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Research Article

How to Estimate Thermodynamic Data and Verify Relationships Using Simple Electrochemistry

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Abstract: Experimental determination of thermodynamic quantities can be very simple, but some suggested procedures can be complicated and cumbersome. They can be almost impossible in the student's laboratory in chemistry education. Electrochemistry provides easy and simple access to those data for chemical reactions which can be executed in an electrochemical cell. Two examples are presented and discussed, their results are critically examined.

Keywords: Thermodynamics, basic laws, enthalpy, free enthalpy, Gibbs energy, entropy

Nomenclature

Term	Description
A	free energy
F	Faraday constant
G	Gibbs energy
H	enthalpy
U	cell voltage
T	temperature
W	work
z	number of transferred electrons

1. Introduction

Enthalpy H, Gibbs energy G (or Gibbs function, the term free enthalpy is popular only in German-speaking places, use of the term according to IUPAC recommendations and local customs seems to vary) and the related quantities isochoric energy U and free energy (also Helmholtz energy) F or A as well as entropy S are standard items in teaching thermodynamics in chemistry bachelor courses both in the classroom and in the student's laboratory (the curriculum as valid for German universities is provided in [1]). They are introduced and derived in the context of the laws of thermodynamics. Definitions and use of symbols differ widely as illustrated before [2], recommendations of IUPAC have brought only limited relief [3]. This apparently also applies to used indices.

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Because in this text only enthalpies, Gibbs energies and entropies and their changes as related to chemical reactions are considered additional indices are not needed (thus ΔG instead of ΔrG). Since chemistry is an experimental science verification, at least examination, of the laws and relationships and further topics addressed in lectures and seminars by experimental work in laboratory courses is a required complement, commonly occupying about 50 % of the time budget allocated to Physical Chemistry [1].

The many experiments possible in a Physical Chemistry lab course [4] are frequently associated with a dubious or even infamous image; frequent failures and imprecise results are only some of the popular complaints. Thus, descriptions of fail-safe procedures and experiments are welcome [4–6].

Calorimetric experiments suitable for the determination of enthalpies, more precisely changes of enthalpy ΔH, during phase transitions and many chemical reactions are well-established, practically helpful descriptions are available [4–6]. Corresponding procedures for determinations of Gibbs energies and entropies of reactions are hard to find, they are seldom found in popular textbooks. With one exception: In case a reaction can be executed as an electrochemical one suddenly many sometimes relatively simple procedures requiring in most cases only rather common and affordable equipment become available.

This report presents a brief introduction into relationships between electrochemical and thermodynamic properties using the popular hydrogen-oxygen fuel cell. Using the derived relationships two experiments are described in sufficient detail to enable the reader reproduction in the student's laboratory. Most likely the student will be familiar with the experiments, at least with their fundamentals, already from the lectures.

2. Thermodynamic Fundamentals

When introducing ΔG as the maximum useful energy (i.e. work) gained from a chemical reaction the hydrogen/oxygen fuel cell is a popular example. Without spending too much time with kinetic hindrances (which are irrelevant in thermodynamics anyway) and catalytic details of three-phase boundaries in gas-fed porous electrodes the open circuit voltage of 1.229 V (also called cell potential or electromotive force EMF) and the number of electrons z transferred in the reaction

$$\mathrm{H_2 + ½\ O_2 \rightarrow H_2O} \tag{1}$$

the electric work W obtained from the cell upon formation of one mole of reaction product is calculated as

$$W = z \cdot F \cdot U_0 \tag{2}$$

Assuming the cell is kept under reversible conditions (rather impractical, but relevant for the moment) at open circuit voltage U_0 this work must be equivalent to ΔG. Accordingly a popular relationship is introduced:

$$\Delta G = -z \cdot F \cdot U_0 \tag{3}$$

The symbol U_0 designing the cell voltage at rest as one option according to IUPAC [3] is used here instead of E (and the term cell potential), because E is again used as the symbol of an electrode potential. The use of U^2 instead of U_0 indicating a cell voltage at rest is not helpful because this superscript may also be used for indicating standard conditions [3]. ΔG of the cell reaction in a galvanic cell has a negative sign. Because no electric work with negative sign is known the eq. 3 has an added minus sign in comparison to eq. 4 below.

The electrochemical cell composed of two electrodes (sometimes also called half-cells) discussed above is a galvanic cell (or element) used for the conversion of chemical energy into electrical energy. Numerous processes and devices are known operating in the opposite way, i.e. for the conversion of electric energy into chemical energy by electrolysis. Whether the conversion itself and the options to store the reaction products (as hydrogen and dioxygen, the latter is not really stored in most cases actually) are of interest as a way to store excess electric energy from e.g. intermittent renewable sources [5] or whether production of substances like chlorine, aluminium or any other element or compounds is of interest the consideration discussed above can be applied also in reverse. Because in this electrolytic cell processes run only when energy is supplied ΔG is positive, eq. 3 changes into

$$\Delta G = z \cdot F \cdot U_0 \tag{4}$$

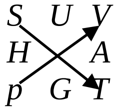
with the minus sign being lost for the reasons outlined above.

Measurement of cell voltages provides an easy access to values of Gibbs energies of reactions ΔG hard to obtain otherwise. Following we will examine in sect. 3 two examples, one of the galvanic and one of the electrolytic type.

The Gibbs equation provides a relationship between the Gibbs energy of reaction, enthalpy and entropy of reaction according to

$$\Delta G = \Delta H - T \cdot \Delta S \tag{5}$$

Using the Maxwell relations and for convenience the Guggenheim scheme



the change of ΔG with temperature can be calculated

$$(\partial \Delta G / \partial T)_{\mathrm{p}} = (\partial \Delta H / \partial T)_{\mathrm{p}} - (\partial T \Delta S / \partial T)_{\mathrm{p}} \tag{6}$$

Assuming the reaction enthalpy ΔH to be constant within the studied range of temperatures the equation can be simplified into

$$(\partial \Delta G / \partial T)_{\mathrm{p}} = -\Delta S \tag{7}$$

or

$$(\partial U_0 / \partial T)_{\mathrm{p}} \cdot z \cdot F = \Delta S \tag{8}$$

Thus determination of the reaction entropy can be based on a rather simple measurement of the cell voltage as a function of temperature, i.e. the determination of the temperature coefficient of the cell voltage.

Following this general introduction of relationships between thermodynamic and electrochemical properties two examples considering both directions of electrochemical conversion of electric energy into chemical energy and back – a topic of highest current interest, too – are presented.

3. Two Examples

Verification of thermodynamic data for cell reactions going both ways from chemical to electric energy in a battery (the galvanic cell) and in the reverse from electric energy to chemical energy in an electrolytic cell are presented in the following sections.

3.1 The Galvanic Cell

In a galvanic cell chemical energy stored in the compounds inside the cell is converted into electric energy, the device is called a battery or in case it is rechargeable it is called an accumulator or a secondary battery [5].

Measurement of the cell voltage provides access to the Gibbs energy of the cell reaction, measurement of the cell voltage as a function of cell temperature provides a way to the reaction entropy. For a revised theory of entropy changes in running galvanic cells see [6]. Both values properly combined yield the reaction enthalpy. The calculations are the same as presented below for the electrolytic cell, only some details regarding signs are different.

Various batteries have been suggested as examples for the student’s lab. With respect to practical relevance lithium-ion batteries and nickel-metal hydride batteries seem to enjoy some popularity according to the results of a simple web search which easily yields student’s laboratory reports from the respective experimental courses. For privacy protection no personal data are revealed here. For both examples the highly important comparison between experimental results and literature data is difficult, practically impossible.

Less practically relevant (the heydays of this battery in railway and telecommunication application were in the 19th century) but experimentally better accessible is the Daniell element (or cell) [7]. It contains a metallic zinc electrode immersed in a zinc sulfate solution as the negative (less noble) electrode or half-cell and a copper electrode in a copper sulfate solution as the positive electrode. Mixing of both half-cell electrode solutions is impeded by a porous diaphragm, instead of a diaphragm use of a salt bridge filled with an aqueous solution of potassium nitrate is an option for laboratory studies (Filling with potassium chloride is not recommended because chloride ions tend to adsorb specifically on many metal surfaces, they may even accelerate corrosion). With or without a salt bridge diffusion potentials may be generated. With the suggested filling of the salt bridge actual values of diffusion potentials will be small; nevertheless this phenomenon must not be overlooked. The electrode and cell reactions are:

Positive electrode (Reduction): $Cu^{2+} + 2\,e^{-} \rightarrow Cu$ (9)

Negative electrode (Oxidation): $Zn \rightarrow Zn^{2+} + 2\,e^{-}$ 10)

$$\text{Cell reaction: } Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu \qquad (11)$$

An earlier description of an experimental approach is available [8]. The generous use of mercury and its salts may possibly inhibit use of the procedure in nowadays student's laboratories. Earlier, more complicated procedures have been described [9, 10]. Measurements of the temperature coefficient of this Daniell cell seem to be an attractive way at first glance to obtain reaction entropy values because thermodynamic data for this cell reaction are well known. The very small reaction entropy of this reaction has already induced earlier researchers to assume that the Daniell cell provides a way for complete conversion of the reaction enthalpy into useful work. The copper electrode tends to form poorly defined surface oxide layers especially when exposed to corrosive environments. The amphoteric nature of the zinc electrode adds further uncertainty, making this cell a less attractive candidate. Nevertheless the authors in [8] found satisfactory agreement for ΔG, with their value of ΔS = -36.9 $J \cdot K^{-1} \cdot mol^{-1}$ significantly larger than the quoted literature value of -21.2 $J \cdot K^{-1} \cdot mol^{-1}$ (the source of the literature value was not provided). A further look at the literature may cause some concerns. In an online text [11] this reaction entropy (again without providing literature sources) is calculated at -104.5 $J \cdot K^{-1} \cdot mol^{-1}$; a theoretical value for comparison is not provided. In the quoted source of data [12] the reaction entropy is found to be ΔS = -13.1 $gibbs \cdot mol^{-1}$, for comparison a literature value of ΔS = -3.73 $gibbs \cdot mol^{-1}$ is quoted. Assuming gibbs to be equivalent to $J \cdot K^{-1}$ the respective values are -55.02 and -15.66 $J \cdot K^{-1} \cdot mol^{-1}$. A value calculated with literature data [19] according to

$$Cu^{2+}_{aq} + Zn \rightarrow Zn^{2+}_{aq} + Cu \qquad (12)$$

and the thermodynamic calculation

$$-S_{Cu^{2+}_{aq}} - S_{Zn} + S_{Cu} + S_{Zn^{2+}_{aq}} = \Delta S \qquad (13)$$

is

$$-(-99.6) - 41.63 + 33.15 + (-112.1) = -20.98 \ J \cdot K^{-1} \cdot mol^{-1} \qquad (14)$$

This rather small value is reasonably close to the literature value quoted in [12]; it is in almost perfect agreement with the literature value of ΔS = -21.1 $J \cdot K^{-1} \cdot mol^{-1}$ provided in [8]. Given the concerns about the use of mercury and its salts recommended in [8] the simple approach in [12] avoiding this detail completely (it remains a mystery why this study was overlooked completely in [8]) comes at a cost: Measured reaction entropy and literature value differ by a factor of four.

The picture becomes even more confusing when inspecting again current student's laboratory reports. In one case a value of ΔS = -75 $J \cdot K^{-1} \cdot mol^{-1}$ is reported without – slightly surprising – giving a comparison with literature values. In a second report from the same place another group of students observed a positive temperature coefficient of the cell voltage – contrary to all literature reports, but in sad agreement with some deplorable observations the present author made when supervising this experiment in a laboratory course many years ago – and consequently a positive reaction entropy of ΔS = 66.25 $J \cdot K^{-1} \cdot mol^{-1}$ is noted. These authors provided a calculated value of ΔS = 12 $J \cdot K^{-1} \cdot mol^{-1}$, but because their calculation is marred by further fundamental errors the discrepancy shall not be explored further here.

Instead another electrochemical galvanic cell was searched for (A further example not explored in the authors lab is the zinc-silver cell again with ample use of mercury [9]). As an example described earlier a silver-copper cell has been suggested [15]. It combines a silver wire immersed in an aqueous solution of 1 **M** $AgNO_3$ with another half-cell of a copper wire immersed in a solution of 1 **M** $CuSO_4$. Both half-cells are combined with a salt bridge filled for said reasons (see above) with an aqueous solution of KNO_3. Measurement of the temperature-dependent cell voltage within a range of 20 °C < T < 80 °C is easily possible. The calculated[1] value of U_0 at room temperature is U_0 = 0.469 V; the experimentally observed one is U_0 = 0.454 V. To identify sources of this difference, the potentials of both electrodes can be measured versus a reference electrode. With a saturated calomel electrode the results are: $E_{\text{Cu vs. SCE}}$ = 0.322 V and $E_{\text{Ag vs. SCE}}$ = 0.775 V. Obviously the deviation is caused by a non-ideal behavior of the copper electrode. Results of the measurements are displayed in Figure 1.

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[1] Mean activity coefficients are $\gamma_{CuSO_4} = 0.047$ and $\gamma_{AgNO_3} = 0.4$

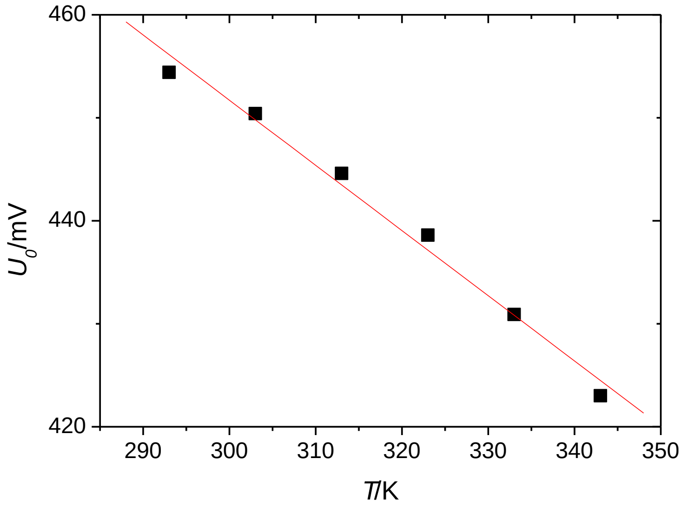

Figure 1. Temperature dependence of the cell voltage of a copper-silver cell (symbols: experimental data, line: interpolation).

Using the temperature coefficient calculated from the plot $\partial U_0/\partial T$ = – 0.63 mV K^{-1} a reaction entropy ΔS = - 121 J·K^{-1}·mol^{-1} can be calculated. The value calculated from thermodynamic data [19] is ΔS = - 145 J·K^{-1}·mol^{-1}. Any obvious uncertainties have not been observed with this cell although the copper electrode may again be a potential source of problems as observed with the Daniell cell. Calculation of reaction enthalpy and Gibbs energy of reaction runs exactly in the same was as described below for an electrolytic cell, they are not repeated here.

3.2 The Electrolytic Cell

Determination of reaction entropy and Gibbs energy is also possible in an approximation with an electrolytic cell. Electrolysis of an aqueous solution of a metal halide yields hydrogen at the negative electrode (which may be called cathode, but to avoid confusion this term is not used here following a suggestion made earlier by Huggins years ago [13, 14]) and the halogens obtain by oxidation of the halide ions. Only minute amounts are formed, but nevertheless safety precautions regarding the use of halogens (ventilation etc.) must be observed. Once electrolysis proceeds the cell is not in equilibrium anymore. This fundamental limitation is taken into account by extrapolating the recorded current vs. voltage relationship (for examples see below) to zero current. The shape of the curve permits – without the need to consider details of the underlying phenomena and processes most likely beyond the present context of the experiment anyway – such extrapolation easily. As example electrolysis of an HCl-solution running as an industrial electrolytic process (the chlor-alkaline electrolysis) on a large scale is considered:

$$\text{at the negative electrode: } H^+ + e^- \rightarrow \tfrac{1}{2} H_2 \tag{15}$$

$$\text{and at the positive electrode: } Cl^- \rightarrow \tfrac{1}{2} Cl_2 + e^- \tag{16}$$

(both equations are rigidly simplified leaving out details not relevant in the following discussion) yielding a slightly extended cell reaction equation

$$2\ H_3O^+ + 2\ Cl^- \rightarrow H_2 + Cl_2 + 2\ H_2O \tag{17}$$

The cell voltage can also be established by running a chlorine-hydrogen fuel cell (a galvanic cell again) fed with hydrogen and chlorine gas to two platinum sheet electrodes immersed into an aqueous solution of HCl. The use of chlorine gas is definitely an unwelcome proposition. Thus chlorine is formed by an electrolytic process here. The negative hydrogen electrode can be established by developing hydrogen by electrolysis, too. This may result in a poorly defined electrode potential. Accordingly in literature descriptions the negative electrode is built as a large surface area (platinized platinum sheet) electrode sparged with a slow stream of hydrogen [15]. Accordingly the current density at the hydrogen electrode is small; the electrode potential is close to E_0. The cell voltage is thus controlled by the potential of the positive chlorine electrode. The experimental setup is depicted in Figure 2, further details can be found in [15].

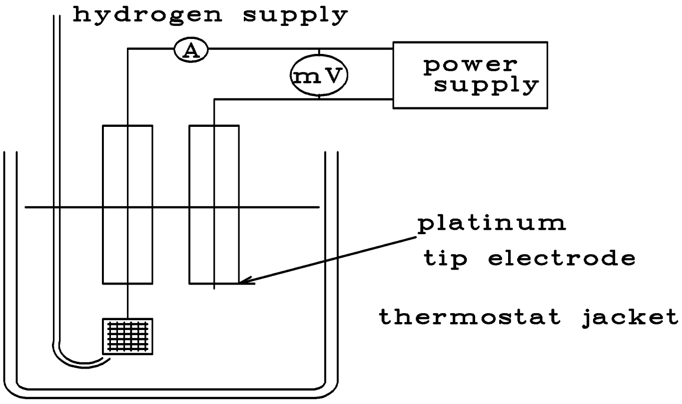

Figure 2. Experimental setup for measurements of HCl-electrolysis

The use of hydrogen gas from pressurized cylinders has been considered a safety risk in some places, thus replacement of the hydrogen electrode by an electrode according to Giner [16] has been suggested and successfully applied [17]. This hydrogen reference electrode (see also [18]) is depicted in Figure 3, a simplified setup available without the assistance of a glass blower has been described [17].

Figure 3. A dynamic hydrogen reference electrode according to Giner

Incorporation of this electrode in a setup for the determination of electrode potentials is shown in Figure 4 with the battery supplying the current for hydrogen evolution at the hydrogen electrode and the resistor limiting the electrolysis current.

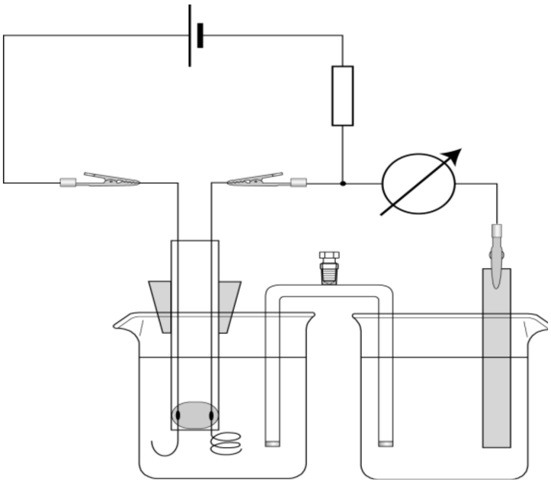

Figure 4. A setup for electrode potential measurements using the dynamic hydrogen electrode (left) and a test electrode (right).

Replacing the test electrode of Figure 4 with the platinum tip electrode with the current source and the ammeter added yield the setup for the measurement of cell voltages shown in Figure 5. Although the amounts of formed hydrogen and halogens are extremely small the experiment should be executed in a well-vented laboratory.

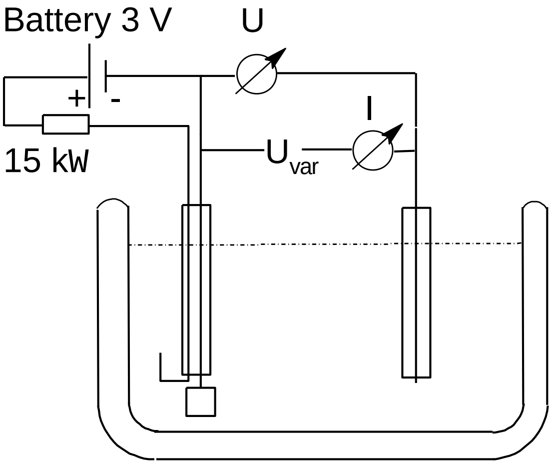

Figure 5. A setup for electrolysis voltage measurements using the dynamic hydrogen electrode (left) and a platinum tip electrode (right).

A set of typical results obtained at $T = 299$ K with various halides (concentrations of HCl 1.2 **M** (at his concentration the proton activity is approximately 1, the hydrogen is thus a standard hydrogen electrode), of Br^- and I^- 1 **M** each) is shown in Figure 6.

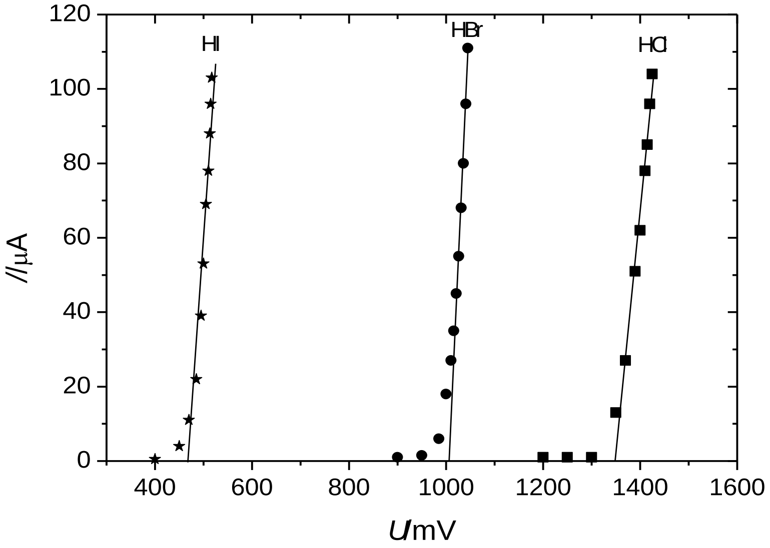

Figure 6. Current vs. cell voltage displays for various acidic halide solutions

Linear extrapolation of the rising part of the line connecting the data point yields at zero current the reversible cell voltage U_0 (at equilibrium or rest), sometimes also called decomposition voltage. The calculated free enthalpy values of the electrolysis reactions are listed in **Table 1** and compared with literature data [19]. Given the rather simple experimental setup agreement between measured and expected/calculated data is satisfying.

Determination of the reaction entropy requires measurements at different temperatures. This was done with the HCl-solution. Results are displayed in Figure 7.

The temperature coefficient of the cell voltage can be obtained by linear regression as shown in Figure 8.

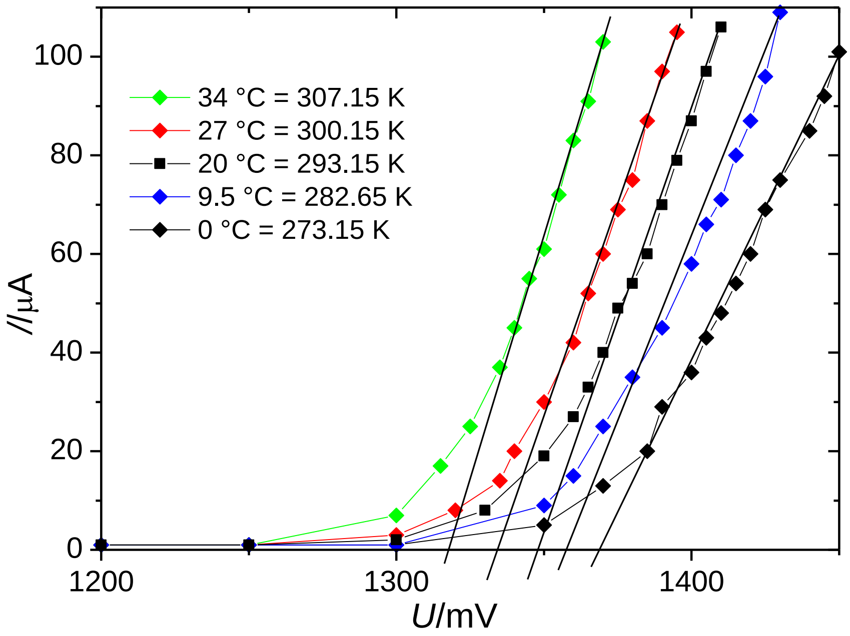

Figure 7. Current vs. cell voltage displays for various temperatures with an acidic aqueous solution of 1.2 **M** HCl

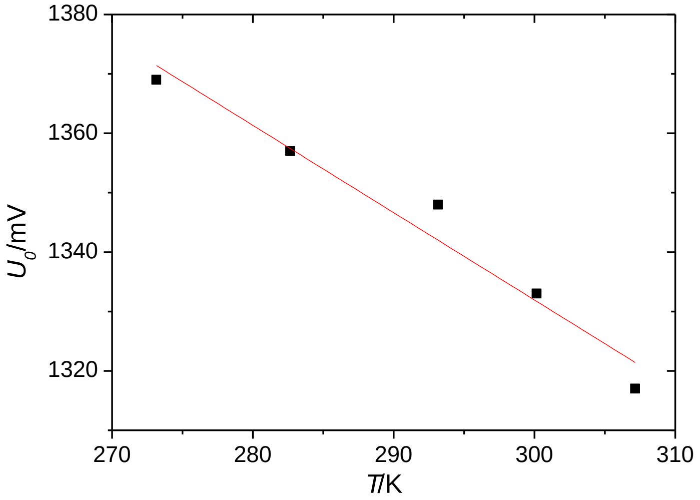

Figure 8. Cell voltage U0 vs. temperature for an acidic aqueous solution of 1.2 M HCl

A value of – 1.47 mV·K^{-1} is obtained. The expected reaction entropy value is calculated assuming a reaction

$$2\ \mathrm{H_3O^+} + 2\ \mathrm{Cl^-} \longrightarrow \mathrm{H_2} + \mathrm{Cl_2} + 2\ \mathrm{H_2O} \tag{17}$$

and the thermodynamic calculation

$$-2S_{\mathrm{H_3O^+_{aq}}} - 2S_{\mathrm{Cl^-}} + S_{\mathrm{H_2}} + S_{\mathrm{Cl_2}} = \Delta S \tag{18}$$

or

$$-\ 2\times 0 - 2\times 56.5 + 130.7 + 223.1 = 240.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}\ [19] \tag{19}$$

Further results are included in Table 1. Using the rearranged Gibbs equation

$$\Delta H = \Delta G + T\cdot\Delta S \tag{20}$$

the reaction enthalpy ΔH can be obtained. Again agreement between experimental data obtained with a rather simple setup and literature data is satisfying.

Table 1. Thermodynamic data for the electrolysis of the studied halide acids (Literature data at T = 298 K, experiments at T = 299 K or as indicated)

	U_0/V	ΔG_{EC}/kJ·mol^{-1}	$\partial U_A/\partial T$/mV·K^{-1}	ΔS_{EC}/J·mol^{-1}·K^{-1}	ΔS_{Lit}/J·mol^{-1}·K^{-1}	ΔH_{EC}/kJ·mol^{-1}	ΔH_{Lit}/kJ·mol^{-1}	ΔG_{lit}/kJ·mol^{-1}
H^{+}_{aq}	1.339	258	-1.47	283	240.8	329	334	262
Cl^{-}_{aq}								
HCl_{aq}								
Br^{-}_{aq}	1.006	194	-	-	118	-	243	207
HBr_{aq}								
I^{-}_{aq}	0.468	90	-	-	24	-	110	103
HI_{aq}								

4. Conclusions

Access to reaction entropies and free enthalpies (Gibbs energies) of electrochemical reactions via simple electrochemical measurements is described with simple laboratory setups. The results agree well with literature data and calculated ones. Their discussion put them into practical contexts of energy conversion and storage [5].

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References

[1] Holze R Lehrinhalte im Bachelor-Studiengang Chemie, Physikalische Chemie. *Bunsen-Magazin* 2016; 18:6-7. Presumably similar curricula exist in other countries and languages, too.

[2] Bittrich HJ *Leitfaden der chemischen Thermodynamik*. Weinheim: Verlag Chemie, 1971. The present author is not aware of an equivalent critical assessment of terminology in English.

[3] *Quantities, units and symbols in physical chemistry* (M. Quack, J. Stohner, H.L. Strauss, M. Takami, A.J. Thor, E.R. Cohen, T. Cvitas, J. Fry, B. Holström, K. Kuchitsu, R. Marquard, I. Mills, F. Pavese Eds.) Cambridge: RSC, 2007.

[4] Holze R *Physikalisch-Chemisches Praktikum*. Weinheim: Wiley-VCH, 2022.

[5] Wu Y, Holze R *Electrochemical energy conversion and storage*. Weinheim: WILEY-VCH, 2022.

[6] Mertin GK, Oldenburger M, Richter R, Hofmann MH, Birke, KP Revised theory of entropy and reversible energy flow in galvanic cells. *J Power Sources* 2021; 482: 228813

[7] *Linden's Handbook of Batteries* (T.B. Reddy Ed.) 4th ed. MacGraw-Hill, New York

[8] Saieed AE, Davies KM A Simple Method for Determining the Temperature Coefficient of Voltaic Cell Voltage. *J. Chem. Educ.* 1996; 73:959-962

[9] Hill DL, Moss SJ, Strong RL Heat of reaction in aqueous soution by potentiometry and calorimetry I. *J. Chem. Educ.* 1965; 42:541-544.

[10] Hill DL, Moss SJ, Strong RL Heat of reaction in aqueous soution by potentiometry and calorimetry II. *J. Chem. Educ.* 1965; 42: 544-546.

[11] P. Fleming, Physical Chemistry, https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(Fleming), accessed 06.12.2022.

[12] Buckbee B, Surdzial RE, Metz CR Temperature Dependence of E^0 for the Daniell Cell. *Proc. Indiana Acad. Sci.* 1969; 79: 123-128.

[13] Huggins RA *Advanced Batteries - Materials Science Aspects*. New York: Springer, 2009.

[14] Huggins RA *Energy Storage*. New York: Springer, 2010.

[15] Holze R *Experimental Electrochemistry: A Laboratory Textbook*. 2nd ed., Weinheim: VCH-Wiley, 2019.

[16] Giner J A practical reference electrode. *J. Electrochem. Soc*. 1964; 111: 376-377.

[17] Roscher J, Holze R Messungen mit Wasserstoffelektroden ohne Druckgas - Measurements with a hydrogen electrode without pressured gas. *CHEMKON*. 2022; 29: 408-411.

[18] Roscher J, Holze R Reference electrodes, *Encyclopedia*. 2023; 3: 478-489.

[19] Atkins PW, de Paula J *Physical Chemistry*. 8th ed., New York: W.H. Freeman and Company, 2006, p. 996