

The Electromotive Force and its Dependence on Activity and Temperature

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Introduction

1.1 Aim of the experiment

The experiments covered in this lab report aim to further the students' understanding of the relation between thermodynamics and electrochemistry in the context of electrochemical cells. The experiment was split into three distinct parts. Firstly, the potential differences of different reference electrodes were measured against one another as to gain insight into the concept of reference electrodes. The second and third experiment examined the correlation between the potential and concentration as well as the potential and temperature in the Daniell cell, a special form of a galvanic cell, respectively.

1.2 Theory

Firstly, in order to be able to apply physical equations on real solutions, despite their intramolecular interactions, a dimensionless "thermodynamically effective quantity", also known as activity a_i was introduced. The calculation of activity based on the concentration b_i , standard molarity b^0 and the activity coefficient γ_i can be seen in the following equation.

$$a_i = \gamma_i \cdot \frac{b_i}{b^0} \text{ with } \lim_{b_i \rightarrow 0} \gamma_i = 1 \quad (1)$$

Furthermore, it is important to define an electrochemical cell. An electrochemical cell enables interchange of chemical and electrical energy based on redox reactions and consists of two half cells. A half cell consists of two metallic conductors, called electrodes, immersed in a solution of an ionic conductor, the electrolyte. An external circuit connecting the two electrode compartments permits electric current flowing from one to another. In the case of two different electrolyte solutions, a salt bridge, may be used to allow selective exchange of ions between them to ensure electrical neutrality [1]. To quantify the effectiveness of an electrochemical cell, the term E , known as thermodynamic or reversible cell potential, was introduced.

$$\Delta G = -n \cdot F \cdot E \quad (2)$$

It is connected to the Gibbs free energy ΔG via the number of electrons exchanged per one electrochemical reaction n and the Faraday constant F . Additionally, E can be described by the Nernst equation.

$$E = E^0 - \frac{R \cdot T}{n \cdot F} \cdot \ln \prod_i a_i^{\nu_i} \quad (3)$$

Here, E^0 is the standard thermodynamic cell potential, R is the ideal gas constant and T the temperature. Additionally, the \prod term is called the reaction quotient, described as a product of the activities of the solvated species, described in (1), to the power of their respective stoichiometric coefficients ν_i . Further, to enable calculation of the enthalpy, ΔH , of the Daniell element, the following equation is derived from the Gibbs-Helmholtz equation [2].

$$\Delta H = -n \cdot F \cdot \left[E - T \cdot \left(\frac{\partial E}{\partial T} \right)_p \right] \quad (4)$$

Results

The raw data is listed in the appendix. Firstly, the expected electrochemical cell potential of different reference electrodes combinations needed to be calculated. For that, the theoretical activity coefficient was determined for the 1 M HCl solution using $\gamma_{HCl} = 0.809$ [2]. Equation 1 was used, resulting in $a_{HCl} = \gamma_{HCl} = 0.809$. To calculate the expected value for the electrochemical potential E , equation 3 was utilized, using a_{HCl} as well as the target temperature (298.15 K). The measured and calculated potentials can be found in table 1.

Table 1: Potentials of the various reference electrode combinations

Electrode	Measured potential		Calculated potential	
	SHE	Calomel	SHE	Calomel
Calomel	246 ± 0	-	268	-
Ag/AgCl	207.56 ± 0.12	-36.56 ± 0.12	223	-45

Remark: Potential given in [mV].

For the second part of the experiment, the potential of a Daniell cell as a function of the concentration was analysed. Once again, the theoretical potential needed to be calculated using equation 3. This time, the activity coefficients were equivalent to the ratio of concentrations of the electrolytes Zn^{2+} and Cu^{2+} . Again, there was no need to calculate the standard deviation for the expected values and for the reaction quotient. The potentials, can be found in the table below.

Table 2: Voltage / concentration dependency of the Daniell cell

Measured potential	Calculated potential	$\ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$
1056.15 ± 0.13	1044.78	4.61
1066.83 ± 0.029	1074.45	2.30
1101.79 ± 0.014	1104.00	0

Remark: Potential given in [mV].

Additionally, the measured as well as the calculated potential got plotted against the reaction quotient in the following graph. It is also worth mentioning, that the standard deviation of the measured values was too small to have displayed error bars meaningfully.

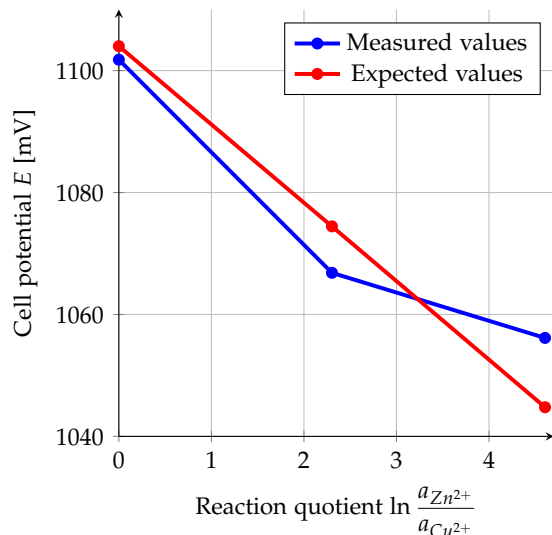


Figure 1: Voltage of the Daniell cell dependent on concentration

In addition, the calculated potential at an activity ratio of one / at a reaction quotient of zero (1104.00 mV) is equal to the standard potential E^0 and can be used to calculate ΔG^0 as per equation (2) resulting in $\Delta G = -213.04 \text{ kJ mol}^{-1}$. Lastly, the potential of a Daniell cell as a function of the temperature was analysed. The averages of the calculated potential and the measured temperatures can be found in the following table.

Table 3: Voltage / temperature dependency of the Daniell cell

Measured potential	Temperature	Enthalpy change
1102.16 ± 0.078	296.82 ± 0.022	-230.17 ± 16.35
1096.66 ± 0.084	308.16 ± 0.058	-229.78 ± 19.63
1095.73 ± 0.018	318.17 ± 0.091	-230.18 ± 8.83

Remark: Potential given in [mV]; Temperature given in [K]; Enthalpy change given in $[\text{kJ mol}^{-1}]$.

Furthermore, the data got visualised, along with linear regression being performed (cf. Error analysis).

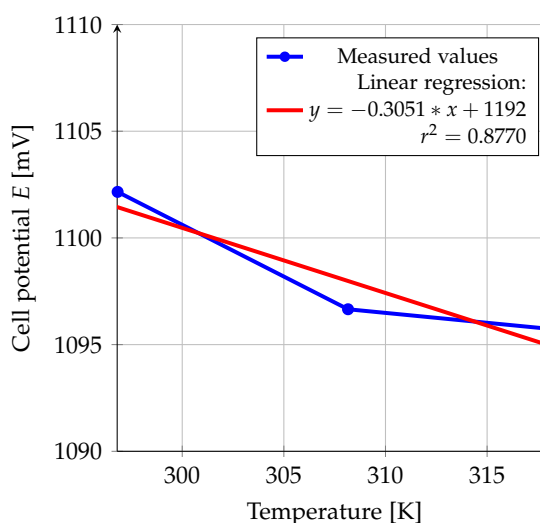


Figure 2: Voltage of the Daniell cell dependent on temperature

The slope of the regression function corresponds to the change of cell potential as a function of temperature at constant pressure, $(\frac{\partial E}{\partial T})_p$. As mentioned in the theory part of this lab report, this can be used to calculate the change in enthalpy by applying equation (4) equating to the results found in table 3.

Discussion

The discrepancy between measured and calculated potentials of the reference electrodes is as following.

- Calomel — SHE is 8.2%
- Ag/AgCl — SHE is 6.9%
- Ag/AgCl — Calomel is 18.8%

The deviation can be attributed to statistical errors, the temperature at the time of measurement not being equal to the target temperature used for the calculation of expected potentials, or mechanical errors such as the electrodes not being properly cleaned. Additionally, the spread of the divergences is relatively similar for both of the SHE measurements, but

is almost thrice as high for the Ag/AgCl — Calomel measurement. Both the measured and calculated potentials make sense in terms of their sequence, as it's in accordance with the reduction potentials of their respective half-cell reactions:

$$\Delta E_{SHE-Calomel}^0 > \Delta E_{SHE-Ag/AgCl}^0 > \Delta E_{Ag/AgCl-Calomel}^0 \quad (5)$$

The deviations between the measured and the calculated potentials in the second part of the experiment can be summarized similarly. The measurements reflect the theoretical relation between the concentration and the potential; the potential changes in accordance to the \ln of the salt activities. As illustrated in figure 1, the cell potential E decreases with a higher reaction quotient. This corresponds to the theoretical relation illustrated by (3). It is worth mentioning that the last two measured cell potential values deviate from the expected value to a certain extent; the measured and the expected values are rather comparable and hence, our experimental result reflects the relationship between cell potential and reaction quotient stated by (3). Besides, the extremely low standard deviation (<0.1) of the measured potential indicates a high precision of the measurements. Figure 2 shows the dependence of the cell potential by the temperature. The higher the temperature gets, the lower the cell potential. This agrees with the mathematical relationship of temperature and cell potential of an electrochemical cell described by (3), which indicates that a higher temperature causes a higher subtrahend, which lowers the cell potential value. The slight deviation of measured values from the regression line can be attributed to unavoidably small amount of shift of metal ion through the salt bridge, which results in change in metal ions concentrations and hence causing deviation from the expected linear relationship. Furthermore, the ΔG^0 of the investigated electrochemical reaction is $-213.04 \text{ kJ mol}^{-1}$, won by extrapolation of figure 1, corresponds with reality, as the type of the cell is galvanic, and the electrochemical reaction is exergonic. Moreover, the Enthalpy change is quite precise, with a mean of roundabout $-230,04 \text{ kJ mol}^{-1}$, which suggests that the electrochemical reaction investigated is exothermic. It is worth mentioning that the errors of the derived enthalpy change of the electrochemical reaction based on Gaussian error propagation are ± 16.35 , ± 19.63 and $\pm 8.83 \text{ kJ mol}^{-1}$ for the three measurements with increasing temperatures respectively. These considerable errors are caused by multiplication with relatively big factors, such as F , signifying the magnitude that error propagation can cause.

Error analysis

Above all, it is worth noting, that the standard deviation (of a measurement series) was specified on all applicable values using the following equation.

$$\sigma_m = \sqrt{\frac{1}{n} \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (6)$$

With n being the amount of measurements, x_i being the i -th measurement and \bar{x} being the arithmetic mean. The final results were reported as follows.

$$\bar{x} \pm \sigma_m \quad (7)$$

Moreover, no standard deviation was noted in cases of expected values, as measured, imperfect quantities weren't used for these calculations. As for the standard deviation of the enthalpy change, an error propagation calculation is needed, as E and T are both inaccurate measurements. To calculate the standard deviation of ΔH (4) involves multiplying the deviation of the variables E and T by possible factors, in this case multiplying σ_T by $\left| \left(\frac{\partial E}{\partial T} \right)_p \right|$. This "intermediate" standard deviation gets added to σ_E and multiplied with the absolute value of the remaining factors n and F . This method isn't perfect, as the $\left(\frac{\partial E}{\partial T} \right)_p$ term, results from the slope of the linear regression and is likewise imperfect, though the standard deviation of that parameter isn't known. To investigate the relationship of the two continuous variables, linear regression is used to find the best-fitting straight line which illustrates the linear relationship. The theoretical relation of cell potential to the temperature is linear, with the slope equal to $-\frac{R \cdot T}{2 \cdot F}$ and the y-intercept equal to E^0 . The formula necessary for the linear regression can be formulated as a general linear function.

$$y = m \cdot x + t \quad (8)$$

Besides, the slope derived from linear regression analysis can serve as partial derivative, which can be utilized in calculation with physics equations. The slope in Figure 2 can be used for calculation of reaction enthalpy with (4). To commence with the calculation of the best-fitting straight line, various statistical variables are introduced from the manual about error

estimation and propagation [3].

$$\begin{aligned}
 S &= \sum_i \frac{1}{\sigma_i^2} \\
 S_x &= \sum_i \frac{x_i}{\sigma_i^2} \\
 S_y &= \sum_i \frac{y_i}{\sigma_i^2} \\
 S_{xy} &= \sum_i \frac{x_i y_i}{\sigma_i^2} \\
 S_x^2 &= \sum_i \frac{x_i^2}{\sigma_i^2}
 \end{aligned} \quad (9)$$

With the above statistical variables, the slope m and y-intercept t can be calculated with the values found in tables 10, 11 and 12 as well as the equations below.

$$\begin{aligned}
 m = \alpha_2 &= \frac{SS_{xy} - S_x S_y}{SS_{x^2} - S_x^2} \\
 t = \alpha_1 &= \frac{S_{x^2} S_y - S_x S_{xy}}{SS_{x^2} - S_x^2}
 \end{aligned} \quad (10)$$

However, the value of slope of the linear regression of 2 is positive ($m = 3.40$), which does not describe the tendency accurately, as the cell potentials decreased with the increasing temperature during the measurements. Hence, alternative way of calculation for the linear regression is used [4]. The alternative way of the calculation is as following.

$$\begin{aligned}
 SS_{xy} &= \sum (x_i - \bar{x})(y_i - \bar{y}) \\
 &= \sum x_i y_i - \frac{(\sum x_i)(\sum y_i)}{n} \\
 SS_{xx} &= \sum (x_i - \bar{x})^2 \\
 &= \sum x_i^2 - \frac{(\sum x_i)^2}{n} \\
 m &= \frac{SS_{xy}}{SS_{xx}} \\
 t &= \bar{y} - m \cdot \bar{x}
 \end{aligned} \quad (11)$$

By applying (11), new regression line with $m = -0.3051$ and $t = 1192$ are obtained, which describes certainly better the data model based on measured values during experiment. Thus, this regression line is used and plotted in figure (2) for further calculation. Besides, to measure the strength of the linear relationship between the temperature and the cell potential, the coefficient of determination r^2 is used. The value of r^2 is always between 0 and 1. The closer of r^2 to 1, the stronger the linear correlation of the

two variables. The calculation of r^2 is as following.

$$\begin{aligned}
 SS_{yy} &= \sum (y_i - \bar{y})^2 \\
 &= \sum y_i^2 - \frac{(\sum y_i)^2}{n} \\
 SSE &= \sum (y_i - \hat{y}_i)^2 \\
 r^2 &= 1 - \frac{SSE}{SS_{yy}}
 \end{aligned} \quad (12)$$

Here \hat{y}_i is equal to expected value of y based on regression line equation. With (12), the r^2 of our postulated regression line is obtained to be 0.8770. It is worth mentioning that all the 21 measurements during the experiments are used to generate the regression line and r^2 . The r^2 of 0.8770 is very close to 1 and hence, indicates a strong linear correlation between temperature and cell potential.

References

- [1] Peter Atkins and Julio Paula. *Atkins' physical chemistry*. Oxford University press, 2008. ISBN: 9780195685220. URL: <http://www.worldcat.org/isbn/9780195685220>.
- [2] Michele Piana et al. *Laboratory Course in Physical Chemistry for Fundamental Studies: Experiments Manual*. 2023.
- [3] Sebastian Günther and Tim Kratky. *G2 - Messfehler einschätzen*.
- [4] J.T. McClave and T.T. Sincich. *Statistics, Global Edition*. Pearson Education, 2017. ISBN: 9781292161563. URL: <https://books.google.de/books?id=mjY9DwAAQBAJ>.

Appendix

Table 4: Raw data of the of reference potentials

Time	T	U	\hat{U}	σ_U
0	24.2	246	246	0
10	24.2	246	-	-
20	24.3	246	-	-
30	24.3	246	-	-
40	24.3	246	-	-
50	24.3	246	-	-
60	24.3	246	-	-
70	24.2	246	-	-
80	24.2	246	-	-
90	24.2	246	-	-
100	24.2	246	-	-
110	24.3	246	-	-
120	24.3	246	-	-
130	24.2	246	-	-
140	24.2	246	-	-
150	24.3	246	-	-
160	24.2	246	-	-
170	24.2	246	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; Half-cell combination: Hydrogen and Calomel.

Table 5: Raw data of the of reference potentials

Time	T	U	\hat{U}	σ_U
0	24.2	208	207.5555556	0.120516921
10	24.2	207	-	-
20	24.2	208	-	-
30	24.2	208	-	-
40	24.2	207	-	-
50	24.2	207	-	-
60	24.2	208	-	-
70	24.2	208	-	-
80	24.2	208	-	-
90	24.2	207	-	-
100	24.2	207	-	-
110	24.2	207	-	-
120	24.2	207	-	-
130	24.2	207	-	-
140	24.2	208	-	-
150	24.2	208	-	-
160	24.3	208	-	-
170	24.3	208	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; Half-cell combination: Hydrogen and Ag/AgCl.

Table 6: Raw data of the of reference potentials

Time	T	U	\hat{U}	σ_U
0	24.2	-36	-36.55555556	0.120516921
10	24.3	-36	-	-
20	24.3	-36	-	-
30	24.3	-37	-	-
40	24.3	-37	-	-
50	24.2	-37	-	-
60	24.2	-37	-	-
70	24.2	-36	-	-
80	24.3	-36	-	-
90	24.3	-37	-	-
100	24.2	-37	-	-
110	24.3	-36	-	-
120	24.2	-37	-	-
130	24.2	-37	-	-
140	24.3	-36	-	-
150	24.2	-37	-	-
160	24.2	-37	-	-
170	24.3	-36	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; Half-cell combination: Calomel and Ag/AgCl.

Table 7: Raw data of the voltage / concentration dependency of the Daniell cell

Time	0	10	20	30	40	50	60
T_1	24	24	24	24	24	24	N/A
T_2	24.2	24.3	24.2	24.2	24.3	24.2	N/A
U	1056.6	1056.4	1056.2	1056	1055.9	1055.8	N/A
\hat{U}	1056.15	-	-	-	-	-	-
σ_U	0.125830574	-	-	-	-	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; $b_{\text{CuSO}_4} = 0.005 \text{ mol}$

Note: The data points for time = 60 s were unavailable.

Table 8: Raw data of the voltage / concentration dependency of the Daniell cell

Time	0	10	20	30	40	50	60
T_1	23.8	23.8	23.9	23.9	23.9	23.9	23.9
T_2	24.1	24.1	24.1	24.1	24.1	24.1	24.2
U	1066.7	1066.8	1066.8	1066.8	1066.9	1066.9	1066.9
\hat{U}	1066.828571	-	-	-	-	-	-
σ_U	0.028571429	-	-	-	-	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; $b_{\text{CuSO}_4} = 0.05 \text{ mol}$.

Table 9: Raw data of the voltage / concentration dependency of the Daniell cell

Time	0	10	20	30	40	50	60
T_1	23.8	23.8	23.8	23.8	23.8	23.8	23.8
T_2	24	24	24	24	24	24	24
U	1101.8	1101.8	1101.8	1101.8	1101.8	1101.8	1101.7
\hat{U}	1101.785714	-	-	-	-	-	-
σ_U	0.014285714	-	-	-	-	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; $b_{\text{CuSO}_4} = 0.5 \text{ mol}$.

Table 10: Raw data of the voltage / temperature dependency of the Daniell cell

Time	0	10	20	30	40	50	60
T_1	296.75	296.75	296.75	296.75	296.85	296.85	296.95
T_2	296.75	296.75	296.95	296.95	296.85	296.75	296.85
U	1102.4	1102.3	1102.3	1102.2	1102.1	1102	1101.8
\hat{U}	1102.157143	-	-	-	-	-	-
σ_U	0.07824608	-	-	-	-	-	-
σ_T	0.022060286	-	-	-	-	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; Target temperature = 298.15 K.

Table 11: Raw data of the voltage / temperature dependency of the Daniell cell

Time	0	10	20	30	40	50	60
T_1	307.95	307.95	307.95	307.95	307.95	307.95	307.95
T_2	308.35	308.45	308.35	308.35	308.35	308.35	308.35
U	1096.9	1096.9	1096.8	1096.6	1096.6	1096.5	1096.3
\hat{U}	1096.657143	-	-	-	-	-	-
σ_U	0.084112008	-	-	-	-	-	-
σ_T	0.057859517	-	-	-	-	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; Target temperature = 308.15 K.

Table 12: Raw data of the voltage / temperature dependency of the Daniell cell

Time	0	10	20	30	40	50	60
T_1	317.75	317.75	317.85	317.85	317.85	317.95	317.95
T_2	318.45	318.45	318.45	318.45	318.55	318.55	318.55
U	1095.7	1095.7	1095.7	1095.7	1095.7	1095.8	1095.8
\hat{U}	1095.728571	-	-	-	-	-	-
σ_U	0.018442778	-	-	-	-	-	-
σ_T	0.090892142	-	-	-	-	-	-

Remark: Potential given in [mV]; Time given in [s]; Temperature given in [K]; Target temperature = 318.15 K.