A23

Measuring the Electromotive Force (EMF)

[redacted]

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Write the chemical reactions.

Show graph.

Estimate error for η

Bitte wieder vorlegen

03.03.17

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Praktikum: A23
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Betreuer:

Objective

I Firstly the electromotive force of the following galvanic cells is measured.

A.) Cu / 1,0 M $CuSO_4$ / sat. KCl - sol. / 1,0 M $ZnSO_4$ / Zn
B) Cu / 1,0 M $CuSO_4$ / sat. KCl - sol. / 0,1 M $CuSO_4$ / Cu
~~B)~~ C) Zn / 1,0 M $ZnSO_4$ / sat. KCl - sol. / 0,1 M $ZnSO_4$ / Zn
D) Cu / 1,0 M $CuSO_4$ / sat. KCl - sol. / AgCl / Ag
E) Zn / 1,0 M $ZnSO_4$ / sat. KCl - sol. / AgCl / Ag
F.) Cu / 0,1 M $CuSO_4$ / sat. KCl - sol. 0,1 M $ZnSO_4$ / Zn

II Also determine the solubility product of AgCl

III At last the temperature dependency of the EMF of cell F, the reaction enthalpy and the reaction entropy is determined.

Basics

In a galvanic cell, electrical energy is generated in a voluntary cell reaction. Among others we are using the Daniell - Element with the overall reaction $Zn + CuSO_4 \rightarrow Cu + ZnSO_4$.

A copper electrode and a zinc electrode are used, which are immersed in $ZnSO_4$ and $CuSO_4$, respectively. The half cells are connected via a salt bridge (eg. KCl).

In Order to link the cell potential to the composition of the reaction mixture, the following Nernst equation is used.

$$\Delta\varphi = \Delta\varphi^0 - \frac{RT}{zF} \ln \prod_i a_i^{\nu_i}$$

$\Delta\varphi$: potential difference $\Delta\varphi^0$: Standard potential difference
R: gas constant T: temperature F: Faraday constant
z: transferred charge a_i: activity of the species i
ν_i: Stöchiometric factor of the species i

The measuring at constant pressure leads to the following equation for the free enthalpy ΔG:

$$\Delta G = -zF \cdot E = -zF \cdot \Delta\varphi \qquad E: \text{EMF}$$

If you combine these equation you get

$$\Delta G = \Delta G^0 + RT \ln \frac{a_{Cu} \cdot a_{Zn^{2+}}}{a_{Zn} \cdot a_{Cu^{2+}}}$$ for the Daniell - Element.

From the Nernst equation you also get $E = E^0 - \frac{RT}{zF} \cdot \ln \frac{a_{Cu} \cdot a_{Zn^{2+}}}{a_{Zn} \cdot a_{Cu^{2+}}}$

with $E = \varphi_{Cu/Cu^{2+}} - \varphi_{Zn/Zn^{2+}}$ and $E^0 = \varphi^0_{Cu/Cu^{2+}} - \varphi^0_{Zn/Zn^{2+}}$

The neglect of a_{Cu} and a_{Zn} leads to

$\varepsilon_{Cu/Cu^{2+}} = \varepsilon^0_{Cu/Cu^{2+}} + \frac{RT}{zF}\ln a_{Cu^{2+}}$ and $\varepsilon_{Zn/Zn^{2+}} = \varepsilon^0_{Zn/Zn^{2+}} + \frac{RT}{zF}\ln a_{Zn^{2+}}$

with $a_\pm^{(x+y)} = a_+^x a_-^y$ and for 1:1 electrolytes $a_\pm = a_+ = a_- = c\gamma_\pm$

of a salt A_xB_y.

All in all we have $E = (\varepsilon^0_{Cu} - \varepsilon^0_{Zn}) - \frac{RT}{zF}\ln\frac{c_{ZnSO_4}\cdot\gamma_{\pm ZnSO_4}}{c_{CuSO_4}\cdot\gamma_{\pm CuSO_4}}$

If you use electrodes of the same material but different concentrations of the solution you can use

$$E = \frac{RT}{zF}\cdot\ln\frac{c^1_{CuSO_4}\cdot\gamma^1_{\pm CuSO_4}}{c^2_{CuSO_4}\cdot\gamma^2_{\pm CuSO_4}}$$

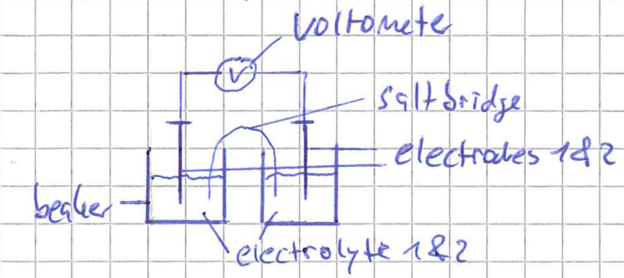
& $c^1_{CuSO_4} \approx c^2_{CuSO_4}$ leads to $E = \frac{RT}{zF}\cdot\ln\frac{c^1_{CuSO_4}}{c^2_{CuSO_4}}$

How? Are you sure about this?

Sources: - description of experiment
- Lecture on the subject "Elektrochemie und Reaktionskinetik"
- Peter Atkins, Physikalische Chemie, WILEY-VCH, Weinheim, 2013

Experiment set-up and procedure

Task I & II:



The salt bridge consists of a cut filter paper soaked in the corresponding salt solution.
Make sure the previously cleared electrodes don't touch neither the beaker walls nor the saltbridge.
The insertion of the salt bridge starts the measurement.

The respective electrodes and electrolytes can be found in the tasks I: A to 7

→ Silver / Silver chloride

For D & E you use a silver chloride electrode as a reference electrode.

For task II the electrolytes contain each 2ml 0,1M $AgNO_3$ +29ml water. For the salt bridge you use 1M KNO_3.
The measurements starts by adding 3ml 0,1M KCl to one half-cell.

The electrodes and all equipment should be cleaned with distilled water after the solution has seen changed.

In the case of task 3, the electrolytes and electrodes are placed in glass apparatus, which are closed at the lower end with a frit.
These are immersed in a double-walled beaker which is filled with KCl solution.
The beaker is connected to a water bath with which the temperature of the solution can be adjusted.
~~For~~ At the beginning the data are collected for about 15 minutes at 25 degrees. Then you heat the water bath to 50°C while the measurement is continued. Record the EMF at regular temperature intervalls.

Source: description of experiment

data evaluation

Write the (electrom) chemical reactions for each case

1) To calculate the electromotoric force (EMF) of the galvanic cells D ~~and~~ respectively E you just have to add the two measured EMFs of the galvanic cells A and D ~~resp~~ or A and E.

$\Rightarrow (A) + (D) = 1{,}096\,V + (-0{,}14\,V) = 0{,}956\,V = (E)$

As you can see, the calculation fits exactly with our measured EMF of E.

$\Rightarrow (E) - (A) = 0{,}956\,V - 1{,}096\,V = -0{,}14\,V = (D)$

This result also fits exactly with the measured EMF (D)

2) The electrode potentials of Zn^{2+}/Zn and Cu^{2+}/Cu we measured are compared to an ~~Ag~~/AgCl-Electrode which has a potential of 0,22233V (refeerece to H_2-Electrode)(1). The calculation to refeence the two halfcell potentials to the H_2-Electrode is equivalent to task 1).

$\Rightarrow (E) + (AgCl/Ag^+ + Cl^-) = -0{,}956\,V + 0{,}22233\,V = -0{,}73367\,V$ which is compared to the literature(2) a very good measurement $((Zn^{2+}/Zn) = -0{,}7618\,V)$.

$\Rightarrow (D) + (AgCl/Ag^+ + Cl^-) = -0{,}14\,V + 0{,}22233\,V = 0{,}08233\,V$ which is just the half Voltage than the literature(3) $(Cu^{2+}/Cu = 0{,}153\,V)$ but because of the mV-scale the error is relatively not so large.

The electrochemical series would be: Zn − H − Cu

What is the concentration of KCl in literature? What is the concentration in the experiment?

3) The given concentrations of $CuSO_4$ and $ZnSO_4$ are inserted into the eqation $E = \frac{RT}{zF} \cdot \ln \frac{c^1_x}{c^2_x}$, with $z = 2$

$\Rightarrow c_1(CuSO_4) = 1M = c_1(ZnSO_4)$, $c_2(CuSO_4) = c_2(ZnSO_4) = 0{,}1M$

$\Rightarrow E = 0{,}0296\,V$ for both galvanic cells B) and C)

4) As you can see in task 3) an approximation for the EMF was used, but this is only correct if the two consentrations are only slightly diffrent which was not given. So in this task the eqation $E = \frac{RT}{zF} \ln \frac{c^1_x \gamma^1_x}{c^2_x \gamma^2_x}$ is used with the same concentrations but also the activity coefficients $\gamma^{1M}_{CuSO_4} = 0{,}041$, $\gamma^{0,1M}_{CuSO_4} = 0{,}149$, $\gamma^{0,1M}_{ZnSO_4} = 0{,}150$, $\gamma^{1M}_{ZnSO_4} = 0{,}0435$ (4)

$\Rightarrow E_{CuSO_4} = 0{,}013\,V$, $E_{ZnSO_4} = 0{,}0137\,V$ which is less than the half Voltage of the result of 3). ~~the~~

The eq. in the protocol is incorrect. Look in the litereture for the right one.

5) To calculate the consentrations of Ag^+- and Cl^-- ions we used the equation $c_1V_1 = c_2V_2$ because the Volume changed in which the mentionded ions were.

$\Rightarrow$ for silver-ions : $0{,}1\frac{mol}{l} \cdot 0{,}002\,l = 0{,}025\,l \cdot c_{Ag^+} \Leftrightarrow c_{Ag^+} = 0{,}008\frac{mol}{l}$

For chlorid-ions : $0{,}1\frac{mol}{l} \cdot 0{,}003\,l = 0{,}025\,l \cdot c_{Cl^-} \Leftrightarrow c_{Cl^-} = 0{,}012\frac{mol}{l}$

With these results the EMF could be calculated like this:

$E = 0{,}059V \cdot \log\left(\frac{c_{Ag^+}}{K_L/c_{Cl^-}}\right)$, E was measured $(-0{,}3V)$, K_L has to be found out

$\Rightarrow$ Converting the equation with $c_{Ag^+} = \frac{K_L}{c_{Cl^-}}$

$-0{,}3V = 0{,}059V \cdot \log\frac{0{,}008\frac{mol}{l} \cdot 0{,}012\frac{mol}{l}}{K_L} \Rightarrow K_L = 7{,}898 \cdot 10^{-10}\frac{mol^2}{l^2}$

compared to the literature⁽⁵⁾ $\left(K_L = 1{,}77 \cdot 10^{-10}\frac{mol^2}{l^2}\right)$ the solubility product of AgCl can be determined with this method, but not very accurate.

What about the amount of Cl^- ions consumed? Write the appropriate chemical reactions.

6) In this last task we used the Gibbs-Helmholtz equation $\Delta G = \Delta H - T\Delta S$ to plot the measured values and do a linear regression to find out the enthapy and entropy of this reaction. First the measured EMFs were transformed with $\Delta G = z \cdot F \cdot E$ into the needed function $(z=2)$. Then, after the linear regreession, the y-intercept was determined by $\Delta H = 200377{,}34\,J$ and the gradient by $\Delta S = 61{,}88\,\frac{J}{K}$. The effectiv work was then given by

Where is the graph/regression?

$\frac{\Delta G}{\Delta H} = \frac{\text{average of } G}{\Delta H} = \frac{213614{,}4\,J}{200377{,}34\,J} = 1{,}036$ use for a single temperature, report which temperature

Because of the definitions of the energy conversion efficiency $\eta = \frac{E_{in}}{E_{out}}$ the effectiv work is the multiplicate inverse of η. (η cannot be > 1)

extra question

with the electrochemical equilibrium condition $\mu_i^{\alpha} = \mu_i^{\beta}$ follows:

$$\mu_i^{\alpha} + z_i F \varphi^{\alpha} = \mu_i^{\beta} + z_i F \varphi^{\beta} \Leftrightarrow \mu_i^{\ominus,\alpha} + RT\ln a_i^{\alpha} + z_i F \varphi^{\alpha} = \mu_i^{\ominus,\beta} + RT\ln a_i^{\beta} + z_i F \varphi^{\beta}$$

$$\Leftrightarrow \Delta\varphi = \varphi^{\alpha} - \varphi^{\beta} = \frac{\mu_i^{\ominus\beta} - \mu_i^{\ominus\alpha}}{z_i F} + \frac{RT}{z_i F}\ln\frac{a_i^{\beta}}{a_i^{\alpha}} = E^{\ominus} + \frac{RT}{zF}\ln\left(\prod a_i^{\nu_i}\right)$$

to what chemica reaction is this related!

Literature CRC Handbook of Chemistry and Physics, 89th edition, CRC Press/ Taylor and Francis 2009,

pages: (1) : 8-25
(2) : 8-24
(3) : 8-21
(4) : 5-80
(5) : 8-119

[redacted]

A	1M CuSO4	1M ZnSO4	1,096 V
B	1M "	0,1M CuSO4	0,0242 V
C	1M ZnSO4	0,1M ZnSO4	0,0239 V
F	0,1M CuSO4	0,1M ZnSO4	1,098 V
D	1M " (+)	AgCl	−0,14 V
E	1M ZnSO4(+)	AgCl	0,958 V 0,956

II 0,1 M AgNO3 + 3M KCl (+) (0,1M) — 0,1 M AgNO3 — −0,241 V

vor KCl −5,7mV — after 2min −0,288 V

rühren −0,3 V

III 0min : 1,099 V 27 °C

1,101

1,126 26°C

1,132

Start 1,134 27°C 12.44

1,137 30°

1,137 32°

1,137 34°

1,139 38° 47

1,14 40

" 42

" 44

1,14 45

" 46

1,14 48

1,139 50

1,138 53

24.02.17

Literature: - description of experiment

- lecture on the subject "Elektrochemie & Reaktionskinetik"
- Peter Atkins, Physikalische Chemie, WILEY-VCH, Weinheim 2013
- CRC Handbook of Chemistry and Physics, 89th edition
CRC Press / Taylor and Francis 2009
(1): 8-25
(2): 8-24
(3): 8-21
(4): 5-80
(5): 8-119

Corrections:

A) R: $Cu^{2+} + 2e^- \rightarrow Cu$
L: $Zn^{2+} + 2e^- \rightarrow Zn$
R-L: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

B) R: $Cu^{2+} + 2e^- \rightarrow Cu$
L: $Cu^{2+} + 2e^- \rightarrow Cu$
R-L: $Cu^{2+} + Cu \rightarrow Cu + Cu^{2+}$

C) R: $Zn^{2+} + 2e^- \rightarrow Zn$
L: $Zn^{2+} + 2e^- \rightarrow Zn$
R-L: $Zn^{2+} + Zn \rightarrow Zn + Zn^{2+}$

D) R: $Cu^{2+} + 2e^- \rightarrow Cu$
L: $2Ag^+ + 2e^- \rightarrow 2Ag$
R-L: $Cu^{2+} + 2Ag \leftarrow Cu + 2Ag^+$

$2AgCl + 2e^- \rightarrow 2Ag + 2Cl^-$

E) R: $Zn^{2+} + 2e^- \rightarrow Zn$
L: $2Ag^+ + 2e^- \rightarrow 2Ag$
R-L: $Zn^{2+} + 2Ag \leftarrow Zn + 2Ag^+$

F) R: $Cu^{2+} + 2e^- \rightarrow Cu$
L: $Zn^{2+} + 2e^- \rightarrow Zn$
R-L: $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

II) $Ag^+ + Cl^- \rightarrow AgCl$

III) graph is attached

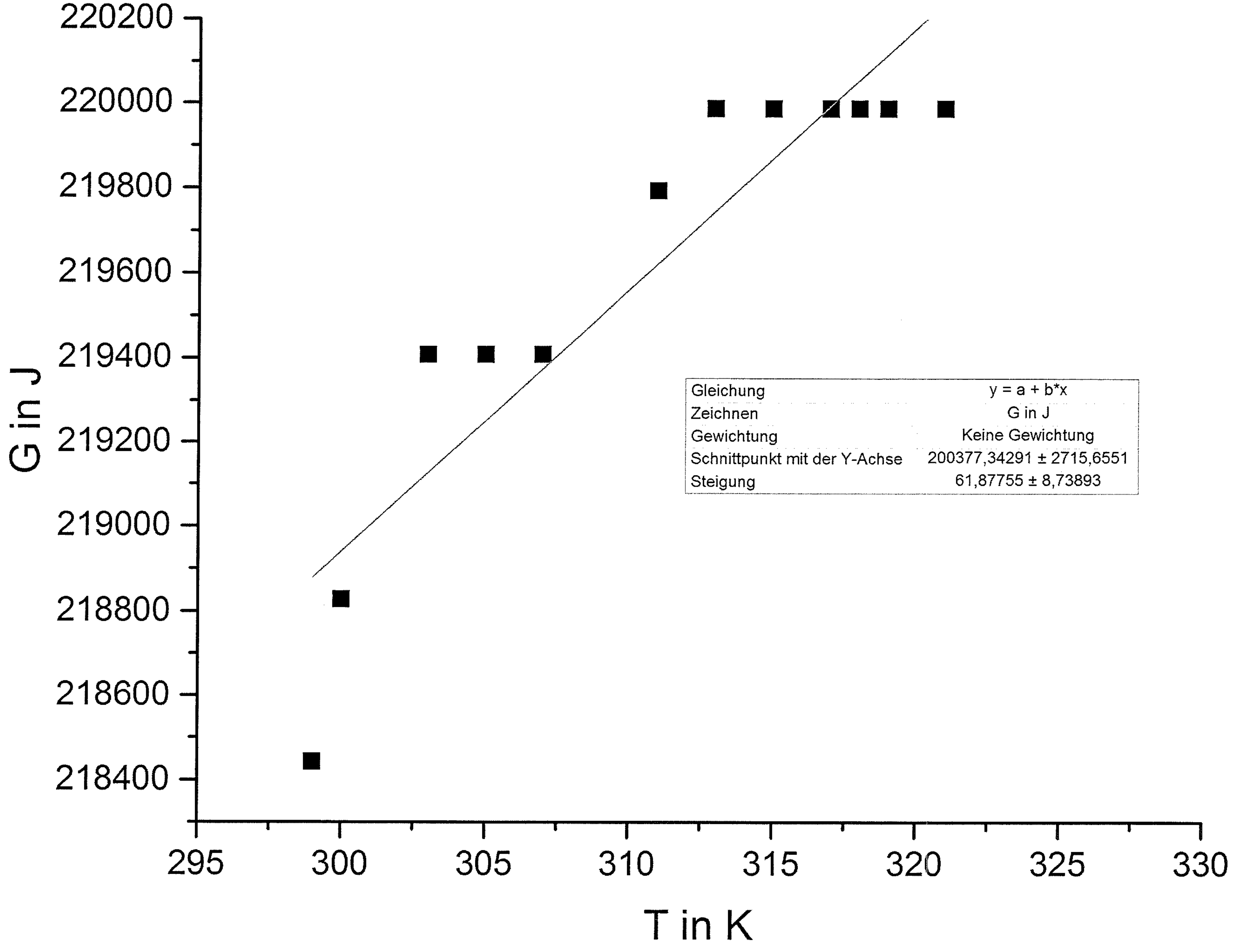
$$\frac{\Delta G}{\Delta H} = \frac{219753{,}6\ J}{200377{,}34\ J} = 1{,}097 \Rightarrow \eta = \frac{\Delta H}{\Delta G} = 0{,}912 = 91{,}2\,\%$$

ΔG at 323 K ($E = 1{,}139\ V$)

$\Delta\eta$?

The error of the effective work is very high, because the deviation of ΔG is very high ($\Delta G_{max} - \Delta G_{min} = 1543{,}8\ J$).

As a consequence the error of η is very small (deviation of η: $\eta_{max} - \eta_{min} = 0{,}0064$



Gleichung	y = a + b*x
Zeichnen	G in J
Gewichtung	Keine Gewichtung
Schnittpunkt mit der Y-Achse	200377,34291 ± 2715,6551
Steigung	61,87755 ± 8,73893