

Understanding the Nernst Equation and Other Electrochemical Concepts: An Easy Experimental Approach for Students

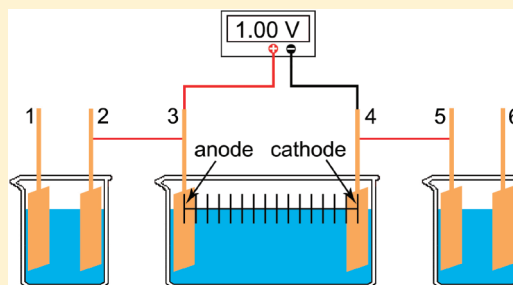
Francisco J. Vidal-Iglesias, José Solla-Gullón,* Antonio Rodas, Enrique Herrero, and Antonio Aldaz

Instituto de Electroquímica, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain

S Supporting Information

ABSTRACT: The goal of the present laboratory experiment is to deepen the understanding of the Nernst equation and some other concepts that are essential in electrochemistry. In this practical laboratory session, students first learn that the equilibrium potential of an electrode is related to the difference between two equilibrium inner electric potentials (also called Galvani potentials), namely, ϕ_M (inner electric potential of the metallic phase) and ϕ_{sol} (inner electric potential of the solution phase). Second, the concept of overvoltage is defined and the method to measure it is described. Finally, it is shown how and why the inner potential of a solution changes with the distance to the working electrode when a current flows through the solution and how the potential difference is distributed in an electrochemical cell when a current is flowing through it.

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Misconceptions/Discrepant Events, Electrochemistry, Electrolytic/Galvanic Cells/Potentials



The Nernst equation is one of the most, if not the most, quoted electrochemical equation.^{1–5} For an ion–metal electrochemical equilibrium such as $M^{n+} + ne^- \rightleftharpoons M$, the equation is normally introduced to students as

$$E_{M^{n+}/M} = E^\circ + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M} \quad (1)$$

where $a_{M^{n+}}$ and a_M are the activities of the oxidized M^{n+} and reduced M species, respectively, E stands for the electrode potential, R for the gas constant, T for the absolute temperature, and F for Faraday's constant. However, if the equation is presented in this way, it is not clear to students that the magnitude given by $E_{M^{n+}/M}$ (which depends on the activities of the species involved in the equilibrium) is related to the difference between two inner electric potentials,⁶ the potential of the metal phase of the electrode ϕ_M , and the potential of the solution phase ϕ_{sol} measured versus a reference electrode.

However, because experimentally the measurement of E is carried out versus a reference electrode, the magnitude measured is the difference between the potential of the metallic phases M and M_{ref} that is,

$$\begin{aligned} E_{M^{n+}/M} &= E_{M^{n+}/M}^\circ + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M} = (\phi_M - \phi_{M,ref}) \\ &= (\phi_M - \phi_{sol}) + (\phi_{sol} - \phi_{sol,ref}) \\ &\quad + (\phi_{sol,ref} - \phi_{M,ref}) \end{aligned} \quad (2)$$

Assuming that the contact potential difference between the two solutions ($\phi_{sol} - \phi_{sol,ref}$) is zero

$$\begin{aligned} E_{M^{n+}/M} &= (\phi_M - \phi_{M,ref}) \\ &= (\phi_M - \phi_{sol}) - (\phi_{M,ref} - \phi_{sol,ref}) \end{aligned} \quad (3)$$

The nature of the reference electrode employed in the measurement of the potential is indicated by the sentence “referred to the saturated calomel electrode”, for example. However, it is also clear from eq 2 that if both inner potentials, ϕ_M and ϕ_{sol} , change, but their difference remains constant, the activities of the species involved in the electrochemical equilibrium must also remain constant (or at least their ratio). Similarly, if the activities remain constant, the inner potentials ϕ_M and ϕ_{sol} can change but in such a way that their difference must remain constant.

Another important electrochemical concept, which is fundamental to understand the behavior of an electrochemical system, is the overvoltage (also called overpotential), η , which is defined as the shift of the potential of an electrode from its equilibrium value when a current I flows through the system

$$\eta = E_{I \neq 0} - E_{I=0} \quad (4)$$

where $E_{I \neq 0}$ stands for the electrode potential for $I \neq 0$ and $E_{I=0}$ for the equilibrium condition, that is, $I = 0$.

Valuable information about the kinetics of the electrochemical reaction taking place on the electrode surface can be obtained from the dependence of the current density on overvoltage, and consequently, its correct measurement is very

important. The overvoltage depends on the current density, j , defined as

$$j = \frac{I}{A} \quad (5)$$

where A is the electrode surface area. According to the IUPAC criteria, the current density is negative for a cathodic (reduction) process and positive for an anodic (oxidation) one. The measurement of the potential $E_{j \neq 0}$ must be carried out when a current is passing through the electrolyte and that can pose a problem to students, who will find that the value of the electrode potential strongly depends on the position of the reference electrode.

In addition, when current flows through an electrochemical cell, the potential needed for this flow is distributed through the cell. Thus, in the electrolyte phase, the inner potential, ϕ_{sol} , changes with the distance to the electrodes and it is more positive near the anode than near the cathode. Thus, there is a potential drop through the electrolyte solution that is normally called the ohmic drop, IR , where R is the resistance of the electrolyte between both electrodes. For a homogeneous parallel field distribution, R is

$$R = \rho \frac{l}{A} \quad (6)$$

where ρ stands for the resistivity of the solution and l for the distance between the electrodes. Because ϕ_{sol}^x changes with distance, so does the potential difference ($\phi_M - \phi_{M,\text{ref}}^x$). Thus, the electrode potential E measured versus a reference electrode placed at a distance x from the electrode is

$$\begin{aligned} E_x &= (\phi_M - \phi_{M,\text{ref}})_x \\ &= (\phi_M - \phi_{\text{sol}}^{x=0}) + (\phi_{\text{sol}}^{x=0} - \phi_{\text{sol}}^x) + (\phi_{\text{sol},\text{ref}} - \phi_{M,\text{ref}}) \end{aligned} \quad (7)$$

For this homogeneous potential distribution and taking $\phi_{\text{sol}}^x = \phi_{\text{sol},\text{ref}}$ (i.e., taking the contact potential as zero):

$$\phi_{\text{sol}}^x = \phi_{\text{sol}}^{x=0} - IR^x \quad (8)$$

where R^x is the resistance at distance x in the solution. Here, I is taken as positive (or negative) for the measurement of the potential of the anode (or cathode).

Thus, the measured electrode potential depends on the position of the reference electrode when a current is circulating through the system. Consequently, the true value of the electrode potential is that measured when the distance between the metallic phase of the electrode and the reference electrode is zero ($IR \rightarrow 0$). However, the position of the reference electrode has to fulfill two opposite conditions. On the one hand, it has to be far from the metallic phase of the electrode to avoid perturbations of the electric potential distribution. On the other hand, it should be as close as possible to the metallic phase of the electrode to reduce the IR potential drop. These two requirements can be partially overcome employing a Luggin capillary (see the Supporting Information). Therefore, it is important to show students that the measurement of an electrode potential when current is flowing is not as simple as it seems and that some experimental precautions must be taken into account.

The aim of this laboratory experiment is to help the students to understand (i) the electrochemical concepts involved in the Nernst equation, (ii) the concept of overvoltage, (iii) the

importance of the position of the reference electrode in the measurement of potential differences in an electrochemical system through which a current is flowing, and (iv) how the potential difference between two electrodes is distributed inside an electrochemical device.

EXPERIMENTAL PROCEDURE

This is a 4-h experiment (one lab session) performed with 24 students working in couples. Students have to prepare, outside of the lab, a lab report of the experiment which should include a detailed response to the questions proposed in the Supporting Information.

In this experiment, three containers, made of glass or transparent PVC, are filled with a 1 M CuSO_4 solution. The central container is a cell with dimensions of $15 \times 5 \times 5$ cm, in which a graph paper was fixed on one of the borders. Six 5×5 cm copper (Cu) pieces are introduced into the solutions and Cu pieces 2 and 3 and 4 and 5 are connected by Cu wires as shown in Figure 1A. The cell is filled with 250 mL of the

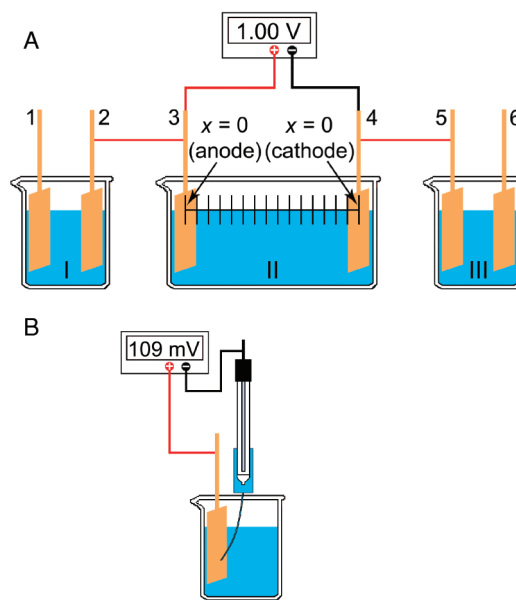


Figure 1. (A) Experimental setup. (B) Potential difference measurement with a capillary connected to the reference electrode.

CuSO_4 solution, giving a liquid height of 3.3 cm. Thus, the Cu electrodic area is $5 \text{ cm} \times 3.3 \text{ cm} = 16.5 \text{ cm}^2$. Initially, the potentials of the six Cu^{2+}/Cu electrodes, 1–6, are measured using a $\text{KCl}/\text{AgCl}/\text{Ag}$ reference electrode with the help of a Luggin capillary placed near the electrode of which is going to be measured, Figure 1B. The measured values should be obviously the same for the six electrodes and should be about 109 mV. Differences among these values, measured with the same reference electrode, bigger than ± 3 mV can be ascribed to a bad treatment of the surface of the Cu metals (the surface can be partially oxidized or contaminated). In addition, the potential differences between Cu(1) and Cu(2) ($E_1 - E_2$), between Cu(5) and Cu(6) ($E_5 - E_6$), and between Cu(1) and Cu(6) ($E_1 - E_6$), as well as the potential difference between solution I and solution III using two reference electrodes are also measured, which in all cases must obviously be zero or near zero (slight difference in the potential of the two reference electrodes may exist).

Then, Cu(3) is connected to the positive pole of a power source and Cu(4) to the negative one. A voltage of 1.00 V is applied between both electrodes and the electrode potentials for electrodes Cu(3) and Cu(4) are measured by placing the capillary of the reference electrode at different distances from the Cu piece. A graph E versus distance is drawn and the values of the two electrode potentials extrapolated at $x = 0$ are noted. The experimental data is used to complete a figure in the Supporting Information (Figure LD8). Again, the potential of the electrodes placed in beakers I and III, the potential difference between solution I and solution III, and the potential differences between Cu(1) and Cu(2) ($E_1 - E_2$), between Cu(5) and Cu(6) ($E_5 - E_6$), and between Cu(1) and Cu(6) ($E_1 - E_6$) are measured and noted filling Figure LD8 in the Supporting Information.

HAZARDS

None of the products is dangerous. However, the wastewater from the experiment should be treated to remove Cu^{2+} ions.

RESULTS AND DISCUSSION

According to the Experimental Procedure, students should measure the potential differences between Cu(1) and Cu(2) ($E_1 - E_2$), between Cu(5) and Cu(6) ($E_5 - E_6$), and between Cu(1) and Cu(6) ($E_1 - E_6$), as well as the potential difference between solutions I and III using two reference electrodes both before and after the 1.00 V is applied between Cu(3) and Cu(4) pieces. Students will find that the values $E_1 - E_2$, and $E_5 - E_6$ remain zero after connecting Cu(3) and Cu(4) to the power source. On the other hand, a potential difference of 1.00 V will be measured between $E_1 - E_6$, and also between solution I and III. But, how is that possible if solutions I and III are identical? Because of the applied voltage, the inner metal potentials, ϕ_{Cu} of Cu(3) and Cu(4) have changed. Moreover, because of the connections between the copper pieces, Cu(3)–Cu(2) and Cu(4)–Cu(5) have the same voltage, $\phi_{\text{Cu(3)}} = \phi_{\text{Cu(2)}}$ and $\phi_{\text{Cu(4)}} = \phi_{\text{Cu(5)}}$. According to the Nernst equation, since the activity of Cu^{2+} ions in solutions I and III has not changed (no current is flowing through solutions I and III), $\phi_{\text{Cu(2)}} - \phi_{\text{sol,I}}$ and $\phi_{\text{Cu(5)}} - \phi_{\text{sol,III}}$ should remain constant. However, $\phi_{\text{Cu(2)}}$ is now more positive (connected to the + pole) than before connection and consequently, to keep the difference $\phi_{\text{Cu(2)}} - \phi_{\text{sol,I}}$ constant, the potential $\phi_{\text{sol,I}}$ must also increase in the same amount. In a similar way, $\phi_{\text{Cu(5)}}$ is now less positive (connected to the – pole) than before connection, and thus, $\phi_{\text{sol,III}}$ should decrease in the same amount. For the same reason, the change of $\phi_{\text{sol,I}}$ and $\phi_{\text{sol,III}}$ forces $\phi_{\text{Cu(1)}}$ and $\phi_{\text{Cu(6)}}$ to change to maintain the differences $\phi_{\text{Cu(1)}} - \phi_{\text{sol,I}}$ and $\phi_{\text{Cu(6)}} - \phi_{\text{sol,III}}$ also constant. This potential reorganization results in a potential difference of 1.00 V between Cu(1) and Cu(6) and between solutions I and III.

Thus, this simple experiment will help students to understand that the equilibrium potential of an electrode, defined by the Nernst equation, is in fact related to the difference between two equilibrium inner potentials (electrode and solution). This difference is controlled by the activities of the compounds involved in the electrode reaction. If these activities are constant, the value of the difference of the inner potentials at the electrode interphase remains constant, irrespective of the particular value of each inner potential. That is to say, if any of the inner potentials change, the other potential must also

change in such a way that the difference between them is kept constant.

Moreover, students have to measure the potentials for electrodes Cu(3), E_3 , and Cu(4), E_4 , while applying the potential difference of 1.00 V between electrodes Cu(3) and Cu(4), by placing the capillary of the reference electrode at different distances from the corresponding Cu piece. The E versus distance representation should be similar to that shown in Figure 2.

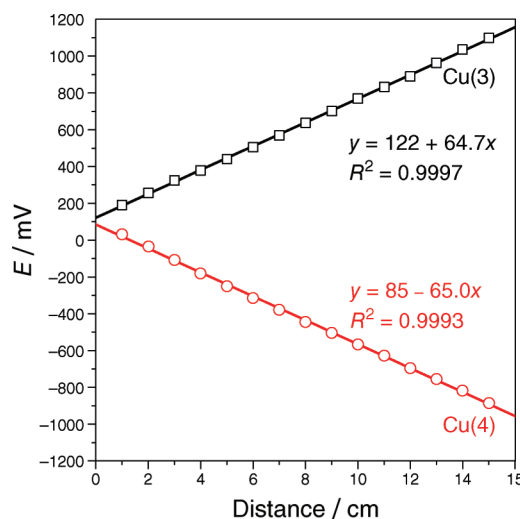


Figure 2. Electrode potentials of Cu(3) (black solid squares) and Cu(4) (red open circles) measured placing the reference electrode at different distances from the corresponding Cu surface.

This representation also allows provides the real values of the two electrode potentials by extrapolating at $x = 0$ the measured potentials at different distances. From the intercepts, the anode, Cu(3) 122 mV, and cathode, Cu(4) 85 mV, potentials were obtained. It should be pointed out that before the connection to the power source, these potentials (equilibrium potentials) were equal to 109 mV.

Consequently, because of the flux of current, an overpotential (η) appears, which is positive for the anode, Cu(3), $\eta_3 = 122 - 109 = 13$ mV and negative for the cathode, Cu(4), $\eta_4 = 85 - 109 = -24$ mV. These values were obtained from the intercept of the linear adjustment. This finding shows students that the potential of an electrode changes when a current flows through the interphase, shifting to more positive (or negative) values than the equilibrium potential when the current is anodic (or cathodic). The former values change if electrode contact areas are different from those mentioned in the Experimental Procedure or if the distance between electrodes Cu(3) and Cu(4) is not 15 cm.

Figure 2 also shows a clear dependence of the measured electrode potential as a function of the position of the reference electrode. The applied potential of 1.00 V is distributed in container II as follows: $1 = E_3 - E_4 + IR_{\text{total}}$, where E_3 and E_4 are the electrode potential of electrodes Cu(3) and Cu(4) at $x = 0$ and IR_{total} is the potential drop caused by the passage of current I through the resistance R_{total} of the electrolyte between both electrodes. IR_{total} can be obtained from the slope of straight lines in Figure 2. These slopes reflect how the potential changes with distance and are, obviously, the same but with opposite sign, positive for the anode and negative for the

cathode (average slope = 65 mV cm^{-1}). One V $\cong 122 \text{ mV} - 85 \text{ mV} + (65 \text{ mV/cm} \times 15 \text{ cm})$

When current flows, the inner potential of the solution, ϕ_{sol} , changes with the distance to the electrode. Thus, the measured potential of the anode will be more positive as the distance between the anode and the reference electrode increases and the cathode potential will be less positive when the distance of the reference electrode to the cathode increases. Experimentally, a better measurement of the real (corrected) potential of the electrode can be obtained directly by placing the capillary tip of the Luggin capillary as near as possible to the cathode or anode.

SUMMARY

These results will help students to realize that the inner potential of an electrolyte solution, ϕ_{sol} , changes when current flows through it and that due to the fact that the electrolyte has non-negligible electrical resistance, the electrode potential measured depends on the position of the reference electrode.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure for the students; student handouts; instructor notes. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jose.solla@ua.es.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Arevalo, A.; Pastor, G. *J. Chem. Educ.* **1985**, *62*, 882.
- (2) Evans, J. S. *J. Chem. Educ.* **1968**, *45*, 532.
- (3) Perrine, D. M. *J. Chem. Educ.* **1984**, *61*, 381.
- (4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley & Sons, Inc.: New York, 2001.
- (5) Compton, R. G.; Sanders, G. H. W. *Electrode Potentials*, 1st ed.; Oxford University Press: Oxford, 1996.
- (6) IUPAC Gold Book. <http://goldbook.iupac.org/I03046.html> (accessed Mar 2012).