

Nernst equation applied to electrochemical systems and centenary of his Nobel Prize in chemistry

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Abstract

Walther Hermann Nernst received the Nobel Prize in Chemistry in 1920 for the formulation of the third law of thermodynamics, thus celebrating a century in this 2020 year. His work helped the establishment of modern physical chemistry, since he researched into fields, such as thermodynamics and electrochemistry, in which the Nernst equation is included. This paper reports on several experiments that used a Daniell galvanic cell working in different electrolyte concentrations for comparing results with the theoretical values calculated by the Nernst equation. The concentration and activity coefficients values employed for zinc sulfate and copper electrolytes showed activity can replace concentrations in thermodynamic functions, and the results are entirely consistent with experimental data. The experimental electromotive force from standard Daniell cell, for ZnSO₄ and CuSO₄, with unitary activity and in different concentrations at room temperature is in agreement with those from theoretical calculations. Cu²⁺ ion concentrations and temperature were simultaneously varied; however, the cell potential cannot be included in calculations of Nernst equation for different temperatures than 25 °C because the standard potential value was set at 25 °C. The cell potential decreases drastically when the Cu²⁺ concentration was reduced and the temperature was above 80 °C.

Keywords: Thermodynamic; Electrochemistry; Nernst Equation; Galvanic Cell; Standard cell potential; Electrolyte Concentrations;

1. Introduction

The first electrochemical studies date from 1786 and were performed by Luigi Galvani, who observed a frog's leg moved when a potential difference was applied to it (GALLONE, 1986; TICIANELLI, 2013; LINDEN, 1995). In 1799, Alessandro Volta developed the voltaic cell, i.e., the first

electrochemical cell comprised of two metal discs - zinc and copper - called electrodes, connected by cardboard soaked with sulfuric acid or saltwater brine as electrolyte (FABBRIZZI, 2019). Those were the first studies of storage and electrochemical energy conversion, and several others on batteries and fuel cell have been currently developed (HWANG, 2015; SOUZA, 2006; LACINA, 2018).

In 1836, John Frederic Daniell designed a galvanic cell using two different compartments (called half-cells) where happens semi-reactions, oxidation (in anode) and reduction (in cathode). Anode and cathode are composed of two metallic plates, respectively, i.e., zinc in a zinc sulfate solution (1.0 mol L⁻¹) and copper in a copper sulfate solution (1.0 mol L⁻¹). Such two compartments are interconnected by an ionic conductor, called salt bridge (FATIBELLO-FILHO, 2019; MARTINS, 1990; MCSWINEY, 1982). A schematic representation of the Daniell galvanic cell is provided in Figure 1 and follows are the halves and overall reactions that occur in the cell.

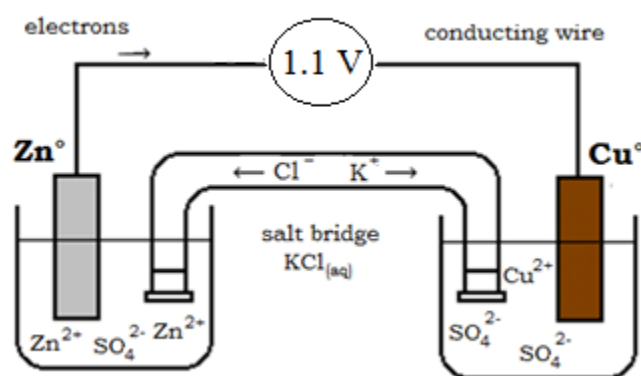
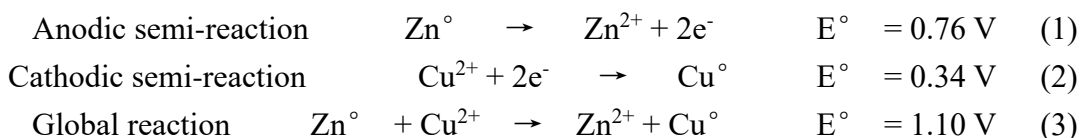


Figure 1. Schematic representation of Daniell galvanic cell.



The standard potential (E°) values are tabulated (WOLYNEC, 2003; MOORE, 1976) for the electrodes as follows: copper (couple (Cu^{2+}/Cu)) reduction = 0.34 V and zinc (couple (Zn^{2+}/Zn)) = 0.76 V, both relative to hydrogen potential at 25 °C and 1 atm pressure.

A historical analysis of the Daniell cell teaching was reported by Boulabiar et al. (2004), and a detailed discussion on the reason why it works was conducted by George F. Martins (1990). Buckbee et al.(1969) investigated the dependence of standard cell potential, E° , of the Daniel cell on the temperature; they observed E° decreased when the temperature increased, and designed a quadratic equation that showed E varied in function of temperature.

The cell potential depict the electrical work of the cell is able to do. The dependence of the cell potential with temperature are applied to other galvanic cells, like Li-ion batteries (WANG, 2018; ROSCHER, 2011; MA, 2018) and nickel–metal hydride battery (SOUZA, 2003, SOUZA 2006, PIEROZYNSKI, 2011) also reported by Li et al. (2015) for Na-FeCl₂ ZEBRA advanced Battery. Additionally, Austin et al. (2018) carried a study on the density function theory (DFT) whose accuracy enabled the obtaining of energy from a zinc/copper voltaic cell and the Daniell cell. All of this electrochemical system presents

spontaneous and exothermic reaction thus, the system heats up with working.

1.1 Thermodynamics and Electrochemical Studies: The Nernst Equation

Walther Hermann Nernst (1864 - 1941), a German chemist, worked in several knowledge areas, including physical chemistry, solid state physics, photochemistry, theory of solutions, and the link between thermodynamics and electrochemistry, which includes Nernst equation, that was developed in 1887 (TICIANELLI, 2013; FATIBELLO-FILHO, 2019; NASCIMENTO, 2019). His studies helped the establishment of modern physical chemistry, researching in theoretical and experimental fields, and the formulation of the Nernst heat theorem, known as the third law of thermodynamics. In 1920, he was awarded The Nobel Prize for Chemistry, thus celebrating a century in this 2020 year (NASCIMENTO, 2019). The Nernst equation has several applications as, it can also be used for oxidation-reduction titration, pH dependence redox couple; determination of equilibrium constants, (THOMPSON, 1999; LU, 2015; WALCZAK, 1997) among others (DANILEWICZ, 2019; RODRIGUES, 2018; NASCIMENTO 2013; SOUZA, 2018).

W.H. Nernst attended the Universities of Zurich, Berlin and Graz, where he studied Physics and Mathematics with Ludwig Boltzmann and Albert Von Ettinghausen. He later obtained his Ph.D. in Würzburg (1887), under the guidance of physicist Friedrich Kohlrausch. After working for some time in Leipzig, he held the position of professor of Physics and Chemistry at the Universities of Göttingen (1891-1905), where he founded the Institute of Chemistry, Physics and Electrochemistry (1895), and Berlin, where he was also director of the Physical-technical Institute of Physical Chemistry (1905-1925). He was appointed President of the Institute of Berlin-Charlottenburg (1922-1933), and from then on, focused on studies of acoustics and astrophysics (NASCIMENTO, 2019; VOGEL, 1979).

The equation developed by W.H. Nernst relates the electromotive force of an electrochemical cell (electrode potential) to the solution concentrations and temperature. In brief, the electrochemical cell potential is determined by cathodic and anodic electrodes, in which happens each reduction semi reaction and oxidation semi reaction as shown in equations 1 and 2, and on the global electrochemical reaction, as showed in equation 3. The electrochemical reactions are carried out often at constant pressure and temperature, and the maximum electrical work (W_e) is the same of the Gibbs free energy change (ΔG), $W_{e,max} = \Delta G$, for reversible transformation. The ΔG of any reaction and standard free energy change, ΔG° , is given by the following relationship:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (4)$$

where Q is the law of mass action of a reaction. For a redox reaction, additionally, the galvanic cell requests a spontaneous global electrochemical reaction, thus, from thermodynamic the variation of Gibbs (ΔG) is negative for a positive cell potential as described by equation 5:

$$\Delta G = -nFE \quad ; \quad G^\circ = -nFE^\circ \quad (5)$$

where: E° is the standard cell potential and E is the cell potential for an electrochemical system; F is the Faraday constant, $F = 96485 \text{ C mol}^{-1}$; and n is an amount in mol of electrons transferred.

The combination of the two equations (4) and (5) gives

$$-nFE = -nFE^\circ + RT \ln Q \quad (6)$$

This equation can be rearranged, so that the Nernst (7) is obtained:

$$E = E^\circ - \left(\frac{RT}{nF} \right) \ln Q \quad (7)$$

where: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant; F is the Faraday constant, $F = 96485 \text{ C mol}^{-1}$; n is an amount in mol of electrons transferred; T is the absolute Kelvin scale temperature ($T = 298.15 \text{ K}$); and Q is the reaction quotient.

The Nernst equation, is the quantitative relationship that enables the calculation of the cell potential, E , in different ion concentrations of a unit; therefore, the cell potential can be easily calculated by Nernst equation and applied to Daniell galvanic cell at 25°C , furthermore, at the standard conditions, i.e, ions unitary concentration, the Daniell cell potential is $E=E^\circ$, because the second thermo of Nernst equation become zero. Moreover, thermodynamics functions can be accessed from electrochemical experiments also (MOORE, 1976; RODRIGUES, 2018; VOGEL, 1979) as will be shown follows.

1.2 Entropy and enthalpy of cell reactions

The application of the Gibbs-Helmholtz equation to equation (5) enables the calculation of the enthalpy change (ΔH) and the entropy change (ΔS) of the cell reaction from the temperature coefficient of the reversible electromotive force. In equation (8), the Gibbs free energy change is equal to the heat reaction corrected for the amount of energy (it cannot be converted to work) (COFEY, 2006).

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

where $T\Delta S$ denotes the heat amount that can be generated in a reversible process.

At constant pressure and according to the preferred representation of Nernst and van't Hoff, equation 8 becomes:

$$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_p = zF \left(\frac{\partial E}{\partial T} \right)_p \quad (9)$$

$$\Delta H = \Delta G + T\Delta S \quad (10)$$

$$\Delta H = -|z|FE + |z|FT \left(\frac{\partial E}{\partial T} \right)_p \quad (11)$$

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p \quad (12)$$

which is the Gibbs-Helmholtz equation. ΔH can be calculated if ΔG is known for all temperatures; however, the reverse is not possible, since it involves an arbitrary integration constant (COFFEY). This technical fact was at the core of the problems faced in the development of the third law of thermodynamics.

Since 1888, scientists have attempted to integrate the differential form of equation (8). Le Chatelier,

Lewis, Theodore Richards, van't Hoff, Fritz Haber, and Nernst (1906), in this chronological order. They aimed to obtain absolute values for the entropy, for the determination of free energy change from thermometric measurements.

T. Richards conducted some reactions in a dilute aqueous solution, such as



in which the exchange of sulfate ion between metals did not refer to temperatures below the water freezing point. Figure 2 shows energy vs. temperature graphs based on Richard's diagram for metal pairs Zn-Cu, Fe-Cu, and Zn-Fe. The points below 0 °C (273.15 K) were obtained by thermodynamic relations, and above 0 °C, free energies and heats of reaction were measured galvanically and calorimetrically, respectively (COFFEY, 2006).

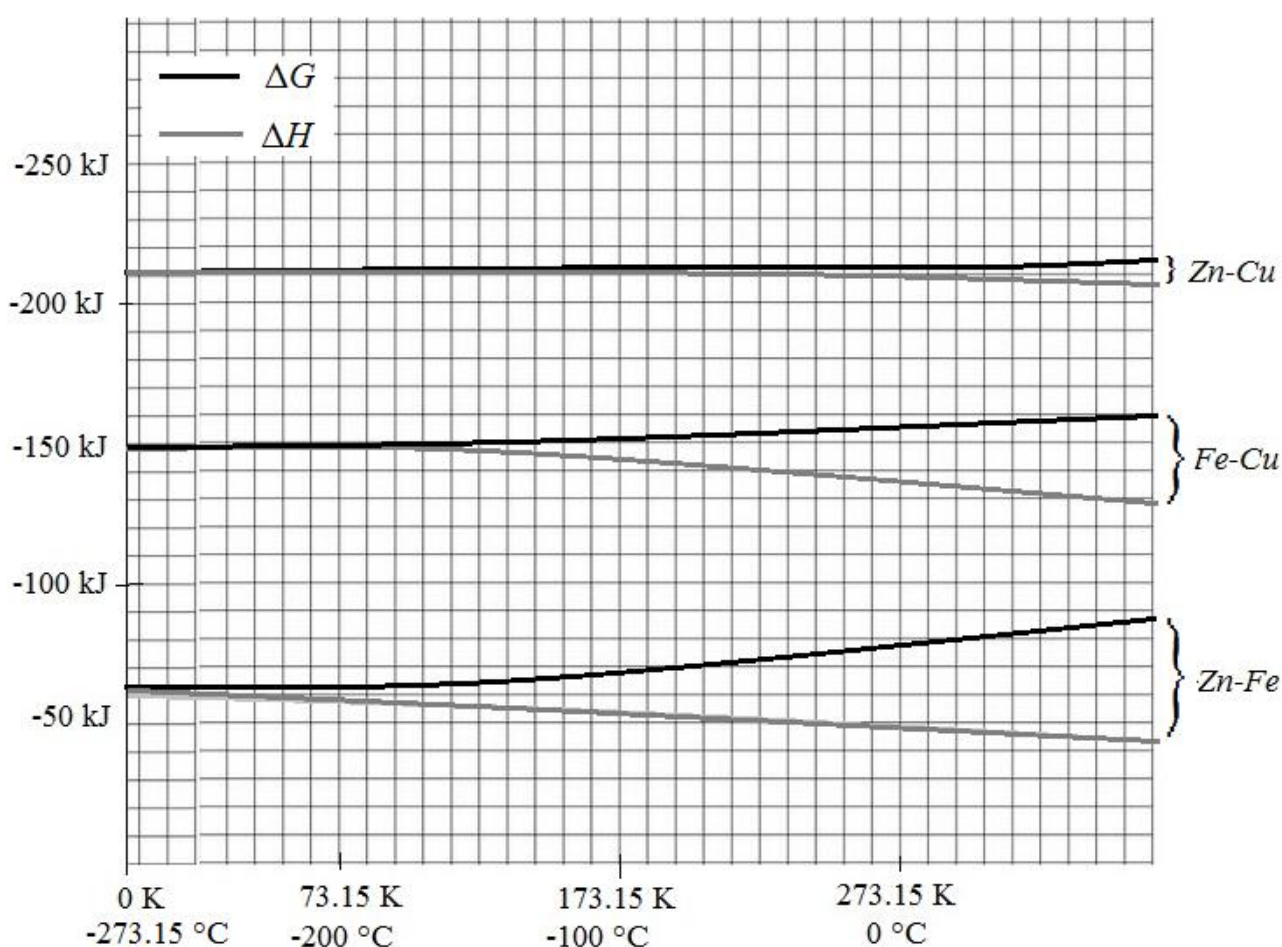


Figure 2 Gibbs free energy (black line – ΔG) and enthalpy (gray line – ΔH) as a function of temperature.

According to the diagram in Figure 2, at 25 °C for metallic pair Zn/Cu (reactions in equations 1-3), the value of ΔG is slightly higher than –210 kJ, and can be compared with that calculated by equation 5 ($\Delta G^\circ = -2 \times 96485 \times 1.1$), thus resulting in $\Delta G = -212.3 \text{ kJ mol}^{-1}$.

Figure 2 shows diagrams with behaviors very similar to those obtained by Richard for some metal pairs. Such behaviors are interesting when ΔG and ΔH are equal in extrapolations to zero Kelvin (absolute zero). W.H. Nernst built a diagram showing the two curves are together when $T \rightarrow 0$, which agrees with condition $\Delta G = \Delta H$ at absolute zero. Lewis then constructed a diagram general pattern in Richards' data.

Lewis had deep knowledge of physics, mathematics, and especially thermodynamics, and had read Gibbs and knew what European scientists had been studying and developing in thermodynamics (COFFEY, 2006). Such a way of measuring free energies also has limited applications. Therefore, Lewis wrote: “*Of all the chemical reactions which we meet in our thermodynamic calculations, comparatively few may be studied by the simple measurement of [voltage]. This is due to the difficulty of finding a galvanic cell in which a given reaction occurs, and occurs with such ease as to permit an approach to complete reversibility*” (COFFEY, 2006).

This study investigates the experimental behavior of Daniel’s galvanic cell for measurements of the cell potential (or electromotive force) in different concentrations of electrolytes and compares Nernst equation calculations at room temperature, considering the electrolyte concentrations and molar ions activity. Experiments conducted at different temperatures in Daniel’s galvanic cell analyzed the dependence on the ions concentration of electrolytes and temperature, although the thermodynamic parameters of the reactions cannot be determined by simple voltage measurements for further theoretical calculations by the Nernst equation.

Additionally, some simple experiments with Daniell cell may be able to demonstrate different chemical concepts such as electrolyte conductivity, electrolyte dissociation, Kohlrausch law, preparation of the Daniell cell preparation, and electromotive force measurements and when the Nernst equation can be applied to galvanic cells. This paper features the Daniel cell working at different electrolytes concentrations and temperatures, the expected cell potential of these conditions were calculated by Nernst equation and a comparison between experimental and theoretical results are shown.

2. Experimental

The Daniell galvanic cell, used in all electrochemical experiments, is basically constituted by two electrodes and two beakers, electrolytic solutions and one salt bridge, cables and one multimeter (Minipa ET-1002).

The electrodes consist of high purity metal sheets (99.9%) zinc (Zn°) and copper (Cu°). Both metal sheets presents 4x25x80 mm (thickness x width x length), totaling a $4.8 \times 10^{-3} \text{ m}^2$ surface area. The electrolytes solution were prepared with distilled water (Quimis, Q341) and $ZnSO_4$ (>99.5%, Dinâmica) and $CuSO_4$ (>99.5%, Nox Lab Solutions). The Agar-Agar KCl saturated salt bridge in U-shaped tubes was prepared also.

2.1 Daniel cell preparation

Previous each any measurement the electrodes were cleaned with sandpaper (Norton 320, Agua T223) afterward it was immersed in HCl solution toward removes surface oxides. The electrode were cleaned with paper tower and immediately inserted in electrolyte.

50 mL of each electrolyte solution was transferred to beakers, the electrodes were connected to a multimeter and the salt bridge was inserted to connect the electrolytes.

2.2 Daniel cell potential measurements

The electrodes were immersed in electrolytes, with $3.2 \times 10^{-3} \text{ m}^2$, the piece out of electrolyte are non-electrochemical active and has no influences in electrochemical data. The salt bridge and the multimeter were connected and the cell was registered after stable value. The solutions were replaced and the electrodes were cleaned before new potential registration.

For cell potential at different temperatures (25, 40, 60, 75 and 80 ° C), the electrochemical system was inserted into a water thermal bath heated by a heating plate with a controller (Fisaton 752A) and whose temperature was measured by a thermometer. The open circuit potential was measured at different temperatures, waiting 10 min for galvanic cell to reach thermal equilibrium.

3. Results and Discussion

3.1 Experimental cell potential and Nernst equation applied as a function of Cu^{2+} and Zn^{2+} concentrations and activity for zinc sulfate and copper electrolytes

Figure 3 shows cell potential measured experimentally (E_M) and cell potential calculated (E_C) by Nernst equation, at room temperature, i.e. 25°C (298.15 K), for different Cu^{2+} concentrations and fixed 1.0 mol L^{-1} Zn^{2+} concentration.

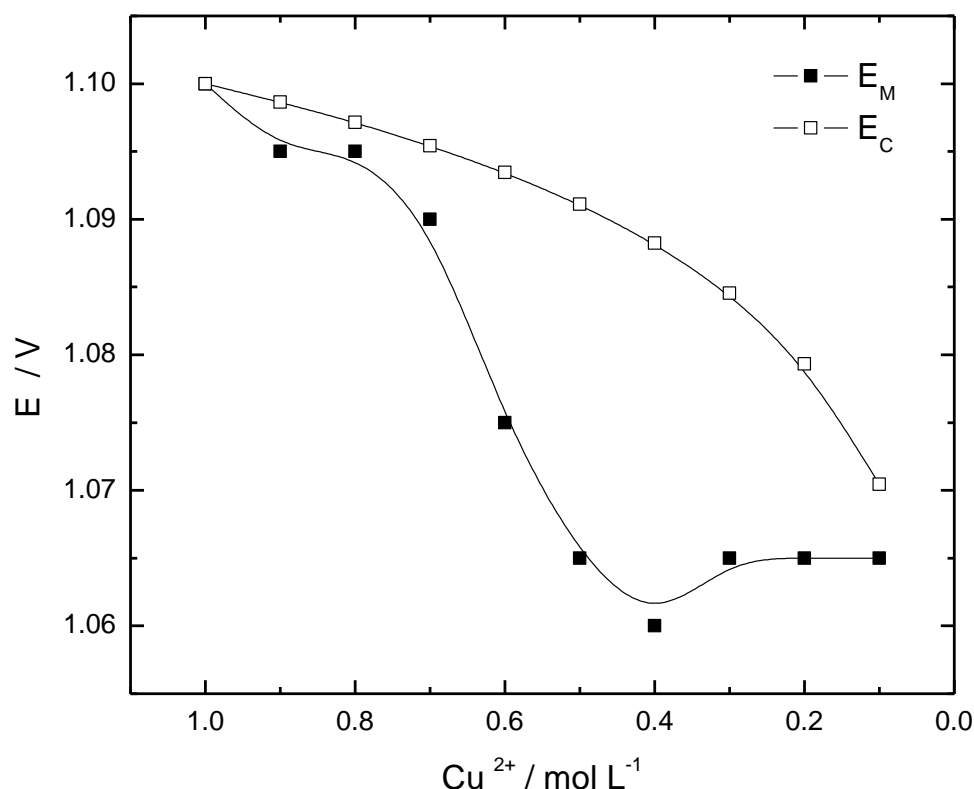


Figure 3. Cell potential calculated (E_C) by Nernst equation and measured experimentally (E_M) for Daniell cell in different Cu^{2+} concentrations. Zn^{2+} concentration fixed in 1.0 mol L^{-1} . $T = 25^\circ \text{C}$.

As knew the cell potential of the cell is a contribution of both electrodes, if one electrode has low activity, the cell shown low performance. The Figure 3 shows discrepancies between theoretical (calculated by Nernst equation) and experimental Daniell cell with different Cu^{2+} ions concentrations. The Nernst equation can be applied at different Cu^{2+} ions concentrations for theoretical calculations of cell potential

at 25°C. Moreover, the operation mechanism of Daniell cell is Zn oxidation and Cu reduction, as shown by the reactions in equations (1-3). Thus the Zn⁰ from electrode became Zn²⁺ in electrolyte at anode and at cathode the Cu²⁺ from electrolyte became Cu⁰. The experimental results in Figure 3 show the cell potential measured different from theoretical. It is expected the experimental cell potential is lower than theoretical and this differences can be assigned to experimental random error instead of the accuracy toward minimize then. The salt bridge saturated in KCl was used to minimize the junction potential, measurement was carried out after cell potential stabilization and triplicate measure were registered, the cell potential drifted 2 mV among the each experiments.

Additionally, the CuSO₄ concentration at room temperature showed little changed to smaller values when Cu²⁺ ≤ 0.7. Such changes can be assigned to others physical-chemistry properties as ion diffusion from bulk to interface electrode/electrolyte; the electrolyte dissociation, and the electrode polarization by mass transfer. According to the Nernst equation, the cell potential behavior is weakly dependent on Cu²⁺ concentration electrolyte in all range calculated because it is an Neperian logarithm mathematical equation, but it do not become the Nernst Equation wrong, the values are close to the Nernst model. Furthermore, at standard conditions i.e. both ions in electrolyte is unitary, e.g. 1.0 mol L⁻¹ of Zn²⁺ and 1.0 mol L⁻¹ of Cu²⁺, or at nonstandard but the second member of eq. 7 become zero, i.e. 0.1 mol L⁻¹ Zn²⁺ and 0.1 mol L⁻¹ Cu²⁺, the calculated and measured cell potential convert to same value when second member of Nernst equation become zero and the large discrepancies on cell potential measured and calculated were observed between 0.7 < [Cu²⁺] < 0.3 (CIRIBELLI, 2018).

3.2 Experimental cell potential as a function of Zn²⁺ and Cu²⁺ concentrations and theoretical results of the Nernst equation (ion concentrations and activity for electrolytes)

According to the law of mass action, the concentration of chemical species is used as variables; therefore the equilibrium constant is independent of such concentrations(MOORE, 1976; NASCIMENTO, 2019). Subsequent studies have shown such a concept is only approximately valid for diluted solutions (the greater the dilution, the greater the approximation of the results) and can be incorrect for more concentrated solutions. Similar discrepancies are large when other thermodynamic quantities, such as electrode potential and free chemical energy are involved. To overcome these difficulties and still retain simple derivative expressions for such quantities, G.N. Lewis introduced a new thermodynamic concept, called activity, which, replacing concentrations in thermodynamic functions, offers results that are perfectly consistent with experimental data. The dimension of this greatness is the same of that of concentration. The activity of a component A, (a_A), is proportional to its effective concentration [A], and can be expressed by:

$$a_A = f_A \cdot [A] \tag{15}$$

where f_A is activity coefficient, dimensionless quantity, which varies according to the concentration. Table 1 shows the activity coefficients for zinc sulfate and copper electrolytes (MOORE, 1976; VOGEL, 2006) at different concentrations.

Table 1. Molar activity coefficients (f_A) for zinc sulfate and copper sulfate electrolytes (VOGEL, 2006)31.

Molar Concentration (C)	0.001	0.01	0.05	0.1	0.2	0.5	1.0	2.0
CuSO ₄	0.74	0.41	0.21	0.16	0.11	0.07	0.05	-
ZnSO ₄	0.70	0.39	-	0.15	0.11	0.07	0.05	0.04

Additional calculation of the cell potential were theoretically calculated at 25 °C for the galvanic cells using the activity and the concentration of the electrolytes and a comparison are shown in Table 2. The comparison among activity and concentration were calculated with the cells:



The Nernst's equation becomes:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{(\text{ZnSO}_4)} \cdot a_{(\text{Cu})}}{a_{(\text{CuSO}_4)} \cdot a_{(\text{Zn})}} \quad (16)$$

Table 2 shows the potential cells at four combinations of concentrations of Zn²⁺ and Cu²⁺ obtained experimentally and calculated by the Nernst equation (theoretical) with concentrations and activity for zinc and copper ions.

Table 2 – Experimental potential cells (E) and calculates by Nernst Equation applying molar ion concentrations (equation 14) and activity (equations 15 and 16) for zinc and copper sulfates electrolytes, at 298.15K.

E (V) – Experimental							
Zn ²⁺ 1.0 mol L ⁻¹		Zn ²⁺ 0.1 mol L ⁻¹		Zn ²⁺ 1.0 mol L ⁻¹		Zn ²⁺ 0.1 mol L ⁻¹	
Cu ²⁺ 1.0 mol L ⁻¹		Cu ²⁺ 1.0 mol L ⁻¹		Cu ²⁺ 0.1 mol L ⁻¹		Cu ²⁺ 0.1 mol L ⁻¹	
1.095		1.095		1.065		1.085	
E (V) – Theoretical							
$a_{\text{Zn}} = f_{\text{Zn}} \cdot [\text{Zn}^{2+}] = 0.05$		$a_{\text{Zn}} = f_{\text{Zn}} \cdot [\text{Zn}^{2+}] = 0.015$		$a_{\text{Zn}} = f_{\text{Zn}} \cdot [\text{Zn}^{2+}] = 0.150$		$a_{\text{Zn}} = f_{\text{Zn}} \cdot [\text{Zn}^{2+}] = 0.015$	
$a_{\text{Cu}} = f_{\text{Cu}} \cdot [\text{Cu}^{2+}] = 0.05$		$a_{\text{Cu}} = f_{\text{Cu}} \cdot [\text{Cu}^{2+}] = 0.160$		$a_{\text{Cu}} = f_{\text{Cu}} \cdot [\text{Cu}^{2+}] = 0.016$		$a_{\text{Cu}} = f_{\text{Cu}} \cdot [\text{Cu}^{2+}] = 0.016$	
Nernst [C]	Nernst <i>a</i>	Nernst [C]	Nernst <i>a</i>	Nernst [C]	Nernst <i>a</i>	Nernst [C]	Nernst <i>a</i>
1.100	1.100	1.130	1.130	1.070	1.071	1.100	1.100

The data presented in Table 2 shows close values of cell potential calculated with Nernst equation using concentration or activity of the electrolytes, the values shift only after four decimal places (data not shown here).

3.3 Cell potential as a function of cell temperature and Zn²⁺ and Cu²⁺ concentrations

Additional investigations of cell potentials were carried out at different temperatures in different CuSO₄ concentrations (fixed ZnSO₄ concentration), and at different temperatures and in different CuSO₄ and

ZnSO₄ concentrations. Figure 4 shows the variation of the cell potential obtained in electrochemical experiments as a function of temperature for the same CuSO₄ and ZnSO₄ concentrations and CuSO₄ concentration lower than those of CuSO₄ and ZnSO₄.

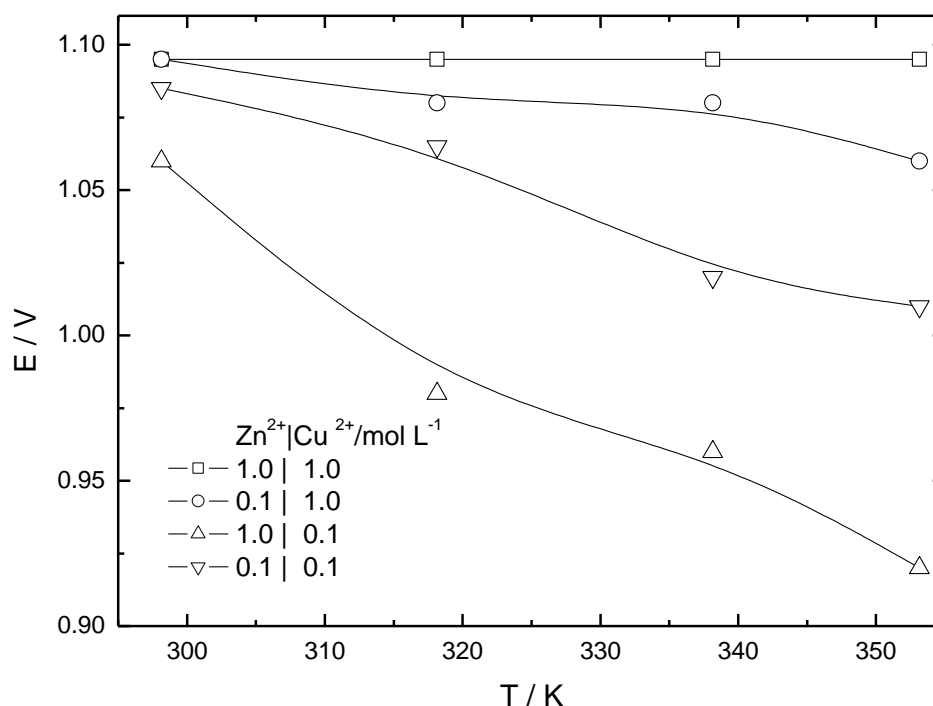


Figure 4. Cell potential obtained experimentally as a function of temperature increase and with variation in Zn²⁺ and Cu²⁺ concentrations.

The cell potential decreased with increases in the temperature for concentrations different from unity. An important concept shown here and often wrongly used is the use of Nernst equation at temperature different from 25 °C. It is not possible to include in the Nernst equation calculates because the value of the standard potential (E°) that appears in this equation is valid only at 25 °C; for application of the Nernst equation at temperatures different from 25 °C, the standard cell potential must be determined (MOORE, 1976) as discussed by Whittemore and Langmuir (1972) on standard electrode potential from 5 to 35 °C using the Fe³⁺/Fe²⁺. Bratsch (1989) presented several standard electrode potential and temperature coefficients. At the same way, Letowsky et al. (1981) showed the Pb/PbSO₄/H₂SO₄ cell potential at 240 °C.

Instead the Nernst equation cannot be directly applied to different temperatures Daniel cell, a qualitative discussion can be done. It was observed from Figure 4, the cell potential is almost independent from temperature when the electrolyte concentrations is high i.e. both are 1 mol L⁻¹. As discussed previews and showed by Buckbee et al. (1969), the standard cell potential decreases with cell temperature increases. Thus, qualitatively the second thermo of Nernst equation increases with temperature at the same intensity of the standard cell potential decreases, for high ion concentration in both electrolytes.

The reduction of the Zn²⁺ concentration has low influences in the cell potential, when the temperature increases, the cell potential present low decreases in comparison with standard cell potential. On the other hand, when the Cu²⁺ concentration is low, the cell potential decreases drastically in comparison with

standard cell potential. The interesting data is low concentration of both electrolytes; of cell potential do not decreases drastically and is not independent from temperature as standard cell potential.

Figure 5 shows the cell potential to the Daniell cell at different temperatures as a function of only Cu^{2+} concentration.

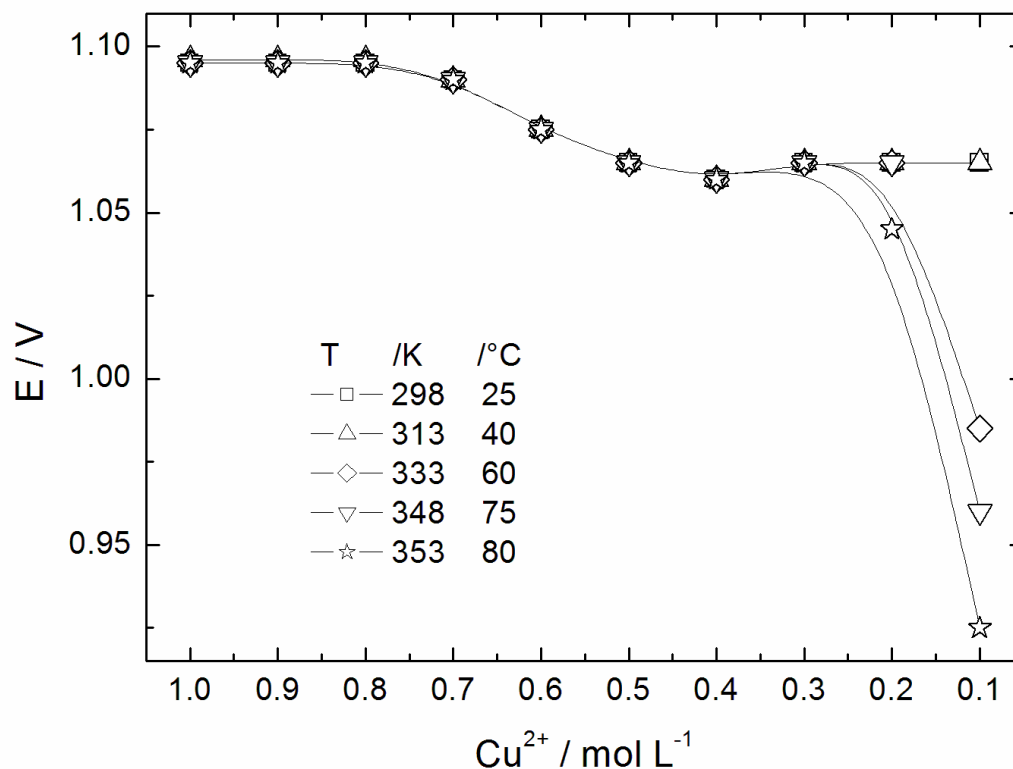


Figure 5. Potential vs. concentration of Cu^{2+} as a function of temperature. $[\text{Zn}^{2+}] = 1.0 \text{ mol L}^{-1}$.

According to Figure 5, the cell potential shows three well-marked regions of concentration relative for all temperatures. The first, from 1.0 to 0.8 mol L^{-1} , shows no variation in the cell potential, regardless of temperature. The second, from 0.8 to 0.4 mol L^{-1} , shows an approximately 4% decrease in the cell potential with a CuSO_4 concentration decrease, all independent from cell temperature. Finally, the third region comprises a Cu^{2+} concentration lower than 0.4 mol L^{-1} , where the cell potential drastically mainly for high temperatures.

As discussed from Figure 4, the Daniel cell potential is more sensitive to Cu^{2+} when the temperature of the cell increases; Figure 5 suggest this cell potential susceptibility is main at lower than Cu^{2+} concentration. Such a different behavior can be assigned to CuSO_4 dissociation. CuSO_4 is a moderate electrolyte, i.e., it is not completely dissociated at high concentrations, and the dissociation increases when get infinitive solubility as Kohlrausch law.

4. Conclusions

The cell potential obtained experimentally for electrolyte solutions of Zn^{2+} and Cu^{2+} investigated at

different concentrations at room temperature are in agreement with those calculated by the Nernst equation (theoretical). Moreover, the calculation of cell potential with using concentrations and the activities of the Zn^{2+} and Cu^{2+} ions in the Nernst equation result close values in all the investigated concentration ranges.

Experimental results showed decrease the cell potential, especially when $[Cu^{2+}]$ is below 0.2 mol L^{-1} . For temperatures above $25 \text{ }^\circ\text{C}$ the Daniel cell potential is more susceptibility to Cu^{2+} concentration.

The study of electromotive force of batteries also led Nernst, this renowned scientist, a century ago (1920-2020) to the discovery of the third law of thermodynamics, thus earning, the Nobel Prize in Chemistry.

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