Temperature Dependence of E° for the Daniell Cell

SISTER BARBARA BUCKBEE[1], RONALD E. SURDZIAL[2] and CLYDE R. METZ[3],
Indiana University

Abstract

EMF measurements for the cell $Zn/ZnSO_4(1M)//CuSO_4(1M)/Cu$ were made at various temperatures over the range of 0-50°C. The equation describing the voltage as a function of temperature is

$$E^\circ(\text{volt}) = (1.1028 \pm 0.0026) - (0.641 \pm 0.425)10^{-3}\,t + (0.72 \pm 0.87)10^{-5}\,t^2$$

where t is the Celsius temperature. This result compares favorably with electrochemical measurements reported in the literature for similar cells, but the derived values of ΔG°, ΔS° and ΔH° differ considerably with accepted thermodynamic values. This disagreement probably results from the presence of a residual voltage and corresponding temperature coefficient inherent in the cell from incomplete elimination of the liquid junction potential.

The conventional Daniell cell, $Zn/Zn^{2+}//Cu^{2+}/Cu$, is often used in general chemistry courses to demonstrate the calculation of overall cell voltage by combining half-cell potentials. Using the data commonly found in textbook tables (3) for the Zn/Zn^{2+} and Cu/Cu^{2+} couples, -0.763 v and 0.337 v, respectively, the predicted value of E° at 25°C is 1.100 v. Upon careful construction of the cell using 0.5M solutions of the nitrates or sulfates of the metals, the observed voltage is somewhat lower than the predicted value (11).

For a cell containing the sulfates of the metals, the overall cell potential E(exp) is given by

$$E(\exp) = E^\circ - \frac{RT}{nF} \ln Q + E(LJ) \qquad [1]$$

where Q, the thermodynamic activity quotient, is defined as

$$Q = a_{Zn^{2+}}\, a_{Cu}/a_{Cu^{2+}}\, a_{Zn} = a^2_{ZnSO_4}\, a_{Cu}/a^2_{CuSO_4}\, a_{Zn} \qquad [2]$$

and E(LJ) is the liquid junction potential arising from the $ZnSO_4$-KCl-$CuSO_4$ interfaces. The activities of the metals in Equation [2] are unity by convention and the product of concentration and mean activity coefficient gives the mean activities for the salts. Using the values given by Robinson and Stokes (8) for the activity coefficients, the emf contribution in Equation [2] for the activity term is negligible for the 1M concentrations.

As written above, the cell contains a salt bridge to minimize the liquid junction potential. MacInnes (5) states that E(LJ) is negligible provided the ionic mobilities of the cation and anion in the bridge are equal. If a saturated KCl bridge is used, this equality is nearly achieved at 25° C. Thus any observed voltage should represent E° for the chemical reaction of interest: $Zn + Cu^{2+} = Zn^{2+} + Cu$.

[1] Current address: St. Joseph High School, Brooklyn, N.Y.
[2] Current address: Highland High School, Highland, Indiana.
[3] Current address: Indiana University-Purdue University at Indianapolis.

Experimental

The half cells consisted of strips of Zn and Cu metal (10x1x0.1 cm) dipping into 1M solutions of $ZnSO_4$ and $CuSO_4$, respectively. To reduce heat transfer from the solutions to the air, the electrodes were thermally insulated using 1-inch thicknesses of plastic foam. The half cells were joined by a salt bridge consisting of a saturated KCl solution suspended on a strip of chromatographic filter paper. To reduce possible interaction between the metals and KCl, the electrodes and a small quantity of solution were isolated from the bulk solution by enclosing them within glass tubing which was drawn to a capillary tip. At each temperature fresh solutions and a newly-constructed salt bridge were used. All chemicals were of reagent grade quality and standard quantitative procedures were used in preparation of the solutions.

The complete Daniell cell was placed in a constant temperature bath and the temperatures of the half cells were monitored by separate thermometers. Once temperature equilibrium was reached, the temperature was recorded to the nearest 0.05° C (corrected for stem immersion) and the open-cell voltage was read from a Honeywell Potentiometric Voltmeter, Model 852, to the nearest 0.1 mv. At the sensitivity used, the input impedance was 10 MΩ, so negligible current was drawn from the cell.

Results

The data appear in Figure 1. Using the method of Bennett and Franklin (1), the regression coefficients for a linear and a quadratic dependence on temperature were determined. An analysis of variance indicated the quadratic term to be significant and the corresponding equation is

$$E^\circ \text{ (volt)} = (1.1028 \pm 0.0026) - (0.641 \pm 0.425)10^{-3}\, t + (0.72 \pm 0.87)10^{-5}\, t^2 \qquad [3]$$

where t is the Celsius temperature and varies from 0° to 50° C. The standard deviation is 1.36 mv and the estimated errors in the regression coefficients are calculated on a 95% probability limit basis.

The maximum random error in the voltage resulting from temperature measurement is negligible, ± 0.02 mv. The error resulting from temperature gradients is estimated as ± 0.5 mv based on observations made with nonisothermal cell conditions.

The important thermodynamic properties ΔG°, ΔS° and ΔH° can be derived from Equation [3]. These are

$$\Delta G^\circ \text{(kcal/mole)} = -nFE^\circ = -50.863 + 0.0296\, t - 0.33\text{x}10^{-3}\, t^2 \qquad [4]$$

$$\Delta S^\circ \text{ (gibbs/mole)} = -d(\Delta G^\circ)/dT = -29.6 + 0.66\, t \qquad [5]$$

$$\Delta H^\circ \text{(kcal/mole)} = \Delta G^\circ + T\Delta S^\circ = -58.948 + 0.1813\, t + 0.33\text{x}10^{-3}\, t^2. \qquad [6]$$

Table 1 contains values of these properties and accepted thermodynamic values (10). Although the quadratic equation for ΔG° allows the estimation of ΔC°_p, the confidence limits in the regression coefficients are too large to provide reliable values.

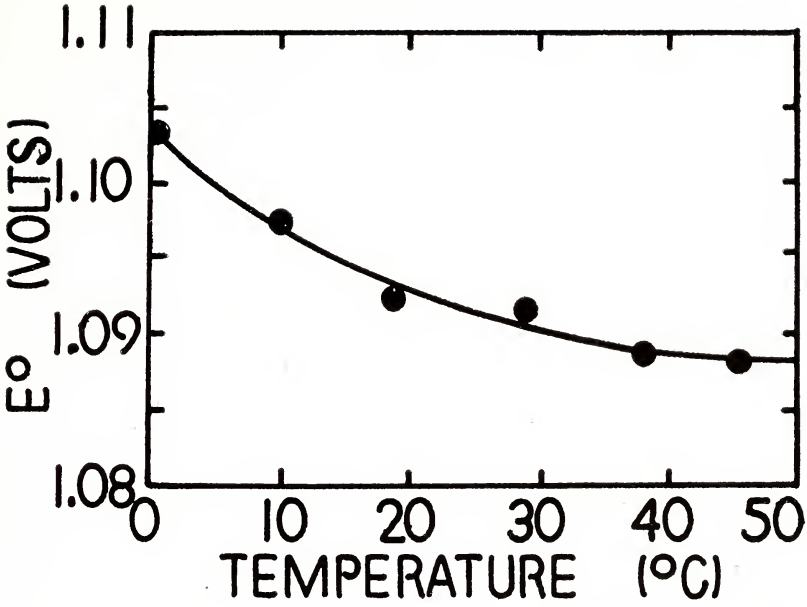

FIGURE 1. *Plot of experimental emfs for the cell $Zn/ZnSO_4(1M)//CuSO_4(1M)/Cu$. The curve is the least squares equation.*

TABLE 1. *Thermodynamic values for the Daniell cell calculated from Equations* [3]-[6].

t (°C)	E° (volt)	ΔG° (kcal/mole)	ΔS° (gibbs/mole)	ΔH° (kcal/mole)
0	1.1028	—50.863	—29.6	—59.948
10	1.0971	—50.600	—23.0	—57.168
20	1.0929	—50.403	—16.4	—55.354
25	1.0913	—50.329(—50.71)*	—13.1(—3.73)*	—54.621(—51.82)*
30	1.0901	—50.272	—9.8	—53.806
40	1.0887	—50.207	—3.2	—52.224

* The values given in parentheses are accepted thermodynamic values (10).

Discussion

The calculated value of E° at 25° C from Equation [3] of 1.0913 ± 0.0026 v is lower than the predicted value of 1.100 v by roughly 9 mv. Reported values for E° at 15° C of 1.09337 by Cohen, Chattaway and Tombrock (2) for a cell consisting of amalgamated electrodes in saturated solutions and 1.0962 v (average) by Jahn (4) give similar differences between experimental and calculated values.

The value of $dE°/dT$ at 25° C calculated from Equation [3] is —0.289 mv/deg. This value compares favorably to —0.429 mv/deg reported by Cohen, Chattaway and Tombrock (2), to —0.2 mv/deg reported by Rosset (9), and to —0.182 mv/deg listed by deBethune and Loud (3) as an experimental determination. These results are considerably more negative than —0.083 mv/deg as predicted by combining half cell values of $dE°/dT$ based on thermodynamic values given by deBethune and Loud (3). The thermodynamic value for $\Delta S°$ in Table 1 corresponds to —0.0809 mv/deg (10). Considering the similarities of the species involved in the cell, the smaller thermodynamic values appear to better express $\Delta S°$ for the reaction than do the electrochemical values.

The source of the discrepancies, 9 mv and 0.2 mv/deg, probably results from the last two terms in the expressions for the overall cell potential, Equation [1], and the corresponding temperature coefficient

$$\frac{dE(exp)}{dT} = \frac{dE°}{dT} - \frac{R}{nF}\left(\ln Q + T\frac{d \ln Q}{dT}\right) + \frac{dE(LJ)}{dT} \qquad [7]$$

which are present because of experimental conditions.

As mentioned earlier, the emf contribution of the second term in Equation [1] is negligible at 25° C and so the 9 mv must be the result of the two liquid junction potentials for the $ZnSO_4$-KCl and KCl-$CuSO_4$ interfaces. MacInnes (5) gives the following general equation

$$E(LJ) = -\frac{RT}{F} \int_{\text{soln I}}^{\text{soln II}} \sum n \frac{t_i}{z_i} d \ln a_i \qquad [8]$$

which must be applied at each interface. Unfortunately Equation [8] cannot be integrated directly, but MacInnes (5) describes two approximate methods for obtaining values of E(LJ).

The first approximation is based on the assumptions that ionic mobilities are independent of concentration and that activities and concentrations are equal. This results in

$$E(LJ) = \frac{RT}{F} \frac{\sum n (\mu_i/z_i)(C_i^{II} - C_i^{I})}{\sum n \mu_i (C_i^{II} - C_i^{I})} \ln \frac{\sum n C_i^{I} \mu_i}{\sum n C^{II} \mu_i} \qquad [9]$$

where μ_i is the ionic mobility. Using data from Milazzo (7) for Equation [9], one obtains

$$E(LJ) = E(LJ)_{ZnSO_4 - KCl} + E(LJ)_{KCl - CuSO_4} = -1.3 + 1.6 = 0.3 \text{ mv}$$

which is considerably less than the 9 mv and has the incorrect sign.

The second technique for obtaining E(LJ) values from Equation [8] is by graphical integration of values of t_+/Cf plotted against Cf between the appropriate concentrations. Following the procedure given by MacInnes (5) and assuming that the activities of the sulfate ion in 1M

$ZnSO_4$ and in 1M $CuSO_4$ are equal and that the changes in the activities of Cl^-, SO_4^{2-} and K_2SO_4 passing from the salt bridge to 1M $ZnSO_4$ and 1M $CuSO_4$ to be identical, the total liquid junction potential is given by

$$E(LJ) = \frac{-RT}{F}\left[\int_{1M\ ZnSO_4}^{sat\ KCl} \frac{t_{Zn^{2+}}}{C_{ZnSO_4}\, f_{ZnSO_4}}\, d(C_{ZnSO_4}\, f_{ZnSO_4}) - \int_{1M\ CuSO_4}^{sat\ KCl} \frac{t_{Cu^{2+}}}{C_{CuSO_4}\, f_{CuSO_4}}\, d(C_{CuSO_4}\, f_{CuSO_4})\right] \quad [10]$$

Using available data (5)-(8) and making the approximation that the activity coefficients for the components of mixtures to be equal to the activity coefficients for the pure components at the concentration of the component, the graphical integration of Equation [10] gives

$$E(LJ) = -38.7 + 38.3 = -0.4 \text{ mv.}$$

Although the magnitude is low, the sign of E(LJ) is correct and if proper data were available, Equation [10] should predict values more in line with the 9 mv. It is felt, therefore, that the 9 mv difference can be accounted for by the value of E(LJ).

From data reflecting the temperature dependence of the limiting ionic conductances (7), Equation [9] can be used to estimate dE(LJ)/dT. For a 2% increase in the ionic mobilities for an increase in temperature of one degree, the value of E(LJ) increases by 0.1 mv. Thus a significant portion of the 0.20 mv/deg discrepancy is accounted for by the dE(LJ)/dT term of Equation [7]. No attempt was made to estimate dE(LJ)/dT from Equation [10] because of the uncertainty in the assumptions regarding the choice of data.

In conclusion, the values of $E°$, $\Delta G°$, $\Delta S°$ and $\Delta H°$ given in Table 1 are valid for the experimental Daniell cell which includes, by necessity, a liquid junction.

Acknowledgment

Two of the authors (SBB and RES) were participants in the Institute for High School Chemistry Teachers sponsored by the National Science Foundation at Indiana University.

Literature Cited

1. BENNETT, C. A., and N. L. FRANKLIN. 1954. Statistical Analysis in Chemistry and the Chemical Industry. John Wiley and Sons, New York. 724 p.

2. COHEN, E., T. D. CHATTAWAY, and W. TOMBROCK. 1907. Zur thermodynamik der normalelemente. Z. Physik. Chem. **60**:706-727.

3. DEBETHUNE, A. J., and N. A. SWENDEMAN LOUD. 1964. Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C. Clifford A. Hampel, Skokie, Ill. 19 p.

4. JAHN, H. 1886. Über die Beziehung von chemischer Energie und Stromenergie galvanischer Elemente. Wied. Ann. **28**:21-28.

5. MACINNES, D. A. 1961. The Principles of Electrochemistry. 2nd. ed. Dover Publications, New York. 478 p.

6. MARON, S. H., and C. R. PRUTTON. 1958. Principles of Physical Chemistry. The Macmillan Company, New York. 789 p.

7. MILAZZO, G. 1963. Electrochemistry. Elsevier Publishing Company, New York. 708 p.

8. ROBINSON, R. A., and R. H. STOKES. 1949. Tables of Osmotic and Activity Coefficients of Electrolytes in Aqueous Solution at 25°C. Trans. Faraday Soc. **45**:612-624.

9. ROSSET, G. 1904. Daniell Cell as Standard Cell for Technical Purposes. Electrochem. Ind. **2**:246.

10. ROSSINI, F. D., D. D. WAGMAN, W. H. EVANS, S. LEVINE, and D. JAFFE. 1952. Selected Values of Chemical Thermodynamic Properties. Nat. Bur. Stand. Circ. 500. 1268 p.

11. YOUNG, J. A., and J. G. MALIK. 1969. Chemical Queries. J. Chem. Educ. **46**:227-228.