A22 Elektrische Leitfähigkeit starker und schwacher Elektrolyte

Gruppe 11: Georg Fleig, Markus Prim

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The corrections are on the last pages.

Basic information

An elektrolyte is any substance containing free ions that make the substance electrically conductive. The conductivity of an electrolyte depends on its solubility. There are two groups of electrolytes:

1) strong electrolytes: (Kohlrausch's law of independent migration of ions)

The definiton of the molar conductivity is $\Lambda_m = \frac{\varkappa}{c}$ ($\varkappa$: measured conductivity, c: electrolyte concentration). For strong elektrolytes the conductivity depends ~~oly~~ only weakly on its concentration. To approximate this we use: $\Lambda_m = \Lambda_m^{\circ} - k\sqrt{c}$

(Λ_m°: molar conductivity of an infinite dilution, k: Kohlrausch coefficient)

2) weak electrolytes: (Ostwald's dilution law)

A weak electrolyte is not fully dissociated. We use the law of mass action onto the equilibrium between the solved ions and the undissociated molecules. We find:

$K_c = \frac{(\Lambda/\Lambda_\infty)^2}{1-\Lambda/\Lambda_\infty} \cdot c$ (K_c: dissociation constant)

Debye-Hückel-Onsager-Theory:

At very low concentration strong elektrolytes should still conduct electricity but they don't. Kohlrausch's law doesn't explain that fact. That is explainable with the Debye-Hückel-Onsager theory. Due the attraction of diferent charged ions ~~aren't all ions free~~ ~~for the~~ they build up an „ion-cloud". Some ions are bound in that cloud so they are not able to transport the electricity. Due that is at low concentrations the conductivity not measurable.

Procedur and Goals

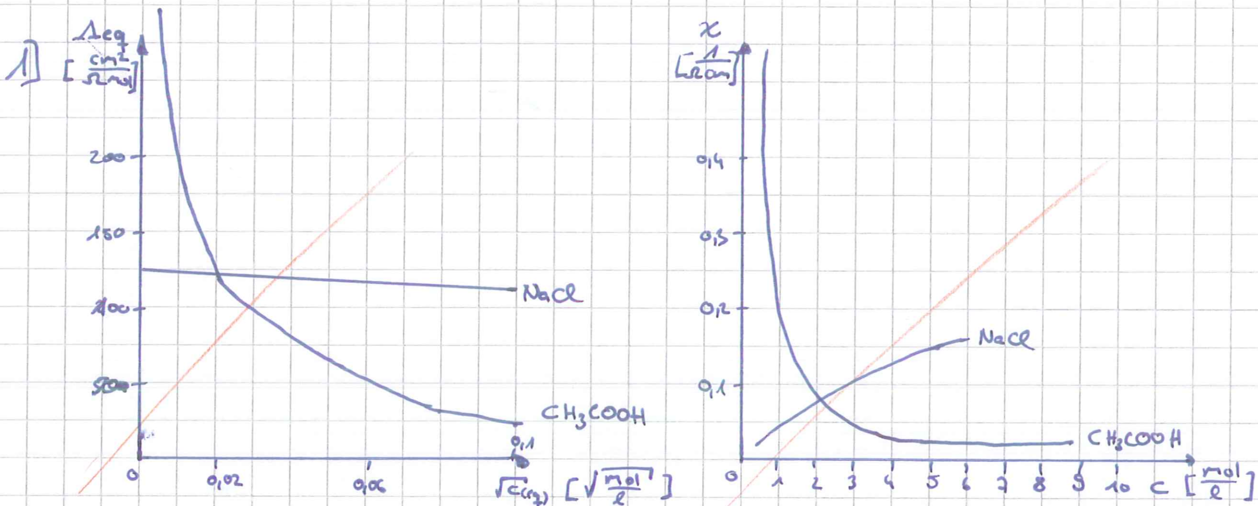
We measure the conductivity of NaCl and CH_3COOH with different concentrations.

For NaCl using extrapolation we want to find Λ_∞ and A.

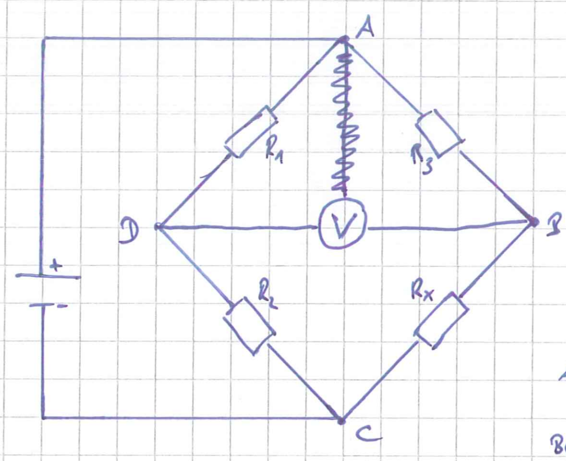
For CH_3COOH we also want Λ_∞ using extrapolation and additional define the dissociation constant K_c.

Additional Questions

1]



2] A Wealtstone bridge is used to measure electrickal resistance. Therefor you have to balance two legs of a bridge circuit and one leg of a bridge circuit which contains the unknown resistance. With this ~~approach~~ approach you can measure very exact, cause you will ~~measure~~ variate until you find a measurement by zero. Then you can use a more exact instrument and repeat the process.



Kirchhoff's first rule:

B: $I_3 - I_x + I_g = 0$

D: $I_1 - I_2 - I_g = 0$

Kirchhoff's second rule:

ABD: $(I_3 R_3) - (I_g \cdot R_g) - (I_1 R_1) = 0$

BCD: $(I_x R_x) - (I_2 R_2) + (I_g R_g) = 0$

The bridge is balanced $\Rightarrow$ $I_g = 0$:

$$I_3 R_3 = I_1 R_1$$
$$I_x R_x = I_2 R_2 \quad \nabla:$$

$$\Rightarrow \quad R_x = \frac{R_2 \, I_2 \, I_3 \, R_3}{R_1 \, I_1 \, I_x}$$

with first rule: $I_3 = I_x$, $I_1 = I_2$:

$$R_x = \frac{R_3 R_2}{R_1}$$

R_x is the measuring cell. So we are ask to find the conductivity of our solution.

3] With raising ~~tempreature~~ temperature the viscosity falls. That makes the ions in the solution ~~more~~ ~~freer~~ more ~~flexible~~ mobile. Because of that the conductivity is higher.

$\Rightarrow \quad \Lambda \sim T$

For weak electrolytes the conductivity raises much faster with raising temperature. That's because the dissosiacion constant raises with the temprature.

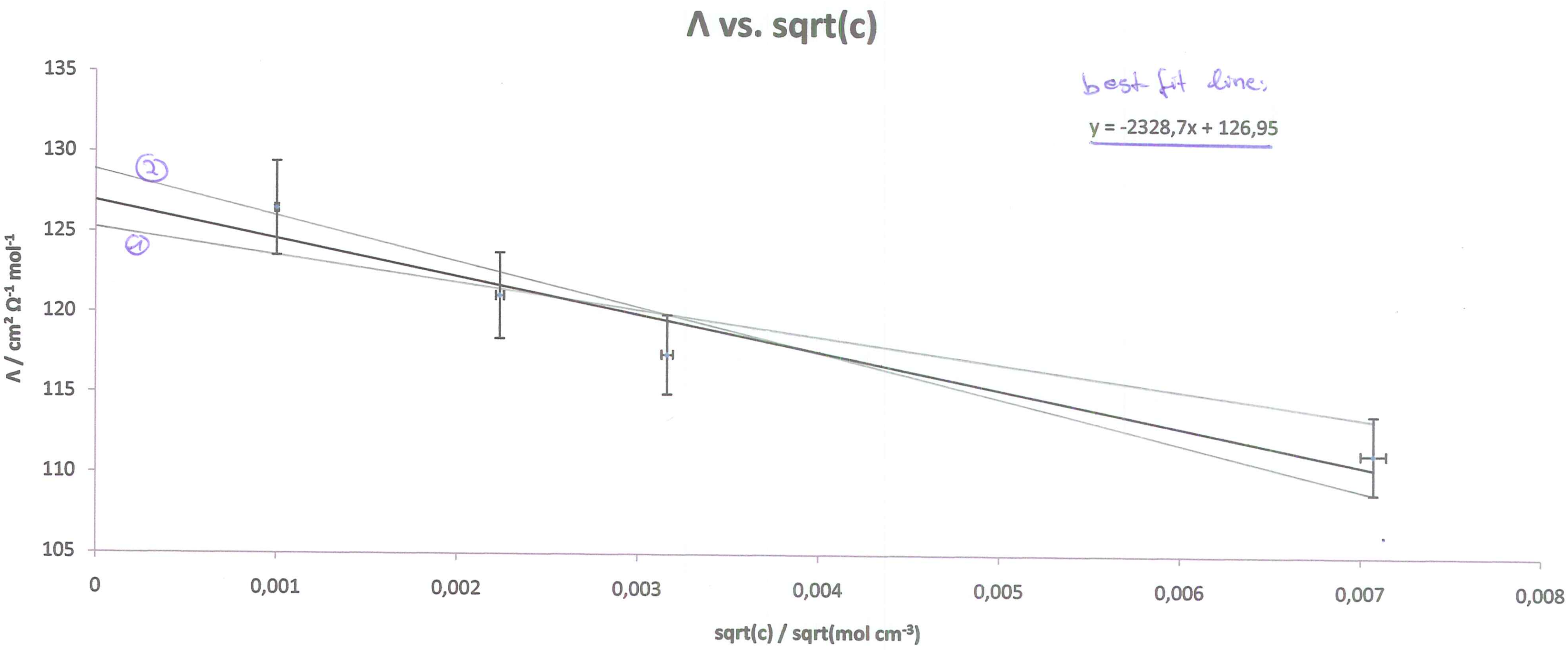
$\Rightarrow \quad \Lambda \sim T$ and $T \sim K_c$ and $K \sim \Lambda \Rightarrow \Lambda^2 \sim T$

Conductivity of different NaCl solutions

χ_{H2O} / µS cm^{-2}	1,5
$\Delta\chi_{H2O}$ / µS cm^{-2}	0,3

c / mol cm^{-3}	Δc / mol cm^{-3}	χ / µ S cm^{-2}	Δχ / µ S cm^{-2}	χ-χ_{H2O} / µS cm^{-2}	$\Delta\chi$-χ_{H2O} / µS cm^{-2}	Λ / cm² Ω^{-1} mol^{-1}	ΔΛ / cm² Ω^{-1} mol^{-1}
0,000001	0,00000002	128,0	0,1	126,5	0,4	126,5	2,93
0,000005	0,0000001	607	1,0	605,5	1,3	121,1	2,68
0,00001	0,0000002	1176	1,0	1174,5	1,3	117,45	2,48
0,00005	0,000001	5570	10,0	5568,5	10,3	111,37	2,43

sqrt(c) / sqrt(mol cm^{-3})	Δsqrt(c) / sqrt(mol cm^{-3})
0,001	0,00001
0,002236068	2,23607E-05
0,003162278	3,16228E-05
0,007071068	7,07107E-05



Conductivity of different HAc solutions

χ_{H2O} / µS cm^{-2} 1,5

$\Delta\chi_{H2O}$ / µS cm^{-2} 0,3

c / mol cm^{-3}	Δc / mol cm^{-3}	χ / µ S cm^{-2}	Δχ / µ S cm^{-2}	χ-χ_{H2O} / µS cm^{-2}	$\Delta\chi$-χ_{H2O} / µS cm^{-2}	Λ / cm^2 Ω^{-1} mol^{-1}	ΔΛ / cm^2 Ω^{-1} mol^{-1}
0,0001	0	522	1,0	520,5	1,3	5,21	0,01
0,00005	0,000001	369	1,0	367,5	1,3	7,35	0,17
0,00001	0,0000002	163,3	0,1	161,8	0,4	16,18	0,36

Dissociation degree and dissociation constant of our HAc solutions

Λ_∞ / cm^2 Ω^{-1} mol^{-1} 393,4

c / mol cm^{-3}	α / unitless	Δα / unitless	K_C / mol l^{-1}	ΔK_C / mol l^{-1}
0,0001	0,013	0,00003	0,0000177	0,000000018
0,00005	0,019	0,00044	0,0000178	0,000000019
0,00001	0,041	0,00092	0,0000176	0,000000018

Measured values and evaluation

1.) The measured values can be found in the corresponding tables.

Calculation of errors:

For the concentration c we assumed a 2% error because of contamination of the containers used and possible inaccuracy of our stock solution.

For χ_{H_2O} we used an error of $\pm 0{,}3\ \frac{\mu S}{cm}$, because the values were alternating in that area. We used the last digit of the meter as the error of each other measured electrical conductivity.

To calculate the error of Λ we used the following error propagation:

$$\Lambda = \frac{\chi}{c} \qquad c \text{ and } \chi \text{ contain errors}$$

$$\Delta\Lambda = \left|\frac{\partial\Lambda}{\partial\chi}\right| \Delta\chi + \left|\frac{\partial\Lambda}{\partial c}\right| \Delta c = \frac{\Delta\chi}{c} + \frac{\chi\,\Delta c}{c^2}$$

The calculated Λ errors can be found in the tables.

For further analysis (drawing the graphs) we also calculated the error of $\sqrt{c}$ the following way:

$$\Delta\sqrt{c} = \left|\frac{\partial\sqrt{c}}{\partial c}\right| \cdot \Delta c = \frac{\Delta c}{2\sqrt{c}} \qquad \text{(for the NaCl solutions only)}$$

2.) After drawing a chart that ~~shw~~ shows $\Lambda(NaCl)$ vs. $\sqrt{c}$ we were able to determinate Λ_∞ through extrapolation.

$\Lambda_\infty = (126{,}95 \pm 2{,}05)\ \frac{cm^2}{\Omega\, mol}$ literature value: $\Lambda_\infty = 126{,}45\ \frac{cm^2}{\Omega\, mol}$

The gradient of the best-fit line equates to the constant factor A of the equation for strong electrolytes:

$$\Lambda = \Lambda_\infty - A \cdot \sqrt{c}$$

$$\Rightarrow A = (-2328{,}7 \pm 643{,}7)\ \frac{cm^2}{\Omega}\ \sqrt[3/2]{\frac{cm}{mol}}$$

To get the error ranges of Λ_∞ and A we fitted two new lines through the data points and the error bars. One with the highest possible gradient and one with the lowest gradient.

The new lines ~~are~~ have the following functions:

① $y_1 = -1685x + 129$

② $y_2 = -2811x + 125$

The differences between the original gradient and the gradients of ① and ② are: 643,7 and 482,3.

So the error of A is $\pm 643{,}7 \ \frac{cm^2}{\Omega} \sqrt[3/2]{\frac{cm}{mol}}$

The differences between the original y-axis intercept and the one of ① and ② are: 1,95 and 2,05

$\Rightarrow$ the error of Λ_∞ is $\pm 2{,}05 \ \frac{cm^2}{\Omega \, mol}$

3) Dissociation degree and dissociation constant of acetic acid:

The following equations were used:

dissociation degree $\alpha = \frac{\Lambda}{\Lambda_\infty}$

dissociation constant $K_c = \frac{\alpha^2}{1-\alpha} \cdot c$

The calculated values can be found in the table.

<u>Error calculation of α:</u>

$$\Delta\alpha = \left|\frac{\partial\alpha}{\partial\Lambda}\right| \Delta\Lambda = \frac{\Delta\Lambda}{\Lambda_\infty}$$

<u>Error calculation of K_c:</u>

$$\Delta K_c = \left|\frac{\partial K_c}{\partial\alpha}\right| \Delta\alpha + \left|\frac{\partial K_c}{\partial c}\right| \Delta c = \left(\frac{2\alpha c}{1-\alpha} + \frac{\alpha^2 c}{(1-\alpha^2)}\right)\Delta\alpha + \frac{\alpha^2}{1-\alpha} \cdot \Delta c$$

The calculated errors can be found in the same table.

Finding Λ_∞ for weak elektrolytes trough extrapolation:

After employing $\alpha = \frac{\Lambda}{\Lambda_\infty}$ in $K = \frac{\alpha^2}{1-\alpha} c$, do some rewriting:

$$K_c = \frac{\Lambda^2 \cdot c}{\Lambda_\infty^2 \left(1 - \frac{\Lambda}{\Lambda_\infty}\right)}$$

$$\Leftrightarrow \quad 1 - \frac{\Lambda}{\Lambda_\infty} = \frac{\Lambda^2 c}{K_c \Lambda_\infty^2}$$

$$\Leftrightarrow \quad \frac{\Lambda}{\Lambda} - \frac{\Lambda}{\Lambda_\infty} = \frac{\Lambda^2 c}{K_c \Lambda_\infty^2}$$

$$\Leftrightarrow \quad \frac{1}{\Lambda} - \frac{1}{\Lambda_\infty} = \frac{\Lambda c}{K_c \Lambda_\infty^2}$$

$$\Leftrightarrow \quad \frac{1}{\Lambda} = \underbrace{\frac{1}{\Lambda_\infty}}_{\text{y-axis intercept}} + \frac{\Lambda c}{K_c \Lambda_\infty^2}$$

By looking at this equation you can essily see, that plotting $\frac{1}{\Lambda}$ vs. $\Lambda \cdot c$ can be used to find Λ_∞.
Using a best-fit line for the data points + extrapolation gives us a y-axis intercept. The inverse of this value is the Λ_∞ we were looking for.

Error analysis

- Contamination of the stock solutions that we used → all concentrations could be wrong
- Dirt on the glass containers might change the concentration.
- Errors in the dilution through inaccurate pipetting.
- Contamination of the distilled water would change all χ values.

	χ / $\frac{\mu S}{cm}$	T / °C	Fehler
Wasser	1,3-1,6 ≈ 145 (15 ± 2)	25,0	–
NaCl 0,001	128,0 ± 0,1	25,0	
NaCl 0,005	607 ± 1	25,0	
NaCl 0,01	1176 ± 1	25,0	
NaCl 0,05	5570 ± 10	25,0	
E.S. 0,1	522 ± 1	25,0	–
E.S. 0,05	369 ± 1	25,0	
E.S. 0,01	163,3 ± 0,1	25,0	

Fehler:

1ml	P.	0,007 ml
5ml	P.	0,01ml
10ml	P.	0,02 ml
25ml	P.	0,03ml
100ml	E.	± 0,1ml

A.J. Atkins

Δc = 2%

Correction

- Model calculation for $\Delta\Lambda$ using the third NaCl solution:

$$\Delta\Lambda = \frac{\Delta\chi}{c} + \frac{\chi\,\Delta c}{c^2} = \frac{1.3\cdot10^{-6}\,\frac{S}{cm}}{1\cdot10^{-5}\,\frac{mol}{cm^3}} + \frac{1.175\cdot10^{-3}\,\frac{S}{cm}\cdot 2\cdot10^{-7}\,\frac{mol}{cm^3}}{\left(1\cdot10^{-5}\,\frac{mol}{cm^3}\right)^2}$$

$$= \underline{\underline{2.48\,\frac{cm^2 S}{mol}}}$$

- The gradient of the best-fit line equates to the constant factor A of the equation for strong electrolytes:

$$\Rightarrow A = (-73{,}639 \pm 20{,}423)\,\frac{cm^4\,l\,S^2}{mol^3}$$

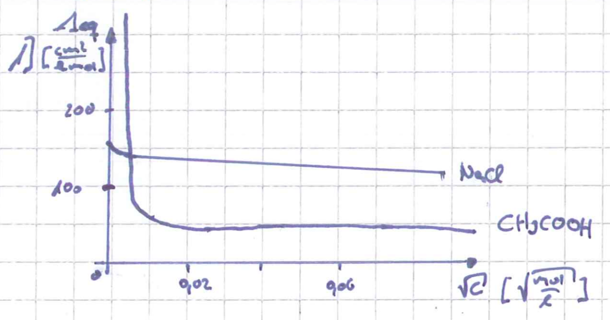
Lines to set the error ranges of A:

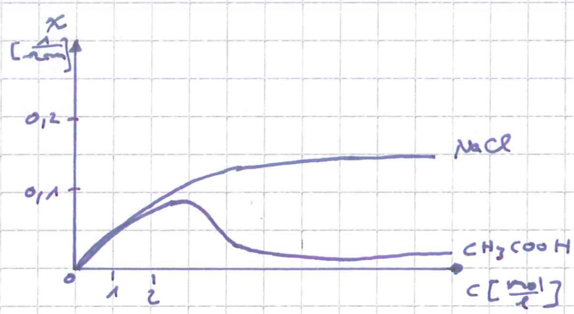
① $y_1 = -53{,}216 + 125{,}252$ Diff. gradient: $\underline{20{,}423}$; Diff. y-Axis: $1{,}694$

② $y_2 = -89{,}132 + 128{,}843$ Diff gradient: $15{,}483$; Diff. y-Axis: $\underline{\underline{1{,}897}}$

- $\underline{\underline{\Lambda = (126{,}946 \pm 1{,}897)\,\frac{cm^2 S}{mol}}}$

Additional Questions

1) 



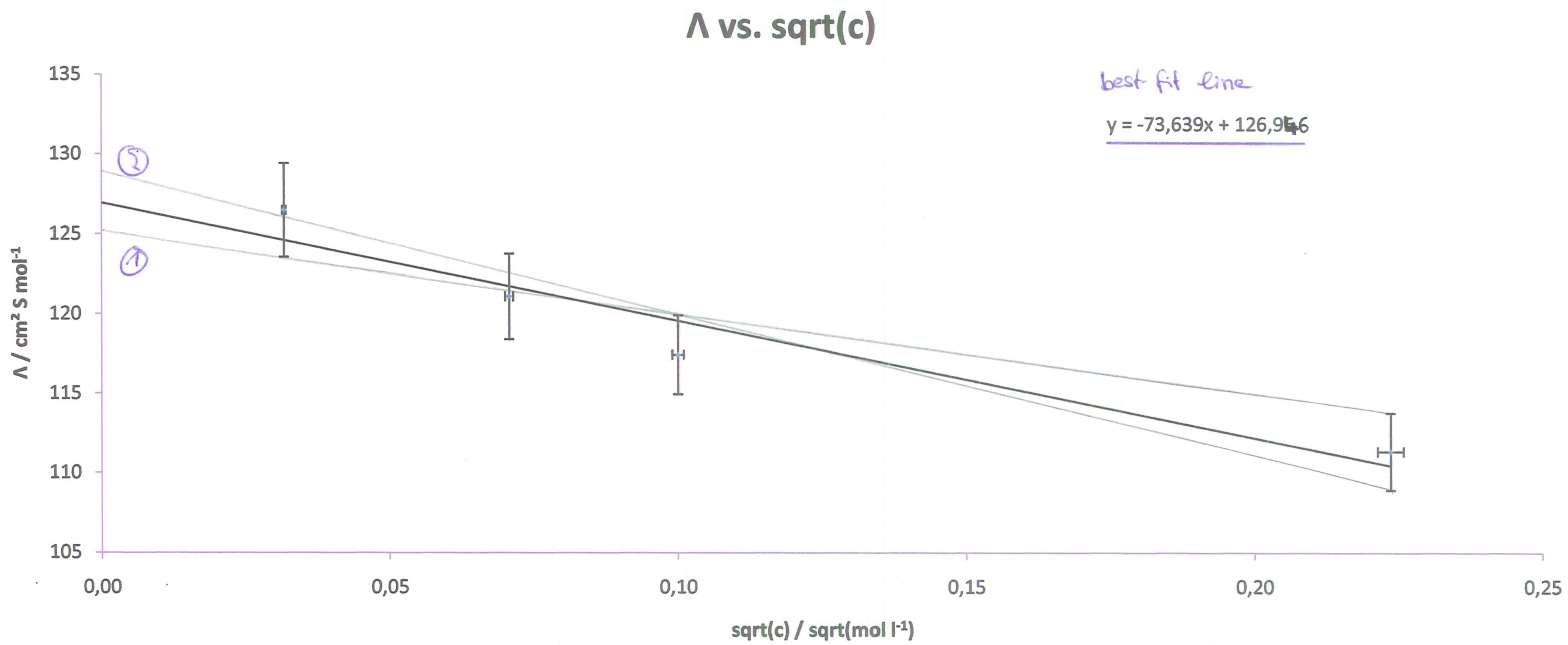
2) We use R_x as our measuring cell. Now we can adjust the resistance of the Bridge and measure the resistance of R_x. With the equation $R = \rho\,\frac{l}{q}$ ~~we are able~~ or better with to known cell parameter C $\kappa = \frac{C}{R}$ we are ask to calculate the specific Conductivity κ of our solution

Conductivity of different NaCl solutions

χ_{H2O} / S cm^{-1}	1,5E-06
$\Delta\chi_{H2O}$ / S cm^{-1}	3,0E-07

c / mol l^{-1}	Δc / mol l^{-1}	χ / S cm^{-1}	Δχ / S cm^{-1}	χ-χ_{H2O} / S cm^{-1}	$\Delta\chi$-χ_{H2O} / S cm^{-1}	Λ / cm² S mol^{-1}	ΔΛ / cm² S mol^{-1}
0,001	0,00002	1,280E-04	1,0E-07	1,265E-04	4,000E-07	126,5	2,93
0,005	0,0001	6,070E-04	1,0E-06	6,055E-04	1,300E-06	121,1	2,68
0,01	0,0002	1,176E-03	1,0E-06	1,175E-03	1,300E-06	117,45	2,48
0,05	0,001	5,570E-03	1,0E-05	5,569E-03	1,030E-05	111,37	2,43

sqrt(c) / sqrt(mol l^{-1})	Δsqrt(c) / sqrt(mol l^{-1})
0,0316	3,162E-04
0,0707	7,071E-04
0,1000	1,000E-03
0,2236	2,236E-03



Conductivity of different HAc solutions

χ_{H2O} / S cm^{-1} 1,5E-06

$\Delta\chi_{H2O}$ / S cm^{-1} 3,0E-07

c / mol l^{-1}	Δc / mol l^{-1}	χ / S cm^{-1}	$\Delta\chi$ / S cm^{-1}	χ-χ_{H2O} / S cm^{-1}	$\Delta\chi$-χ_{H2O} / S cm^{-1}	Λ / cm^2 S mol^{-1}	$\Delta\Lambda$ / cm^2 S mol^{-1}
0,1	0,002	5,220E-04	1,0E-06	5,205E-04	1,300E-06	5,21	0,01
0,05	0,001	3,690E-04	1,0E-06	3,675E-04	1,300E-06	7,35	0,17
0,01	0,0002	1,633E-04	1,0E-07	1,618E-04	4,000E-07	16,18	0,36

Dissociation degree and dissociation constant of our HAc solutions

Λ_∞ / cm^2 S mol^{-1} 393,4

c / mol l^{-1}	α / unitless	$\Delta\alpha$ / unitless	K_C / mol l^{-1}	ΔK_C / mol l^{-1}
0,1	1,32E-02	3,30E-05	1,77E-05	1,78E-08
0,05	1,87E-02	4,40E-04	1,78E-05	1,86E-08
0,01	4,11E-02	9,24E-04	1,76E-05	1,85E-08