filtrates & residues

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A Simple Method for Determining the Temperature Coefficient of Voltaic Cell Voltage

An Application in Exploring the Gibbs–Helmholtz Equation

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Although use of the Nernst equation to illustrate the dependence of cell potential on half-cell concentrations is routinely covered in first-year college chemistry and high school AP chemistry classes, the temperature dependence of cell voltages is rarely encountered outside of the undergraduate physical chemistry laboratory. Even there, its coverage is somewhat limited because of the cost and sophistication of the instrumentation required. This article describes a relatively simple method for preparing voltaic cells, and through their temperature coefficient, $\partial E°/\partial T$, it explores relationships between $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the cell reactions involved. Calculated values of the three parameters are compared to values estimated using standard thermodynamic data available in the literature.

The experiments effectively demonstrate that the electromotive force produced by exothermic redox reactions varies inversely with the temperature and uses the cell temperature coefficient, $\partial E/\partial T$, to calculate the enthalpy and entropy changes for cell reactions through the familiar thermodynamic equations

$$\Delta G° = -nFE° \qquad (1)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (2)$$

Since from eqs 1 and 2

$$-\,\partial\Delta G°/\partial T = nF(\partial E°/\partial T) = \Delta S°$$

substitution for $\Delta G°$ and $\Delta S°$ in the Gibbs–Helmholtz equation

$$\Delta H° = \Delta G° + T\Delta S°$$

gives

$$\Delta H° = -nF[E° - T(\partial E°/\partial T)] \qquad (3)$$

Also, by substituting $E° = (\partial E°/\partial T)T + b$ into eq 3, one gets

$$\Delta H° = -nFb \qquad (4)$$

where b is the y-intercept of the voltage vs. temperature plot. The measurement of emf values at various temperatures therefore provides a very convenient way of obtaining thermodynamic values for chemical reactions. The relationship between enthalpy and entropy changes for the cell reactions may also be arrived at graphically through plots of the free energy ($\Delta G° = -nFE°$) vs. temperature and their values obtained directly from the intercept and the negative of the slope of the plot.

The equipment and materials used in the experiments we describe are less sophisticated than those used in similar experiments reported by Hill, Moss, and Strong (*1–3*) for the calculation of heats of reaction, and the results obtained are consequently slightly less accurate. The experiments described, however, do enable the enthalpy, entropy, and free energy changes accompanying both homogeneous and heterogeneous redox reactions to be calculated with an acceptable degree of accuracy for advanced high-school or first-year college chemistry students. The simplicity of the methods described also make the experiments more readily available for study in routine laboratory instruction.

Part I: Heterogeneous Equilibrium

A simple Cu/Cu^{2+}– Zn/Zn^{2+} cell was employed in the experiment. We are not aware of anyone previously determining this cell's heat of reaction using the procedure described in this article. The cell notation is:

$$Zn(s)\,|\,ZnSO_4\,(1.0\ M)\,\|\,CuSO_4(\,1.0\ M)\,|\,Cu(s)$$

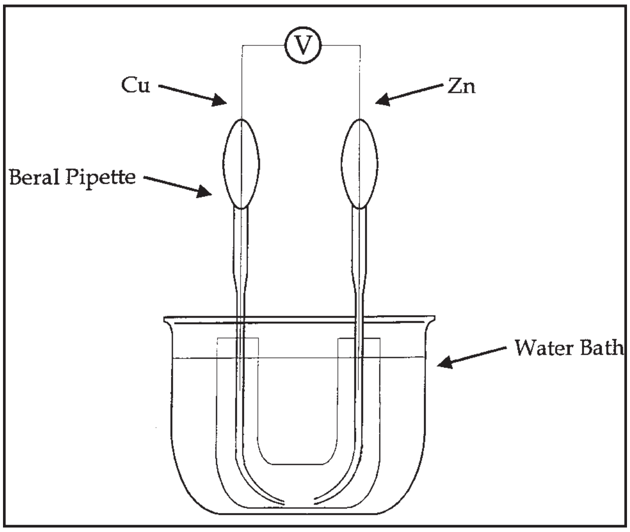

Figure 1. Diagram of Cell Arrangement.

A Kelvin 200 battery operated voltmeter accurate to one millivolt was used for potential measurements. The cell design for the Cu/Cu^{2+}–Zn/Zn^{2+} cell is illustrated in Figure 1. An open liquid junction was employed, eliminating the problems associated with porous cups and agar salt bridges. The use of Beral pipets to construct electrochemical cells was adapted from the method reported by H. P. Williams (*4*).

The Zn electrode was prepared by cutting a 12 cm × 3 mm strip of zinc from larger zinc strips obtained from Cenco (catalog number 79306). The thickness was estimated to be about 1/50 inch. It is not desirable to use a thickness of 1/100 inch, since the strip becomes brittle and breaks easily when amalgamated with mercury. The lower 5 cm of the Zn strip was immersed in 30% sulfuric acid just long enough to clean the surface. After rinsing with distilled water, it was amalgamated by placing it in a saturated solution of mercurous nitrate for ten minutes. The zinc was then rinsed with distilled water and with 1 M zinc sulfate (*3*). The amalgamated zinc prevents the zinc from deteriorating rapidly. The Zn/Zn^{2+} couple was constructed by making an incision at the top of the bulb of a Beral-type pipet and inserting the amalgamated zinc through the slit made in the pipet. The pipet tip was stretched and cut to give a small opening (*5*). Caulk was used instead of glue to seal the zinc strip, since the caulk not only seals the electrode rapidly but can also be easily removed. After the caulk had dried, the bulb of the pipet was squeezed to draw up enough 1.0 M zinc sulfate to cover the amalgamated part of the zinc strip.

The Cu/Cu^{2+} half-cell was prepared by cutting a strip of copper with the same dimensions as the zinc. After sealing the copper in the pipet, the bulb of the pipet was squeezed to draw up enough 1.0 M copper(II) sulfate to cover the lower 5 cm of the copper strip.

Immediately after preparation, the Zn/Zn^{2+} and Cu/Cu^{2+} couples were placed opposite each other in a 10-cm high U-tube, which was 3/4 filled with 1.0 M sodium nitrate. When the lower 10-cm portions of the two pipets were inserted in the U-tube, their tips were about 2 cm apart and slightly bent towards each other.

Temperature Dependence of Cell Voltage and Calculation of Thermodynamic Values

The U-tube containing the half-cells was placed in a thermostated water bath, initially at 35 °C, and the potential measured at intervals of 5 °C down to 10 °C. To check on the reproducibility of the data, the bath temperature was then raised to 35 °C and finally lowered again to 15 °C with further periodic measurement of the cell voltage. The data obtained, which show an excellent linear dependence of cell potential on temperature, are summarized in Table 1. Heats of reaction may be calculated using eq 3, where the temperature coefficient of the cell emf, $\partial E°/\partial T$, is the slope of the voltage–temperature plot and the standard cell potential, $E°_{298}$, is the value of the voltage on the y-axis that corresponds to 298 K on the x-axis on the best straight line obtained from linear regression of the $E°$ vs. temperature (K) data. Alternatively, $\Delta H°$ may be obtained more directly from eq 4 using the y-intercept of the voltage–temperature plot.

Table 1. Cell Voltage – Temperature Dependence for Zn/Zn^{2+} – Cu/Cu^{2+} Cell

Temperature (K)	Measured Cell Potential, *E* (Volts)		
	Descending Temperature	Ascending Temperature	Descending Temperature
308	1.101	1.098	1.098
303	1.102	—	—
298	1.103	1.099	1.099
293	1.1035	—	—
288	1.104	1.103	1.101
283	1.105	—	—
Linear Regression for Voltage – Temperature Data			
Slope (V/K)	-0.000151	-0.000250	-0.000150
$E°_{298}$ (V)	1.1027	1.100	1.099
Correlation coefficient (*R*)	-.991	-.945	-.982
y-Intercept (V)	1.1478	1.1745	1.1440

Table 2. Summary of Electrochemical and Thermodynamic Data obtained for Zn/Zn^{2+} – Cu^{2+}/Cu Cell

	Mean Experimental Value	Literature Value
$E°_{298}$	1.100 V	1.100 V
$\partial E/\partial T$	-1.838×10^{-4} V/K	—
$\Delta H°$ (potentiometric)	-223 kJ	-219 kJ
$\Delta H°$ (calorimetric)	-218 kJ	—
$\Delta S°$	-36.9 J/K	-21.1 J/K
$\Delta G°$	-212 kJ	-213 kJ

For the initial data set of descending temperatures

$$\Delta H° = -nF[E°_{298} - T(\partial E°/\partial T)]$$

$$\Delta H° = -(2 \text{ mol of e}^-)(96{,}500 \text{ C/mol of e}^-)[1.1027 \text{ V} - 298 \text{ K}(-0.000151 \text{ V/K})] = -2.22 \times 10^5 \text{ J}$$

or

$$\Delta H° = -nFb = -(2)(96500)(1.1478) = -2.22 \times 10^5 \text{ J}$$

Corresponding values of $\Delta H°$ calculated from $\partial E°/\partial T$ and $E°_{298}$, obtained from subsequent ascending and descending temperature data, are -227 and -221 kJ, respectively. The mean calculated value is -223 kJ. A value of $\Delta H°$ = -219 kJ is estimated for the reaction

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

using standard state $\Delta H_f°$ values (*6*) for $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$. In view of the simplicity of the method involved, we feel the error of less than 2% in our determination compared to the literature value is very good. No special attempt was made to allow the cell to equilibrate at any temperature for more than a few minutes, and no consideration is given to changes in liquid junction potential with temperature. The integrity of the electrodes was maintained over at least three cycles of temperature variation, though experiments starting at the low temperatures appeared somewhat less reproducible and required a short incubation period. There was also evidence of some electrode deterioration taking place at the lowest temperatures. Notwithstanding these limitations, the reproducibility of the data obtained is good, and the simplicity of the experimental method offers definite advantages for routine instruction.

The data in Table 2 were also used to calculate a reaction free energy of -212 kJ ($\Delta G° = -nE°F$) and a reaction

Table 3. Cell Voltage –Temperature Dependence for Fe^{2+}/Fe^{3+} – Ce^{4+}/Ce^{3+} Cell Using Pt Wire

Temperature (K)	Measured Cell Potential, *E* (Volts)	
	Descending Temperature	Ascending Temperature
308	0.716	0.7265
303	0.722	0.7295
298	0.728	0.7325
293	0.733	0.7355
288	0.7385	0.7385
Linear Regression for Voltage vs. Temperature Data		
Slope (V/K)	-0.00112	-0.00060
$E°_{298}$ (V)	0.7275	0.7325
Correlation coefficient (*R*)	-0.999	-1.000
y-Intercept (V)	1.061	0.911

Table 4. Summary of Data for Fe^{2+}/Fe^{3+} – Ce^{4+}/Ce^{3+} Cell Using Platinum

	Mean Experimental Value	Literature Value for Standard States
$E°_{298}$	0.730 V	—
$\partial E/\partial T$	-0.00087 V/K	—
$\Delta H°$	-95.2 kJ	-118 kJ
$\Delta G°$	-70.4 kJ	-93.7 kJ
$\Delta S°$	-83.2 J/K	-82.8 J/K

entropy of 0.0369 kJ/K [$\Delta S° = (\Delta H° - \Delta G°)/T$, or $\Delta S = nFm$, where m = slope of the voltage vs. temperature plot].

Graphical treatment of the combined 12 data points in Table 1 as a plot of ΔG (= $-nFE°$) vs. temperature, giving equal weighting to all 12 points, affords values of -224.1 ± 0.3 kJ for $\Delta H°$ and -38.7 ± 11.4 J/K for $\Delta S°$, from intercept and slope, respectively.

Calorimetric Determination of ΔH°

Since it is generally satisfying and instructive for students to see that the value of $\Delta H°$ obtained potentiometrically is in agreement with the value obtained calorimetrically, a simple calorimetric determination of $\Delta H°$ was also carried out. Excess zinc dust was added to 100 mL of 0.10 M copper(II) sulfate in a Styrofoam cup. The resulting increase in temperature of the solution was 5.20 °C. Assuming the density and the specific heat of the solution to be 1.00 g/mL and 4.184 J/g°C, respectively, the heat liberated was 2.18 kJ and the corresponding heat of reaction was -218 kJ/mol, in good agreement with the potentiometric value. The experimentally determined values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ are compared in Table 3 to values estimated from literature data.

Part II. Homogeneous Equilibrium

The cerium(IV)–iron(II) reaction

$$Fe^{2+}(aq) + Ce^{4+}(aq) = Fe^{3+}(aq) + Ce^{3+}(aq)$$

was chosen for the homogeneous cell reaction. The cell notation for the experimental conditions employed is:

$$\text{Pt} \mid Fe^{2+}(0.10\ M),Fe^{3+}(0.025\ M),H_2SO_4(1.0\ M) \parallel$$
$$H_2SO_4(1.0\ M),Ce^{4+}(0.10\ M),Ce^{3+}(0.025\ M) \mid \text{Pt}$$

The salts $FeSO_4$, $Fe_2(SO_4)_3$, $Ce(SO_4)_2$, and $CeCl_3$ were used as the source of the ions in the Fe^{2+}/Fe^{3+}–Ce^{4+}/Ce^{3+} cell. $CeCl_3$ was used because $Ce_2(SO_4)_3$ was unavailable.

The electrochemical cell used in Part II was constructed as in Part I, except that platinum wire was used in place of the copper and zinc strips. A straight pin was used to make a tiny hole at the top of the bulb of the Beral pipet. An appropriate length of platinum wire (about 26 gauge B&S) was inserted and sealed with caulk. The bulb of the pipet was squeezed to draw up enough of the solution containing 0.10 M iron(II) sulfate and 0.025 M iron(III) sulfate to cover the lower 5 cm of the platinum wire. The bulb of the other pipet with platinum wire inserted was similarly squeezed to draw up enough of the 0.10 M Ce(IV)/0.025 M Ce(III) solution to cover the lower 5 cm of the platinum. The two half-cells were placed in a U-tube 3/4 filled with 1.0 M H_2SO_4. The U-tube was placed in a water bath at 35 °C, and the voltage was measured. Similar measurements were made at 5° temperature intervals down to 15 °C. The bath temperature was then slowly raised to 35 °C with voltage measurements again being taken at 5° intervals. The data obtained are shown in Table 3. Good linear dependence of measured cell emf on temperature was found in both cases, although a slower voltage response was apparent when starting at the lower temperatures. The data in Table 3 lead to mean values for the thermodynamic parameters $\Delta H = -95.2$ kJ, $\Delta G = -70.4$ kJ, and $\Delta S = -83.2$ J/K, as summarized in Table 4.

The plot of $\Delta G(= -nFE)$ vs. T(K), using the combined data in Table 3, yields $\Delta H = -95.2 \pm 0.3$ kJ and $\Delta S = -83.0 \pm 15.0$ J/K. Corresponding values of $\Delta H°$ and $\Delta G°$ estimated from standard-state data (*6*) are -118 kJ and -93.7 kJ, respectively. The data are compared in Table 4. Although differences between our values and those calculated for standard states are expected, these differences do not appear to be solely attributable to the nonstandard state concentrations in our cell. Significant differences also exist between our measured cell potential at 25 °C, 0.728 V, and a calculated value of 0.831 V obtained through the Nernst equation. Using cyclic voltammetry we determined $E_{1/2}$ for the Ce^{4+}/Ce^{3+} in 1.0 M H_2SO_4 at a Pt working electrode to be 1.45 V, in good agreement with the value of 1.44 V cited in the literature for both 1.0 M H_2SO_4 (*7*) and 0.5 M H_2SO_4 (*8*). Lange's handbook (*8*) gives a value of 0.67 V for Fe^{3+}/Fe^{2+} in 0.5 M H_2SO_4 and Hill et al. cite 0.68 V for Fe^{3+}/Fe^{2+} in 1.0 M H_2SO_4 (*2*). Combining the value of 0.68 V for the Fe^{3+}/Fe^{2+} couple with 1.44 V for Ce^{4+}/Ce^{3+} leads to $E°_{cell}$ = 0.76 V. Although application of the Nernst equation to our experimental conditions yields a value of 0.831 V, the assumption that activity coefficients will be equal to one for the highly charged cations, at the high ionic strengths operating in our cell, appears inappropriate and makes accurate concentration dependence of cell voltage difficult to assess. The complex ionic interactions existing in the mixed Cl^- and SO_4^{2-} medium of our cell, as well as possible temperature-dependent changes both in the nature of complex species at equilibrium in solution and in junction potentials, may also be partly responsible for the discrepancy between the literature and measured values of the cell potentials and thermodynamic parameters. Moss and Hall (*2*), using more sophisticated instrumentation and double the concentrations employed by us, obtained an experimental value of 0.843 V, in closer agreement with the calculated value.

Finally, because of the expense of routinely using Pt wire in a classroom situation, we repeated our experiment using Chromel A wire (B&S 24 gauge). Although reproducible data were obtained with a correlation coefficient of close to unity, illustrating the inverse temperature dependence of the cell voltage, it yielded a different value for the cell temperature coefficient, $-(0.00147 \pm 0.00007)$ V/K, and the measured standard cell emf was some 0.14 V lower than obtained with Pt. Some Cr^{2+} was probably generated in the 1M H_2SO_4 solution and interfered with the cell reaction. Although the average value of -99.2 kJ, calculated for $\Delta H°$ was in surprisingly good agreement with that obtained using the platinum wire, such agreement appears fortuitous. Use of Chromel A wire does, however, afford an inexpensive way of demonstrating the inverse temperature dependence of the $Ce^{4+}/Ce^{3+}–Fe^{2+}/Fe^{3+}$ cell emf, in accord with Le Chatelier's principle.

In summary, the experiments described afford a simple and inexpensive method of demonstrating that the electromotive force of exothermic redox reactions varies inversely with temperature. The finding can be rationalized qualitatively through Le Chatelier's principle and discussed in terms of increasing temperature lowering the driving force of the redox change. The variation in measured cell potential with temperature may be used to calculate $\Delta H°$, $\Delta G°$, and $\Delta S°$ for the cell reactions and the data compared with values calculated using available thermodynamic data. The experiments utilize inexpensive and readily available materials. If desired, they can be formulated as a miniproject, with students involved in all stages of the experiment from cell construction to data collection and thermodynamic data calculation. Since the goals of this paper can be satisfactorily achieved using either the $Zn/Zn^{2+}–Cu^{2+}/Cu$ or the $Ce^{4+}/Ce^{3+}–Fe^{2+}/Fe^{3+}$ cell, in light of the chemical safety problems associated with mercury salts, we feel that the latter cell is probably more appropriate for use in the high school environment (*11*).

Hazards

Mercury and all its compounds are toxic. Prolonged exposure to even low concentrations should be avoided, since chronic and toxic effects can result from inhalation, ingestion, or skin contact. The dust from salts of mercury is also poisonous and can irritate the eye and skin (*9*). Sulfuric acid is severely corrosive to eyes, skin, and other tissue.

Disposal

Mercury and cerium compounds should be converted to their insoluble sulfide salts and disposed of in a landfill designed for toxic chemicals. The Zn/Hg electrodes should also be disposed of in suitable solid-waste disposal sites. Detailed disposal procedures are provided in standard reference sources (*9, 10*). Prior to disposal, the amalgamated zinc electrodes may be stored for reuse by securely sealing them in a plastic bottle.

Note

1. Retired.

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11. The experiments described in this article were developed and done at George Mason University as part of the Chemistry 529 course requirements.