Chem. Educator **2000,** *5*, 17–19

Experimental Evaluation of ΔS^o_{rxn}, ΔH^o_{rxn}, and ΔG^o_{rxn} Using Voltaic Cells: A First-Year College Chemistry Laboratory

Donald E. Mencer* and Elaine Anne Elliott

Department of Chemistry, The Pennsylvania State University-Hazleton, Hazleton, PA 18201, dxm53@psu.edu

Abstract: Six voltaic cells have been evaluated for their suitability in the determination of thermodynamic parameters. The cells were prepared with all species present at conditions that approximate standard-state conditions and cell potentials were measured as a function of temperature. From these measurements graphs of voltage versus temperature were prepared. From these graphs it was possible to determine the standard heats of reaction (ΔH^o_{rxn}), standard change in entropy or disorder (ΔS^o_{rxn}), and the Gibbs free energy (ΔG^o_{rxn}) for the spontaneous oxidation–reduction reactions. The standard cell potential (E^o_{cell}) values were also calculated. Two cells with opposite temperature dependence of the cell potential were found to produce good agreement with the literature values of ΔG^o_{rxn}, ΔH^o_{rxn}, ΔS^o_{rxn}, and E^o_{cell}. Criteria for identifying additional cells that may be suitable for potentiometric studies of thermodynamic parameters are also included.

Introduction

Generally, both thermodynamics and equilibrium electrochemistry are covered during the second semester of the college chemistry curriculum. Over the years, a number of papers have appeared in the literature that discuss the use of the temperature dependence of cell potential to determine ΔS^o_{rxn}, ΔH^o_{rxn}, and ΔG^o_{rxn} for certain cells [1–7]. At least one commercially available laboratory manual also contains this type of experiment [8]. Some of these experiments use materials that may not be on hand in all laboratories, are expensive, or pose hazards: a storage battery positive plate [1], Pt-wire electrodes [6, 7], and the use of mercury or mercury containing salts [2, 6], respectively. One of these studies [7], however, points out that "lead" pencil carbon can be substituted for Pt wire electrodes. Another [8] uses iron electrodes that are prone to surface oxidation and $Fe^{2+}(aq)$ solutions that are subject to oxidation in the presence of dissolved oxygen. This can lead to results with relatively large errors. Furthermore, the temperature dependence of some of the cells suggested for study are relatively small. This can also lead to large relative errors [6].

The present paper examines six voltaic cells (see Table 1) that can be assembled from supplies and materials available in most first-year college chemistry or high school chemistry laboratories. Ready availability of the supplies was a primary criterion for selecting these cells; however, some other criteria used in selecting these cells stemmed from a desire to identify at least two cells that provided consistently good student results and also displayed opposite temperature dependence of the cell potential (entropy changes of opposite sign). Cells should possess a reasonably large cell potential (on the order of 0.5 V or larger) in order to minimize the relative error in each measurement of cell potential. The cells should also possess a reasonably large temperature dependence for the cell potential. Over a 60 ºC temperature change, a ΔS^o_{rxn} value of 100 J K^{-1} mol^{-1} results in a change in potential of only about 30 mV for a reaction that involves 2 mol of electrons per mol of reaction. Finally, the source of the metal ions should allow the preparation of 1.0 M solutions. Most first-year college chemistry texts identify the standard state as one that involves concentrations of 1.0 M. Although this is not strictly true, use of 1.0 M solutions produces results that approximate the standard state values.

The findings discussed in this paper have been used to develop an experiment that allows students to investigate two voltaic cells with opposite entropic contributions to cell spontaneity. The experiment is carried out in the second-semester laboratory course in a first-year college chemistry curriculum. It could also be completed in an advanced high school chemistry laboratory course. The experiment is performed after the students have completed a separate laboratory in which the basic principles of electrochemistry are covered. The equipment requirements are modest: a high-impedance meter capable of measuring voltages smaller than about 1.5 volts (a pH meter will work), a thermometer, a hotplate/stirrer (a Bunsen burner with ring stand and a stirring rod can be substituted), filter paper, metal electrodes, metal salt solutions, beaker, test tubes, and cardboard. A student handout (510020dms1.pdf) and list of supplies and materials needed for a section of 24 students (510020dms2.pdf) are available as supporting materials. The experimental results are used to illustrate the relationship between the signs of ΔH^o_{rxn} and ΔS^o_{rxn} and the sign of ΔG^o_{rxn}. The results also highlight the relationship between cell potential and free energy change. One important finding is that reactions that look very similar can have very different changes in entropy (not only different in magnitude, but opposite in sign).

Experimental Procedure

Six cells were constructed using supplies available in most chemistry laboratories (see Table 1). Clearly, some of the cells listed in Table 1 do not meet all of the criteria listed above; however, all six cells were evaluated experimentally and the results compared to the accepted values [9]. The experimental apparatus consists of the following: four small test tubes (one for each half-cell compartment, one for the salt bridge electrolyte, and one for a thermometer in water) supported in a piece of cardboard, a beaker on a hot plate/stirrer for the constant temperature bath, a thermometer supported from a ring stand, and a meter capable of measuring voltages (either a pH

© 2000 Springer-Verlag New York, Inc., S1430-4171(00)01352-7, 10.1007/s00897990352a, 510017dm.pdf

Table 1. Listing of Cells Investigated along with Accepted Values of Thermodynamic Parameters (at 25 ºC) in Order of Decreasing Value of $\Delta S^{\circ a}$

Cell notation	E°_{cell} (volts)	ΔS°_{rxn} (J K^{-1} mol^{-1})	ΔH°_{rxn} (kJ mol^{-1})	ΔG°_{rxn} (kJ mol^{-1})
Pb|Pb^{2+}(aq) (1.0 M)||Cu^{2+}(*aq*) (1.0 M)|Cu	0.466	78.5	–66.5	–89.9
Fe|Fe^{2+}(aq) (1.0 M)||Cu^{2+}(aq) (1.0 M)|Cu	0.777	32.2	–153.9	–144.4
Zn|Zn^{2+}(aq) (1.0 M)||Fe^{2+}(aq) (1.0 M)|Fe	0.323	11.3	–64.8	–68.2
Zn|Zn^{2+}(aq) (1.0 M)||Cu^{2+}(aq) (1.0 M)|Cu	1.100	–20.9	–218.7	–212.6
Zn|Zn^{2+}(aq) (1.0 M)||Pb^{2+}(aq) (1.0 M)|Pb	0.638	–99.4	–152.2	–122.7
Fe|Fe^{2+}(aq) (1.0 M)||Pb^{2+}(aq) (1.0 M)|Pb	0.315	–110.7	–87.4	–54.5

[a] From ref. 9.

meter or multimeter with high-impedance input will work). A figure is included in the student handout that is supplied as one of the supplements to this paper. 1.00 M solutions of the required species were prepared from either the sulfate or nitrate salts and used to fill two of the four test tubes. In the case of the Fe^{2+}(aq) solutions, students prepared fresh solutions from $FeSO_4{\cdot}7H_2O$ just prior to each trial. Salt bridges were constructed from filter paper strips and saturated with 1.0 M KNO_3 solution. These salt bridges connected each half-cell compartment (test tube) to the test tube filled with KNO_3. Salt bridges were replaced with each new trial. A thermometer is carefully centered in a test tube of water to monitor the temperature of the system. The voltage was measured by placing the appropriate metal electrodes attached to a voltmeter in each solution. The beaker was initially filled with an ice/water mixture and is stirred (with a magnetic stir bar) to improve temperature uniformity in the beaker. The temperature was increased slowly (at a rate of about 2 ºC min^{-1}) and voltage measurements were recorded every five degrees from 5 ºC (298 K) to 65 ºC (338 K). Two trials were performed on each cell. Electrodes were sanded and rinsed for each new trial.

Results and Discussion

This experiment introduces students to the following relationships between thermodynamics and equilibrium electrochemistry.

$$\Delta G^\circ_{rxn} = -nFE^\circ_{cell} \tag{1}$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} \tag{2}$$

where ΔG°_{rxn} is the Gibbs free energy of the oxidation–reduction reaction (typically expressed in kJ mol^{-1}), n is the number of moles of electrons per mole of reaction, F is Faraday’s constant (96,485 C mol^{-1}), ΔH°_{rxn} is the standard enthalpy change of the reaction (typically expressed in kJ mol^{-1}), and ΔS°_{rxn} is the standard entropy change of the reaction (typically expressed in J K^{-1} mol^{-1}). These equations can be combined to yield a linear relationship between standard cell potential and temperature (the subscript rxn for reaction will be dropped for convenience for the rest of the paper).

$$E^\circ = \left(\frac{\Delta S^\circ}{nF}\right)T - \frac{\Delta H^\circ}{nF} \tag{3}$$

The slope (m) and the y intercept (b) of this straight line are used to find ΔS° and ΔH° for the reaction using the relationships

$$\Delta S^\circ = nFm \tag{4}$$

$$\Delta H^\circ = -nFb \tag{5}$$

with n = 2 mol of electrons per mol of reaction in all of the cells used in this study. A spreadsheet is used to plot the data (voltage versus absolute temperature), and the slope and intercept are found using the linear regression feature of the software. The experimental values are discussed below and compared with literature values. The literature values of ΔS° and ΔH° can either be provided, or students can calculate them from tabulated values of enthalpies of formation (ΔH_f°) and standard molar entropies (S°) for the reactants and products involved in each oxidation–reduction reaction. The value of ΔG° can be calculated at 298 K using eq 2. Finally, students can find E°_{cell} from ΔG° at 298 K using eq 1 and compare the result to the tabulated value.

The experiments performed on the six cells in Table 1 resulted in only two cells that met all of the criteria discussed above. All the cells that involved the Fe|Fe^{2+}(aq) half-cell (either as the anode or cathode compartment) produced inconsistent data and resulted in a ΔS° values with large errors compared to the literature values (sometimes higher than 200%). The errors in ΔH°, ΔG°, and E°_{cell} were smaller. The cell that produced the least accurate results was Zn|Zn^{2+}(aq) (1.0 M)||Fe^{2+}(aq) (1.0 M)|Fe. This cell has a small literature value for ΔS° leading to only a small change in voltage over the temperature range studied. It also has one of the smaller values of E°_{cell}, which increases the relative error in each voltage measurement, and it included the Fe|Fe^{2+}(aq) half-cell. It is worth noting that the color change expected to accompany the oxidation of Fe^{2+}(aq) to Fe^{3+}(aq) was observed in every trial involving this half-cell. The zinc/copper cell has a large E°_{cell} value and thus provides for smaller relative errors in each voltage measurement. In fact, this cell produces very good results for ΔH°, ΔG°, and E°_{cell} (typical experimental values: ΔH° = –213.5 kJ mol^{-1}, ΔG° = –209.7 kJ mol^{-1}, and E°_{cell} = 1.086 V); however, this cell has a rather small ΔS°, and even a small difference in the slope of the plot of voltage versus absolute temperature translates into large percentage errors (individual student values can range from –10 to –40 J K^{-1} mol^{-1}, producing errors of about 50 to 100%). It is worth noting that the results observed in our laboratory are in reasonable agreement with another study of this same cell. [6].

The other cells: Pb|Pb^{2+}(aq) (1.0 M)||Cu^{2+}(aq) (1.0 M)|Cu and Zn|Zn^{2+}(aq) (1.0 M)||Pb^{2+}(aq) (1.0 M)|Pb produce much better results. Representative data for these cells are plotted in Figure 1. This figure shows graphs of measured cell voltage versus absolute temperature for the two cells under discussion. The points represent averages of actual data for two trials for each cell. The solid line represents the best straight-line fit of the experimental data. Additionally, Table 2 lists the mean experimental results obtained from a single laboratory section. Clearly these cells produce data that are in good agreement with the accepted values in a reproducible manner. Although

Table 2. Accepted Values,[a] Typical Class Average Results, and Percentage Errors for Two Voltaic Cells

Cell notation	E^o_{cell} (V)	ΔS^o_{rxn} (J K^{-1} mol^{-1})	ΔH^o_{rxn} (kJ mol^{-1})	ΔG^o_{rxn} (kJ mol^{-1})
Pb|Pb^{2+}(aq) (1.0 M)||Cu^{2+}(aq) (1.0 M)|Cu				
Accepted values	0.466	78.5	–66.5	–89.9
Mean class values	0.472	69.9	–70.3	–91.1
% Error	~1%	11%	5.7%	1.3%
Zn | Zn^{2+}(aq) (1.0 M) || Pb^{2+}(aq) (1.0 M) | Pb				
Accepted values	0.638	–99.4	–152.2	–122.7
Mean class values	0.618	–108.6	–151.7	–119.3
% Error	3.1%	9.3%	~0.3%	2.8%

[a] From ref 9.

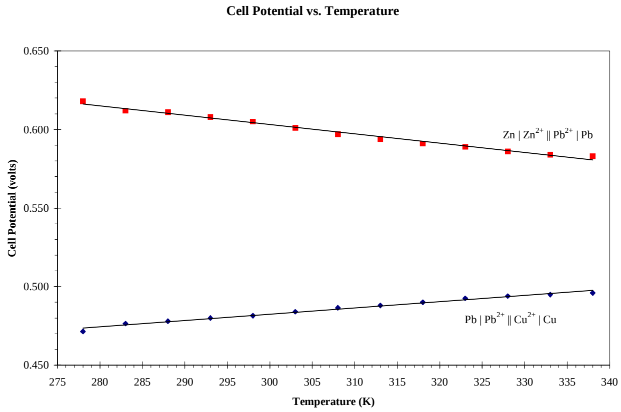

Figure 1. Cell potential (average of two trials) versus temperature (in K) for Pb|Pb^{2+}(1.0 M)||Cu^{2+}(1.0 M)|Cu (the lower curve) and Zn|Zn^{2+}(1.0 M)||Pb^{2+}(1.0 M)|Pb (the upper curve). Also included are the best-fit straight lines for these data sets.

the errors in ΔS^o are higher than the errors in the other parameters, the class average error is on the order of 10% and individual student errors are usually 15% or smaller. The results for ΔH^o, ΔG^o, and E^o_{cell} produce class average errors of about 5% or less and individual student errors on the order of 10% or smaller. The value of E^o_{cell} for the zinc/copper cell has a larger percentage error than that for the lead/copper cell. A previous paper [7] has shown that buffering the half-cell compartment containing a zinc electrode at a pH of 4 will improve the stability of voltage readings taken from the voltaic cell. The zinc half-cell compartments in this experiment were not buffered, yet still yielded quite reasonable data. Finally, the students are required to try to explain reason for the very different temperature dependence of the cell potentials of these two reactions that appear to be quite similar:

$$Pb(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu(s)$$

$$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$$

Students are asked to look beyond the first level of explanation: “Because the entropy changes are opposite in sign.” to think about the physical changes occurring in each oxidation–reduction process.

Conclusion

This paper has identified two voltaic cells that can be used to conveniently measure thermodynamic parameters with good reproducibility and accuracy. The cells are prepared using supplies and materials that are inexpensive and present in most chemistry laboratories. Both cells have relatively large cell potentials that vary substantially over the temperature range studied. Also, the two cells identified have ΔS^o values of opposite sign yielding cell potentials that have the opposite temperature dependence. Finally, the authors would propose that additional cells suitable for these potentiometric studies of thermodynamic parameters can be identified using the following selection criteria: (a) cells should possess a reasonably large cell potential (on the order of 0.5 V or larger), (b) the magnitude of the absolute value of ΔS^o should be on the order of 50 J K^{-1} mol^{-1} or larger, (c) electrodes and metal cations should be stable with respect to undesirable reactions, and (d) the source of the metal ions should allow the preparation of 1.0 M solutions approximating true standard-state conditions while conforming to the introductory chemistry text presentation of standard-state conditions.

Acknowledgment. The authors would like to thank the general chemistry laboratory students who labored to collect much of the data used in this paper.

References and Notes

1. Johnson, R. S.; Crawford, D. E. *J. Chem. Educ.* **1969,** *46,* 52–53.
2. Vincent, C.A. *J. Chem. Educ.* **1970,** *47,* 365–368.
3. Beaulieu, L. P., Cpt. *J. Chem. Educ.* **1978,** *55,* 53–54.
4. McSwiney, H. D. *J. Chem. Educ.* **1982,** *59,* 165.
5. Smith, M. J.; Vincent, C. A. *J. Chem. Educ.* **1989,** *66,* 529–531.
6. Saieed, A. E.; Davies, K. M. *J. Chem. Educ.* **1996,** *73,* 959–962.
7. Probst, D. A.; Henderson, G. *J. Chem. Educ.* **1996,** *73,* 962–964.
8. Monroe, M. B.; Abrams, K. F. *Experimental Chemistry: A Laboratory Course;* Star Publishing Co.: Belmont, CA, 1991; Experiment 32a.
9. Masterton, W. L.; Hurley, C. N. *Chemistry: Principles and Reactions;* Saunders College Publishing: New York, 1997; Appendix 1, pp A.2–A.3.