Laboratory Courses in Physical Chemistry
for students the study courses chemical engineering
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Elaboration of the experiment 6.1

First Order Reaction

Group 3
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1 Problem

In this expertiment we examined the activation energy of a first-order chemical reaction. To accomplish that we measured the temperature dependent rates of the reaction.

2 Theory

The rate of a first-order reaction is all the time proportional to the concentration of a responding substance.

$$\frac{dc}{dt} = -kc \tag{1}$$

k is the rate constant.

The rate is the highest at the beginning and is declining with diminishing concentration to zero. Through intergration of the differential equation:

$$\int_{c_0}^{c} \frac{dc}{c} = -\int_{0}^{t} kdt \tag{2}$$

$$\Rightarrow \ln\frac{c}{c_0} = -kt \tag{3}$$

So we get the rate constant k:

$$k = \frac{\ln\frac{c_0}{c}}{t} \tag{4}$$

And for the half-lives:

$$t_{1/2} = \frac{1}{k}\ln 2 \tag{5}$$

The rate constants of most reactions increase as the temperature is raised. It is found experimentally for many reactions that a plot of $\ln k$ against $1/T$ gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the Arrhenius equation.

$$\ln k = \ln A - \frac{E_A}{RT} \tag{6}$$

The parameter A is called the pre-exponential factor or the frequency factor. The parameter E_A is called activation energy.

The fact that E_A is given by the slope of the plot of $\ln k$ against $1/T$ means that, the higher the activation energy, the stronger the tempature dependence of the rate constant (that is, the steeper the slope). a high activation energy signifies that the rate constant depends strongly on temperature. If a rection has zero activations energy, its rate is independent of temperature.

3 Experiment

3.1 Procedure

In our experiment we examine the decay of tertiary amylbromid.

$$\begin{aligned} C_2H_5(CH_3)CBr &\xrightarrow{\text{slow}} \left[C_2H_5(CH_3)C^+\right] + Br^- \\ \left[C_2H_5(CH_3)C^+\right] + H_2O &\xrightarrow{\text{fast}} C_2H_5(CH_3)CH + H^+ \end{aligned}$$

A cell is filled with 80 ml of 80% ethanol and a magnetic stir bar; the electrodes and the thermometer are installed. The electrodes should be parallel. now the whole equipment is put on a magnetic stirrer. Then 0,5 ml of teriary amylbromid is filled in and the reacion starts. The measurements will be taken at 25 °C, 30 °C and 35 °C. At 25 °C and 30 °C the registration will be done for 30 min and then stopped before the end of the reaction. At 35 °C it will be tacken until the resistance stays constant. This value is the resistance of the cell and is needed for the equation. We get the other two resistances by cooling down the solution and by measuring the values.

3.2 Evaluation

3.2.1 Reaction at 25 °C

We got the plot in figure 1 (you will find the measured values in the appendix):

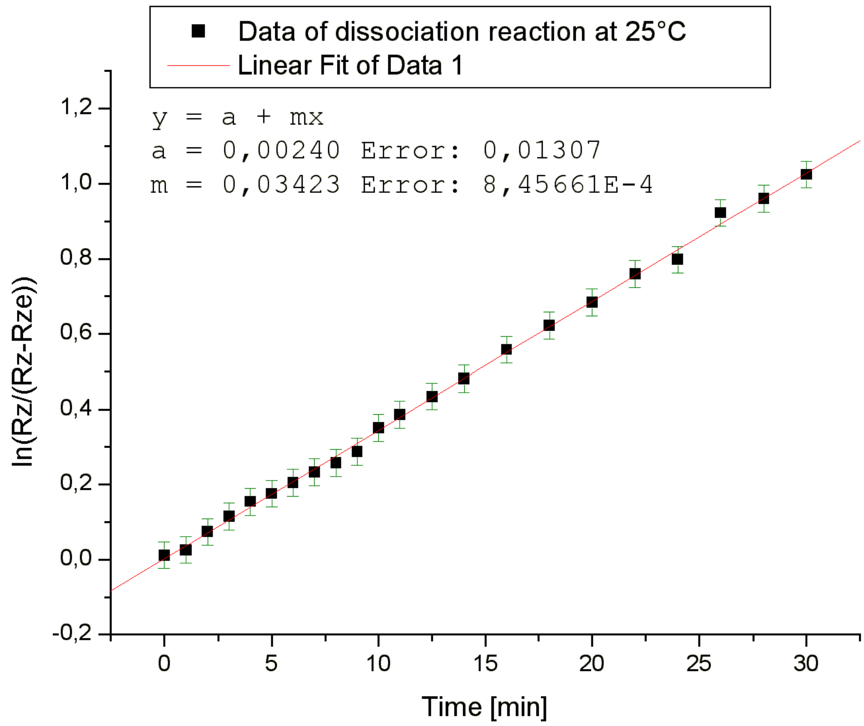

Figure 1: Dissociation reaction at 25 °C

The slope m of the line is:

$$\underbrace{\ln\frac{R_Z}{R_Z - R_{ZE}}}_{c_0/c} = k \cdot t \tag{7}$$
$$y = m \cdot x \Rightarrow k = m$$

So the rate constant k is equal to the slope of the plot:

$$k_{25°\mathrm{C}} = 0,0342 \pm 0,0008 \text{ min}^{-1}$$

The error bars for the ordinate were calculated in part 4. The error range has been determinated graphically.
With equation (5) we got for the half-live at 25 °C: $t_{1/2} = \frac{1}{0{,}0342} \cdot \ln 2 \text{ min} = 20,27 \text{ min}$

3.2.2 Reaction at 30 °C

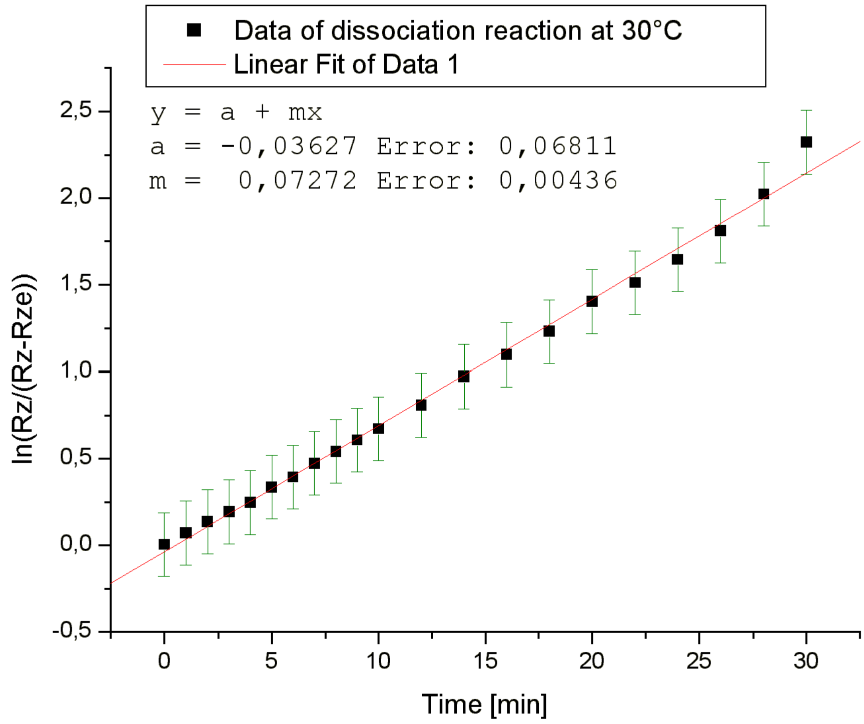

Figure 2: Dissociation reaction at 30 °C

So we got for the rate constant $k_{30°C}$:

$$k_{30°C} = 0,0727 \pm 0,0044 \text{ min}^{-1}$$

And for the the half-live at 30 °C:

$$\begin{aligned} t_{1/2} &= \frac{1}{0,0727} \cdot \ln 2 \ \text{[min]} \\ &= 9,532 \text{ min} \end{aligned}$$

3.2.3 Reaction at 35 °C

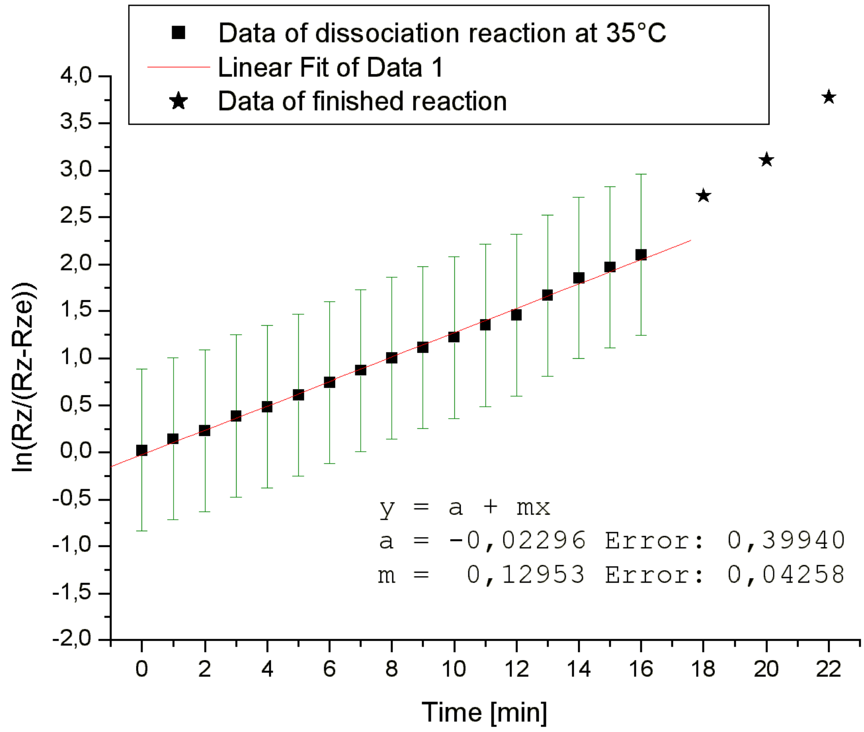

Figure 3: Dissociation reaction at 35 °C

So we got for the rate constant $k_{35^\circ\mathrm{C}}$:

$$k_{30^\circ\mathrm{C}} = 0,1295 \pm 0,0426 \text{ min}^{-1}$$

And for the the half-live at 30 °C:

$$\begin{aligned} t_{1/2} &= \frac{1}{0,12953} \cdot \ln 2 \ \ [\text{min}] \\ &= 5,351 \text{ min} \end{aligned}$$

3.2.4 Calculation of the activation energy

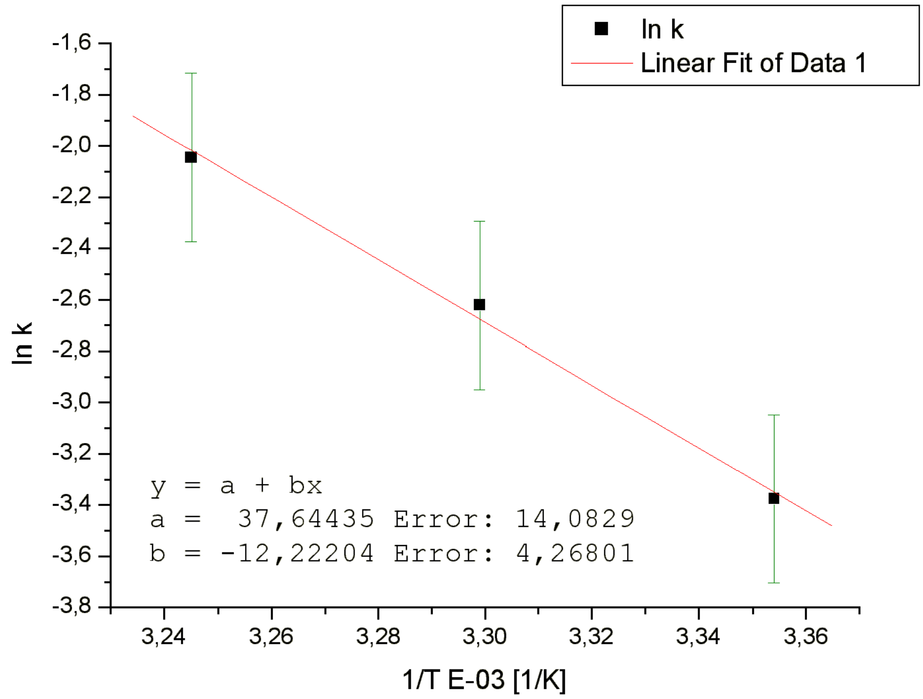

Figure 4: Arrhenius plot

T [°C]	$1/T \cdot 10^{-3}$ [K^{-1}]	$\ln k$
25 °C	3,354	-3,3755
30 °C	3,299	-2,6214
35 °C	3,245	-2,0438

Table 1: Data of the Arrhenius plot

The Arrhenius plot in figure 4 is described by equation (6). The slope m of gives $-E_A/R$ and the intercept a gives $\ln A$. So we got for the activation energy:

$$\begin{aligned} E_A &= -m\,[\mathrm{K}] \cdot R \\ &= -(-12,2204 \pm 4,26801) \cdot 10^3 \cdot 8,3143 \cdot \ \mathrm{J/mol} \\ &= 101604,07 \pm 35485,52\ \frac{\mathrm{J}}{\mathrm{mol}} = 101,60 \pm 35,49\ \frac{\mathrm{KJ}}{\mathrm{mol}} \end{aligned}$$

4 Error calculation

The only error during the experiment due to the measurements are the values for the resistence R_Z and R_{ZE}. The error for reading these values is 0,01 Ω, so we get for the errors $\Delta R_Z = R_Z \cdot 0,01\ \Omega$ and $\Delta R_{ZE} = R_{ZE} \cdot 0,01\ \Omega$.

Now we have to calulate the partial derivative of the equation (7) to get the maximum error for the ordinate $\ln k$ by error propagation:

$$\begin{aligned} F(R_Z, R_{ZE}) &\stackrel{(7)}{=} \ln \frac{R_Z}{R_Z - R_{ZE}} = kt \\ \Delta F &= \left| \frac{\partial F}{\partial R_Z} \cdot \Delta R_Z \right| + \left| \frac{\partial F}{\partial R_{ZE}} \cdot \Delta R_{ZE} \right| \qquad (8) \\ &= \left| -\frac{R_{ZE}}{R_Z\,(R_Z - R_{ZE})} \cdot R_Z \cdot 0,01 \right| + \left| \frac{1}{R_Z - R_{ZE}} \cdot R_{ZE} \cdot 0,01 \right| \\ &= \left| 0,02 \cdot \frac{R_{ZE}}{R_Z - R_{ZE}} \right| \qquad (9) \end{aligned}$$

We get for the maximum errors at 25, 30 and 35 °C following values (see tables 2, 3 and 4 in the appendix for data):

$$\begin{aligned} \Delta F_{25^\circ\mathrm{C},max} &= \pm 0,03571 \\ \Delta F_{30^\circ\mathrm{C},max} &= \pm 0,18400 \\ \Delta F_{35^\circ\mathrm{C},max} &= \pm 0,86000 \end{aligned}$$

It is save to use these maximal errors as error bars for the ordinate in the plottings.
For the error of $\ln k$ in the Arrhenius plot we have to calculate the partial derivative of (6):

$$\begin{aligned} F2(k) &= \ln k \qquad (10) \\ \Delta F2 &= |1/k \cdot \Delta k| \qquad (11) \end{aligned}$$

We get the following maximum errors at 25, 30 and 35:

$$\begin{aligned} \Delta F2_{25^\circ\mathrm{C},max} &= \pm \frac{1}{0,0342} \cdot 0,0008 = \pm 0,02339 \\ \Delta F2_{30^\circ\mathrm{C},max} &= \pm 0,06052 \\ \Delta F2_{35^\circ\mathrm{C},max} &= \pm 0,32896 \end{aligned}$$

For the Arrhenius plot it seems save to take $\Delta \ln k = 0,32896$ as maximum error.

5 Appendix

R_{ZE} [Ω]	Time [min]	R_Z [Ω]	$R_Z - R_{ZE}$ [Ω]	$\frac{R_Z}{R_Z - R_{ZE}}$ (∗)	ln(∗)	Δ ln(∗)
250	0,0	22000	21750	1,01149	0,01143	0,00023
	1,0	10000	9750	1,02564	0,02532	0,00051
	2,0	3500	3250	1,07692	0,07411	0,00154
	3,0	2300	2050	1,12195	0,11507	0,00244
	4,0	1750	1500	1,16667	0,15415	0,00333
	5,0	1550	1300	1,19231	0,17589	0,00385
	6,0	1350	1100	1,22727	0,20479	0,00455
	7,0	1200	950	1,26316	0,23361	0,00526
	8,0	1100	850	1,29412	0,25783	0,00588
	9,0	1000	750	1,33333	0,28768	0,00667
	10,0	845	595	1,42017	0,35078	0,00840
	11,0	780	530	1,47170	0,38642	0,00943
	12,5	710	460	1,54348	0,43404	0,01087
	14,0	655	405	1,61728	0,48075	0,01235
	16,0	585	335	1,74627	0,55748	0,01493
	18,0	540	290	1,86207	0,62169	0,01724
	20,0	505	255	1,98039	0,68329	0,01961
	22,0	470	220	2,13636	0,75911	0,02273
	24,0	455	205	2,21951	0,79729	0,02439
	26,0	415	165	2,51515	0,92233	0,03030
	28,0	405	155	2,61290	0,96046	0,03226
	30,0	390	140	2,78571	1,02450	0,03571

Table 2: Measurements for the reaction at 25 °C ($R_{ZE} = 250$ Ω)

R_{ZE} [Ω]	Time [min]	R_Z [Ω]	$R_Z - R_{ZE}$ [Ω]	$\frac{R_Z}{R_Z - R_{ZE}}$ (∗)	ln(∗)	Δ ln(∗)
230	0,0	43000	42770	1,00538	0,00536	0,00011
	1,0	3300	3070	1,07492	0,07224	0,00150
	2,0	1800	1570	1,14650	0,13671	0,00293
	3,0	1300	1070	1,21495	0,19471	0,00430
	4,0	1050	820	1,28049	0,24724	0,00561
	5,0	805	575	1,40000	0,33647	0,00800
	6,0	705	475	1,48421	0,39488	0,00968
	7,0	610	380	1,60526	0,47329	0,01211
	8,0	550	320	1,71875	0,54160	0,01438
	9,0	505	275	1,83636	0,60779	0,01673
	10,0	470	240	1,95833	0,67209	0,01917
	12,0	415	185	2,24324	0,80792	0,02486
	14,0	370	140	2,64286	0,97186	0,03286
	16,0	345	115	3,00000	1,09861	0,04000
	18,0	325	95	3,42105	1,22995	0,04842
	20,0	305	75	4,06667	1,40282	0,06133
	22,0	295	65	4,53846	1,51259	0,07077
	24,0	285	55	5,18182	1,64516	0,08364
	26,0	275	45	6,11111	1,81011	0,10222
	28,0	265	35	7,57143	2,02438	0,13143
	30,0	255	25	10,20000	2,32239	0,18400

Table 3: Measurements for the reaction at 30 °C ($R_{ZE} = 230$ Ω)

R_{ZE} [Ω]	Time [min]	R_Z [Ω]	$R_Z - R_{ZE}$ [Ω]	$\frac{R_Z}{R_Z - R_{ZE}}$ (∗)	ln(∗)	Δ ln(∗)
215	0,0	10000	9785	1,02197	0,02173	0,00044
	1,0	1600	1385	1,15523	0,14430	0,00310
	2,0	1050	835	1,25749	0,22911	0,00515
	3,0	670	455	1,47253	0,38698	0,00945
	4,0	560	345	1,62319	0,48439	0,01246
	5,0	470	255	1,84314	0,61147	0,01686
	6,0	410	195	2,10256	0,74316	0,02205
	7,0	370	155	2,38710	0,87008	0,02774
	8,0	340	125	2,72000	1,00063	0,03440
	9,0	320	105	3,04762	1,11436	0,04095
	10,0	305	90	3,38889	1,22050	0,04778
	11,0	290	75	3,86667	1,35239	0,05733
	12,0	280	65	4,30769	1,46040	0,06615
	13,0	265	50	5,30000	1,66771	0,08600
	14,0	255	40	6,37500	1,85238	0,10750
	15,0	250	35	7,14286	1,96611	0,12286
	16,0	245	30	8,16667	2,10006	0,14333
	18,0	230	15	15,33333	2,73003	0,28667
	20,0	225	10	22,50000	3,11352	0,43000
	22,0	220	5	44,00000	3,78419	0,86000
	24,0	215	0			

Table 4: Measurements for the reaction at 35 °C ($R_{ZE} = 215\ \Omega$)