# A Student-Constructed Galvanic Cell for the Measurement of Cell Potentials at Different Temperatures

Anna Jakubowska*

Department of Physical Chemistry, Adam Mickiewicz University, Umultowska 89 b, 61-614 Poznan, Poland

S Supporting Information

ABSTRACT: A student-made galvanic cell is proposed for temperature measurements of cell potential. This cell can be easily constructed by students, the materials needed are readily available and nontoxic, and the solution applied is in an attractive color. For this cell, the potential values are excellently reproducible at each temperature, and the potential−temperature coefficient is well measurable. This experiment illustrates the determination of thermodynamic properties of a cell reaction, such as changes in entropy, enthalpy, and Gibbs energy through measurements of cell potential as a function of temperature. Students are led to understand the significance of those quantities. They also get to know the role of a supporting electrolyte in the electrochemical system.
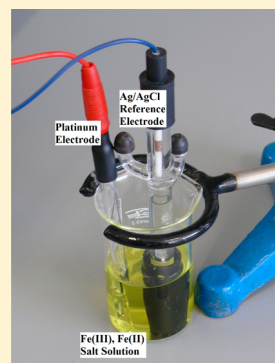
Although electrochemistry is an important topic in the curriculum of physical chemistry, students frequently have problems with electrochemical concepts. For example, the student misconceptions involve the movement of electrons and ions in the galvanic cell, and the resulting charge sign given to the anode and cathode.[1] Students often think that electrons move through the solution. Moreover, students do not understand why the supporting electrolyte is introduced into the solution used in the galvanic cell. They also often have problems with understanding what thermodynamic quantities mean or why they are significant to chemists. This experiment should help students to understand thermodynamic properties of the galvanic cells.

In the galvanic cells presented recently in this *Journal*, toxic materials such as cadmium,[2] or lead[2,3] and lead oxide[3] were used, salt bridges had to be prepared,[4,5] during the cell operation hydrogen gas bubbles[3] or deposits[6] were formed on the electrode surfaces, and/or the electrode mass changed,[6] and recycling of electrodes used during one experiment was necessary for their use by other students.[3] In many galvanic cells described recently in the *Journal*, zinc and copper electrodes were used.[1,2,4,6,7] Because of aqueous corrosion of zinc electrodes and because of surface oxidation of copper electrodes, the potentials of these electrodes are unstable and irreproducible.

A stable cell potential is especially important for thermodynamical studies of galvanic cells. In this *Journal*, the galvanic cell, represented by

$$(-)Zn(s)|Zn^{2+}(1.0\ M)||(Fe(CN)_6{}^{3-}(0.1\ M),\ Fe(CN)_6{}^{4-}(0.1\ M)|Pt(+)$$
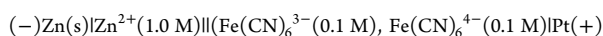
(where || means a salt bridge), has been proposed to be used by students for temperature measurements of cell potential.[8] However, the potential of such a cell is unstable and irreproducible because in this cell a zinc electrode is used.[9] Therefore, we decided to make such a galvanic cell in which a suitable electrode of a constant potential would be used instead of a zinc electrode. So we constructed a galvanic cell

$$(-)Ag(s)|AgCl(s)|KCl(sat\ at\ 25\ °C)||\ Fe(CN)_6{}^{3-}(0.01\ M),\ Fe(CN)_6{}^{4-}$$
$$(0.01\ M)|Pt(+)$$
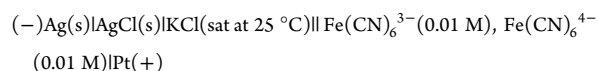
in which the following electrochemical reaction takes place:

$$Ag(s) + Cl^-(sat\ at\ 25\ °C) + Fe(CN)_6{}^{3-}(0.01\ M)$$
$$\rightleftharpoons Fe(CN)_6{}^{4-}(0.01\ M) + AgCl(s)$$
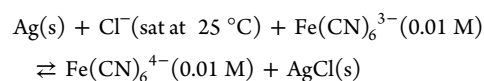
In comparison with the galvanic cells presented recently in this *Journal* (see the second paragraph of this section), in our cell the materials used are nontoxic and no preparation of glassware or salt bridges is necessary. Moreover, the electrodes of this cell can be used many times until their mechanical damage, and during the cell operation, no changes in mass and surfaces of the electrodes are observed, as well as no deposits are formed on the electrode surfaces. Therefore, the values of the galvanic cell potential are excellently reproducible at each temperature.
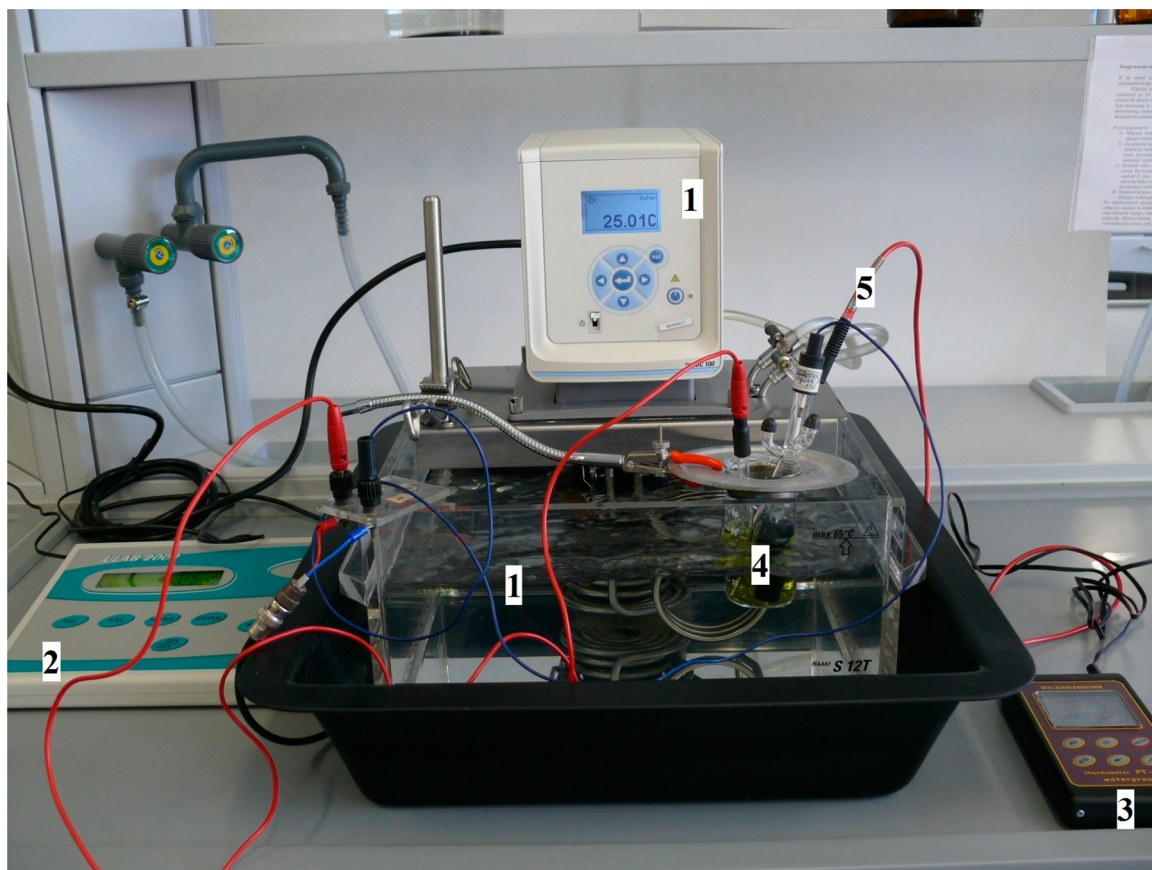
Figure 1. Measuring system used in the experiment for temperature measurements of galvanic cell potentials; 1, thermostat; 2, millivoltmeter; 3, digital thermometer; 4, student-made galvanic cell; 5, thermocouple probe.

In this paper, we propose a galvanic cell simple to construct, made of readily available and nontoxic materials, and the solution applied shows a spectacular color. In this laboratory experiment, students learn to make a simple galvanic cell, study and explain its thermodynamic properties, determine potential–temperature coefficients for the half-cells and the galvanic cell, and use the Nernst equation for prediction of cell potentials at different temperatures

$$E(T) = E_{\text{Pt/Fe(III),Fe(II)}}{}^{\circ}(T) - E_{\text{Cl}^-/\text{AgCl/Ag}}{}^{\circ}(T)$$

$$+ \frac{2.303RT}{nF} \log\left(\frac{a_{\text{Fe(III)}}}{a_{\text{Fe(II)}}} a_{\text{Cl}^-}\right) \tag{1}$$

where $E(T)$ is the galvanic cell potential at a given temperature T, $E^{\circ}(T)$ is the standard potential of a given half-cell at a temperature T, and a_i is the ion activity. For a galvanic cell similar to the one proposed, the potential–temperature coefficient has been determined,[10−12] but no student-measured potential–temperature dependence has been presented.

CONSTRUCTION OF THE GALVANIC CELL

The aqueous solutions of 0.01 M $K_3[\text{Fe(CN)}_6]$ in 0.5 M KCl and 0.01 M $K_4[\text{Fe(CN)}_6]$ in 0.5 M KCl are prepared in volumetric flasks of 25 mL in capacity. In the solutions of the iron salts, potassium chloride is used as a supporting electrolyte; that is, KCl is introduced into the solution studied in a high concentration in order to keep a constant ionic strength. A beaker of 100 mL in volume is filled with 25 mL of Fe(III) salt solution and with 25 mL of Fe(II) salt solution.

After mixing the two solutions in the beaker, a platinum electrode and a silver–silver chloride reference electrode (RE) are inserted in the Fe(III), Fe(II) salt solution. Nice yellow color of this solution attracts the attention of students.

Optionally, one can use a student-made Ag/AgCl reference electrode whose various preparation versions have been reported.[13−15] However, our students use the commercial Ag/AgCl RE with a double salt bridge to minimize precipitation. This Ag/AgCl/Cl⁻ half-cell eliminates the problems associated with preparation of glassware or salt bridges. In our laboratory, students also use the commercial platinum electrode.

As shown in this paragraph, we propose the galvanic cell, very simple to construct by students, made of nontoxic and readily available materials.

EXPERIMENTAL PROCEDURE

Students work in groups of two. The entire experiment together with calculations takes about 4 h.

The measuring system used in this experiment, presented in Figure 1, consists of a galvanic cell described above, a thermostat, a digital millivoltmeter, and a digital thermometer. A millivoltmeter with high input impedance should be used to achieve near-reversible conditions of the cell reactions. Such a millivoltmeter, of a sensitivity of 0.1 mV, is used to measure the cell potential for 5 different temperatures at 5 °C intervals in the range from 20 to 40 °C. The temperature of the galvanic cell is controlled by the digital thermometer with the thermocouple probe immersed in the Fe(III), Fe(II) salt

solution. For each temperature, the solution of iron salts should be thermostated together with the electrodes and thermocouple probe, for a minimum of 10 min. Between the E measurements, the electrodes must be disconnected from the digital millivoltmeter so that no current flows in the cell.

■ HAZARDS

Potassium hexacyanoferrate(II) (or -potassium ferrocyanide) is nontoxic because it does not decompose to cyanide in human organism. Potassium ferrocyanide may cause long-term adverse effects in the aquatic environment. Therefore, it is not to be released to the environment. Potassium hexacyanoferrate(III) (or -potassium ferricyanide) has very low toxicity. Its main hazard being that it is a mild irritant to the eyes and skin. Potassium ferricyanide is harmful if swallowed, inhaled, or in contact with skin and eyes. Solutions of these compounds should be collected in separate waste containers and disposed of according to EPA standards. Students are required to wear goggles, a lab coat, and protective gloves during the experiment.

■ RESULTS AND DISCUSSION

The laboratory experiment is divided into three stages. In the first stage, instructors initiate prelab discussion to introduce students to subject of galvanic cells. Students should discuss about half-cells (what is a half-cell), their types, and galvanic cells (what is a galvanic cell, which quantity characterizes them, in which way this quantity can be determined experimentally and theoretically). Electrochemical concepts employed in this experiment present a lot of teaching material, and during prelab discussion, the instructor himself should decide which issue should be particularly emphasized to explain students' problems. For example, students may be asked to propose a schematic diagram and to construct a galvanic cell according to this diagram, and a system for temperature measurements of cell potential. Moreover, with instructor assistance, students can discuss the function of the cell components, the transfer of electrons and the ions in the galvanic cell as the cell reaction proceeds, which electrode is the cathode and which one is the anode, which electrode is positive and which one is negative. During this discussion, on the schematic diagram of the galvanic cell, students should mark the movement of electrons and ions, and the charge sign of the electrodes. Students should also write the half-cell reactions taking place in the cell studied, discuss the ion activity (how to evaluate it), and estimate the value of ionic strength of the solution studied.

In the second stage, students construct the galvanic cell and measure its potential as a function of temperature in the range from 20 to 40 °C. Next, they plot the dependence of the galvanic cell potential, E, versus the absolute temperature, T, as shown in Figure 2. The equation relating E to T, determined with the use of linear regression, is

$$E = -1.551 \cdot T + 760.6 \qquad (2)$$

with the temperature coefficient of the cell potential, $(\delta E/\delta T)_p$, equal to -1.55 mV/K; for the line presented in Figure 2, the squared correlation coefficient, r^2, is equal to 0.999. It is worth emphasizing that for each temperature, the potential values measured by a given group of students were excellently reproducible to within ± 0.1 mV. Moreover, the difference between the values of E determined for a given temperature by 10 groups of students was very small, within $1-3$ mV, and the $(\delta E/\delta T)_p$ values estimated by various groups of students were reproducible to within ± 0.1 mV/K.
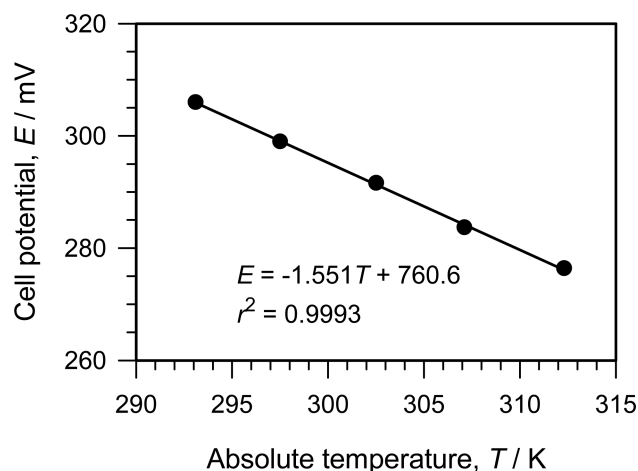

Figure 2. Temperature dependence of the student-made galvanic cell potential.

In the third stage of the laboratory experiment, students prepare a lab report including the experimental results and all calculations. Using the Nernst equation (eq 1), students estimate the theoretical values of E for each temperature. The values of $E_{Pt/Fe(III),Fe(II)}^\circ$ and $E_{Cl^-/AgCl/Ag}^\circ$ for a given temperature are determined from[16]

$$E^\circ(T_2) = E^\circ(T_1) + (dE^\circ/dT)(T_2 - T_1) \qquad (3)$$

where $E_{Cl^-/AgCl/Ag}^\circ$ $(T_1 = 298$ K$) = 0.2226$ V and $E_{Pt/Fe(III),Fe(II)}^\circ$ $(T_1 = 298$ K$) = 0.356$ V. For a given half-cell, the dE°/dT value is estimated from

$$dE^\circ/dT = \frac{\Delta_{r\_half-cell}H^\circ - \Delta_{r\_half-cell}G^\circ}{nFT} \qquad (4)$$

where $T = 298$ K. The standard enthalpy, $\Delta_{r\_half-cell}H^\circ$, and the standard Gibbs energy, $\Delta_{r\_half-cell}G^\circ$, for the half-cell reaction are calculated from the standard enthalpies and Gibbs energies of formation of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and Cl^- ions, as well as $AgCl(s)$.

Further details about the calculations can be found in the Supporting Information.

In postlab discussion, students compare the E values obtained (for a given temperature) from experiment to those determined from the Nernst equation (eq 1). Differences between the measured and calculated values of the cell potentials are significant (see Table 1), and students should discuss the possible reasons for these differences. These differences may partly result from the fact that temperature changes in the ionic activity coefficients (in the ionic strength) are disregarded and that no terms representing the liquid junction potential, E_j, are used in eq 1. However, for the galvanic cell presented here, the E_j potential is much reduced

Table 1. Experimental and Theoretical Values of Cell Potential in the Presence of Supporting Electrolyte

Temperature, T/K	$E_{experiment}$/mV calculated from eq 2	$E_{theoretical}$/mV calculated from eq 1
293	306.2	259.9
298	298.4	253.5
303	290.6	247.1
308	282.9	240.9
313	275.1	234.6

because Ag/AgCl RE with the double salt bridge is applied. Then, differences between the $E_{\text{experiment}}$ and $E_{\text{theoretical}}$ values mainly result from the fact that the $E_{\text{theoretical}}$ values were determined with the use of the Debye–Hückel equation (eq 2S in the Supporting Information) which is valid for the ionic strength, $I \leq 0.1$ M. Because of the presence of 0.5 M KCl as a supporting electrolyte, the ionic strength of the solution studied is very high, so eq 2S cannot be valid and the $E_{\text{theoretical}}$ values in Table 1 must be wrong. In that case, students proposed the repetition of the whole experiment but with the use of the iron salt solution without the supporting electrolyte.

In the absence of the supporting electrolyte, the equation relating E to T is

$$E = -1.523 \cdot T + 665.4 \qquad (5)$$

with $r^2 = 0.999$ and the values of cell potentials are collected in Table 2.

Table 2. Experimental and Theoretical Values of Cell Potential in the Absence of Supporting Electrolyte

Temperature, T/K	$E_{\text{experiment}}$/mV calculated from eq 5	$E_{\text{theoretical}}$/mV calculated from eq 1
293	219.2	226.3
298	211.5	219.1
303	203.9	211.8
308	196.3	204.6
313	188.7	197.4

As follows from data in Table 2, the differences between the measured and theoretical values of the cell potentials are not significant. However, the E values obtained in the absence of the supporting electrolyte are much lower than those obtained in its presence (compare the E values from Table 2 with those from Table 1). Consequently, students learn that the supporting electrolyte affects the ion activities (activity coefficients) in the cell solution in such a way that in the presence of this electrolyte the values of E are much higher than without it, so in its presence, the E values are measured to a higher accuracy. The supporting electrolyte does not affect the cell potential–temperature coefficient (the $(\delta E/\delta T)_p$ values in eqs 2 and 5 are the same).

In literature, the potential–temperature coefficient is given only for the Pt/Fe(III), Fe(II) half-cell and the $(\delta E_{\text{Pt/Fe(III),Fe(II)}}/\delta T)_p$ value is about -2 mV/K.[11] The $(\delta E/\delta T)_p$ coefficient of the galvanic cell proposed by us is related to the $(\delta E_{\text{Pt/Fe(III),Fe(II)}}/\delta T)_p$ coefficient through the relation:

$$(\delta E/\delta T)_p = (\delta E_{\text{Pt/Fe(III),Fe(II)}}/\delta T)_p - dE_{\text{Cl}^-/\text{AgCl/Ag}}^{\circ}/dT \qquad (6)$$

So, knowing that $dE_{\text{Cl}^-/\text{AgCl/Ag}}^{\circ}/dT = -0.65$ mV/K (this value is calculated in the Supporting Information) and $(\delta E/\delta T)_p = -1.55$ mV/K (the experimental value obtained in this laboratory), the $(\delta E_{\text{Pt/Fe(III),Fe(II)}}/\delta T)_p$ coefficient estimated in this experiment is equal to -2.2 mV/K. Consequently, $\Delta_{\text{r\_half-cell}}S$ for our Pt/Fe(III), Fe(II) half-cell is

$$\Delta_{\text{r\_half-cell}}S = nF(\delta E_{\text{Pt/Fe(III),Fe(II)}}/\delta T)_p$$
$$= -212.3 \text{ J/(mol·K)}$$
$$= -50.5 \text{ cal/(mol·K)} \qquad (7)$$

The literature value of $\Delta_{\text{r\_half-cell}}S$ is -49 cal/(mol·K).[17] Thus, the $(\delta E_{\text{Pt/Fe(III),Fe(II)}}/\delta T)_p$ and $\Delta_{\text{r\_half-cell}}S$ values determined by students are in good agreement with the literature data.

In the end, students calculate changes in entropy ($\Delta_{\text{r\_cell}}S$), enthalpy ($\Delta_{\text{r\_cell}}H$), and Gibbs energy ($\Delta_{\text{r\_cell}}G$) for the cell reaction:

$$\Delta_{\text{r\_cell}}G = -nFE_{\text{experiment}} \qquad (8)$$

$$\Delta_{\text{r\_cell}}S = nF(\delta E/\delta T)_p \qquad (9)$$

$$\Delta_{\text{r\_cell}}H = \Delta_{\text{r\_cell}}G + T\Delta_{\text{r\_cell}}S \qquad (10)$$

The values of $\Delta_{\text{r\_cell}}G$, $\Delta_{\text{r\_cell}}S$, and $\Delta_{\text{r\_cell}}H$ determined by students are given in the Supporting Information in Table S4. Students analyze and discuss the results obtained. (In this part of postlab discussion, the role of the instructor is that of coach or facilitator.) They note that all values are negative and try to find out what it means for the thermodynamic system. Negative $\Delta_{\text{r\_cell}}G$ values imply that the electrochemical reaction takes place spontaneously in the galvanic cell. Because a change in enthalpy is equal to the energy supplied as heat at constant pressure, negative values of $\Delta_{\text{r\_cell}}H$ imply that the cell reaction is exothermic. Then, the students try to interpret the fact that with increasing temperature the values of $\Delta_{\text{r\_cell}}G$ become less negative, so the electrode processes that take place are less spontaneous. Moreover, students note that the absolute values of $\Delta_{\text{r\_cell}}G$ are lower than the absolute values of $\Delta_{\text{r\_cell}}H$. They recall from the lectures on thermodynamics that the change in Gibbs energy is equal to the maximum nonexpansion work ($w_{e,\text{max}}$) done in thermodynamic system when the quasi-static (reversible) process takes place at $p = $ const and $T = $ const. Then, in the instructor-led discussion, students find that the heat given off during the electrochemical reaction in a galvanic cell is converted into electrical energy and the cell is capable of doing useful work. Students conclude that if $|\Delta_{\text{r\_cell}}G| < |\Delta_{\text{r\_cell}}H|$, then electrical energy is smaller than thermal energy (the reaction heat) of the cell studied. Thus, the exothermic process dominates in the cell because only part of the reaction heat is consumed on the cell work and the rest of this heat is transferred to the surroundings. Therefore, the entropy (thermodynamically defined by the idea of energy dispersal,[18,19] instead of the usual "disorder", and $\Delta S = q_{\text{rev}}/T$, where q_{rev} is the heat exchanged between a system and its surroundings, when the reversible process occurs) of our cell decreases and $\Delta_{\text{r\_cell}}S < 0$. Since the entropy of the cell decreases, the entropy of the surroundings increases. Afterward, the students are led to understand what it means that the potential–temperature coefficient of the galvanic cell studied is negative. They conclude that the higher the temperature, the lower the cell potential and, consequently, the lower the ability of this cell to do electric work (this work is proportional to the cell potential by the relation: $\Delta_{\text{r\_cell}}G = -nFE = w_{\text{cell,max}}$).

Finally, the students compare the values of thermodynamic quantities obtained in the presence of the supporting electrolyte with those obtained in its absence. They discuss that at each temperature, the values of $\Delta_{\text{r\_cell}}G$ and $\Delta_{\text{r\_cell}}H$ are more negative in the presence of a supporting electrolyte than in its absence. Thus, this electrolyte causes an increase in the ability of the galvanic cell to do electric work and the thermal effect of the electrochemical reaction. On the other hand, the $\Delta_{\text{r\_cell}}S$ values determined in the presence of the supporting electrolyte are similar to those obtained in its absence. Thus,

the supporting electrolyte does not affect the exchange of heat from the cell to its surroundings.

CONCLUSION

Our student-made galvanic cell exhibits good potential stability at each temperature. The potential–temperature coefficient of this cell is relatively high and well measurable, and its experimental value agrees very well with literature ones. The experiment presented here is readily understood and executed, and allows students to receive valuable hands-on experience with a galvanic cell and to gain deeper understanding of cell thermodynamics. Students learn about the construction of the galvanic cell, the principles of measurement of the cell potential, and role of the supporting electrolyte in the electrochemical system. The construction of galvanic cells and the study of their thermodynamics provide experience to investigate the cell reactions at different temperatures, and to determine and interpret thermodynamic quantities of these reactions. In this experiment, students learn that through the determination of the $(\delta E/\delta T)_p$, $\Delta_{r\_cell}G$, $\Delta_{r\_cell}S$, and $\Delta_{r\_cell}H$ values, one can estimate if the galvanic cell produces more electric or thermal energy, what is the cell capability of doing electric work, and if heat is exchanged from the cell to its surroundings or from the surroundings to the cell.

ASSOCIATED CONTENT

ⓢ Supporting Information

. The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00124.

> Handouts for students and notes for instructors; details to calculate the ion activity (particularly, ionic activity coefficients) and the $dE°/dT$ values for half-cells; an abridged table of student results (PDF, DOC)

AUTHOR INFORMATION

Corresponding Author

*E-mail: annajak@amu.edu.pl.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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