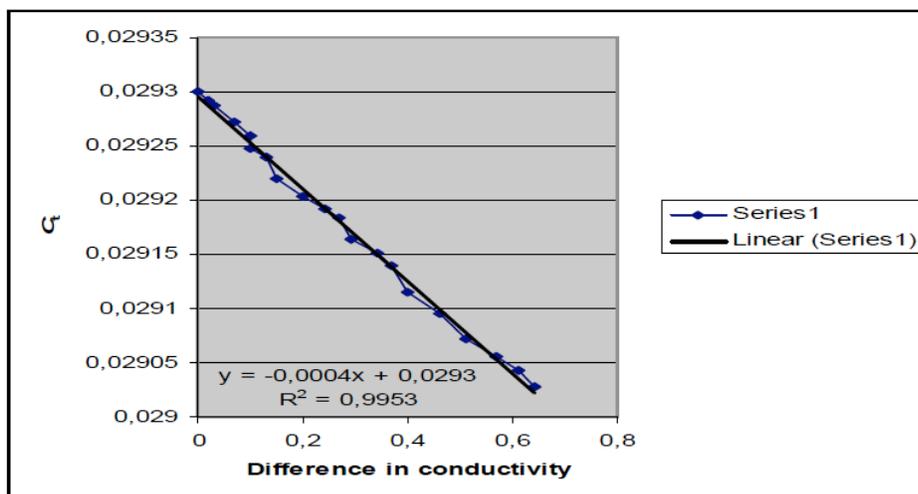
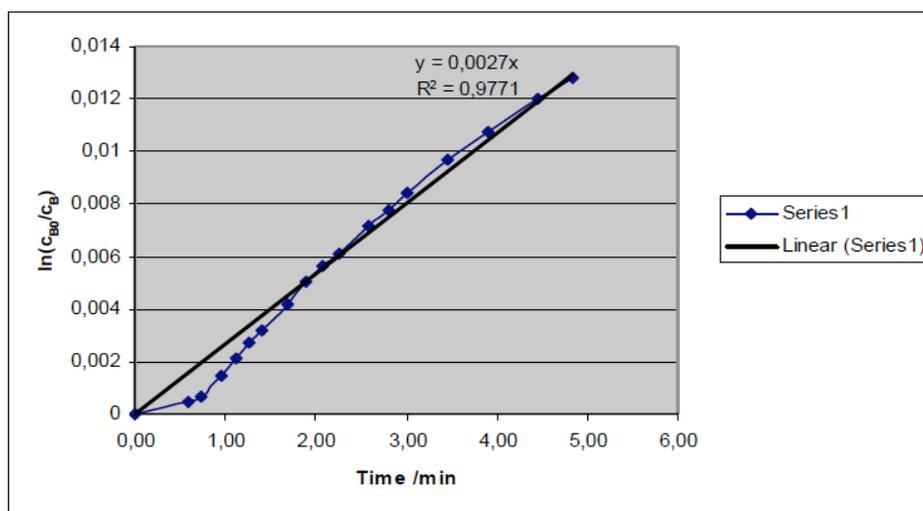**Figure 10:** Concentration as a function of difference in conductivity.

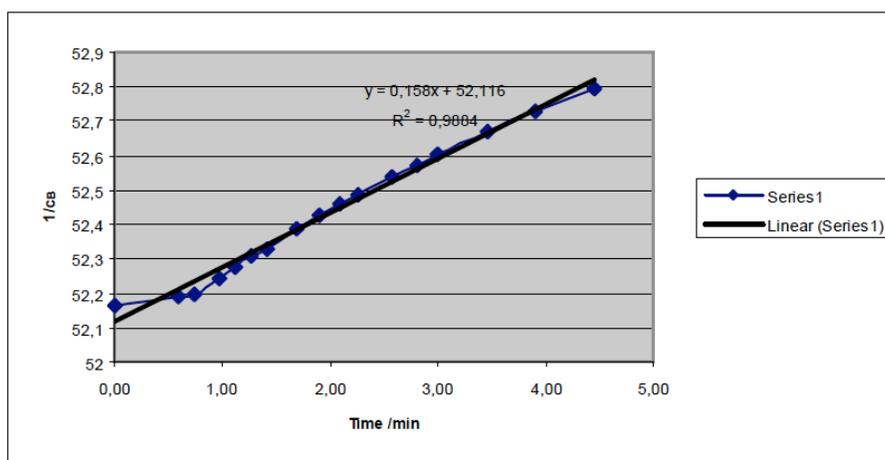**Figure 11:** The plot of $\ln(c_{B0}/c_B)$ as a function of time at 18.5 °C.

Figure 12: The plot of $(1/c_B)$ as a function of time at 18.5 °C.

law is second order with respect to benzoic acid concentration, under given reactive conditions, for excess sodium hydroxide. The slope represents the rate constant k (eq. 4.10). The rate constant was found to be 0.158 L/(mol min^{-1}) at 18.5 °C. The data shows the reaction is second order under all temperatures studied (Table **5**).

Table 5: The Reaction Rate Constant, *k*

	First order		Second order	
T/ºC	**k min^{-1}**	**R^2**	**k L/(mol min^{-1})**	**R^2**
16.1	0.0010	0.9867	0.0539	0.9915
17.4	0.0012	0.9772	0.0686	0.9841
18.5	0.0027	0.9771	0.158	0.9884

The experiment at temperatures 16.1 ºC and 17.4 ºC was repeated using the same procedure. Taking the logarithm of the Arrhenius equation (eq. 4.11) and the activation energy is 303.92 kJ/mol (Figure **13**):

$$\ln k = \ln k_0 - \frac{E_a}{R \cdot T} \tag{5.9}$$

$$E_a = 36\,556\,\text{K} \cdot 8.314\,\text{J} / (\text{mol K}) = 303.92\,\text{kJ} / \text{mol} \tag{5.10}$$

The slope of the graph is:

$$-E_a/R = -36\,556\,\text{K} \tag{5.11}$$

6. CONCLUSIONS

The double-linear extrapolation method is an alternative method for determining concentration, by measuring the conductivity of a strong electrolyte. This double-linear extrapolation method is a very simple method over two stages, each stage looks at different constants (conductivity and concentration) from the sloped-lines of different diagrams (the linear time dependence regarding the difference in conductivity and the linear difference in conductivity, depending on concentration). Each reaction has specific characteristic double-linear constants, which can be determined by using double mathematical linear extrapolation. Conductivity for a specific reaction has a specific characterization, therefore, certain linear constants can be determined, being constant during the specific reaction.

The kinetics of sodium benzoate was determined by measuring the conductivity of a strong electrolyte – sodium hydroxide as a reactant, in a batch reactor. Conductivity for a specific reaction has a specific characterization, therefore, the conductivity and concentration constants can be determined, being constant during the specific reaction. Once both the conductivity and concentration constants are known, which can be calculated after only a few known parameters, the desired concentration can be further calculated.

The chemical kinetics of sodium benzoate production from sodium hydroxide and benzoic acid were determined by measuring the conductivity of sodium hydroxide using double-linear extrapolation. The reaction was of second order regarding sodium hydroxide and the same order for benzoic acid. The rate constant was found to be 0.0671 L/(mol min^{-1}) at 18.5 $^{\circ}$C regarding sodium hydroxide. The rate constant was found to be 0.158 L/(mol min^{-1}) at 18.5 $^{\circ}$C regarding benzoic acid. The total reaction order is the sum of both, therefore it is of the fourth order.

The order of reaction, with respect to a certain reactant, is defined as the power to which its
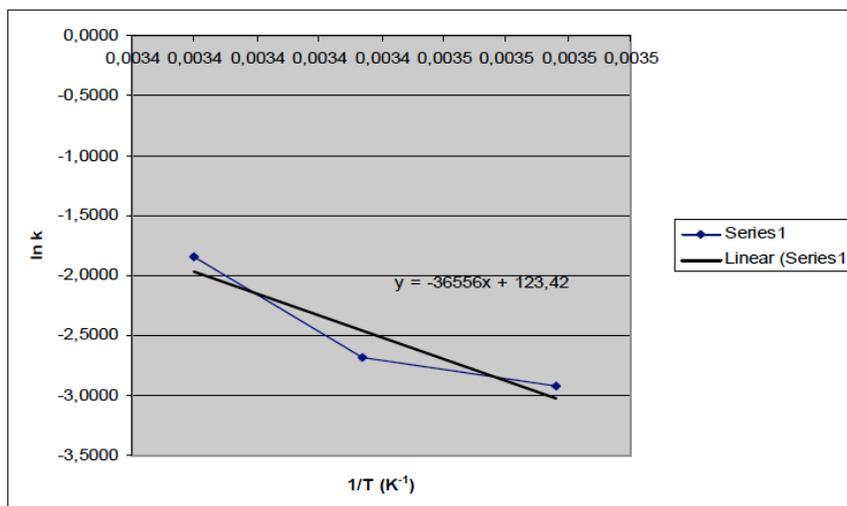

Figure 13: The plot of ln*k* and *1/T*.

concentration term is raised in the rate equation. Rate order presents the speed of reaction change if the concentration of the reactant is changed. If enlargement of the reaction's speed is required, the concentration with higher order must be in excess - in our case the concentrations of both reactants (sodium hydroxide and benzoic acid) were very important. The synthesis of sodium benzoate is a very fast reaction, as evidenced by the high value for activation energy. The activation energy was 303.92 kJ/mol.

Chemical kinetics plays an important role in chemical engineering, so it could represent both continuous and non-continuous methods for determining concentration. The continuous method, by using conductivity, was very useful for uninterrupted concentration measures.

NOMENCLATURE

c =   concentration, mol/L

K =   constant in Kohlrausch equation, mS $m^2/((mol\ L^{-1})^{1/2}\ mol)$

k =   reaction rate constant

n, m =   rate order, /

r =   rate of reaction

R =   gas law constant, J/(mol · K)

T =   temperature, K

t =   time of reaction, min

X =   degree of conversion, 1

κ =   conductivity, mS/dm

Λ_m^o =   molar conductivity at infinite dilution, S m^2 mol^{-1}

Λ_m =   molar conductivity, S m^2 mol^{-1}

ADDITION A

Program (in FORTRAN):

```
zc =0.17
H=221.3
10 c=(H+ 2458*zc**1.5)/2492
eps=abs((c-zc)/zc)
zc=c
if(eps.ge.0.0001) go to 10
write (6,*) zc,c,eps
stop
end
```

REFERENCES

[1]   Eldridge JW, Piret EL, Continuous-flow stirred-tank reactor system I. Design equations for homogeneous liquid phase reactions, Experimental data. Chem Eng Prog 1950; 46: 290.

[2]   Shatyski JJ, Hanesian D. Adiabatic kinetics studies of the cytidine/acetic anhydride reaction by utilizing temperature versus time data. Ind Eng Chem Res 1993; 32: 594. http://dx.doi.org/10.1021/ie00016a004

[3]   Haji S, Erkey C. Kinetics of hydrolisis of acetic anhydride by in situ FTIR spectroscopy. Chem Eng Ed 2005; 56-61.

[4]   Cosmetic Ingredient Review Expert Panel Bindu Nair, Final Report on the Safety Assessment of Benzyl Alcohol, Benzoic Acid, and Sodium Benzoate. Int J Tox 2001; 20(Suppl 3): 23-50.Atkins PW. Physical chemistry, Oxford, Melbourne, Tokyo: Oxford University Press, cop. 1998.

[6]   Vas Bhat R, Kuipers J, Versteeg G. Mass transfer with complex chemical reaction in gas–liquid system: two-steps reversible reactions with unit stoichio-metric and kinetic orders. Chem Eng J 2000; 76: 127-52. http://dx.doi.org/10.1016/S1385-8947(99)00104-7

[7]   Simmie JM. Detailed chemical kinetic models for the combustion of hydrocarbon fuels. Prog Energy Combust Sci 2003; 29: 599-34. http://dx.doi.org/10.1016/S0360-1285(03)00060-1

[8]   Elliott L, Ingham DB, Kyne AG, Mera NS, Pourkashanian M, Wilson CW. Generic algorithms for optimisation of chemicalkinetics reaction mechanisms. Prog Energy Combust Sci 2004; 30: 297-28. http://dx.doi.org/10.1016/j.pecs.2004.02.002

[9]   Heinichen H, Heyl A, Rutsch O, Weichmann J. Modeling of the coplex chemicalkinetics of the thermal decomposition of tetrachloromethane in methane. Chem Eng Sci 2001; 56: 1381-86. http://dx.doi.org/10.1016/S0009-2509(00)00361-4

[10]   Smith JM, Ness HCV. Introduction to Chemical Engineering Thermodynamics, McGraw-Hill 1975.

[11]   Poling BE, Prausnitz JM, O'Connell JP. The Properties of Gases and Liquids, McGraw-Hill 2000.

[12]   Weinan E, Liu D, Vanden-Eijnden E. Nested stochastic simulation algorithm for chemical kinetic systems with disparate rates. J Chem Phys 2005; 123.

[13]   Gibson MA, Bruck J. Efficient exact stochastic simulation of chemical systems with many species and many channels. J Phys Chem 2000; 104: 1876-89. http://dx.doi.org/10.1021/jp993732q

[14]   McQuarrie DA. Stochastic approach to chemicalkinetics. J Appl Probab 1967; 4: 413-78. http://dx.doi.org/10.2307/3212214

[15]   Delogu F, Monagheddu M, Mulas G, Schiffini L, Cocco G. Some kinetic features of mechanical alloying transformation processes. J Non-Cryst Solids 1998; 383-89. http://dx.doi.org/10.1016/S0022-3093(98)00550-X