ABSTRACT

RODRÍGUEZ-VELÁZQUEZ, SORÁNGEL. Development of an Electrochemistry Teaching Sequence using a Phenomenographic Approach. (Under the direction of Maria T. Oliver-Hoyo).

Electrochemistry is the area of chemistry that studies electron transfer reactions across an interface. Chemistry education researchers have acknowledged that difficulties in electrochemistry instruction arise due to the level of abstraction of the topic, lack of adequate explanations and representations found in textbooks, and a quantitative emphasis in the application of concepts. Studies have identified conceptions (also referred to as misconceptions, alternative conceptions, etc.) about the electrochemical process that transcends academic and preparation levels (e.g., students and instructors) as well as cultural and educational settings. Furthermore, conceptual understanding of the electrochemical process requires comprehension of concepts usually studied in physics such as electric current, resistance and potential and often neglected in introductory chemistry courses. The lack of understanding of physical concepts leads to students’ conceptions with regards to the relation between the concepts of redox reactions and electric circuits. The need for instructional materials to promote conceptual understanding of the electrochemical process motivated the development of the electrochemistry teaching sequence presented in this dissertation.

Teaching sequences are educational tools that aim to bridge the gap between student conceptions and the scientific acceptable conceptions that instructors expect students to learn. This teaching sequence explicitly addresses known conceptions in electrochemistry and departs from traditional instruction in electrochemistry to reinforce students’ previous knowledge in thermodynamics providing the foundation for the explicit relation of redox
reactions and electric circuits during electrochemistry instruction. The scientific foundations of the electrochemical process are explained based on the Gibbs free energy (G) involved rather than on the standard redox potential values (E°_{ox/red}) of redox half-reactions. Representations of the core concepts from discipline-specific models and theories serve as visual tools to describe reversible redox half-reactions at equilibrium, predict the spontaneity of the electrochemical process and explain interfacial equilibrium between redox species and electrodes in solution. The integration of physics concepts into electrochemistry instruction facilitated describing the interactions between the chemical system (e.g., redox species) and the external circuit (e.g., voltmeter).

The “Two worlds” theoretical framework was chosen to anchor a robust educational design where the world of objects and events is deliberately connected to the world of theories and models. The core concepts in Marcus theory and density of states (DOS) provided the scientific foundations to connect both worlds. The design of this teaching sequence involved three phases; the selection of the content to be taught, the determination of a coherent and explicit connection among concepts and the development of educational activities to engage students in the learning process. The reduction-oxidation and electrochemistry chapters of three of the most popular general chemistry textbooks were revised in order to identify potential gaps during instruction, taking into consideration learning and teaching difficulties. The electrochemistry curriculum was decomposed into manageable sections contained in modules. Thirteen modules were developed and each module addresses specific conceptions with regard to terminology, redox reactions in electrochemical cells, and the function of the external circuit in electrochemical process.
The electrochemistry teaching sequence was evaluated using a phenomenographic approach. This approach allows describing the qualitative variation in instructors’ consciousness about the teaching of electrochemistry. A phenomenographic analysis revealed that the most relevant aspect of variation came from instructors’ expertise. Participant A expertise (electrochemist) promoted in-depth discussions of fundamental theories and models that explain the electrochemical process while participant B expertise (general chemistry instruction) emphasized a coherent and explicit presentation of such theories and models to students. Other categories of variation were identified as: recognizing students’ conceptions, the use of teaching resources and instructors’ expectations for the teaching sequence. For example, while Participant B depended heavily on representations and explanations found in textbooks, participant A recognized misleading representations and oversimplified statements in general chemistry textbooks. Participant A was also more inclined to question the significance of some conceptions such as the correlation between the use of the term circuit and students’ conceptions related to the movement of electrons in solution in an electrochemical cell. The electrochemistry teaching sequence in this dissertation fulfils each of the instructors’ expectations with regards to the content that incorporated discipline-specific theories and models, explicit connections and flow among concepts, and addressing students’ conceptions via the educational activities developed.
Development of an Electrochemistry Teaching Sequence using a Phenomenographic Approach

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Chemistry

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Robert J. Beichner               Lin He
DEDICATION

To my dearest mom, you are my inspiration and motivation. I will always make you proud.
BIOGRAPHY

Sorángel Rodríguez-Velázquez was born on June 2\textsuperscript{nd}, 1984 in Ponce, Puerto Rico. She was a blessing to her mom Maritza Velázquez. She grew up in a very humble neighborhood in Ponce with her brother (Julio Rodríguez), sister (Maria “Guty” González) and her lovely grandparents (“buelito” and “buelita”). She attended Joaquín Ferrán Elementary school, Eduardo Newman Gandía Middle school and Thomas Armstrong Toro High school. Her love for science motivated her to begin a career in chemistry at the University of Puerto Rico in Ponce where she spent two years and then transferred to the University of Puerto Rico in Mayagüez (UPRM) where she completed a Bachelor’s of Science degree in Chemistry in May 2007. After graduating with Magna Cum Laude from UPRM, Sorángel realized her potential as a scientist and decided to pursue a doctoral degree in chemistry at North Carolina State University. Graduate school brought her many challenges, including learning a new language and being away from home, but she knows that these experiences are shaping her life in many positive ways.
ACKNOWLEDGMENTS

This work could not have been possible without the support of my family, mentors and friends. First, I must recognize the blessings that God has given me with the most loving and supporting family in the world. I am extremely proud of my mom, who has worked very hard to support me and my siblings. Mom, I love and thank you. I must also recognize the invaluable role that my grandparents had contributed in my life. The values they instilled in me are the most valuable gifts that I have. Thank you “buelito” and “buelita”, you are both the love of my life. I also would like to acknowledge the support of my aunt Patricia, who helped me translate many of my college assignments from Spanish to English and vice-versa. I want you to know that you helped overcome the language barrier.

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# TABLE OF CONTENTS

**LIST OF TABLES** ............................................................................................................... viii  
**LIST OF FIGURES** ........................................................................................................... ix  
**LIST OF ABBREVIATIONS** .............................................................................................. xii

Chapter 1 Introduction and literature review ........................................................................ 1  

1.1 Introduction .................................................................................................................... 1  
1.2 Literature review ........................................................................................................... 4  
  1.2.1 Language in science ................................................................................................. 4  
  1.2.2 Chemistry textbooks ............................................................................................... 5  
  1.2.3 Rote application of the concepts ........................................................................... 6  
  1.2.4 Prevalence of students’ conceptions in electrochemistry ....................................... 7  
  1.2.5 Teaching difficulties and instructor conceptions in electrochemistry .................... 11  
  1.2.6 Discrepancies between chemistry and physics instruction .................................... 12  
  1.2.7 Educational activities in electrochemistry ............................................................... 15  
  1.2.8 Teaching sequences as educational tools ............................................................... 17  
References ............................................................................................................................. 20

Chapter 2 Educational theoretical framework and discipline-specific theories and models ................................................. 25  

  2.1 Educational theoretical framework: “Two Worlds” ..................................................... 25  
  2.2 Electrochemistry models and theories ....................................................................... 33  
References ............................................................................................................................. 44

Chapter 3 Research proposal and methodology ................................................................ 47  

  3.1 Research proposal ........................................................................................................ 47  
  3.2 Research methodology ............................................................................................... 48  
    3.2.1 Design of an electrochemistry teaching sequence ............................................... 48  
    3.2.2 The phenomenographic approach ...................................................................... 57  
    3.2.3 Rationale for the use of phenomenography in this study .................................... 58  
    3.2.4 Data collection ..................................................................................................... 59  
References ............................................................................................................................. 61

Chapter 4 Electrochemistry teaching sequence .................................................................. 64  

  4.1 Redox reactions terminology ...................................................................................... 64  
  4.2 Redox nomenclature ................................................................................................... 67  
  4.3 Electrochemical series ................................................................................................. 71
LIST OF TABLES

CHAPTER 2
Table 2.1 Different methods used by experts and novices in the interpretation of representations ................................................................. 28
Table 2.2 Compilation of representative experimental $E_{pzc}$ values versus the normal hydrogen electrode (NHE) reported by Trasatti ........................................ 35

CHAPTER 3
Table 3.1 Compilation of student and instructor conceptions in electrochemistry .. 48

CHAPTER 4
Table 4.1 IUPAC definitions for reduction and oxidation reactions ...................... 64
Table 4.2 Compilation of definitions for oxidizing and reducing agents found in general chemistry textbooks ......................................................... 70
Table 4.3 Proposed redox nomenclature ............................................................. 71
Table 4.4 Compilation of $\Delta H^\circ$ values for the oxidation of metals (calculated using tabulated values) .............................................................. 76
Table 4.5 Comparison between the density of electronic states model for redox species in solution and band theory model for metal electrodes ....................... 96

CHAPTER 5
Table 5.1 Description of categories resulting from the phenomenographic study of instructors’ consciousness about electrochemistry instruction ............. 135
# LIST OF FIGURES

## CHAPTER 2

| Figure 2.1 | Representation of the rendition to the Two Worlds theoretical framework | 27 |
| Figure 2.2 | Electrochemical cell connected to a voltmeter | 30 |
| Figure 2.3 | Representation of the DOS model of metal electrodes (band theory) and redox species (Gerischer model) | 31 |
| Figure 2.4 | Electrochemical cell at the interfacial equilibrium (equilibrium in each half-cell between electrode and redox species in solution) | 33 |
| Figure 2.5 | Relation between Φ and E\textsubscript{pzc} for different crystal faces of Cu, Ag, and Au | 37 |
| Figure 2.6 | Effects of the applied potential (E\textsubscript{applied}) on the Gibbs free energy of redox species in solution | 39 |
| Figure 2.7 | Density of electronic states for redox species in solution | 41 |

## CHAPTER 3

| Figure 3.1 | Proposed sequence of changes for the electrochemistry curriculum | 51 |

## CHAPTER 4

<p>| Figure 4.1 | Representation of the mechanism of the reaction between nitrite and hypochlorous acid | 64 |
| Figure 4.2 | Representation of a 1-electron transfer process | 72 |
| Figure 4.3 | Representation of the thermodynamic cycle for the oxidation of a metal inaqueous solution | 74 |
| Figure 4.4 | Thermodynamic cycle for the oxidation of H\textsubscript{2(g)} to H\textsuperscript{+}\textsubscript{(hyd)} (BD = bond dissociation energy) | 79 |</p>
<table>
<thead>
<tr>
<th>Figure 4.5</th>
<th>Scale for ΔG° values using H$<em>2$(1atm) to H$^+$$</em>{(a=1)}$ oxidation reaction as a reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 4.6</td>
<td>Gibbs free energy representation for a redox half-reaction at equilibrium</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>Gerischer model for the density of electron energy states. Shading designates occupied states. The figure represents a redox solution with equimolar concentrations of Ox and Red as can be deduced from the equal areas under the two curves</td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Distribution of electron energy states for two redox half-reactions and the energy states available for electron transfer between the two redox half-reactions. The diagram shown is for a reaction where electrons (represented by ↑) can flow spontaneously from redox couple #1 to redox couple #2</td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>Representation of an electrochemical cell connected to a voltmeter in which each half-cell contains a solution with both forms of a redox couple present</td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>Electrochemical cell comprised of a redox half-cell at standard conditions connected to SHE. H$<em>2$(1atm) is bubbled through the solution containing Pt wire immersed in H$^+$$</em>{(a=1)}$ solution so that dissolved H$^+$ is in equilibrium with H$_2$(1atm)</td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>Electronic band structure of Au metal for s-type electrons. As the number of atoms increases (N), the number of interactions to form bonding and antibonding crystal orbitals also increases. As an extended structure is approached (N →∞), the discrete energy levels corresponding to the crystal orbitals can be considered as a continuum, hence the formation of an energy band</td>
</tr>
<tr>
<td>Figure 4.12</td>
<td>Before and after the establishment of electrochemical equilibrium between redox species in solution and a metal electrode surface</td>
</tr>
<tr>
<td>Figure 4.13</td>
<td>Electrochemical equilibrium between redox couple and electrode in solution for two redox half-cells</td>
</tr>
<tr>
<td>Figure 4.14</td>
<td>Electrochemical cells using Pt and Au electrodes. $E_{cell}$ calculated from ΔG values</td>
</tr>
</tbody>
</table>
Each electrochemical cell is connected to a low resistance circuit (100 Ω), which let electron transfer to take place between the two redox half-cells.

Basic circuit of a voltmeter in which current is measured in the ammeter and $E_{\text{cell}}$ is determined according to Ohm’s Law.

Relation between external circuit resistance and electron transfer in an electrochemical cell.

Representation of electrochemical cell as shown in textbooks.

Representation of an electrochemical cell for the following redox process: $\text{Cu}^{2+}\text{(aq)} + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}\text{(aq)}$ $E_0^{\text{cell}} = + 1.1$ V. Each redox couple in solution with an electrode represents a redox half-cell (one in each container). The two half-cells are connected by a porous material saturated with electrolyte solution (e.g. KCl) known as the salt bridge. Each redox half-cell is connected to one end of a shunt resistor and the potential is measured in volts using a voltmeter.

(Graph 1) Measured cell potential as shunt resistance changes. (Graph 2) Measured cell potential as the magnitude of current through the cell changes.

Representation of interfacial equilibrium in an electrochemical cell.

Representation of density of states model for a concentration cell. Each graph represents a redox half-reaction containing the ferro/ferri-cyanide redox couple at different concentrations. $G$ values were identified from graphical analysis of the intersection points. $\Delta G$ was determined by subtracting $G$ values of redox half-reactions 1 and 2 as follows: $G^0_2 - G_1 = -31.38 \text{ kJ/mol} - (-26.12 \text{ kJ/mol}) = -5.26 \text{ kJ/mol}$.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Activity of the specie</td>
</tr>
<tr>
<td>BD</td>
<td>Bond dissociation energy</td>
</tr>
<tr>
<td>C</td>
<td>Coulombs</td>
</tr>
<tr>
<td>$C_i^\alpha$</td>
<td>Concentration of species $i$ in phase $\alpha$</td>
</tr>
<tr>
<td>$C_{\text{Red}}$</td>
<td>Concentration of the reduced species</td>
</tr>
<tr>
<td>$C_{\text{Ox}}$</td>
<td>Concentration of the oxidized species</td>
</tr>
<tr>
<td>$C_R(0,t)$</td>
<td>Concentration of reduced species at the electrode surface</td>
</tr>
<tr>
<td>$C_O(0,t)$</td>
<td>Concentration of oxidized species at the electrode surface</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>$D_{\text{vacant}}$</td>
<td>Density of electron- vacant states</td>
</tr>
<tr>
<td>$D_{\text{occupied}}$</td>
<td>Density of electron-occupied states</td>
</tr>
<tr>
<td>$E^{\circ}_{\text{ox/red}}$</td>
<td>Standard redox potential</td>
</tr>
<tr>
<td>$E^{\circ}_{\text{cell}}$</td>
<td>Standard cell potential</td>
</tr>
<tr>
<td>$E_{\text{cell}}$</td>
<td>Cell potential</td>
</tr>
<tr>
<td>$E_{\text{applied}}$</td>
<td>Applied potential</td>
</tr>
<tr>
<td>$E_{\text{eq}}$</td>
<td>Equilibrium potential</td>
</tr>
<tr>
<td>$E_{\text{pzc}}$</td>
<td>Potential of zero charge</td>
</tr>
<tr>
<td>$E^{\circ}$</td>
<td>Energy corresponding to the standard potential</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>G</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$G^{\circ}$</td>
<td>Standard Gibbs free energy</td>
</tr>
<tr>
<td>$\Delta G^{\circ}$</td>
<td>Standard Gibbs free energy change</td>
</tr>
<tr>
<td>$G_{\text{red}}$</td>
<td>Gibbs free energy of the reduced species</td>
</tr>
<tr>
<td>$G_{\text{ox}}$</td>
<td>Gibbs free energy of the oxidized species</td>
</tr>
<tr>
<td>$G^{\text{redox}}_{\text{e}}$</td>
<td>Gibbs free energy of the redox electron(s)</td>
</tr>
<tr>
<td>$G_{\text{cathode}}$</td>
<td>Gibbs free energy for the cathode half-cell</td>
</tr>
<tr>
<td>$G_{\text{anode}}$</td>
<td>Gibbs free energy for the anode half-cell</td>
</tr>
<tr>
<td>$\Delta G^{M}_{\text{e}}$</td>
<td>Gibbs free energy change of the metal</td>
</tr>
<tr>
<td>$\Delta H^{\circ}$</td>
<td>Standard enthalpy change</td>
</tr>
<tr>
<td>$\Delta H^{\circ}_{\text{atom}}$</td>
<td>Standard enthalpy of atomization</td>
</tr>
<tr>
<td>$\Delta H^{\circ}_{\text{hyd}}$</td>
<td>Standard enthalpy of hydration</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>J</td>
<td>Joules</td>
</tr>
<tr>
<td>K</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>M</td>
<td>Metal</td>
</tr>
<tr>
<td>$M^+$</td>
<td>Metal ion</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>N</td>
<td>Number of atoms</td>
</tr>
<tr>
<td>N___</td>
<td>Number of electrons</td>
</tr>
<tr>
<td>n_e_</td>
<td>Number of moles of electrons</td>
</tr>
<tr>
<td>n_{(vac)}</td>
<td>Vacuum electron(s)</td>
</tr>
<tr>
<td>n_{(redox)}</td>
<td>Redox electron(s)</td>
</tr>
<tr>
<td>N_A</td>
<td>Avogadro's number</td>
</tr>
<tr>
<td>N___HE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>Ox</td>
<td>Oxidized species</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>Q</td>
<td>Reaction quotient</td>
</tr>
<tr>
<td>Red</td>
<td>Reduced species</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>ΔS__</td>
<td>Standard entropy change</td>
</tr>
<tr>
<td>T</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>vac</td>
<td>Vacuum</td>
</tr>
<tr>
<td>W_R(λ,E)</td>
<td>Probability density function for the reduced species</td>
</tr>
<tr>
<td>W_R(λ,E)</td>
<td>Probability density function for the oxidized species</td>
</tr>
<tr>
<td>Z__</td>
<td>Effective charge</td>
</tr>
<tr>
<td>z_i</td>
<td>Charge of the species i</td>
</tr>
<tr>
<td>μ_i</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>μ_0__</td>
<td>Standard chemical potential</td>
</tr>
<tr>
<td>μ_α</td>
<td>Electrochemical potential of species i in phase α</td>
</tr>
<tr>
<td>μ__M</td>
<td>Chemical potential of a metal</td>
</tr>
<tr>
<td>Φ</td>
<td>Work function</td>
</tr>
<tr>
<td>Φ</td>
<td>Electrostatic potential</td>
</tr>
<tr>
<td>γ_i</td>
<td>Activity coefficient of species i in phase α</td>
</tr>
<tr>
<td>ν</td>
<td>Stoichiometric coefficient</td>
</tr>
<tr>
<td>λ</td>
<td>Reorganization energy</td>
</tr>
<tr>
<td>χ__M</td>
<td>Surface electrostatic potential</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction and literature review

1.1 Introduction

One of the challenges in chemistry instruction is for instructors to be able to explain the relation between the observable events (macro level) and the corresponding scientific models (micro level)\(^1,2,3\). The multilevel of representations in chemistry were described by Johnstone as micro, macro and symbolic\(^4\). The micro representation refers to concepts such as atoms, molecules and electrons while the macro representation includes the observation and descriptions of the events. The equations and chemical formulas used to represent chemical processes correspond to the symbolic representation. It is found that instructors usually transition between levels of representation without an explicit motivation, purpose or connection between the three levels\(^1\). Instructors often explain events at the micro level without an explicit reference to the phenomena assuming that students understand the purpose and limitations of the micro representations and can apply accurately the symbolism involved\(^3\).

Research has been done with the aim to help students in the connection and transition between levels of representation in chemistry\(^5,6,7,8,9,10\). Computer software has been developed to help students visualize processes at the micro level and to simultaneously relate the micro, macro and symbolic levels of representation during a chemical process\(^8,9\). Teaching strategies that emphasize the three levels of representation during instruction have shown to promote conceptual understanding\(^11,12\). Results indicate that the introduction of a concept departing from macro phenomena followed with explanations using micro
representations may increase students’ motivation as well\textsuperscript{13}. However, in-depth research and more teaching resources to help students in the conceptual understanding of diverse topics in chemistry is needed\textsuperscript{2}.

Electrochemistry is found to be one of the most difficult topics in chemistry for students at different levels of instruction\textsuperscript{14,15,16}. One of the reasons is that most of the concepts studied in electrochemistry are at the micro level of understanding\textsuperscript{17}. For example, students have to understand that electrons are transferred during an electrochemical process even when they are not able to directly observe such process. The symbolic language manifests itself as an additional challenge as students must relate the concepts (e.g., reduced species and oxidized species) to the processes (e.g., reduction and oxidation) in order to successfully apply the terms. Furthermore, the study of electrochemistry requires the understanding of concepts studied in physics such as potential, electric current and electric circuits. However, there is a lack of adequate explanations about these concepts in electrochemistry chapters in general chemistry textbooks\textsuperscript{18,19}. Consequently, one of the difficulties in electrochemistry instruction is to explicitly relate the concepts of redox reactions and electric circuits\textsuperscript{20,21,22,23}.

This project attempts to address the challenges that the study of electrochemistry presents to students by developing a teaching sequence to promote conceptual understanding about the electrochemical process. Teaching sequences are teaching tools aimed to bridge the gap between the concepts to be taught (scientific knowledge) and students’ conceptions\textsuperscript{24,25}. For our purpose the term conceptions will be used when referring to ideas that do not
represent the scientific accepted knowledge, which are commonly defined as misconceptions or alternative conceptions\textsuperscript{23,26}. For example, one common students’ conception is that a voltmeter measures the current through the electrochemical cell\textsuperscript{20}. The development of the teaching sequence should be theoretically framed taking into consideration students’ conceptions\textsuperscript{27}. We used Tiberghien \textit{et al.} proposed framework for the design of teaching sequences that involves the explicit relation between the scientific theories and models to the material world (objects and events)\textsuperscript{25}. The proposed electrochemistry teaching sequence aims at facilitating the explicit connection between the electrochemistry concepts (theories and models) and the observed phenomena (e.g., measurements). The design of the teaching sequence involved the reconstruction of the electrochemistry curriculum, as presented in textbooks,\textsuperscript{18,19} considering teaching and learning difficulties. During the development of the proposed electrochemistry teaching sequence we integrated educational theoretical frameworks and discipline-specific theories and models. This resulted in the incorporation of scientific models and theories often neglected in general chemistry textbooks during the study of electrochemistry, which permitted the explicit and coherent connection among the concepts of redox reactions and electric circuits during instruction.

In our approach, the teaching sequence served as well as a research tool to investigate instructors’ consciousness about the teaching of electrochemistry using a phenomenographic approach. The phenomenography study consisted on identifying the qualitative variation in instructors’ consciousness about different aspects of the teaching of electrochemistry such as: students’ conceptions, educational resources (e.g. textbooks), subject knowledge, and
teaching expectations. Each instructor evaluated each module of the teaching sequence and discussed with the researcher their expectations for the teaching of electrochemistry. The results from these discussions allowed the development of an electrochemistry teaching sequence from the instructors’ perspective. The literature review, research proposal, methodology, electrochemistry teaching sequence, conclusions and proposed future work are presented in this dissertation.

1.2 Literature review

1.2.1. Language in science

Students have to learn a new language when they are learning science. Often students spent more time trying to understand and interpret the language used in chemistry than in learning the actual concepts\(^{28}\). The terminology used to describe the concepts is one of the sources of students’ conceptions in electrochemistry\(^{23,29}\). Most of the terms used in chemistry have their meaning in everyday language and for novices that is the only meaning that they know\(^{30}\). For example, the term “reduction” in everyday language might refer to a decrease in size, amount or degree but electrochemistry reduction refers to a gain of electrons. Conflicts with language come when students fail to translate the everyday meaning of a word to chemistry language, or are unaware of the difference. For example, when referring to the electrochemical cell as an electric circuit, the use of the term circuit can create confusion regarding the movement of charge in the electrochemical process\(^{31}\). In everyday language the movement in a circuit is in a closed, continued, circular pattern. In electrochemistry this is
not the case, where current through the circuit involves the movement of ions in opposite
directions in solution and electrons (from anode to cathode) through the external circuit.
Students often fail to solve a problem in chemistry because they do not comprehend the
scientific language used. This illustrates the need for instructors to explicitly define terms
used during instruction. When instructors use a word to describe a concept there is a chance
that the students construct a completely different mental picture of what the instructor is
trying to convey.

1.2.2. Chemistry textbooks

Textbooks are frequently used as a primary resource during instruction. This practice
benefits students and teachers since textbooks are sources of valuable information. However,
sometimes the statements, diagrams, and terminology used in textbooks could lead to
different interpretations and eventually to inaccurate conceptions. Figures representing
electrochemical cells in textbooks could communicate wrong ideas about the electrochemical
process. As an example, most of the diagrams of electrochemical cells found in textbooks
show the anode on the left and the cathode on the right and this may promote students’
conceptions regarding the dependency of the position of the electrodes and the direction of
the current flow. When an electrochemical cell is represented connected to a voltmeter, a
continuous flow of electrons through the external circuit of the electrochemical cell is often
illustrated. This generates crucial students’ conceptions regarding the characteristics and
function of the voltmeter, since the current through a high resistance voltmeter is almost
zero.
Direct connection between the language used in textbooks and some of the conceptions that students develop has been found. The use of general statements and the lack of explanations of concepts such as electric circuits lead to misinterpretations\textsuperscript{20,23}. For example, the use of the term “the salt bridge completes the circuit”\textsuperscript{19} to define the function of the salt bridge in the electrochemical cell reinforces the students’ conception that electrons flow through the salt bridge and solution during an electrochemical process\textsuperscript{20}.

1.2.3. Rote application of the concepts

Research demonstrated that students who can succeed in chemistry courses often fail questions that require a conceptual understanding of the topic\textsuperscript{2}. Students often memorize rules and equations in order to successfully solve problems without reasoning about the validity of the answers\textsuperscript{36}. Unfortunately, electrochemistry instruction often emphasizes the quantitative aspect of the subject resulting in a lack of conceptual knowledge among students\textsuperscript{16}. It is reported that often instructors promote the use of algorithms found in textbooks without giving an appropriate explanation about the physical meaning of the concepts\textsuperscript{21}. For example, Greenbowe and Sanger indicated that the additive method to calculate the standard cell potential used during instruction $E^{\circ}_{\text{cell}}$ ($E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$), might promote students confusion about the nature of the $E^{\circ}_{\text{cell}}$ value, which is a potential difference between two redox half-cells\textsuperscript{23,34}. 
1.2.4. Prevalence of students’ conceptions in electrochemistry

Students around the world share the same conceptions about electrochemistry, although differences in culture, educational resources and curricula\textsuperscript{14,15,20,21,22,23,29}. Ogude \textit{et al.} studied pre-college and college African students’ conceptions regarding ionic conduction and electrical neutrality\textsuperscript{20,37}. Some of students’ conceptions are that electrons flow through the solution\textsuperscript{15,20,22,23,29,37} and that electrical neutrality in the electrochemical cells means that one half-cell is positively charged with cations in solution and the other half-cell is negatively charged with an equal number of anions\textsuperscript{20}.

Garnett and Treagust reported the challenges that Australian high school students confront when studying electrochemistry\textsuperscript{22,29}. The results indicated that students often are unable to successfully apply the concept of cell potential ($E_{\text{cell}}$) to determine the direction of electron transfer in electrochemical cells. One students’ conception is that the $E_{\text{cell}}$ is due to a difference in electron concentration between two redox half-cells\textsuperscript{22}. In addition, students often described the electron transfer as from high electron concentration (anode) to low electron concentration (cathode)\textsuperscript{29}. Sanger and Greenbowe replicated Garnett and Treagust study and found that American college students’ experience the same students’ conceptions as reported for Australian high school students\textsuperscript{23}.

De Jong and Treagust compiled the studies mentioned above and identified the main areas of difficulties as: confusion when applying the multiple models to identify reduction and oxidation reactions, misinterpretation of the use of plus and minus signs designation when identifying the anode and cathode in electrochemical cells, failure to recognize the
need of a standard reference electrode to measure \( E_{\text{cell}} \), lack of understanding about the concept of electrolytic conduction, rote application of the Nernst equation and instructional gaps in the connection between the concepts (e.g., electron transfer) and the observed phenomena (e.g., measured \( E_{\text{cell}} \))\(^{38}\).

**Difficulties related to the topic of redox reactions**

One common students’ conception is that the three definitions provided for reduction and oxidation reactions can be used simultaneously to identify all redox reactions\(^{22}\). However, the use of multiple definitions (e.g., oxidation = increase in the oxidation state, removal of electrons, or gain of oxygen) can generate confusion among students\(^{16,22,32,39,40}\). For example, the use of oxidation states to identify redox reactions can lead to wrongful assumptions as this is a hypothetical method that does not indicate a transfer of electrons between the reactants. Furthermore, the use of “loss of oxygen and/or gain of hydrogen” to indicate reduction can be confusing as not all redox reactants are organic substrates. Davis suggested the use of multiple definitions in order to describe redox reactions in different contexts; although the definitions provided do not apply to all redox processes\(^{39}\). However, this may lead to inconsistencies in the identification of the redox reactions. There is a need for a more consistent approach when defining redox reactions to emphasize the phenomena of electron transfer, which is essential for the understanding of the redox process.
**Difficulties related to identifying the anode and cathode**

Greenbowe and Sanger found that most students mistakenly identified the anode and cathode in galvanic cells according to the placement of the electrodes in diagrams in textbooks (the anode commonly depicted on the left and the cathode on the right)\(^\text{23}\). In addition, in many instances, students were unable to describe the redox processes occurring in electrolytic cells when the same electrodes (e.g., same metal) or inert metals (not taking part of the redox reaction) were used.

Furthermore, it is found that the plus and minus signs designation for the electrodes generate confusion among students\(^\text{23,29,37}\). For example, one student conception is that the redox process occurring in the anode and cathode depends on the charge on the electrode. Subsequently, students incorrectly assume that the anode undergoes oxidation in galvanic cells (where the anode is negative) and reduction in electrolytic cells (where the anode is positive)\(^\text{23}\). Although the use of plus and minus signs to identify the electrodes is common in textbooks, this concept is not necessary for the understanding of the fundamental aspects of the electrochemical process\(^\text{16,37}\).

**Difficulties related to recognizing the need for a reference**

Students confront difficulties understanding the need for a reference to determine the standard redox potential of a half-cell \((E^\circ_{\text{ox/red}})\)\(^\text{23,29}\). One student conception is that \(E^\circ_{\text{ox/red}}\) is an absolute value and can be used to determine the spontaneity of a redox process (e.g., a negative potential will indicate that the redox half-reaction is spontaneous)\(^\text{23}\). In addition, it
is found that students confront difficulties understanding the fact that $E^{\circ}_{\text{ox/red}}$ for the standard hydrogen electrode (SHE) is arbitrarily assigned as zero. One student common conception is that this value depends on the chemistry of $H^+$ and $H_2^{29}$.

**Difficulties related to the concept of electrolytic conduction**

Some students confront difficulties describing the concept of electrolytic conduction in electrochemical cells$^{15,20,22,23,29}$. One common conception is that electrons flow through the electrolyte solution in electrochemical cells$^{15,19,20,22,23,29}$. It is found that students often describe the movement of electrons in electrochemical cells as: “electrons flowing from the anode through the cathode along the wire, entering the solution from the cathode, traveling through the solution and the salt bridge, and emerging at the anode to complete the circuit”$^{23}$. In addition, students often confront difficulties understanding the function of the salt bridge$^{15,22,23,29,37}$. Some of the reported students’ conceptions are represented by statements such as: “the salt bridge can be replaced by a piece of metal wire”$^{23}$ and “the salt bridge is used if you want the reaction to last longer”$^{37}$.

**Difficulties related to understanding the physical meaning of the Nernst equation**

There is a lack of conceptual understanding of the relations among the concepts of $E^{\circ}_{\text{cell}}$, $E_{\text{cell}}$ and the reaction quotient (Q) for redox processes in electrochemical cells$^{23,29}$. It is found that students often confront difficulties determining Q for redox reactions in concentration cells due to the fact that the reactants and products species are the same. In addition, they confront difficulties understanding the difference between $E^{\circ}_{\text{cell}}$ and $E_{\text{cell}}$ described in the
Nernst equation\textsuperscript{23}. Not surprisingly, students were able to calculate $E_\text{cell}^0$ value, although they confronted difficulties recognizing that $E_\text{cell}^0$ is always zero for spontaneous redox processes in concentration cells. These findings support the need for a conceptual approach to reinforce the relation among $E_\text{cell}^0$, $E_\text{cell}$ and redox couples concentration.

1.2.5. Teaching difficulties and instructor conceptions in electrochemistry

Students learning process depends strongly on the teacher performance during instruction. Instructors’ expertise influences their success in teaching electrochemistry, as it is crucial when conveying conceptual understanding from teacher to student\textsuperscript{14,16,21,38}. It has been found that teachers and students have similar conceptions about electrochemistry. Ozkaya et al. replicated Garnett and Treagust study and investigated conceptual difficulties in electrochemistry experienced by Turkish prospective instructors\textsuperscript{14,21}. The studies showed that instructors and students experience similar difficulties understanding the concepts of potential, electrolytic conduction and redox reactions in electrochemical cells. For example, one instructors’ conception is that the placement of the electrodes in diagrams (anode on the right and cathode on the left) is an International Union of Pure and Applied Chemistry (IUPAC) convention\textsuperscript{14}. Furthermore, the results of the study demonstrated a lack of knowledge among the instructors about the fact that the electrochemical process involves an interfacial equilibrium between the electrodes and redox couples in electrochemical cells\textsuperscript{21}.

De Jong et al. studied the challenge that Dutch high school instructors confronted when teaching the topic of redox reactions\textsuperscript{16}. Teaching difficulties and instructors’ conceptions about their teaching were investigated based on four conditions (intelligible, plausible,
necessary and fruitful) suggested by Posner to facilitate students' conceptual understanding. The results indicated that the instructors were not conscious about most of the teaching difficulties identified by the researcher during instruction due to the lack of time and subject expertise. For example, the instructors claimed the necessity of using the oxidation state model to identify redox species even though this concept was removed from the Dutch curriculum due to the potential conceptions it can generate. Furthermore, redox terminology used by the instructors is inconsistent. For example, instructors often use different terms (e.g., oxidizing agent and oxidant) to refer to the same specie (e.g., reactant that gain electrons during the redox process), which might promote students’ confusion when identifying redox species in a reaction. In addition, the use of phrases such as “the reductant is oxidized” refer to the specie (reactant losing electrons) and the state of this specie (oxidized) can be confusing.

1.2.6. Discrepancies between chemistry and physics instruction

There are discrepancies in the use of teaching models and concept definitions between physics and chemistry instruction. Consequently, students perceive chemistry and physics as disconnected subjects. For example, some students believe that physics is more related to the real world than chemistry. Garnett and Treagust investigated the difference in students’ conceptions about the electrochemical process between physics and non-physics students. The results showed that students taking physics and chemistry courses confront more difficulties understanding the movement of electrons through the external circuit of an electrochemical cell than students not taking physics. Al-Soudi reported the discrepancy in
the models of electric current between chemistry and physics as one of the sources of students’ difficulties in electrochemistry. In electrochemistry the concept of electric current is described as the movement of electrons in a metal conductor and ions (cations and anions) in solution. However, in physics electric current is modeled as the movement of electrons and positive charge. The direction of the movement of positive charge through the conductive material is defined as conventional current. The movement of electrons is defined as electron current and it flows in opposite direction to the conventional current. This model of electric current is introduced in basic physics in order to study the electric and magnetic properties of a metal surface. However, the concept of conventional current can promote conceptions in electrochemistry about positive charge (e.g., protons) flow through the wires (external circuit) and electrolyte solution in an electrochemical cell. Therefore, a unified approach between chemistry and physics could benefit electrochemistry instruction.

**Difficulties related to physics instruction**

The understanding of concepts studied in physics courses such as resistance, electric current and potential is essential during the study of electrochemistry. However, there is a lack of adequate explanations about electric circuits during electrochemistry instruction leaving the electrical part of the electrochemical process ambiguously explained. Consequently, a lack of understanding about the function of the external circuit of electrochemical cells when studying electrochemistry is described in this literature review. The literature review shows the critical importance of the incorporation of
explanations about electric circuits into the electrochemistry curriculum in order to promote
conceptual understanding about the electrochemical process.

Researchers in physics education are also concerned about the students’ difficulties in
relating the macro phenomena with the micro representations. It is reported that physics
students confront difficulties in constructing mental models about the mechanism of current
flow in electric circuits\textsuperscript{47,48}. Thacker \textit{et al.} found that students experienced difficulties
connecting the scientific explanations about electric circuits (micro representations) to the
real phenomena (macro representation)\textsuperscript{47}. They found that students often were unable to
construct models of electric circuits to describe the mechanism of a capacitor in practice. One
common conception among physics students is that electrons “jump” from one plate of the
capacitor to the other. Physics students also experience difficulties with the language used
during instruction as they confront problems in differentiating between the physics
terminology and everyday meaning of a concept\textsuperscript{49}. For example, the meaning of the term
impulse in physics is related to the changes in force with time, but in everyday language the
term impulse is related to a spontaneous response. In addition, there is no differentiation in
the use of the terms current, electricity, energy and power in everyday language\textsuperscript{50}. This
interchangeable use of the terms in everyday language limited the students to distinguish
between these concepts in the study of electric circuits\textsuperscript{51}. It is common among students to use
current and energy as synonymous when they refer to an electrical process\textsuperscript{50,52}. Furthermore,
it is found that physics and chemistry instructors experience similar problems when they
teach electric circuits\textsuperscript{39}. Students in both courses experienced similar conceptions regarding
potential, current and resistance\textsuperscript{40}. For example, as in electrochemistry, physics students
confront difficulties understanding that $E_{\text{cell}}$ refers to a difference rather than to an absolute value\textsuperscript{53}. Therefore, educational tools that promote conceptual understanding about electric circuits are needed.

### 1.2.7. Educational activities in electrochemistry

Educational activities to address students’ conceptions in electrochemistry have been developed. Greenbowe and Sanger reported the development of computer animations to address student conceptions regarding the electrochemical process occurring at the micro level\textsuperscript{8,9}. Computer animations aim to help students connect micro and macro events during an electrochemical process. The results indicated that the use of computer animations during instruction promote conceptual understanding. However, the use of computer animations during instruction depends on the students’ learning strategies\textsuperscript{54} and requires to be coupled to other educational tools\textsuperscript{6}. Huddle \textit{et al.} reported the development of a physical model of the electrochemical cells\textsuperscript{10}. In this model the ions and electrons are tangible objects that students manipulate. This model addresses students’ conceptions regarding the flow of ions and electrons during an electrochemical process. However, since this is a static model, it does not show the dynamic behavior of the process potentially misleading students about the nature of the process.

The traditional teaching approach to electrochemistry consists of the explanation of concepts and the application of routine calculations such as the determination of $E_{\text{cell}}$ using the Nernst equation\textsuperscript{38}. Ahmad and Yeboah developed an experiment that illustrates the validity of using the Nernst equation to describe the redox process\textsuperscript{55}. The experiment consists
of measuring the $E_{\text{cell}}$ of a cell containing the ferro/ferri-cyanide redox couple at different concentrations. A graphical analysis of the results indicates that the $E_{\text{cell}}$ changes with concentration according to the Nernst equation. Thompson and Kateley developed an educational activity that aims to describe the validity of using the Nernst equation to determine the formation constant ($K_{\text{form}}$) of diammine silver (I) complex\textsuperscript{56}. The activity consists of constructing a concentration cell for the Ag/Ag\textsuperscript{+} redox couple. $E_{\text{cell}}$ is measured as the concentration of silver ions changes in one of the half-cells by adding a known amount of ammonia. $K_{\text{form}}$ for the diammine silver (I) complex is determined by calculating the remaining concentration of silver ions using the Nernst equation. However, these activities lack conceptual explanations about fundamental aspects of the electrochemical process such as the relation between the external circuit and redox couples in electrochemical cells when measuring $E_{\text{cell}}$ and the relation between redox concentration and $E_{\text{cell}}$ predicted by the Nernst equation.

Previous studies have introduced concepts studied in physics into the study of electrochemical cells with the aim of helping students understand the electrochemical process and the functionality of the electrochemical cells. Kelter et al. developed an educational activity where students apply Ohm’s law to an electrochemical cell connected to a clock. Students relate current, potential and resistance in order to determine the efficiency of the cell when using orange juice as the electrolyte solution\textsuperscript{57}. Williamson and Morikawa developed an experiment to describe the second law of thermodynamics by modeling an electrochemical cell as a calorimeter\textsuperscript{58}. The experiment consists of measuring the heat absorbed or generated in the cell (calorimeter) as the external resistance changes in order to
determine enthalpy change ($\Delta H$), entropy change ($\Delta S$) and Gibbs free energy change ($\Delta G$) during the electrochemical process. The effect of these activities in promoting conceptual understanding about the electrochemical process has not been investigated. Therefore, research on the effect of educational resources that address students’ conceptions and conceptually relate the electrical and chemical aspects of an electrochemical process are needed.

1.2.8. **Teaching sequences as educational tools**

Teaching sequences are educational tools to facilitate the link between the teaching and learning of a topic\textsuperscript{59}. The design of a teaching sequence involves identifying the teaching goals and strategies needed to present the scientific knowledge to the students aiming for the explicit and coherent connection between the concepts during instruction\textsuperscript{24}. The development of teaching sequences has shown to promote conceptual understanding among students through the explicit connection between scientific explanations and students’ conceptions during instruction\textsuperscript{59,60}. In this dissertation the development of a teaching sequence in electrochemistry is proposed to explicitly relate the concepts of redox reactions and electric circuits taking into account students’ conceptions.

**Teaching sequences in science**

Researchers have developed teaching sequences that aim to address learning and teaching difficulties for diverse topics including solubility, modeling in science and classical mechanics\textsuperscript{61,62,63}. Kabapinar \textit{et al.} developed a teaching sequence to address Turkish middle
school students’ conceptions about the concept of solubility. The teaching sequence applies the “particle model” to facilitate the understanding of the relation between the macro (e.g., mass of the solute) and micro (e.g., movement of the particles) properties of the phenomenon. The teaching sequence aims to address students’ difficulties related to the language used when referring to concepts at the macro and micro level. For example, students tend to erroneously use the term melting instead of dissolving when describing the solubility of particles in a solvent. Although most of the students were able to successfully describe the concepts of dissolving and melting using the particle model, the results of the study indicated no significant difference in students’ understanding of the concept of mass conservation and the macroscopic and quantitative aspects of solubility compared to the traditional approach.

Saari developed a teaching sequence to investigate seventh-grade students’ learning difficulties regarding the concept of modeling. This study was motivated by the discrepancies in the scientific conception and students’ everyday understanding of models. The teaching sequence consisted of educational activities that aim to promote discussions about modeling in science. During the activities students had to construct macro and micro models to describe different states of matter (gas, liquid and solid). The teaching sequence allowed the students to describe and construct scientific models according to the following categories: definition of model, use and purpose of the models, fitness of the model and reasons for changing the model. The analysis of these categories before and after intervention revealed a significant improvement in students’ understanding of scientific models.
Arriassecq and Greca developed a teaching sequence for the introduction of the Special Relativity Theory (SRT) at the high school level. The teaching sequence describes historical, scientific and social aspects of the SRT taking into consideration students’ conceptions about the concepts of time, space, observer, reference frame and simultaneity. A qualitative evaluation of educational tools such as conceptual maps and graphical presentations generated by students during instruction revealed that the teaching sequence allowed the students’ to describe these concepts in terms of classical mechanics.

Teaching sequences have shown to be valuable tools in addressing students’ conceptions in science; however the development of a teaching sequence to address difficulties in electrochemistry instruction has not been reported. This work developed an electrochemistry teaching sequence aimed to provide students and instructors with the scientific foundations required for the understanding of the electrochemical process.
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Chapter 2: Educational theoretical framework and discipline-specific theories and models

The development of the teaching sequence for electrochemistry instruction used an educational theoretical framework (Two Worlds) and discipline-specific theories and models (Marcus theory and Density of States) in order to create a robust instructional resource. The theoretical framework guided the development of the conceptual progression within the electrochemistry sequence as well as the design of the components required to support the implementation of the teaching sequence such as the activities developed for this sequence (found in Appendices A-H). Concurrently, discipline-specific theories and models provided the knowledge-based foundation necessary for effective electrochemistry instruction.

2.1. Educational theoretical framework: “Two Worlds”

Grand theories such as socio-constructivism (Vygotski ) and cognitive development (Piaget) are useful tools to support the design of educational materials1. However, grand theories do not provide specific guidance for the use of teaching strategies; therefore the development of teaching resources requires a theoretical framework with a practical approach2,3. The need for theories that provide specific direction in the design of educational materials motivated Tiberghien et al. to develop the Two Worlds theoretical framework for the design of a teaching sequence in physics3. The “world” of objects and events include the measurements and observations. The “world” of theories and models include the scientific explanations to the observable events. The world of theories and models relates to the world of objects and events through the “modeling activity”, which involves the construction of
mental models of the concepts to explain the observable events. The Two Worlds theoretical framework was adopted for the design of an electrochemistry teaching sequence that explicitly relates the concepts of redox reactions and electric circuits to explain electrochemical processes. In this proposed electrochemistry teaching sequence, students’ conceptions in electrochemistry are addressed by relating the “world” of theories and models using terminology, diagrams and analogies as teaching tools. Observations and experiments are used to explore the “world” of objects and events. Figure 2.1 is my own rendition of this framework relating objects, events, theories and models with the incorporation of teaching tools such as observations, experiments, terminology, diagrams and analogies.

In this application of the Two worlds framework, the objects represent concepts studied in electrochemistry (energy, oxidation, reduction, equilibrium) and the measurements (e.g. potential, current) are considered the events. Experimentation provides the means to connect objects and events since experiments allow the measurement of the events. The objects and events connect to theories and models through the modeling activity (illustrated by the double arrows) which may facilitate the interactions between the Two Worlds.
Consistent use of terminology is essential in communicating clearly the knowledge-base about concepts and processes. Definitions of the terms allow describing models and theories in electrochemistry and connecting concepts in the teaching sequence. For example, the concept of redox reactions is defined in terms of the electron transfer mechanism involved in an electrochemical process. This approach facilitates connecting the concepts (oxidized and reduced species) to the process (oxidation and reduction) in a consistent manner.

Diagrams effectively used as teaching tools facilitate identifying and relating concepts during instruction. Furthermore, diagrams allow tracking a particular event during an electrochemical process. In this way, the concretization of abstract concepts and events in electrochemistry is facilitated. In this dissertation, representations of the core concepts of the
density of states (DOS)\textsuperscript{5,6} and Marcus theory\textsuperscript{5} allow the qualitative description of the relation between the $E_{\text{cell}}$ and the chemical nature of the redox process. For example, an increase in the density of electronic states of the oxidized species (increase the concentration of oxidized species in solution) shifts the position of the Fermi level in the half-cell, resulting in an increased $\Delta G$ which is reflected in a more positive $E_{\text{cell}}$.

We aim to represent models and theories used by electrochemistry experts keeping in mind that students (novices) and experts differ on the methods used for the interpretation of representations\textsuperscript{7}. Table 2.1 summarizes a compilation of different methods used by experts and novices in the interpretation of representations\textsuperscript{7,8}. Expert interpretations of representations involve a more holistic and integrated view of the components, whereas novices concentrate their efforts understating local features of the representation, resulting in a more compartmentalized view of the system\textsuperscript{9,10}. One of the challenges is to overcome the knowledge barrier between students (novices) and instructors (experts). In order to bridge the gap between novices and experts, we need to explicitly guide the students through the tasks required for scientific understanding of the representations (expert like).
Table 2.1: Different methods used by experts and novices in the interpretation of representations.

<table>
<thead>
<tr>
<th>Expert</th>
<th>Novice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addresses the meaning, location and behavior of the components</td>
<td>Lacks recognition about integral components</td>
</tr>
<tr>
<td>Recognizes higher order relationships between the components</td>
<td>Shows deficiencies relating components</td>
</tr>
<tr>
<td>Uses scientific models and theories to explain events</td>
<td>Uses common sense to explain events</td>
</tr>
<tr>
<td>Views the representation as a whole</td>
<td>Sees representation as disconnected components</td>
</tr>
</tbody>
</table>

Two of the most important aspects in the interpretation of diagrams are the discrimination and relation among components\(^4\),\(^11\). The level of discriminatory reasoning depends on previous knowledge about the concepts that the representation aims to convey. The relation between the concepts depends on placement and meaning given to the components in the representation. In order to promote a scientific approach in the interpretation of diagrams we aim to guide the students through distinct descriptions of the static and dynamic models as well as the outcomes of the models\(^8\). Static models represent the relative location of the components (anode, cathode, oxidized species, reduced species, ions, electrons) in a single situation. For the static model in Figure 2.2, electrochemistry experts may identify the anode and cathode according to the electrochemistry convention for measuring \(E_{\text{cell}}\) as follows: \(E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{red}} - E_{\text{black}}\); while students (novices) often assume that the anode is always located on the left and cathode on the right side of the electrochemical cell as commonly depicted in textbooks\(^12\). In our approach, we introduce the concept of electrochemistry conventions to address students’ difficulties identifying the anode and cathode in electrochemical cells. The dynamic model describes processes such as
transfer of electrons, equilibrium and ionic conduction. The modeling of these dynamic processes involves identifying and relating the components in the representation which allow describing the outcomes of these processes. An expert-like interpretation of the dynamic model in Figure 2.2 would predict an interfacial equilibrium between the electrode and redox species in solution; however, a novice-like interpretation may reveal a disconnected view of the external circuit and electrochemical cell as students confront difficulties relating the concepts of electric circuits and redox reactions to predict electron transfer between the redox half-cells\textsuperscript{13,14,15,16,17}.

Figure 2.2: Electrochemical cell connected to a voltmeter.

In our approach, each of the components and processes in the electrochemical cell and external circuit are modeled using individual representations demonstrating: Gibbs free energy of redox couples, Fermi level, current through the cell and the basic circuit of a
voltmeter. Relating the components of the representations allows explaining events such as interfacial equilibrium and electron transfer between redox half-cells.

Analogies are important in the explanation of unfamiliar and abstract ideas and have been successfully used during instruction to bridge the gap between students’ conceptions and the target concept\textsuperscript{18,19,20}. Analogies may assist the learning process by connecting the new concepts to situations or ideas that students are familiar with and making the target concept less intimidating. The use of analogies in the teaching sequence facilitates connecting theories and models to the knowledge-base that we intend students’ to learn (target concept). For example, the introduction of the concept of interfacial equilibrium is facilitated by comparing similarities and differences between the DOS of redox species and metal electrodes in solution; within such models, the following components can be compared: Gibbs free energy, Fermi level, electron-occupied states and electron-vacant states as shown in Figure 2.3.

![Figure 2.3: Representation of the DOS model of metal electrodes (band theory) and redox species (Gerischer model).](image)
We developed educational activities to address students’ conceptions by connecting scientific models and theories to electrochemical measurements (events). For example, one of the activities aims for the students to describe the concept of interfacial equilibrium by comparing and integrating the DOS of redox species (Figure 2.3B) and metal electrodes (Figure 2.3A). This activity addresses students’ conceptions regarding the function of inert electrodes in electrochemical processes (see Appendix D).

### 2.2. Electrochemistry models and theories

The introduction of fundamental aspects of models and theories used by experts to describe the electrochemical process allow explaining concepts and processes that are missing or oversimplified by the traditional approach. The following discipline-specific models and theories were incorporated into the design of the teaching sequence in electrochemistry.

**Electrochemical potential**

The electrochemical potential describes the energy for the chemical and electrical interactions of the redox species and solvent molecules in solution. The relation between Gibbs free energy (G) and chemical composition of species is defined by the chemical potential \( \mu_i^\alpha \) as follows:

\[
\mu_i^\alpha = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j\neq i}}
\]

where \( n_i \) is the number of moles of i in phase \( \alpha \).
The electrical energy required to move charged species from one point to another is proportional to the electrostatic potential ($\varphi$). Thus, the electrochemical potential ($\mu_i^\alpha$) is defined as follow:

$$\mu_i^\alpha = \mu_i^\alpha + z_i F \varphi^\alpha = \mu_i^{0 \alpha} + RT \ln a_i^\alpha + z_i F \varphi^\alpha$$

where $z_i$ represents the charge of the species $i$, $F$ is the Faraday constant (96,485 C/mol), $\mu_i^{0 \alpha}$ is the standard chemical potential and $a_i^\alpha$ is activity.

Figure 2.4 shows an electrochemical cell for the following redox reaction:

At equilibrium,

$$\text{Fe}^{3+} \text{(aq)} + e^-\text{(Pt)} \rightleftharpoons \text{Fe}^{2+} \text{(aq)}$$

$$\text{Cr}^{2+} \text{(aq)} \rightleftharpoons \text{Cr}^{3+} \text{(aq)} + e^-\text{(Pt')}$$
\[ e^-(\text{Pt}) + \text{Cr}^{2+}(\text{aq}) + \text{Fe}^{3+}(\text{aq}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + \text{Cr}^{3+}(\text{aq}) + e^-(\text{Pt}) \]

Then,

\[ \bar{a}_{e}^{\text{Pt}} + \bar{a}_{\text{Cr}}^{2+} + \bar{a}_{\text{Fe}}^{3+} = \bar{a}_{\text{Fe}}^{2+} + \bar{a}_{\text{Cr}}^{3+} + \bar{a}_{e}^{\text{Pt}} \]

\( \mu_i^a = 0 \) for species in their most stable configuration under standard conditions (pure substances and \( p = 1 \) atm).

Furthermore,

\[ \bar{a}_{e}^{\text{Pt}} - \bar{a}_{e}^{\text{Pt}'} = \frac{\Delta G^\circ + R T \ln (a_{\text{Fe}}^{2+}) \cdot (a_{\text{Cr}}^{3+})}{(a_{\text{Fe}}^{3+}) \cdot (a_{\text{Cu}}^{2+})} \]

where

\[ \Delta G^\circ = \mu_{\text{Fe}}^{0s} + \mu_{\text{Cr}}^{3s} - \mu_{\text{Fe}}^{3s} - \mu_{\text{Cr}}^{2s} = \text{FE}_{\text{cell}}^\circ \]

Thus, we arrive at

\[ E_{\text{cell}} = E_{\text{cell}}^\circ + R T \ln \left( \frac{(a_{\text{Fe}}^{2+}) \cdot (a_{\text{Cr}}^{3+})}{(a_{\text{Fe}}^{3+}) \cdot (a_{\text{Cu}}^{2+})} \right) \]
which is the Nernst equation for the electrochemical cell.

**Potential of zero charge**

Excess charge on a metal electrode surface is related to its electrostatic potential and the nature of the metal – solution interface. The electrode potential at which the excess charge on the metal surface is zero is known as the potential of zero charge ($E_{pzc}$). Table 2.2 is a compilation of representative experimental $E_{pzc}$ values obtained by various authors using different experimental techniques\textsuperscript{21}.

Table 2.2: Compilation of representative experimental $E_{pzc}$ values *versus* the normal hydrogen electrode (NHE) reported by Trasatti\textsuperscript{21}.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E_{pzc}$ (V) vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-0.63</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.62</td>
</tr>
<tr>
<td>Al</td>
<td>-0.52</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.44</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.35</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.30</td>
</tr>
<tr>
<td>Pt</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>0.09</td>
</tr>
<tr>
<td>Au</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The $E_{pzc}$ value is dependent on the chemical free energy of the valence electrons in an uncharged metal in vacuum. For example, the free energy of the valence electrons of Pt metal in vacuum is lower than for the energy of the valence electrons in Zn. This is reflected in the difference in $E_{pzc}$ values for the metals shown in Table 2.2.
Efforts have been made to relate fundamental properties of the metal to the $E_{\text{pzc}}$. The chemical potential of a metal ($\mu_e^M$) describes changes in the chemical free energy when an electron is removed or added from the metal surface according to the following equation:

$$\mu_e^M = \left( \frac{\partial G}{\partial n_e} \right)_{T,P,n_i\neq i}$$

where $\partial G$ is the change in chemical free energy and $n_e$ is the number of moles of electrons on the metal at constant temperature and pressure.

Experimental determination of $\mu_e^M$ is obtained by measuring the work function $\Phi$ of the metal. $\Phi$ is defined as the minimum energy required to remove an electron from the Fermi level of an uncharged metal into vacuum$^{22}$. Analogous to the ionization energy (IE), which is the minimum energy required to remove an electron from a free gaseous atom.

The relation between $\Phi$ and $\mu_e^M$ is described by the following equation:

$$\Phi = -\mu_e^M + F \chi^M$$

where $F$ is the faraday constant 96,500 C/mol e- and the $\chi^M$ value is the surface electrostatic potential which accounts for the difference in metal crystal face.

The measured value of $\Phi$ is related to $E_{\text{pzc}}$ according to the following equation:

$$E_{\text{pzc}} = \frac{\Phi}{F} + \text{const}$$
The $E_{pzc}$ values indicate the energy required to remove an electron from the inert metal surface. For example, according to the values reported in Figure 2.5, in order to remove an electron from a Au metal surface, a potential greater than 0.5 V is required. Electrons are removed from or added to the metal surface depending on the sign and magnitude of the potential applied. For example, according to the $E_{pzc}$ values reported in Table 2.2, if a potential of -0.30 V is applied, excess negative charge would be induced on Au ($E_{pzc} = 0.18$ V) whereas Zn ($E_{pzc} = -0.63$ V) would develop excess positive charge.

The value of $E_{pzc}$ also includes the effects of electrolyte solution, temperature and metal crystal face on the electrostatic potential. When a metal is immersed in solution a surface potential develops due to the dipole interactions between the solvent molecules in the electrolyte solution and the electrons at the metal surface. Surface potential differs depending on the nature of the electrolyte solution. The orientation of the solvent molecules
at the metal surface depends on the thermal motion of the molecules in solution and the arrangement of atoms in the metal.

**Marcus theory for electron transfer**

Marcus theory, introduced by Rudolph A. Marcus, predicts electron transfer rates in terms of Gibbs free energy and molecular configuration (bond angle, bond length, etc.) of donor (reduced) and acceptor (oxidized) species in solution. Changes in molecular configuration result from vibrational and rotational motions of the reduced and oxidized species and from the reorientation of the solvent molecules due to electron transfer. The theory assumes that changes in molecular configuration are slow compared with the process of electron transfer, according to the Frank-Condon principle. Electron transfer has been modeled for heterogeneous (between redox species in solution and electrode) reactions where the donor and acceptor are close enough for the electron to “jump” from one species to the other. At the moment of electron transfer, the total Gibbs free energy and nuclear configurations of the electron donor (reduced species) and the electron acceptor (oxidized species) are the same.

The point where the energy and nuclear configuration of the reduced and oxidized species are the same is known as the transition state. The energy required to transform the nuclear configurations of the reduced species and solvent to those of oxidized species in solution is known as the reorganization energy ($\lambda$). Figure 2.6 represents an energy diagram for electron transfer between reduced and oxidized species. One parabola corresponds to the total Gibbs free energy of the reduced species and the other to the oxidized species and
electron. The bottom of the curves represents the Gibbs free energy at equilibrium which corresponds to the equilibrium potential ($E_{eq}$) for the redox couple.

![Diagram](image)

**Figure 2.6:** Effects of the applied potential ($E_{applied}$) on the Gibbs free energy of redox species in solution. When potential is applied to the electrode the total energy of the shift by $F(E_{applied} - E_{eq})$; therefore the corresponding curve moves up or down by that amount.
Density of electronic states (DOS)

The DOS model introduced by Gerischer describes the number of available electronic states per energy interval for a redox couple in solution. Electron occupied states correspond to the reduced species and electron vacant states to the oxidized species. The energies of the electronic states for the reduced and oxidized species are distributed over a range according to the concentration density functions of electron-occupied states $D_{\text{occupied}}$ and electron-vacant states $D_{\text{vacant}}$, respectively. $D_{\text{occupied}}$ and $D_{\text{vacant}}$ are defined in terms of concentration as follow:

$$D_{\text{occupied}}(\lambda, E) = N_A C_R(0,t) W_R(\lambda, E)$$

$$D_{\text{vacant}}(\lambda, E) = N_A C_O(0,t) W_O(\lambda, E)$$

where $E$ is energy, $N_A$ is Avogadro’s number, $t$ is time in seconds, $C_R(0,t)$ and $C_O(0,t)$ are concentrations of reduced and oxidized species at the electrode surface and $W_R(\lambda, E)$ and $W_O(\lambda, E)$ are the probability density functions for the reduced and oxidized species, respectively.

This model assumes a Gaussian distribution of energy states resulting from thermal fluctuations of the molecules and solvent in solution. $W_R(\lambda, E)$ and $W_O(\lambda, E)$ describe this Gaussian distribution as follows:

$$W_R(\lambda, E) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(E - E^o + \lambda)^2}{4\lambda kT}\right]$$

$$W_O(\lambda, E) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(E - E^o - \lambda)^2}{4\lambda kT}\right]$$
where $k$ is the Boltzmann constant ($1.3806 \times 10^{-23}$ J/K), $T$ is temperature in Kelvins and $E^o$ is the energy corresponding to the standard potential.

According to the equation above, the Gaussian curves have a mean at $E = E^o \pm \lambda$ and a standard deviation of $0.53\lambda^2$ as shown in Figure 2.7. The energy at $E^o$ is defined as the energy level of the highest occupied electronic state of the redox couple, also known as the Fermi level of the solution. Electron transfer occurs between the Fermi level of the electrode and the Fermi level of the redox species in solution. The solution Fermi level is a direct reflection of the location of the energy state for the electron transferred, i.e., the “redox electron”.

Figure 2.7: Density of electronic states for redox species in solution$^{5,6}$. 

42
The relative positions of these curves (\(D_{\text{occupied}}\) higher than \(D_{\text{vacant}}\)) results from the interactions and reorientations of solvent dipoles with the two redox states, which are differently charged. In this model, distributions of \(D_{\text{occupied}}\) and \(D_{\text{vacant}}\) have the same shape, but \(D_{\text{vacant}}\) is centered on \(E^o + \lambda\) and \(D_{\text{occupied}}\) on \(E^o - \lambda\) as shown in Figure 2.7. For example, in the case of the redox couple \(\text{Fe}^{3+}/\text{Fe}^{2+}\), the oxidized state carries the higher charge, which exerts relatively greater attraction for the negative ends of solvent dipoles. This, in turn, produces a more negative electrostatic field at the redox orbital, thus raising its energy. The reduced state, on the other hand, carries the lower charge, which results in a less negative electrostatic field at the redox orbital due to weaker attraction to the negative ends of solvent dipoles and therefore a lower relative electron energy level.
REFERENCES


Chapter 3: **Research proposal and methodology**

3.1. Research proposal

The research motivation for this work is rooted on the difficulties experienced by instructors and students alike during the teaching and learning of electrochemistry which have been well documented\(^1,2,3,4,5,6,7,8,9\). Some of the difficulties are related to the nature of the topic which is highly abstract and integrative of concepts from other disciplines. The oversimplification of concepts\(^2,3,4\), inaccurate representations used in textbooks\(^10,11\) and an emphasis on a quantitative approach in electrochemistry instruction\(^8,9\) results in a lack of conceptual knowledge such as the interactions between electric circuits and redox reactions during electrochemical processes and the thermodynamic nature of the $E_{\text{cell}}$ values. An example identified as a source of conceptions is the transfer of electrons and the function of the external circuit in electrochemical cells\(^1,3,12\). Remarkably, findings reveal that similar electrochemistry conceptions are persistence among students and instructors worldwide.

The teaching sequence developed addresses students’ conceptions in electrochemistry through the explicit connection between the concepts of redox reactions and electric circuits. A theoretical framework was used to incorporate discipline-specific models and theories into the electrochemistry curriculum in order to facilitate conceptual explanations about the scientific nature of the electrochemical process. The proposed teaching sequence was used as a tool to investigate the different ways in which chemistry instructors experience the teaching of electrochemistry. A phenomenographic study allows describing the qualitative variation in instructors’ consciousness during the development of an electrochemistry teaching sequen
3.2 Research methodology

The methodology in this study involved the design of the instructional material (teaching sequence) based on the “Two Worlds” theoretical framework and discipline-specific theories and models along with discussions about such materials with chemistry instructors following a phenomenographic approach.

3.2.1 Design of an electrochemistry teaching sequence

Teaching sequences aim to bridge the gap between student conceptions and the scientific acceptable conceptions students are expected to learn. Buty et al. approaches the development of teaching sequences in three phases; selection of the content, determination of the order in which the content is to be presented and adoption of educational tools and teaching strategies to introduce concepts. The first phase includes the identification of knowledge to be taught taking into consideration learning objectives and students conceptions.

Selection of content for the development of the teaching sequence

We listed the most predominant electrochemistry conceptions among students and instructors found in the literature as shown in Table 3.1
Table 3.1: Compilation of student and instructor conceptions in electrochemistry.

<table>
<thead>
<tr>
<th>Concept</th>
<th>Conceptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox terminology</td>
<td>“The multiple definitions provided for oxidation and reduction can be used interchangeably to identify redox species in all chemical reactions”</td>
</tr>
<tr>
<td>Redox thermodynamic</td>
<td>“The $E^{\circ}_{\text{ox/red}}$ value of a redox half-reaction determines the spontaneity of the reaction rather than the potential difference”</td>
</tr>
<tr>
<td>Reference electrode</td>
<td>“The $E^{\circ}_{\text{ox/red}}$ value for the standard hydrogen electrode (SHE) depends on the chemical nature of the $\text{H}_2(\text{1 atm})$ and $\text{H}^+(\alpha=1)$ species (not realizing that it is arbitrarily assigned to be zero)”</td>
</tr>
<tr>
<td>Electrodes</td>
<td>“No reaction will occur if inert electrodes are used”</td>
</tr>
<tr>
<td>Electrochemistry conventions</td>
<td>“$E^{\circ}_{\text{cell}}$ for non-spontaneous processes in electrolytic cells can be positive”</td>
</tr>
<tr>
<td>Electrochemistry nomenclature</td>
<td>“The cathode undergoes reduction in a galvanic cell and oxidation in an electrolytic cell”</td>
</tr>
<tr>
<td>Electrolytic conduction</td>
<td>“Electric current in the electrochemical cells is due to the movement of electrons and protons in opposite directions”</td>
</tr>
<tr>
<td>Salt bridge</td>
<td>“A metal can be used as a salt bridge”</td>
</tr>
<tr>
<td>Voltmeter</td>
<td>“The voltmeter measures the electron flow through the electrochemical cell”</td>
</tr>
<tr>
<td>Nernst equation</td>
<td>“Determining $E^{\circ}<em>{\text{cell}}$ equal to zero and obtaining a nonzero $E^{\circ}</em>{\text{cell}}$ is inconsistent with spontaneous redox reactions in concentration cells”</td>
</tr>
<tr>
<td></td>
<td>“The reaction quotient (Q) for redox reactions in concentration cells cannot be calculated because products and reactant species are the same”</td>
</tr>
</tbody>
</table>

These findings motivated the analysis of the oxidation-reduction and electrochemistry chapters of three of the most popular general chemistry textbooks. When reviewing the textbooks, the focus was on the terminology, representations, and content gaps as it was
hypothesized that these were the main sources of students’ conceptions. For example, the terminology used in electrochemistry to differentiate concepts and processes include redox species (oxidized ad reduced), redox processes (oxidation and reduction) and electrodes in an electrochemical cell (anode and cathode). Multiple terms and definitions are used to identify reducing agents (reduced specie, electron donor and reductant) and the oxidation process (e.g., an increase in the oxidation number of any atom within any substrate, the complete net removal of one or more electrons from a molecular entity or gain of oxygen and/or loss of hydrogen of an organic substrate). In many instances, the terminology found in textbooks to describe scientific concepts and processes is inconsistent and confusing and can potentially contribute to students difficulties identifying redox reactions in electrochemical processes\textsuperscript{19,9}.

The relation between concepts and processes in electrochemistry is often represented in an inaccurate and oversimplified manner. A single representation of an electrochemical cell is used to identify the chemical (redox species) and electrical (electrodes and external circuit) components, relate the concept and process (anode / oxidation, cathode / reduction) and introduce physics concepts such as electric current and potential. This results in omitting explanations about important aspects of the electrochemical process such as the Fermi level difference and the interfacial equilibrium in electrochemical cells. Furthermore, these representations explicitly promote the erroneous conception about electrons flowing through an electrochemical cell when connected to a voltmeter\textsuperscript{10}.

The thorough analysis of the textbooks pointed at a crucial gap between chemistry (e.g., Gibbs free energy, chemical equilibrium) and physics (e.g., potential, current) concepts during the explanation of the electrochemical process leaving the electrical components of
the electrochemical cell (external circuit) ambiguously explained. Vague explanations about electric circuits, the characteristics of the voltmeter and the relation between the electrochemical process and the $E_{\text{cell}}$ were consistently found. The proposed teaching sequence aims to address students’ conceptions by integrating scientific models and theories to explicitly relate the redox reactions and electric circuits in electrochemical processes. The proposed teaching sequence reinforces students’ previous knowledge in thermodynamics and introduces physics concepts in order to explain the electrochemical process.

Students’ and instructors conceptions were identified from the literature and textbooks were analyzed as they provide the tools to identify conceptions that needed to be addressed and instructional gaps in content knowledge. These led the way to the appropriate selection of content.

**The process of designing the teaching sequence**

The development of the teaching sequence involved the decomposition of the curriculum into small segments, reconnection of each segment and the integration of activities through an explicit and theoretically-based manipulation of the concepts to be taught as suggested by Buty et al.\(^{13}\). This proposed teaching sequence shifts the frame of reference of electrochemistry instruction from a quantitative approach based on $E^{\circ}_{\text{ox/red}}$ to a conceptual approach based on the Gibbs free energy ($G$) of the redox reaction. The electrochemistry curriculum was decomposed into manageable sections contained in modules. Each module addresses a particular student conception (presented in Table 3.1) as related to terminology, redox process or the relation between the electric circuits and redox reactions in electrochemical cells. The ordering of the modules took into account a coherent
and explicit connection between concepts. Figure 3.1 describes the proposed sequence of changes for electrochemistry instruction. Each “block” represents a module in which the introduction of concepts is highly dependent on the content from previous modules. Blocks highlight the main difference this teaching sequence presents.

Figure 3.1: Proposed sequence of changes for the electrochemistry curriculum.

The following actions were taken in order to connect student conceptions to the knowledge that was intended for students to learn:

1. In order to avoid students confusion when using multiple definitions provided by IUPAC for reduction and oxidation reactions, we adopted a single definition (reduction is defined as the transfer of one or more electrons to a molecular entity and
oxidation is the complete removal of one or more electrons from a molecular entity) to emphasize the role of electron transfer mechanism involved in electrochemical processes and facilitate identifying reduction and oxidation reactions in a consistent manner.

2. Redox terminology is related to the electron transfer process rather than using the various terms found in textbooks (e.g., reducing agents = reduced species, electron donor and reductant) which are complex and confusing for students to apply. For example, the oxidized and reduced species are defined in terms of electron donor and electron acceptor respectively.

3. Instead of building the electrochemistry foundation departing from the concept of $E^{\circ}_{\text{ox/red}}$, the relative activity of the redox species is determined by comparing enthalpy change ($\Delta H$) values, which are obtained by constructing thermodynamic cycles for the oxidation process. For example, by comparing $\Delta H$ for different metals we can justify the low activity of Pt ($\Delta H = 1601$ kJ/mol) relative to others metals. These cycles are not currently used even though they provide not only an appropriate sequence, but also reinforce previous concepts and build on a thematic coherent approach describing energy as the driving force.

4. In this sequence, the chemical nature of electrochemical processes is described in terms of the Gibbs free energy of the redox electron(s) ($G_{\text{redox}}$) for redox half-reactions at equilibrium: $\text{Red} \rightleftharpoons \text{Ox} + n\text{e}^-_{(\text{redox})}$. The following aspects are currently avoided in general chemistry textbooks:
a. The core concepts of Marcus theory are introduced to describe $G_e^{\text{redox}}$ and equilibrium between redox species$^{20,21}$. This approach allows determining $G_e^{\text{redox}}$, which is an approximation to the standard Gibbs free energy change ($\Delta G^\circ$) value for a reversible redox half-reaction at equilibrium.

b. The core concepts of the DOS model are introduced to indicate the relative position of $G_e^{\text{redox}}$ (Fermi level) and predicts the spontaneity of redox reactions$^{20,21,22}$. This approach allows defining $E_{\text{cell}}$, which is a measure of the difference in $G_e^{\text{redox}}$ of the redox half-cells at equilibrium.

5. The textbooks analyzed do not emphasize the significance of using reference electrodes for determining $E_{\text{ox/red}}^\circ$. In this sequence, $E_{\text{ox/red}}^\circ$ is determined using the SHE as a reference and compared to tabulated values.

6. We avoid using the oversimplify explanations of the electrochemical process found in textbooks, instead the concept of interfacial equilibrium is introduced to explain the interactions between electrodes and redox species in solution using analogies as teaching tools. This teaching sequence utilizes representations from DOS to illustrate the equilibrium that occurs between the solution Fermi level and metal Fermi level when the electrode is immersed in the redox solution.

7. In this sequence, the function of electrodes in electrochemical processes is described in terms of thermodynamic values. This approach allows differentiating between active and inert electrodes using $\Delta G$ values. For example, we describe the function of silver (Ag) metal as an inert or active electrode according to the Gibbs free energy value of the redox species in the electrochemical cell. Unfortunately, there is lack of
adequate descriptions of active and inert electrodes in textbooks which may promote the lack of understanding among students with regard to the function of those electrodes in electrochemical processes.

8. The electrochemical set-up (cathode connected to the red lead of the voltmeter and the anode to the black lead) is commonly illustrated in textbooks without referring to the relation between the sign of the measured potential and the electrochemical conventions. In this sequence, electrochemical conventions are introduced in order to relate the sign of $E_{\text{cell}}$ to the spontaneity of an electrochemical process in a consistent manner. For example, an electrochemical set-up where the $G$ value of the anode half-cell is higher than that of the cathode half-cell results in a positive $E_{\text{cell}}$. This approach facilitate identifying the cathode and anode in an electrochemical cells.

9. Representations of electrochemical cells found in textbooks commonly use signs designations (plus and minus) to identify the cathode and anode; however, the sign designations for electrodes in electrochemical cells have shown to promote students’ conceptions\(^1,2,3,4\); therefore they are removed from the teaching sequence and fundamental concepts in electrochemistry are explained without addressing the sign of the charge on the electrode.

10. The misinterpretation of general statements and language used in textbooks has been identified as source of student conceptions regarding the concept of electric current in electrochemical cells\(^5\). This sequence explains the concept of electric current taking into consideration students’ conceptions about the function of the salt bridge and the movement of charge through the salt bridge, solution and external circuit.
11. The study of electrochemical processes requires the integration of redox reactions and electric circuits; however, there is lack of explanations about physics concepts such as resistance, current and electric circuits in the electrochemistry chapters revised. In this sequence, we describe the basic circuit of a voltmeter and the $E_{\text{cell}}$ is measured according to Ohm’s law.

12. Remarkably, representations found in textbooks erroneously illustrate a significant flow of electrons in electrochemical cells connected to a voltmeter, when in fact the current through a high resistance voltmeter is almost zero. In this sequence, students determine the electrical (resistance and current) and chemical conditions for measuring $E^{\circ}_{\text{cell}}$. This is crucial for students to understand the function of the voltmeter and integrating the concepts of redox reactions and electric circuits. For example, when measuring the $E^{\circ}_{\text{cell}}$ with a high resistance voltmeter, the amount of current through the cell is almost zero and the redox half-reactions are at the interfacial equilibrium.

13. Instead of following the quantitative approach describing the Nernst equation as shown in textbooks, we use DOS representations of redox half-cells to provide conceptual explanations about the electrochemical process and track shifts in $E_{\text{cell}}$ with redox species concentration for a concentration cell. This approach facilitates differentiating between the concepts of $E^{\circ}_{\text{cell}}$ and $E_{\text{cell}}$ when describing the electrochemical process.
3.2.2 The phenomenographic approach

This study used a phenomenographic approach to identify chemistry instructors’ conceptions about the teaching of electrochemistry. Findings were then used to evaluate and modify modules and activities developed for the teaching sequence. Within this approach, we focused on the following research question: What is the qualitative variation in instructors’ consciousness during the development of an electrochemistry teaching sequence?

Phenomenography is a qualitative research methodology developed by Marton et al. that aims to investigate the different ways in which people perceive a phenomenon. This approach assumes that people perceive a phenomenon in different ways due to their experiences or understanding of the phenomenon. The outcome of the investigation is a set of categories describing the most distinct aspects of the relation between the individual and the phenomena as seen by the researcher. The phenomenographic analysis involves relating the categories in order to describe the significance of the variation.

Researchers have used a phenomenographic approach to describe the different ways in which instructors’ experience their own teaching. Alexandersson investigated instructors’ variation in the direction of consciousness during their own teaching. The lessons of twelve primary school instructors’ were video recorded and used during interviews. The results indicated that the most distinct aspects of instructors’ consciousness about their own teaching were directed toward the teaching activity itself (e.g., how the pupils are communicating, listening, and thinking during the lesson), the aims for the teaching outcomes (rarely related to the content) and towards the teaching of specific content. The phenomenographic analysis showed a significant variation towards the teaching activity itself without regard to the
instructors’ skills (e.g., teaching experience and working methods). Trigwell K. *et al.*
described different approaches in relating teaching strategies used during instruction and the
intentions of using those strategies of twenty-four physical science instructors$^{25}$. The
instructors were interviewed about their teaching approach, learning conceptions and
teaching conceptions. The phenomenographic analysis revealed a correlation between the
instructors’ teaching approaches and the students’ approaches to learning investigated by
Marton and Säljö$^{26}$. The intention of instructors using teacher-focused strategies was to
transmit knowledge to the students expecting that the students will understand the concepts.
Results indicated that a teacher-focused approach correlates with a students’ surface
approach to learning in which learning is obtained in a superficial fashion (e.g.,
memorization of concepts) rather than focusing on understanding the significance of the
concepts. Instructors using a student-focused approach intended to motivate students to
develop their own knowledge by constructing relations among the concepts. This approach
correlates with a students’ deep approach to learning in which students acquire conceptual
knowledge and develop an insightful understanding of the subject.

3.2.3 Rationale for the use of phenomenography in this study

The developed electrochemistry teaching sequence addresses students and instructors’
conceptions about electrochemistry and a phenomenographic approach is well suited to
investigate instructors’ variation in their consciousness about the reported conceptions. The
study consisted of two phases. During the first phase the instructors were confronted with the
reported conceptions in order to stimulate discussions about how the teaching of
electrochemistry might address those conceptions. During the second phase each of the
topics in the electrochemistry teaching sequence was presented to the instructors in module format. The modules consist of a claim stating student conceptions about a specific topic in electrochemistry, a rationale explaining the sources of student difficulties and the proposed approach to address the conceptions. Each module was continuously modified by the researcher according to instructors’ views on the teaching of the subject. The phenomenographic analysis involved the qualitative identification and categorization of the most predominant aspects of variation in instructors’ consciousness about the electrochemistry teaching sequence.

3.2.4. Data collection

The data was collected during weekly discussions about the teaching of electrochemistry with two general chemistry instructors for an average of two hours per week during 80 weeks (aprox. 160 hrs). One of the instructors (participant A) is a discipline expert (electrochemist) with over 30 years of research experience in analytical chemistry and electrochemistry research plus teaching experience in electrochemistry at the undergraduate and graduate levels. The other instructor (participant B) is a mature chemistry professor with over 28 years of experience mostly dedicated to general chemistry. Each of the instructors revised each module individually. During the weekly meetings the modules were discussed as a group (instructors and researcher) where all the details of the discussion were collected by the researcher. These discussions allowed modifying each module according to instructors’ comments and suggestions. This process continued until each module fulfilled instructors’ expectations.
The discussions focused on specific aspects of the teaching of electrochemistry such as students’ conceptions, intended knowledge, connection between concepts, reliability of the explanations, use of teaching resources (e.g., representations and analogies) and core aspects of models and theories used by experts to explain the electrochemical process. During the discussions the researcher was able to identify variation in instructors’ expectations for the sequence. For example, these experts tend to be concerned about the significance of explaining electrochemistry concepts through the use of models and theories used by experts which might differ from other practitioners whom may use the models and theories without questioning its instructional relevance or value. However, participant A tended to give in-depth considerations to the fundamental theory of a particular model while participant B was more focused on how the presentation of a particular model might be interpreted by students. In addition, participant A identified particular aspects of the diagrams used in chemistry textbooks as sources of misconceptions. In contrast, the expectations of participant B were more related to the connection and consistency in the explanations of the concepts during instruction. A detailed discussion about these findings is presented in the conclusions chapter of this dissertation.
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Chapter 4: Electrochemistry teaching sequence

4.1. Redox reactions terminology

Argument:

The simultaneous use of available definitions for reduction and oxidation found in general chemistry instructional materials creates confusion among students as the definitions used to identify redox reactions depend on the context\textsuperscript{1}. There is a need for a consensus with regard to the definitions used to introduce the concept of redox reactions during electrochemistry instruction in general chemistry courses\textsuperscript{2}. We propose the use of a single definition that provides a common ground for the explanation of fundamental concepts in electrochemistry.

Rationale:

The International Union of Pure and Applied Chemistry (IUPAC) provides multiple definitions for reduction and oxidation processes (Table 4.1). These definitions are used to identify and explain redox reactions in chemistry textbooks. However, it is important to understand the pedagogical consequences that can arise if these definitions are used interchangeably to explain a single redox reaction. Researchers have found that one of the sources of student misunderstanding is the rote application of these definitions when studying redox reactions\textsuperscript{1,3,4}. 
Table 4.1: IUPAC definitions for reduction and oxidation reactions⁵.

<table>
<thead>
<tr>
<th>Definition</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A decrease in the oxidation state of any atom within any substrate.</td>
<td>An increase in the oxidation state of any atom within any substrate.</td>
</tr>
<tr>
<td>2</td>
<td>The complete transfer of one or more electrons to a molecular entity.</td>
<td>The complete, removal of one or more electrons from a molecular entity.</td>
</tr>
<tr>
<td>3</td>
<td>Loss of oxygen and/or gain of hydrogen of an organic substrate.</td>
<td>Gain of oxygen and/or loss of hydrogen of an organic substrate.</td>
</tr>
</tbody>
</table>

Definitions 1 and 2 are the most prevalent textbook definitions for explaining the electrochemical process. However, the oxidation state model (definition 1) is a hypothetical method that does not provide information about the mechanism of the reaction, which can lead to wrongful assumptions. In some cases, a change in oxidation number does not indicate that a transfer of electrons has occurred between the reactants⁶. For example, Figure 4.1 shows the oxidation of nitrogen and the reduction of chlorine according to definition 1. The reaction mechanism does not involve electron transfer between the species but rather the change in oxidation state is due to the following nucleophilic substitution:

Figure 4.1: Representation of the mechanism of the reaction between nitrite and hypochlorous acid⁶.

Furthermore, the indiscriminate use of the definitions can lead to inconsistencies in the identification of redox reactions. For example, students used definition 3 to identify the
reduction of the carbonate ion although it is not applicable to this reaction since these species are not technically considered organic substrates\(^1\).

\[
2\text{H}_3\text{O}^+ (\text{aq}) + \text{CO}_3^{2-} (\text{aq}) \rightarrow 3\text{H}_2\text{O} (\text{l}) + \text{CO}_2 (\text{g})
\]

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Definition 1</td>
<td>C in CO(_3^{2-}): +4</td>
<td>C in CO(_2): +4</td>
</tr>
<tr>
<td>Definition 3</td>
<td>CO(_3^{2-})</td>
<td>CO(_2)</td>
</tr>
</tbody>
</table>

Moreover, students have incorrectly used definitions 2 and 3 to state that the transfer of electrons is distributed among both reactants, H\(^+\) and to MnO\(_4^-\), in the following balanced redox half-reaction:

\[
\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})
\]

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Definition 2</td>
<td>8H(^+)</td>
<td>4H(_2)O</td>
</tr>
<tr>
<td>Definition 3</td>
<td>MnO(_4^-)</td>
<td>Mn(^{2+})</td>
</tr>
</tbody>
</table>

It should be clear that the definitions used to identify redox reactions depend on the context. For example, definition 3 is commonly used in organic chemistry to identify oxidation reactions but it does not apply for reactions that do not involve oxygen or hydrogen\(^3\). Also, the oxidation state model (definition 1) does not provide the scientific foundations to physically explain electrochemical phenomena and is not necessary in order to understand the electrochemical processes. Actually, the oxidation state model was officially removed from the Dutch curriculum more than twenty years ago although instructors still use this definition in their classrooms today\(^1,7\).
Electrochemistry is the chemistry topic in which electron transfer reactions across an interface are studied. Based on the pedagogical implications discussed above, we propose to use definition 2 to emphasize the essential role of the electron transfer mechanism involved in the electrochemical process. Definition 2 is also consistent with definition 1 since, when electron transfer occurs, the oxidation states of the species in the reaction change. Furthermore, the use of an electron transfer model provides a clear physical foundation that lends itself to the use of thermodynamic representations as educational tools in electrochemistry. Accordingly, our goal is to promote the understanding of and connections between fundamental thermodynamic concepts such as Gibbs free energy (G), Fermi level and equilibrium in order to explain the electrochemical process in an unambiguous and logical manner.

4.2. Redox nomenclature

Argument:

The variety of terms and related statements used in general chemistry textbooks to describe redox nomenclature can generate confusion among students when identifying the reduced and oxidized species involved in a redox reaction\(^3\). The terms used can refer to the specie *per sé* and/or to the redox process involved, thereby creating added difficulty for students trying to apply such terms\(^4\). In our approach we propose a consistent redox nomenclature that aims to facilitate student connection between terminology and the electrochemical process.
**Rationale:**

The most common terms used in textbooks to identify redox species are oxidizing agent, reducing agent, oxidant, reductant, oxidized species and reduced species. As an example, Table 4.2 is a compilation of definitions currently used for oxidizing and reducing agents in general chemistry textbooks. Definition 1(b) seems to be confusing and contradicting; however, it is commonly used in popular general chemistry textbooks. Also, the terminology used to identify redox species is inconsistent. For example, four different terms are used to identify the reducing agent (reduced specie, electron donor and reductant). Furthermore, the linguistics used to distinguish between the states of the species (oxidized or reduced), the processes these species undergo themselves (reduction or oxidation), and the processes induced in reactants by oxidizing or reducing agents can be confusing. For example, reducing agents became oxidized when they undergo oxidation thereby inducing other species to become reduced.
Table 4.2: Compilation of definitions for oxidizing and reducing agents found in general chemistry textbooks.

<table>
<thead>
<tr>
<th>Definition</th>
<th>Reducing agent</th>
<th>Oxidizing agent</th>
</tr>
</thead>
</table>
| 1          | a) Substance that gives up electrons, thereby causing another substance to be reduced\(^8\).  
             b) Chemical species causing reduction (become oxidized)\(^9\).  
             c) Chemical species losing electrons\(^10\). | a) Substance that makes it possible for another substance to become oxidized\(^8\).  
             b) Chemical species causing oxidation (become reduced)\(^9\).  
             c) Chemical species gaining electrons\(^10\). |
| 2          | Substance that donates electron(s) to another specie in a redox reaction\(^11\). | Substance that accepts electron(s) from another reactant in a redox reaction\(^11\). |
| 3          | Substance that causes the reduction of an electron acceptor\(^11\). | Substance that causes the oxidation of an electron donor\(^11\). |
| 4          | Reducing agent is the reductant\(^8\). | Oxidizing agent is the oxidant\(^8\). |

De Jong and Treagust suggested replacing these confusing definitions by simpler descriptions such as: “the oxidant gains electrons” and “the reductant loses electrons”\(^7\). However, these descriptions are oversimplified excluding the standard terminology used to describe the redox process (reduction and oxidation). We propose a simplified redox nomenclature that relates the process (oxidation and reduction) to the terminology (oxidized and reduced species) in a consistent manner.

Electrochemistry involves electron transfers that occur between electron acceptor or electron donor species and an electrode.

A specie that accepts electrons (n) undergoes reduction:

\[
\text{Acceptor} + n\text{e}^- \rightarrow \text{Donor}
\]

A specie that donates electrons (n) undergoes oxidation:
Donor → Acceptor + ne-

Electron acceptors are commonly referred to as oxidized species (Ox) and electron donors as reduced species (Red).

Table 4.3 summarizes our proposed approach for identifying redox species and describing oxidation and reduction processes. We aim to provide a simpler, consistent, and precise electrochemistry nomenclature to facilitate the identification of redox species in the electrochemical process.

Table 4.3: Proposed redox nomenclature.

<table>
<thead>
<tr>
<th>Species</th>
<th>Donor = reduced species</th>
<th>Acceptor = oxidized species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Donation (loss) of electrons = oxidation</td>
<td>Acceptance (gain) of electrons = reduction</td>
</tr>
</tbody>
</table>

Figure 4.2 is a representation of the electron transfer process between oxidized species (acceptor) and reduced (donor) species. The redox species are represented as spheres and the electrons as arrows. The electron-vacant sphere represents the electron acceptor species (oxidized species) and the electron-occupied sphere represents the electron donor species (reduced species).
We aim for students to be able to conceptualize a redox reaction as the process in which oxidized species (electron acceptors) undergo reduction (accept electrons) and reduced species (electron donors) undergo oxidation (donate electrons).

### 4.3. Electrochemical series

**Argument:**

The electrochemical series refers to the arrangement of redox species according to their relative redox activity (easy of oxidation). Typically, the construction of the electrochemical series during general chemistry instruction is based on the observation of physical changes during a redox reaction (e.g., color change, phase change) and/or the comparison between standard redox potential ($E^\circ_{\text{ox/red}}$) values of half-cells (e.g., the more negative the value, the easier for the specie to become oxidized). However, the sole use of physical changes and/or $E^\circ_{\text{ox/red}}$ values to construct the electrochemical series presents the following educational challenges:
1. Connections between the electrochemical series and periodic table trends are presented in an oversimplified manner.

2. Tools for developing a scientific foundation that includes energy as the driving force in electrochemical reactions are not provided.

3. Any explanation regarding the chemical nature of inert metals such as Pt, which are commonly used in electrochemical cells, is excluded.

Therefore, the proposal to use a thermodynamic approach to construct the electrochemical series in order to provide the scientific foundations necessary to explain the redox process is justifiable.

**Rationale:**

Different approaches have been proposed to explain the electrochemical series. The relative redox activity of some elements has been explained using periodic trends such as the atomic radius and nuclear effective charge ($Z_{\text{eff}}^{12,13}$). In this approach, elements with large atomic radii and small $Z_{\text{eff}}$ are more active than elements with small atomic radii and large $Z_{\text{eff}}$. However, the relation between redox activity and the periodic table trends is too general and inconsistent. For example, according to this trend, platinum should be more active than lead since the atomic radius of platinum is larger. Furthermore, these periodic trends are not fully consistent with the $E^{\circ}_{\text{ox/red}}$ values of the redox species. For example, although lithium is the most active metal in the periodic table according to its $E^{\circ}_{\text{ox/red}}$ value (e.g., more negative), it is less active (less vigorous reaction) than the other members of the alkali metals family due to its small radii and large $Z_{\text{eff}}^{12}$. 

72
The use of the thermodynamic cycle has been suggested as a teaching tool to explain the electrochemical series\(^\text{14,15}\). Enthalpy changes during the oxidation of a metal in aqueous solution can be described by the thermodynamic cycle shown in Figure 4.3. \(\Delta H^\circ\) represents the energy required to remove an electron from a reduced species such as from the metal to the vacuum level. According to Hess’ law, \(\Delta H^\circ\) is calculated by summing of the enthalpy of atomization (\(\Delta H^\circ_{\text{atom}}\)), the total ionization energy \(\Sigma(IE)\) and the enthalpy of hydration (\(\Delta H^\circ_{\text{hyd}}\)).

![Thermodynamic Cycle Diagram](image)

Figure 4.3: Representation of the thermodynamic cycle for the oxidation of a metal in aqueous solution\(^\text{14,15}\).

Laing proposed the use of this thermodynamic approach to classify the relative activities of redox species according to their \(\Delta H^\circ\), \(E^\circ_{\text{ox/red}}\) and oxidation states\(^\text{14}\). However, his proposed approach is presented as a mathematical model that lacks scientific explanations about the relationship between those concepts. Martins\(^\text{15}\), as well as Probst and Henderson\(^\text{16}\), suggested the use of the thermodynamic cycle to determine relative activities of the redox species by exploring the relation between \(\Delta H^\circ\) and \(E^\circ_{\text{ox/red}}\). This model aims for students to realize that
more positive \( \Delta H^\circ \) values correspond to less active redox species. Although this model is better aligned to conceptual underpinnings, some limitations are evident. First, the model assumes that the standard entropy of reaction (\( \Delta S^\circ \)) is negligible; this is not accurate, however, especially when comparing redox couples undergoing different phase changes. For example, the \( \Delta H^\circ \) values for the redox couples \( \text{Li/Li}^{1+} \) and \( \text{Fe}^{3+}/\text{Fe}^{2+} \) are not comparable for predicting relative activities. In addition, for the trend between \( \Delta H^\circ \) and \( E^{\circ}_{\text{ox/red}} \) to be consistent, we can only compare oxidation reactions involving the same number of electrons transferred.

The teaching sequence in this dissertation proposes a modified thermodynamic approach to construct the electrochemical series acknowledging the limitations discussed above. Thermodynamic representations were incorporated as teaching tools to explain how energy drives the redox process. This approach aims to more clearly connect electrochemistry and thermodynamics concepts discussed in general chemistry such as \( \Delta H^\circ \), \( \Delta S^\circ \), standard Gibbs free energy (\( \Delta G^\circ \)) and Hess’ Law.

The next building block is for students to explore the relative activities of metals in the electrochemical series by constructing thermodynamic cycles to determine \( \Delta H^\circ \). For example, with \( \Delta H^\circ \) values for the oxidation of \( \text{Cu}, \text{Zn} \) and \( \text{Pt} \) at hand, students have data to justify the low redox activity of \( \text{Pt} \) metal compared to other metals as shown in Table 4.4. Furthermore, the use of the thermodynamic cycle allows students to make connections between the relative activities and the chemical nature of species. For example, the high
oxidative reactivity of F$_2$(g) can be understood as arising from the low energy required for its reduction ($\Delta H^\circ = -28$ kJ/mol) where $\Delta H^\circ$ values were calculated using tabulated values$^{17,18}$.

Table 4.4: Compilation of $\Delta H^\circ$ values for the oxidation of metals (calculated using tabulated values$^{17,18}$).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(s) to Zn$^{2+}$(aq)</td>
<td>726</td>
</tr>
<tr>
<td>Cu(s) to Cu$^{2+}$(aq)</td>
<td>942</td>
</tr>
<tr>
<td>Pt(s) to Pt$^{2+}$(aq)</td>
<td>1601</td>
</tr>
</tbody>
</table>

The use of thermodynamic cycles is expected to facilitate the connections between thermodynamics and electrochemistry as it provides the scientific foundations to explain the relative activity of redox species. These thermodynamic representations were considered to be essential educational tools to convey a clearer scientific justification of the electrochemical process. The thermodynamic cycle described in Figure 4.3 serves as a teaching tool to explain the relative activity of the redox species keeping in mind the limitations described above.

4.4. Representational models of Gibbs free energy

Argument:

Electrochemistry chapters in most general chemistry textbooks exhibit a lack of conceptual explanation relating $E^\circ_{\text{ox/red}}$ values to the thermodynamic parameters involved in a redox process$^{19}$. Consequently, students often confront difficulties understanding the thermodynamic nature of $E^\circ_{\text{ox/red}}$$^{2, 20, 21}$. Sanger and Greenbowe found that one predominant
students’ conception is that the reduction potential of a half-cell determines the spontaneity of a reaction rather than the potential difference between half-cells. The teaching sequence proposed here aims to utilize thermodynamic concepts and representations to explain scientific models used by electrochemists. The proposed Gibbs free energy (G) representations aim to emphasize the dynamic electron transfer process in redox half-reactions. The relation between the components in the representational models provides the basis for connecting concepts of G, electron transfer reactions, equilibrium and E°_ox/red for an electrochemical process. In our approach the use of representational models to provide conceptual explanation regarding the thermodynamic nature of E°_ox/red is emphasized. The proposed approach aims to bridge the gap between thermodynamic properties and physical models that are used by electrochemists to explain the electrochemical process.

**Rationale:**

*Gibbs free energy value*

The thermodynamic cycle can serve as a teaching tool to construct the electrochemical series by calculating ΔH° as previously proposed. For the reaction:

Red → Ox + ne^−_(vac)

ΔH is the energy required to remove n electrons from the reduced species to the vacuum level. However, this approach by itself does not provide an adequate scientific foundation to explain the relation between ΔH, ΔG, and E°_ox/red in the electrochemical series. Therefore representational models for ΔG to promote conceptual explanations that enable the
thermodynamics of a redox reaction to be directly connected to the concept of \( E^\circ_{\text{ox/red}} \) were adopted.

The \( \Delta H \) value calculated from a thermodynamic cycle relates to the change in \( \Delta G \) of the system according to the following equation:

\[
\Delta G = \Delta H - T \Delta S
\]

where \( T \) is absolute temperature.

For many redox couples is impossible to obtain 1 M concentration. In this case, the standard cell potential (\( E^\circ_{\text{cell}} \)) can be closely approximated as long as the reduced and oxidized species concentrations have the same value. At standard conditions (pure substances and pressure = 1 atm) and \( T = 298.15 \) K:

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

The \( \Delta G \) value for the oxidation of a redox species is commonly determined using the following oxidation reaction as a reference\(^{22}\):

\[
vH_2(1\text{atm}) + v\text{Ox} \rightarrow vH^+(a = 1) + v\text{Red}
\]

where \( v \) is the stoichiometric coefficient and \( a \) is the activity of the specie.

According to the thermodynamic cycle for the oxidation of \( H_2(1\text{atm}) \) (see Figure 4.4), the energy required to remove two electrons from \( H_2(1\text{atm}) \) to the vacuum level at standard conditions, \( \Delta H^\circ \), is equal to 876 kJ/mol \( H_2(1\text{atm}) \).
Using the ΔH° value we can determine ΔG° for the oxidation of H₂(1atm) according to the following equation (using tabulated values\textsuperscript{17,18}):

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

\[
= 876 \text{ kJ/mol} - (298 \text{ K} \cdot (-0.1307 \text{ kJ/mol·K}))
\]

\[
= 915 \text{ kJ/mol H}_2(1\text{atm})
\]

Using this value as a reference ΔG° can be determined for the oxidation of other reduced species. For example, the ΔG° value for the oxidation of Fe\textsuperscript{2+}(aq) to Fe\textsuperscript{3+}(aq) is determined as follows:

\[
\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + e^-(\text{vac})
\]

From the thermodynamic cycle we obtain:

\[
\Delta H^\circ = -\Delta H^\circ_{(\text{hyd})} + \Sigma(\text{IE}) + \Delta H^\circ_{(\text{hyd})} = 1946 \text{ kJ/mol} + 2957 \text{ kJ/mol} + -4430 \text{ kJ/mol}
\]
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

\[ = 473 \text{ kJ/mol} - (298.15 \text{ K} \cdot -0.1782 \text{ kJ/mol} \cdot \text{K}) \]

\[ = 526 \text{ kJ/mol} \text{ Fe}^{2+} \]

Figure 4.5 presents a visual depiction of \( \Delta G^\circ \) for the oxidation of \( \text{Fe}^{2+} \) using the \( \text{H}_2(1\text{atm}) \) to \( \text{H}^+(a=1) \) oxidation reaction as a reference.

This approach emphasizes the significance of a reference in thermodynamic and electrochemical measurements. The determination of \( \Delta G^\circ \) provides a way to connect thermodynamic parameters to \( E^\circ_{\text{ox/red}} \) values for a redox reaction.  

79
Gibbs free energy curves

For a reversible redox reaction at equilibrium, electron transfer occurs between redox couples rather than from the reduced specie to vacuum as previously described for oxidation reactions. Therefore, for redox half-reactions a double arrow is used to describe the process:

\[
\text{Red} \rightleftharpoons \text{Ox} + n\text{e}^-_{\text{(redox)}}
\]

or

\[
\text{Donor} \rightleftharpoons \text{Acceptor} + n\text{e}^-_{\text{(redox)}}
\]

The total Gibbs free energy curve for an individual substance is typically depicted by plotting $G$ with respect to the reaction coordinate. The reaction coordinate is a multi-dimensional function of the molecular structure (bond angles, bond lengths, etc.) therefore, it is reasonable to refer to it as molecular configuration. Gibbs free energy fluctuates continuously as the positions of atoms change due to thermal motion. In Figure 4.6 the two curves represent the individual redox species, with the left curve representing the Gibbs free energy of the reduced species ($G_{\text{red}}$) with respect to molecular configuration and the right curve corresponds to the Gibbs free energy of the oxidized species ($G_{\text{ox}}$) and the redox electron(s) ($G_{\text{e\,redox}}$). The bottom of each curve indicates the Gibbs free energy at the most stable molecular configuration. The position of each curve represents $G$ for redox species in a redox half-reaction at equilibrium as a function of molecular configuration. Electron transfer can occur when the molecular configurations of the reduced species and oxidized species are the same as represented by the intersection of the two curves.
Figure 4.6: Gibbs free energy representation for a redox half-reaction at equilibrium.\(^{22}\)

\(\Delta G\) describes the Gibbs free energy difference between products and reactants in a reaction.

At equilibrium:

\[ \Delta G = 0 \]

Therefore,

\[ G_{\text{red}} = G_{\text{ox}} + G_{e}^{\text{redox}} \]
Gibbs free energy values depend on the composition of the species in the system. The property that relates \( G \) to species composition at constant pressure and temperature is known as the chemical potential \( (\mu_i^\alpha) \) for the specie \( i \) in phase \( \alpha \). The relation between \( G \) and \( \mu_i^\alpha \) is expressed as follow:

\[
\mu_i^\alpha = \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq i}
\]

where \( \mu_i^\alpha \) and chemical composition are related according to the following equation:

\[
\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln C_i^\alpha
\]

In the latter equation \( \mu_i^{0\alpha} \) is the standard chemical potential and \( C_i^\alpha \) is concentration (assuming that the activity coefficient \( (\gamma_i^\alpha) \) is equal to 1).

Values of \( \mu_i^{0\alpha} \) for ideal gaseous or dissolved substances at standard conditions (pure substances and \( p = 1 \text{ atm} \)) have been tabulated using \( H^+_{(aq)} \) as a reference (\( \mu_i^{0\alpha} = 0 \)).

\( G_e^{\text{redox}} \) for a redox half-reaction can be determined as follows:

\[
\mu_e^\alpha = \mu_{\text{red}}^\alpha - \mu_{\text{ox}}^\alpha = \left( \frac{\partial G_e^{\text{redox}}}{\partial n_i} \right)_{T, p, n_j \neq n_i} = \left( \frac{\partial G_{\text{red}}}{\partial n_i} \right)_{T, p, n_j \neq n_i} - \left( \frac{\partial G_{\text{ox}}}{\partial n_i} \right)_{T, p, n_j \neq n_i}
\]

At standard conditions:

\[
\mu_e^{\circ \alpha} = \mu_{\text{red}}^{\circ \alpha} - \mu_{\text{ox}}^{\circ \alpha} = \left( \frac{\partial G_e^{\circ \text{redox}}}{\partial n} \right)_{T, p, n_j \neq n_i} = \left( \frac{\partial G_{\text{red}}^{\circ}}{\partial n} \right)_{T, p, n_j \neq n_i} - \left( \frac{\partial G_{\text{ox}}^{\circ}}{\partial n} \right)_{T, p, n_j \neq n_i}
\]
For example, for the following redox half-reaction:

$$\text{Fe}^{2+}_{\text{(aq)}} \rightleftharpoons \text{Fe}^{3+}_{\text{(aq)}} + e^-$$

We obtain (from tabulated $\mu_i^{0\alpha}$ values$^{23}$):

$$\frac{\partial G^\circ_{\text{e redox}}}{\partial n}_{\text{T,P}, n_j \neq n_i} = \left( \frac{\partial G^\circ_{\text{Fe}^{3+}}}{\partial n}_{\text{T,P}, n_j \neq n_i} \right) - \left( \frac{\partial G^\circ_{\text{Fe}^{2+}}}{\partial n}_{\text{T,P}, n_j \neq n_i} \right)$$

$$= (-78.87 \text{ kJ/mol}) - (-4.60 \text{ kJ/mol}) = -74.27 \text{ kJ/mol}$$

$G^\circ_{\text{e redox}}$ is an approximation to the $\Delta G^\circ$ value for a reversible redox half-reaction at equilibrium. For example, if we compare the calculated $G^\circ_{\text{e redox}}$ and $\Delta G^\circ$ values for the Fe$^{3+}$/Fe$^{2+}$ redox couple we obtain comparable values that students may use to relate concepts in the proposed teaching sequence.

$$G^\circ_{\text{e redox}} = -74.27 \text{ kJ/mol} \text{ versus } \Delta G^\circ = -69 \text{ kJ/mol}$$

Summarizing, Gibbs free energy curves can be used as a teaching tool to facilitate students’ understanding of the following concepts:

- For a reversible redox half-reaction at equilibrium: $G_{\text{red}} = G_{\text{ox}} + G_{\text{e redox}}$
- $G_{\text{e redox}}$ represents the Gibbs free energy difference between reduced and oxidized species in a redox half-reaction at equilibrium.
**Density of electronic states**

The number of electronic states, whether occupied or vacant, per energy interval is defined as the density of states (DOS). Electronic states are filled from lower to higher energy until all electrons have been accounted for. Figure 4.7 depicts electron energy for redox species in solution with respect to the density of electron-occupied states $D_{\text{occupied}}$ and the density of electron-vacant states $D_{\text{vacant}}$. Gaussian distributions of energy states due to thermal fluctuations of the molecules and solvent in solution are commonly assumed\textsuperscript{22}. This model was developed primarily by Gerischer, to rationalize semiconductor photo-electrochemistry phenomena. The point where $D_{\text{occupied}}$ overlaps $D_{\text{vacant}}$ corresponds to the solution Fermi level, which denotes the energy level of the highest occupied electronic state of the solution.
Figure 4.7: Gerischer model for the density of electron energy states\textsuperscript{24,25}. Shading designates occupied states. The figure represents a redox solution with equimolar concentrations of Ox and Red as can be deduced from the equal areas under the two curves.

\( D_{\text{occupied}} \) and \( D_{\text{vacant}} \) represent the reduced and oxidized forms of a redox couple at equal concentration in solution, respectively. The solution Fermi level is a direct reflection of the \( G_e^{\text{redox}} \) value for the redox half-reaction\textsuperscript{22,24}. However, absolute experimental measurements of \( G_e^{\text{redox}22,25} \) cannot be obtained

It is proposed in this dissertation to use the density of electron energy states model to illustrate the difference in \( G_e^{\text{redox}} \) between two redox half-reactions. Figure 4.8 depicts an
arbitrary $G_e^{\text{redox}}$ difference for the following net redox reaction, where 1 and 2 refer to two individual redox couples, $\text{Ox}_1/\text{Red}_1$, and $\text{Ox}_2/\text{Red}_2$

$$\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2$$

or

$$\text{Donor}_1 + \text{Acceptor}_2 \rightarrow \text{Acceptor}_1 + \text{Donor}_2$$

The placement of the curves will depend on the actual $G_e^{\text{redox}}$ values for the redox processes (higher energy on the top and lower energy on the bottom). The $G_e^{\text{redox}}$ difference between two redox half-reactions is equal to the total change in Gibbs free energy for the net redox reaction as follow:

$$\Delta G = G_2^{\text{redox}} - G_1^{\text{redox}}$$

where $G_1^{\text{redox}}$ and $G_2^{\text{redox}}$ refers to the electron Gibbs free energy for the redox half-reactions 1 and 2 respectively.

At standard conditions:

$$\Delta G^\circ = G_2^{\circ, \text{redox}} - G_1^{\circ, \text{redox}}$$

In Figure 4.8 the energy states available for electron transfer between the two redox half-reactions are represented. As depicted, spontaneous electron transfer occurs from the higher energy state (electron on the top) to the lower energy state (available energy states on the bottom).
Figure 4.8: Distribution of electron energy states for two redox half-reactions and the energy states available for electron transfer between the two redox half-reactions. The diagram shown is for a reaction where electrons (represented by ↑ ) can flow spontaneously from redox couple #1 to redox couple #2.

$\Delta G$ values can be experimentally measured using electrochemical cells such as the one shown in Figure 4.9. Electrochemical cells are composed of a chemical system (containing the redox couples) and metals (known as electrodes) in solution. Each redox couple and electrode in solution represents a redox half-cell. The solutions of the two half-
cells are ionically connected by a liquid junction whose function is to restrict flow between half-cells and therefore minimize mixing. The salt bridge is a common liquid junction composed of a porous material saturated with electrolyte solution (e.g. KCl).

![Diagram of an electrochemical cell connected to a voltmeter.](image)

Figure 4.9: Representation of an electrochemical cell connected to a voltmeter in which each half-cell contains a solution with both forms of a redox couple present.

Each redox half-cell is connected to an external circuit (e.g., current load, voltmeter). In Figure 4.9, the electrochemical cell in connected to a voltmeter which is an electrical instrument that measures the cell potential \( E_{\text{cell}} \). \( E_{\text{cell}} \) is a measure of \( \Delta G \) for the net redox reaction that occurs in an electrochemical cell:

\[
\Delta G = -nFE_{\text{cell}}
\]

where \( n \) is moles of electrons/mol of reactant and \( F \) is the Faraday constant (96,500 C/mol e-)

At standard conditions:
\[ \Delta G^o = -nF \Delta E_{\text{cell}} \]

This approach illustrates and explains the relation between \( \Delta G \) and \( E \) in an electrochemical process. The representations provided serve as visual resources to reinforce the concepts of \( E_{\text{cell}} \), Fermi level, electrochemical equilibrium and Nernst equation that are subsequently discussed during electrochemistry instruction.

4.5. Reference electrode

Argument:

Students confront difficulties understanding the meaning of a reference electrode when determining thermodynamic values in electrochemistry. For example, one students’ conception is that the \( E^o \) value for the standard hydrogen electrode (SHE) depends on the chemical nature of the \( H_2(1 \text{atm}) \) and \( H^+(a=1) \) species, not realizing that it is arbitrarily assigned to be zero. Ozkaya et al. suggested that instructors should emphasize the nature of \( E^o_{\text{ox/red}} \) values and the significance of using a reference electrode for measuring \( E^o \) during electrochemistry instruction. In our approach, the concept of electrochemical conventions for determining \( E^o_{\text{ox/red}} \) values is introduced using a reference electrode in an electrochemical cell. Students determine the \( E^o_{\text{ox/red}} \) for a single redox couple using \( \Delta G^o \) values and SHE as a reference.

Rationale:

As previously discussed, the teaching sequence calls for students to use thermodynamic representations to visually relate \( \Delta G^o \) and \( E^o \) values for two redox half-
reactions. $E^\circ_{cell}$ is a measure of $\Delta G^\circ$ for the following redox reaction in an electrochemical cell:

$$\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2$$

$E^\circ_{\text{ox/\text{red}}}$ is not measurable\textsuperscript{22,25}. Instead, one can determine $E^\circ_{\text{ox/\text{red}}}$ values for redox half-reactions at equilibrium with respect to a reference electrode\textsuperscript{22}. Using representations, we aim for students to recognize that in order to determine $E^\circ_{\text{ox/\text{red}}}$ for a single redox couple, another redox half-reaction (reference electrode) is needed as a basis for comparison and to complete the electrical circuit.

W. Nernst suggested the use of the SHE as a reference electrode due to the reproducibility and reliability of its potential, and it is now internationally accepted as the primary reference electrode\textsuperscript{22,28}. SHE consists of a platinum wire immersed in an acid solution through which $H_2$ is bubbled as shown in Figure 4.10. The $E^\circ_{\text{ox/\text{red}}}$ value for SHE was arbitrarily chosen as zero at all temperatures ($E^\circ_{\text{SHE}} = 0$).
For an electrochemical cell,

\[ E_{\text{cell}} = E_{\text{red}} - E_{\text{black}} \]

In the proposed approach, students determine \( E^\circ_{\text{ox/red}} \) from \( \Delta G^\circ \) values for a single redox couple using SHE as a reference as follows:

\[ E^\circ_{\text{cell}} = E^\circ_{\text{ox/red}} - E^\circ_{\text{SHE}} \]

For example, we can determine the \( E^\circ_{\text{ox/red}} \) value for the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) half-reaction against SHE as follows:
\[ \text{H}_2(\text{aq}=1) + \text{Fe}^{3+}(\text{aq}=1) \rightleftharpoons 2\text{H}^+(\text{aq}=1) + \text{Fe}^{2+}(\text{aq}=1) \]

Using the Fe\(^{3+}/\text{Fe}^{2+}\) value obtained from the calculated \(\Delta G^\circ\) (see Figure 3.5),

\[ E_{\text{ox/red}}^\circ = -\frac{\Delta G^\circ}{nF} \]

Therefore,

\[ E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = -\frac{-69}{\text{kJ/mol Fe}^{2+}} \cdot \frac{1}{\text{mol e}^-} \cdot \frac{96500}{\text{C/mol e}^-} \cdot \frac{1000}{\text{J/kJ}} = 0.72 \frac{\text{C}}{\text{J}} = 0.72 \text{V} \]

When students compare the calculated \(E_{\text{ox/red}}^\circ\) value with the tabulated value found in standard reduction potential tables\(^{22}\), they observe that the values are similar. In this case, for Fe\(^{3+}/\text{Fe}^{2+}\), the calculated and tabulated are:

\[ E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ \text{(cal)} = 0.72 \text{ V} \approx E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ \text{(tab)} = 0.771 \text{ V} \]

In the traditional approach, students typically use the standard reduction table as a resource for \(E_{\text{ox/red}}^\circ\) values. The approach taken here provides greater inside regarding the thermodynamic nature of \(E_{\text{ox/red}}^\circ\) and the role of the reference electrode.

### 4.6. Redox solutions and inert metal electrodes

**Argument:**

Oversimplified explanations about the electrochemical processes that occur between redox species and inert metal electrodes (electrodes that do not appear explicitly in the redox reaction) can generate confusion among students\(^{19}\). Sanger and Greenbowe found that
students confront difficulties understanding the function of inert electrodes in the electrochemical process\textsuperscript{19,26}. One reported students’ conception is that “no reaction will occur if inert electrodes are used”\textsuperscript{26}. A teaching tool to address students’ conceptions about the function and characteristics of inert metal electrodes is needed. It was considered that the incorporation of the concept of interfacial equilibrium (equilibrium between solution and electrode) would be appropriate to describe the interaction between redox species and inert metal electrodes.

**Rationale:**

According to the density of electronic states model, the solution Fermi level is positioned at the energy level where DOS curve for the reduced species ($D_{\text{occupied}}$) and the DOS curve for the oxidized species ($D_{\text{vacant}}$) cross each other. The Fermi level of a metal used as an inert electrode is described using band theory, which depicts the distribution of the energies of valence electrons in the solid. For our purposes, Fermi level of the metal can be taken to correspond to the highest occupied level of a partially filled band as shown in Figure 4.11, which is a simple representation of the distribution of the valence electrons in metal (Au). It was deemed valuable to compare and connect the concepts of solution Fermi level and metal Fermi level in order to explain the function of inert metal electrodes in the electrochemical process.
Figure 4.11: Electronic band structure of Au metal for s-type electrons. As the number of atoms increases (N), the number of interactions to form bonding and antibonding crystal orbitals also increases. As an extended structure is approached (N → ∞), the discrete energy levels corresponding to the crystal orbitals can be considered as a continuum, hence the formation of an energy band.

The minimum energy required to remove an electron from the Fermi level of an uncharged metal into vacuum is known as the work function (Φ). The experimental Φ value is an approximation to the magnitude of the Gibbs free energy change (ΔG_{eM}^M) that occurs when an electron is removed from the metal surface to vacuum or vice-versa. Assuming that the surface electrostatic potential of the metal is negligible, the relation between Φ and G_{eM}^M can be described using the following equation\textsuperscript{25}:

$$\Phi = \frac{\partial G_{eM}^M}{\partial n_e T_P n_{j/e}}$$
where \( n_e \) is the number of moles of electrons in the metal at constant temperature and pressure.

\( \Delta G_e^M \) is analogous to \( \Delta G_e^{\text{redox}} \) for a redox couple in solution, as described earlier. Students compare the similarities and differences between the density of electronic states model for redox species in solution and the band theory model for metal electrodes as shown in Table 4.5.

Table 4.5: Comparison between the density of electronic states model for redox species in solution and band theory model for metal electrodes.

<table>
<thead>
<tr>
<th>Concept</th>
<th>Redox solution</th>
<th>Metal electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of electronic states</td>
<td>Gerischer model(^{25}). Distribution due to thermal fluctuations</td>
<td>Band theory. Distribution due to the quantum mechanical structure of the metal</td>
</tr>
<tr>
<td>Electron occupied-states</td>
<td>( D_{\text{occupied}} ) – reduced species</td>
<td>Electron-filled portion of the partially filled band</td>
</tr>
<tr>
<td>Electron vacant-states</td>
<td>( D_{\text{vacant}} ) – oxidized species</td>
<td>Electron-vacant portion of the partially filled band</td>
</tr>
<tr>
<td>Fermi level</td>
<td>Highest occupied electron state located at the region where ( D_{\text{red}} ) and ( D_{\text{ox}} ) overlap.</td>
<td>Highest occupied electronic state of the partially filled band</td>
</tr>
<tr>
<td>Gibbs energy at the Fermi level</td>
<td>Minimum energy required to remove an electron from the Fermi level of the redox solution to the vacuum level (( G_e^{\text{redox}} ))</td>
<td>Minimum energy required to remove an electron from the Fermi level of the metal surface into vacuum (( G_e^M ))</td>
</tr>
</tbody>
</table>

When an inert metal is inserted into a solution containing redox species, electron transfer occurs between the redox species and the metal due to a difference between the Fermi levels. Electrons will transfer from higher energy states to lower energy states. Consequently, the inert metal becomes either positive or negative charged depending on the
direction of net electron transfer. This process causes the metal Fermi level to shift in the
direction of the solution Fermi level. Interfacial equilibrium is established when the Fermi
level of the redox couple in solution and the Fermi level of the metal have the same value\textsuperscript{25}.
Therefore, at interfacial equilibrium,

\[ \Delta G_e^M = \Delta G_e^{\text{redox}} \]

The concept of interfacial equilibrium can be explained using a representation that
integrates density of electronic states models for redox solutions and metal electrodes as
shown in Figure 4.12. In this example, the Fermi level of an uncharged metal is arbitrarily
depicted at lower energy than the Fermi level of the solution. When the metal is immersed in
the redox solution, electron transfer occurs spontaneously from the solution to the metal and
as a result the metal surface becomes negatively charged, which raises its electronic energy.
Consequently, the net electron transfer proceeds until the metal Fermi level is raised to the
solution Fermi level, at which electrochemical equilibrium has been established.
Figure 4.12: Before and after the establishment of electrochemical equilibrium between redox species in solution and a metal electrode surface.

Figure 3.12 can be systematically used to identify and connect the concepts of density of electronic states, electron occupied states, electron-vacant states, Fermi level and electron Gibbs free energy for redox solutions and inert metal electrodes. This representation can be extended to an electrochemical cell composed of two half-cells, each of which containing a redox couple in equilibrium with an inert electrode (see Figure 4.13). These representations serve as teaching tools to explain the concept of interfacial equilibrium in an electrochemical cell.
Students do not conceptualize that one important function of inert metal electrodes is to provide a conductive surface with a Fermi level that adjusts to $G_e^{\text{redox}}$ values of redox half-reactions in solution in order to determine $E_{\text{cell}}$. Therefore, when $G_e^M$ values for two different
inert metal electrodes immersed in the same redox solution are compared, values should be the same. In our approach, students measure $E_{\text{cell}}$ for the same electrochemical cell using two different inert metal electrodes. For example, Figure 4.14 shows two electrochemical cells: platinum electrodes are used in one cell and gold electrodes in the other. However, the redox process in both cells is the same:

$$\text{[Fe(CN)}_6\text{]}^{4-}_{(aq)} + \text{Fe}^{3+}_{(aq)} \rightleftharpoons \text{[Fe(CN)}_6\text{]}^{3-}_{(aq)} + \text{Fe}^{2+}_{(aq)} \quad E^\circ_{\text{cell}} = 0.41 \text{ V}$$

E\text{cell}$ is a measure of the difference in $G_e^{\text{redox}}$ between two redox half-cells, which is the same as the difference in $G_e^{\text{M}}$ according to the description above. At electrochemical
equilibrium, $E_{\text{cell}}$ values for the electrochemical cells in Figure 4.14 should be the same since both inert metal electrodes are in the same redox solution.

4.7. Electrodes

**Argument:**

Explanations about the function and characteristics of active and inert electrodes are commonly lacking during traditional electrochemistry instruction$^{19}$. As a result, students confront difficulties when predicting the role of the electrodes in the electrochemical process$^{19,26}$. As previously mentioned, one student conception is that “no reaction occurs if inert electrodes are used”$^{26}$. Sanger and Greenbowe suggested that textbooks should describe the characteristics that make electrodes inert during electrochemical processes$^{19}$. In this teaching sequence student conceptions are addressed by describing the function and characteristics of active and inert electrodes in electrochemical cells according to thermodynamic parameters.

**Rationale:**

Electrodes serve as electronic conductors during electrochemical processes. Active electrodes take part in the redox reaction, whereas inert electrodes serve as a source of or sink for electrons in solution. The traditional approach emphasizes the use of active electrodes in galvanic cells and inert electrodes in electrolytic cells, despite the fact that the role of the electrodes is independent of the type of cell. In our approach, students describe the function of Ag as inactive or active electrode during an electrochemical process.
The density of states model proposed to represent interfacial equilibrium refers to the electron transfer process occurring between redox couples in solution and inert electrodes. However, this model does not describe the electrochemical process occurring when metal electrodes take part in the redox reaction. For active metal electrodes we have:

\[ \text{M} \rightleftharpoons \text{M}^{n+} + \text{ne}^- \]

where M is the metal (reduced specie) and M^{n+} is the metal ion (oxidized specie).

As previously discussed, the Gibbs free energy for redox half-reactions at interfacial equilibrium is described as follow:

\[ G_e^{\text{redox}} = G_{\text{red}}^\circ - G_{\text{ox}}^\circ \]

Substituting for the species we obtain:

\[ G_e^{\text{redox}} = G_M^\circ - G_{M^+}^\circ \]

Since, \( G_M^\circ = 0 \), therefore;

\[ G_e^{\text{redox}} = - G_{M^+}^\circ \]

which is an approximation to \( \Delta G^\circ \) for the redox reaction.

In this part of the teaching sequence, students construct electrochemical cells for the two scenarios in Figure 4.15. We aim for students to determine the spontaneity of the redox processes in cells A and B according to \( \Delta G \) values.
Figure 4.15: Each electrochemical cell is connected to a low resistance circuit (100 Ω), which let electron transfer to take place between the two redox half-cells.

In electrochemical cell A, Ag is taking part in spontaneous redox reaction as follows:

\[
2\text{Ag}^{+}(aq) + \text{Zn}(s) \rightarrow 2\text{Ag}(s) + \text{Zn}^{2+}(aq)
\]

In electrochemical cell B, the Ag metal electrode is introduced into a solution containing \([\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}\) redox couple. The experimental conditions (e.g., absence of \(\text{Ag}^+\) in solution) and the well positive \(E^{\circ}_{\text{ox/red}}\) of the \(\text{Ag}^+/\text{Ag}\) couple (hence Ag does not oxidize) allows the reduction of \([\text{Fe(CN)}_6]^{4-}\) as follows:

\[
2[\text{Fe(CN)}_6]^{3-}(aq) + \text{Zn}(s) \rightarrow 2[\text{Fe(CN)}_6]^{4-}(aq) + \text{Zn}^{2+}(aq)
\]

This indicates that Ag is functioning as an inert electrode.
Students should be able to distinguish between the two scenarios in Figure 3.15 when replacing Ag electrode with Pt, which will function as an inert electrode in both cells. It is observed that the $E_{\text{cell}}$ value for electrochemical cell B remains the same, whereas for electrochemical cell A, $E_{\text{cell}}$ will be different from that obtained when using Ag. This approach allows the characterization of active and inert electrodes in electrochemical processes. We aim for students to be able to describe the function of the electrodes using thermodynamic values.

4.8. Electrochemistry conventions

Argument:

Students confront difficulties understanding the relation between the sign of the potential and the spontaneity of the redox reaction, such as mistakenly calculating positive cell potentials for non-spontaneous processes in electrolytic cells\textsuperscript{26}. In this part of the teaching sequence, the sign of the measured $E_{\text{cell}}$ is related to the spontaneity of the redox process according to electrochemical conventions.

Rationale:

At this point of the proposed teaching sequence, students should be able to describe the electrochemical process as follows:

1. $E_{\text{cell}}$ is a measure of $\Delta G$ between two redox half-reactions in an electrochemical cell defined as: $\Delta G = -nFE_{\text{cell}}$. 

2. \( E^\circ \) values for individual redox couples are measured versus a reference electrode in an electrochemical cell.

3. The convention for measuring \( E_{\text{cell}} \) using a voltmeter is described as:

\[
E_{\text{cell}} \equiv E_{\text{cathode}} - E_{\text{anode}}.
\]

4. When measuring an \( E^\circ_{\text{cell}} \) value, the current through the cell is almost zero and interfacial equilibrium must be established.

Assuming student understanding of the concepts described in the teaching sequence, we propose to relate the sign of \( E_{\text{cell}} \) to the spontaneity of the electrochemical process. The main learning objective is for students to reflect on the electrochemical processes occurring at the anode and cathode in electrochemical cells when determining \( E_{\text{cell}} \).

Chemistry instruction commonly includes the convention that the measured \( E_{\text{cell}} \) for a galvanic cell is positive. However, there is often no precise explanation about the fact that the sign of a measured \( E_{\text{cell}} \) is defined by electrochemistry convention as follows:

\[
E_{\text{cell}} \equiv E_{\text{cathode}} - E_{\text{anode}} = E_{\text{red}} - E_{\text{black}}
\]

A positive \( E_{\text{cell}} \) indicates a spontaneous redox reaction where the Gibbs free energy of the anode half-cell is higher than that of the cathode half-cell; this is a galvanic cell. A negative \( E_{\text{cell}} \) indicates a non-spontaneous redox reaction where the Gibbs free energy of the anode half-cell is lower than that of the cathode half-cell; this is an electrolytic cell.
In our approach, students determine the spontaneity of an electrochemical process by connecting the electrochemical cell to the voltmeter according to electrochemistry conventions. For example, for the following redox reaction:

\[ \text{Cu}(s) + \text{Zn}^{2+} \text{(aq)} \rightarrow \text{Cu}^{2+} \text{(aq)} + \text{Zn}(s) \]

The Cu/Cu^{2+} half-cell is connected to the black terminal of the voltmeter and the Zn/Zn^{2+} half-cell to the red resulting in a negative \( E_{\text{cell}} \), which indicates a non-spontaneous electrochemical process for which the Gibbs energy of the anode half-cell is lower than that of the cathode half-cell.

Likewise, \( E_{\text{cell}} \) can be determined from Gibbs free energy values as follows:

\[ \Delta G = -nF E_{\text{cell}} \]

which leads to:

\[ \Delta G = G_{\text{cathode}} - G_{\text{anode}} \]

where \( G_{\text{cathode}} \) and \( G_{\text{anode}} \) correspond to the Gibbs free energy for the cathode and anode half-cells reactions at the interfacial equilibrium, respectively.

For example,

\[ \Delta G = G^o_{\text{Zn/Zn}^{2+}} - G^o_{\text{Cu/Cu}^{2+}} = 147.03 \text{ kJ/mol} - (-65.52 \text{ kJ/mol}) = 212.55 \text{ kJ/mol} \]

Therefore,

\[ E^o_{\text{cell}} = -1.10 \text{ V} \]
This value is similar to the $E_{\text{cell}}$ calculated using tabulated values found in reduction potential tables ($E^\circ_{\text{cell (tab)}} = -1.1026 \text{ V}$)\textsuperscript{22}.

This approach facilitates describing the relation between the sign of the measured $E_{\text{cell}}$ and the spontaneity of the redox process in a consistent manner.

4.9. Electrochemistry nomenclature

Argument:

Researchers reported the use of minus (-) and plus (+) signs to identify the electrodes as the source of the following students’ conceptions\textsuperscript{2,20,21,30}:

1. Redox processes occurring at the anode and cathode depend on the type of cell. For example, one students’ conception is that the cathode undergoes reduction in a galvanic cell and oxidation in an electrolytic cell\textsuperscript{21}.

2. For a galvanic cell:
   a. The anode is negatively charged because it has lost electrons; the cathode is positively charged because it has gained electrons\textsuperscript{2,21,30}.
   b. In solution, cations are attracted to the anode and anions are attracted to the cathode\textsuperscript{21}.
   c. Electrons flow from regions of high electron concentration to low electron concentration\textsuperscript{2}.

This teaching sequence shows that the elimination of the plus and minus designations is feasible as they are not necessary for understanding the fundamentals concept in electrochemistry, thereby potentially minimizing students’ conceptions.
Rationale:

Figures found in textbooks often label the cathode as positive (+) in galvanic cells and negative (-) in electrolytic cells without providing adequate explanations about the significance of the signs. The positive and negative signs are generally intended to indicate relative charges on the electrodes at interfacial equilibrium assuming that for a spontaneous process the anode is more negative than the cathode, whereas for a non-spontaneous process the anode is more positive than the cathode. However, this is not always the case as the excess charge of metal electrodes depends on their potential of zero charge ($E_{pzc}$) which is the potential at which the excess charge on the metal surface is zero (see section 2.2). For example, according to $E_{pzc}$ values (see table 2.2), if a potential of -0.20 V is applied, an excess negative charge would be induced on Cu ($E_{pzc} = 0.18$ V)\(^{22}\) whereas Zn ($E_{pzc} = -0.63$ V)\(^{22}\) would develop excess positive charge; however, spontaneous electron transfer occurs from Cu/Cu\(^{2+}\) ($E^{°}_{ox/red} = +0.32$ V)\(^{22}\) to Zn/Zn\(^{2+}\) ($E^{°}_{ox/red} = -0.78$ V)\(^{22}\) redox couples in an electrochemical cell according to their $E^{°}_{ox/red}$ values.

Al-Soudi mentioned that, while representing signs on the electrodes for galvanic cells, students might wonder why the anode is negative if electrons are leaving. Furthermore, for electrolytic cells, how electrons can flow from positive to negative is not intuitive\(^{31}\). Garnett and Treagust reported that some students who have previously taken physics were confused when defining current in electrochemical cells\(^{2,21}\). One student conception is that electron flow is from cathode to anode in a galvanic cell according to conventional current (movement of positive charge). Ogude and Bradley indicated that the use of positive or
negative signs when identifying electrodes is irrelevant to understanding the electrochemical process.  

Students’ conceptions regarding the signs on the electrodes have been addressed in the teaching sequence as follows:

1. In the “Electrochemistry conventions” module the cathode and anode were defined without regard to the type of cell, which permits the electrode potentials to be related to the spontaneity of the redox process in a consistent manner.

2. In the “Redox solutions and inert metal electrodes” module, the concept of electrode charge is mentioned when explaining interfacial equilibrium. However, our approach emphasizes the relative positions of the Fermi levels of the redox half-cells as the fundamental concept required for understanding the electrochemical process.

3. In the “Representational models of Gibbs free energy” module the process of electron transfer is described using a thermodynamic approach, which allows the spontaneity of redox reactions to be explained based on differences in Fermi levels between redox half-reactions and not on differences of electrode charge.

In the modules mentioned above fundamental concepts in electrochemistry are addressed without the need to designate the sign of the charge on the electrode. Therefore, in order to avoid unnecessary confusion, it is reasonable to propose that the use of plus and minus sign designations on electrodes be removed from electrochemistry instruction.
4.10. Electric current in electrochemical cells

Argument:

Garnett and Treagust reported that one student’s conception is that electrons flow through the salt bridge and electrolyte solution in order to complete the circuit\textsuperscript{21}. Furthermore, they found that students taking both physics and chemistry were more likely to confront difficulties understanding the movement of electrons through the electrochemical cell than students not taking physics\textsuperscript{2}. One student’s conception is that electric current in an electrochemical cell is due to the movement of electrons and protons in opposite directions. In this part of the teaching sequence, we describe the function of the salt bridge and the movement of charge in an electrochemical cell while taking into consideration potential students’ conceptions.

Rationale:

Different models are used in chemistry and physics to describe the concept of electric current. Electric current is defined as the flow of charge through a conductive material. In physics, the concept of electric charge is modeled as the movement of positive and negative charges. The direction of the movement of positive charge through the surface is defined as conventional current. The movement of electrons through the metal surface is defined as electron current and it flows in opposite direction to the conventional current. These models of electric current are introduced in basic physics in order to study the electric and magnetic properties of conductive materials. However, this model can give rise to the students’
conception in electrochemistry mentioned above regarding proton flow in an electrochemical cell.

Schmidt et al. indicated that when referring to the electrochemical cell as an electric circuit, the use of the term “circuit” can also be a source of students’ conceptions in regard to the movement of charge in the electrochemical process. In everyday language movement in a circuit is often viewed as occurring in a closed, continuous, circular pattern. In electrochemistry this is not the case, where current involves the movement of ions in opposite direction in solution and salt bridge while electrons are moving from anode to anode through the external circuit. We aim for instructors to emphasize the direction of the current and the nature of charge carriers (electron or ions) in electrochemical cells while describing electric current as follows:

1. Electrons flow through the external circuit of the electrochemical cell from the anode to the cathode.

2. Cations and anions move in opposite directions in the salt bridge and in solution in order to address the charge imbalance resulting from the transfer of electrons between half-cells.

Ozkaya et al. found that one conception among prospective chemistry instructors is that a metal can be used as a salt bridge. In this part of the teaching sequence, students connect half-cells using a metal wire in place of a salt bridge and observe that the cell is not operational. By using this approach, we aim for students to understand that electric current in
solution is due to the movement of ions and not electrons, and that a metal cannot provide the electrolytic conduction required for the electrochemical cell to function.

4.11. The external circuit

Argument:

Conceptual understanding of electrochemical processes requires the integration of physics concepts such as potential, current and resistance. However, explanations regarding the characteristics and function of electrical components (e.g., voltmeter) are often lacking in chemistry textbooks. Remarkably, the same researchers who set out to identify misconceptions failed to recognize that a predominant conception among students is that a significant flow of electrons is permitted through an electrochemical cell connected to a voltmeter despite the fact that this conception was explicitly shown during the studies. We propose to explain the function of the voltmeter by introducing the concepts of resistance, current and potential during electrochemistry instruction in order to promote conceptual understanding about the role of the electrical components when connected to an electrochemical cell.

Rationale:

In electrochemistry we study the integration of chemical reactions and electrical circuits. Therefore, understanding of concepts studied in physics courses such as resistance, current, potential, and electrical circuits is essential during the study of the electrochemical process. Educational activities that use the properties of resistance, current and potential in an
electrochemical cell have been published\textsuperscript{34,35}. In these activities, the concepts of resistance and current have been introduced to explore the applicability of electrochemical cells as electrical devices. For example, Kelter et al. developed an activity where students construct an electrochemical cell (using orange juice as the electrolyte solution) to deliver current through a clock\textsuperscript{35}. Students used Ohm’s Law to relate current, voltage and resistance in the electrochemical cell. However, explanations about the characteristics and significance of these concepts in the electrochemical process were missing. For instance, this activity does not provide any explanation about the role of the external circuit with regards to the electrochemical process. The concept of resistance is only explained in the context of the chemical system (solution resistance), excluding the external circuit (e.g. voltmeter resistance). Kelter \textit{et al.}’s approach emphasizes calculations of solution resistance and voltage drop, resulting in a lack of conceptual learning among students\textsuperscript{4}. The teaching sequence developed proposes a teaching model that explicitly defines and relates the electrical and chemical components of the electrochemical cell. Conceptual understanding is fostered by relating the function of the electrical components of the cell to the resulting electrochemical process.

An examination of fourteen general chemistry textbooks, including the most popular current ones reveals a lack of explanations about the electrical requirements for measuring $E^\circ_{\text{cell}}$ between two half-cells\textsuperscript{8-11,38}. Consequently, during electrochemistry instruction the voltmeter is commonly introduced to students as a “black box” used to measure a potential. In this module the “black box” problem is addressed by exposing students to the basic circuit
of a voltmeter (see Figure 4.16) and relating the resistance in the external circuit (voltmeter resistance) with the redox processes occurring in the cell.

![Diagram of a basic voltmeter circuit](image)

Figure 4.16: Basic circuit of a voltmeter in which current is measured in the ammeter and $E_{cell}$ is determined according to Ohm’s Law.$^{39}$

The activity involves students constructing a basic voltmeter according to Figure 4.16 and measuring the current through a cell at various resistance values. Figure 4.17 shows electrochemical setups for two values of voltmeter resistance, one high (left hand cell) and one low (right hand cell). The resistance in the voltmeter sets the electrical conditions for the two scenarios shown in Figure 4.17. The amount of current through the cell is almost zero at high resistance ($1.0 \times 10^6 \ \Omega$), whereas at low resistance (100 $\Omega$) a significant amount of electrons is allowed to flow through the cell. The fact that these scenarios are not investigated in traditional instruction might contribute to the student’s conception that the voltmeter measures the charge flow in an electrochemical cell.$^{32}$
Figure 4.17: Relation between external circuit resistance and electron transfer in an electrochemical cell.

The relation between current, external circuit resistance and potential in an electrochemical cell is explored by determining cell potentials and electric current for the two scenarios shown in Figure 4.17 according to Ohm’s law. This approach prompts students to identify the electrical conditions required (negligible current and high resistance) and the electrochemical process occurring (interfacial equilibrium) when measuring $E^\circ_{\text{cell}}$ for an electrochemical process later in this teaching sequence.

### 4.12. Relating redox reactions and electric circuits

**Argument:**

Representations of electrochemical cells used in textbooks often communicate wrong ideas about the electrochemical process\textsuperscript{19,36}. For example, when a voltmeter is connected to
an electrochemical cell, the current through the cell is almost zero due to the high resistance of the voltmeter. This fact is contradicted by figures presented in many textbooks (see Figure 4.18), where illustrations specifically show a flow of electrons through the voltmeter\textsuperscript{36}.

![Figure 4.18: Representation of electrochemical cell as shown in textbooks\textsuperscript{9}.](image)

Consequently, one of the most common students’ conception is that the voltmeter measures the charge flow through the electrochemical cell\textsuperscript{32}. We propose to address this key misunderstanding by explicitly studying the function of the voltmeter. We aim for the students to relate the measurements (potential, current and resistance) to the electrochemical process and to view the external circuit and chemical species in an electrochemical cell in an integrated fashion.
Rationale:

Garnett and Treagust identified the lack of explanations about electrical circuits during electrochemistry instruction while Sanger and Greenbowe identified statements used in textbooks to describe concepts as important sources of student conceptions. For example, the use of the term “external circuit” to refer to the electrical components connected to the electrochemical cell promotes the idea about classifying the voltmeter as not being part of the electrochemical process. In this module, Ohm’s law is used to relate the properties of the external circuit (resistance, current and potential) and the redox process. Ohm’s law is used in physics instruction to describe the relation between potential, resistance and current in a resistive electrical circuit. However, Periago and Bohigas reported that physics students confront difficulties understanding the applicability of Ohm’s law. One student conception is that a potential can be measured between two points on a wire despite the assumption that the conducting wire connecting the points is essentially resistance free. Through this module of the teaching sequence this conception is taken into consideration where Ohm’s law is used to relate current and potential of an electrochemical cell at various resistance values. It is expected that as students observe potential measurements made at various external circuit resistance values in an electrochemical process, they will deduce that these data do not follow the linear relationship that is usually encountered in physics.

The activity involves students constructing an electrochemical cell according to Figure 4.19, where a shunt resistor is connected in parallel to an electrochemical cell and potential is measured using a voltmeter. The shunt resistor serves as an alternative pathway
for electrons to flow through the external circuit when measuring the cell potential. This allows \( E_{\text{cell}} \) to be measured while different magnitudes of current flow through the cell. By constructing graphs of potential as a function of shunt resistance and current, we aim for students to relate the electrical conditions for measuring \( E^\circ_{\text{cell}} \) to the electrochemical process. Graphs 1 and 2 show resistance, current and potential trends for the electrochemical process represented in Figure 4.19. According to Graph 1, as the shunt resistance increases, \( E_{\text{cell}} \) reaches a plateau which corresponds to the equilibrium \( E^\circ_{\text{cell}} \) for the redox reaction. Graph 2 indicates that a decrease in electric current occurs as the \( E_{\text{cell}} \) approaches \( E^\circ_{\text{cell}} \). This approach allows the determination of the electrical condition required for measuring \( E^\circ_{\text{cell}} \) for a redox reaction, namely, high resistance corresponding to negligible current through the cell.
Figure 4.19: Representation of an electrochemical cell for the following redox process:
\[ \text{Cu}^{2+}(\text{aq}) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(\text{aq}) \quad E^\circ_{\text{cell}} = +1.1 \text{ V}. \]
Each redox couple in solution with an electrode represents a redox half-cell (one in each container). The two half-cells are connected by a porous material saturated with electrolyte solution (e.g. KCl) known as the salt bridge. Each redox half-cell is connected to one end of a shunt resistor and the potential is measured in volts using a voltmeter.
This module focuses on the relationship between these conditions to the electron transfer occurring in the electrochemical cell. Chemistry instruction commonly includes the
convention that during a net electrochemical reaction the flow of electrons is always through the external circuit from the anode to the cathode disregarding the fact that when the cell is connected to a voltmeter, electron transfer is not allowed between the two half-cells but instead interfacial equilibrium prevails in each half-cell as shown in Figure 4.21 (double arrows between the electrode and solution).

\[
\begin{align*}
\text{Cu}_\text{(s)} & \rightleftharpoons \text{Cu}^{2+} \text{(aq)} + 2e^- \\
\text{Zn}_\text{(s)} & \rightleftharpoons \text{Zn}^{2+} \text{(aq)} + 2e^- 
\end{align*}
\]

Figure 4.21: Representation of interfacial equilibrium in an electrochemical cell.

This module of the teaching sequence emphasizes the concept of interfacial equilibrium and illustrates the transfer of electrons when a voltmeter is connected to an electrochemical cell as shown in Figure 4.21. Using this approach the relation between the electrical conditions (high resistance and current almost zero) and the electron transfer in an electrochemical cell when measuring $E^\circ_{\text{cell}}$ is determined.
4.13. Nernst equation

Argument:

Electrochemistry instruction often emphasizes the quantitative aspects of the subject, which can result in a lack of conceptual understanding among students\(^4\). Sanger and Greenbowe reported student conceptions regarding the concept of potential and reaction quotient (Q) for redox reactions in concentration cells\(^2\). Although students were able to calculate \(E_\text{cell}^o\), they confronted difficulties recognizing that \(E_\text{cell}^o\) is always zero for concentration cells. Furthermore, students confronted difficulties recognizing the relation between \(E_\text{cell}\) and Q; they were often unable to calculate Q due to the fact that there is no net reaction because products and reactants are the same. We propose the use of representational models for the conceptual explanation of the relation among \(E_\text{cell}^o\), \(E_\text{cell}\) and Q in electrochemical cells.

Rationale:

Concentration cell refers to a cell composed of two redox half-cells, each containing both the oxidized and reduced forms of the same redox couple, but at different concentrations. In the traditional approach, the relation among \(E_\text{cell}^o\), \(E_\text{cell}\) and redox species concentration is described using the Nernst equation:

\[
E_\text{cell} = E_\text{cell}^o + \frac{RT}{nF} \ln Q
\]

where R is the gas constant (8.314472 J/K·mol), T is temperature in Kelvins, and Q is the reaction quotient. For,
Red$_1$ + Ox$_2$ → Ox$_1$ + Red$_2$

\[ Q = \frac{[\text{Ox}_1][\text{Red}_2]}{[\text{Red}_2][\text{Ox}_2]} \]

During electrochemistry experiments students usually measure $E_{\text{cell}}$ as the ratio of oxidized and reduced species concentrations is varied in the electrochemical cell$^{41}$. These experiments emphasize the quantitative aspect of the Nernst equation but lack conceptual explanation regarding the relations among $E^\circ_{\text{cell}}$, $E_{\text{cell}}$, $Q$ and the electrochemical process.

In our approach, we explain how changes in Gibbs free energy ($G$) of redox half-cells at interfacial equilibrium result from changes in redox species concentration by using representations involving the density of states model. Figure 4.22 depicts the density of states model for two redox half-reactions in a concentration cell. The density of states ($D$) relates to concentration according to the following equations:

\[ D_{\text{(occupied)}} = C_{\text{Red}} \cdot \exp \left[ \frac{- (G - G^\circ + \lambda)^2}{4\lambda kT} \right] \]

\[ D_{\text{(vacant)}} = C_{\text{Ox}} \cdot \exp \left[ \frac{- (G - G^\circ + \lambda)^2}{4\lambda kT} \right] \]

where $G^\circ$ is equal to $G^\circ_{\text{redox}}$ for the redox half-reaction, $C_{\text{Red}}$ and $C_{\text{Ox}}$ are the respective concentrations of the reduced and oxidized species respectively, $k$ is the Boltzmann constant ($1.3806 \times 10^{-23}$ J/K), $T$ is temperature in Kelvin and $\lambda$ is the reorganization energy (see section 2.2). In figure 4.22, $\lambda$ was set equal to $4.1 \times 10^4$ J/mol, a value that conveniently gives rise to an easily identifiable intersection point between $D_{\text{ox}}$ and $D_{\text{red}}$. 

122
For half-cell 1, curves were calculated for equimolar (0.1 M) concentrations of the oxidized and reduced forms of the ferri/ferro-cyanide redox couple, which correspond to $E_{\text{cell}} = E^{\circ}_{\text{cell}}$. For half-cell 2, the concentration of ferricyanide was decreased tenfold to 0.01 M, leaving ferrocyanide set at 0.1 M. The dashed curves of half-cell 2 indicate $D_{\text{(vacant)}}$ for the 0.1 M case ($E_{\text{cell}} = E^{\circ}_{\text{cell}}$).
Figure 4.22: Representation of density of states model for a concentration cell. Each graph represents a redox half-reaction containing the ferro/ferri-cyanide redox couple at different concentrations. G values were identified from graphical analysis of the intersection points. ΔG was determined by subtracting G values of redox half-reactions 1 and 2 as follows: $G^\circ_2 - G_1 = -31.38 \text{ kJ/mol} - (-26.12 \text{ kJ/mol}) = -5.26 \text{ kJ/mol}$. 
The representation above allows the determination of $G$ for a given concentration of oxidized and reduced species in a redox half-cell. For a concentration cell with each half-cell at standard conditions,

$$\Delta G^\circ = -nFE^\circ_{cell} = 0$$

We can determine $\Delta G^\circ$ from Figure 4.22 as follows:

$$\Delta G^\circ = G^\circ_2 - G^\circ_1 = 0$$

According to the density of states model, changes in the total Gibbs free energy of the redox reaction results in changes in the positions of the Fermi level for the redox half-cell. One learning objective in this module is for students to describe the relation between $\Delta G$ and the concentration of redox couples as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

For the reaction:

$$[\text{Fe(CN)}_6]^{4-}(0.1\text{M}) + *[\text{Fe(CN)}_6]^{3-}(0.1\text{M}) \rightarrow [\text{Fe(CN)}_6]^{3-}(0.01\text{M}) + *[\text{Fe(CN)}_6]^{4-}(0.1\text{M})$$

we have:

$$Q = \frac{(0.01 \text{ M}) \cdot (0.1\text{M})}{(0.1 \text{ M}) \cdot (0.1\text{M})} = 0.1$$

Substituting we obtain,

$$\Delta G = 0 + ((8.314472 \text{ J/K\cdot mol}) \cdot (298 \text{ K}) \cdot \ln(0.1)) = -5.71 \text{ kJ/mol}$$
This calculated value ($\Delta G = -5.71 \text{ kJ/mol}$) is comparable to the value obtained from the density of states model shown in Figure 4.22 ($\Delta G = -5.26 \text{ kJ/mol}$). This allows for the use of the density of states model as a teaching tool for determining $E^\circ_{\text{cell}}$ and $Q$, explaining the effects of concentration in the electrochemical process at a fundamental level, and differentiating between $\Delta G^\circ$ and $\Delta G$ values for a redox reaction in a concentration cell.

We aim for the student to understand the effects of concentration on the position of the Fermi level of a redox half-cell, which are reflected in the measured $E_{\text{cell}}$ value. As previously discussed, $\Delta G$ relates to $E_{\text{cell}}$ according to the following equation:

$$\Delta G = -nF E_{\text{cell}}$$

Substituting we obtain,

$$-nF E_{\text{cell}} = -nF E^\circ_{\text{cell}} + RT \ln Q$$

Then,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

which is the Nernst equation.

In this part of the teaching sequence, students predict shifts of $E_{\text{cell}}$ as concentration changes according to the density of states model and compare to the measured $E_{\text{cell}}$ values for a concentration cell. By using this representation, we aim for students to recognize the difference between $E_{\text{cell}}$ and $E^\circ_{\text{cell}}$ for a redox reaction in an electrochemical cell.
This approach allows the Nernst equation to be explained according to the density of states model. Using the proposed representations, we aim for students to understand that the Nernst equation describes changes in $\Delta G$ as redox species concentration changes in an electrochemical cell, which results in shifts of the Fermi levels of redox half-cells at interfacial equilibrium.
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41. Evans, J. S., Verification of form of Nernst equation - An experiment for introductory chemistry. *Journal of Chemical Education* 1968, 45 (8), 532-533.
Chapter 5: Results, conclusions and future work

5.1. Phenomenographic analysis

A phenomenographic analysis of the data collected during this study revealed the different ways in which participant A (expert electrochemist) and participant B (mature chemistry professor) experienced the teaching of electrochemistry. The most predominant aspects of the qualitative variation in instructors’ consciousness about the teaching of electrochemistry are categorized and described in Table 5.1. The subject knowledge category shows the most significant variation between participants in this study. Instructor expertise plays an essential role in the development of teaching sequences. The expertise of participant A allowed for insightful discussions about the electrochemical process in terms of discipline-specific theories and models whereas participant B expertise (general chemistry instruction) allowed for translating such in-depth theories and models into a context that was meaningful, specific and coherent for students. When confronting instructors with the reported students’ conceptions, participant A often questioned the correlation between some of the students’ conceptions and the traditional approach in electrochemistry instruction. For example, participant A questioned the use of the term circuit when referring to the function of the salt bridge (e.g., “the salt bridge completes the circuit”) and students’ conceptions regarding the movement of charge through the electrochemical cell. However, participant B found itself promoting some of the students’ conceptions due to the lack of awareness and deep understanding of the intricacies of the subject matter. The emphasis on a quantitative approach found in the general chemistry textbooks reviewed was found to hamper a more
accurate and scientifically sound approach by participant B. Participant B recognized using the additive method to calculate $E^{\circ}_{\text{cell}}$ ($E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$) during instruction which can potentially generate students conceptions regarding the thermodynamic nature of the $E^{\circ}_{\text{cell}}$ value.

Another relevant aspect of discussion was the use of teaching resources such as textbooks and educational activities during instruction. Both instructors acknowledged the potential degree of confusion that terminology and oversimplified statements in textbooks could raise. Participant A identified errors in textbook representations illustrating electrochemical cells connected to a voltmeter (e.g., the significant flow of electrons through an electrochemical cell connected to a voltmeter). However, participant B used textbooks as the primary teaching resource without recognizing that the illustration and statements used in textbooks are potential sources of students’ conceptions.
Table 5.1: Description of categories resulting from the phenomenographic study of instructors’ consciousness about electrochemistry instruction.

<table>
<thead>
<tr>
<th>Category</th>
<th>Participant A</th>
<th>Participant B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subject knowledge</td>
<td>Refers to scientific models and theories when explaining the electrochemical process.</td>
<td>Refers to the subject knowledge found in general chemistry textbooks.</td>
</tr>
<tr>
<td>Recognizing student conceptions</td>
<td>Recognizes student conceptions although sometimes questioning the significance of some of the student difficulties.</td>
<td>Recognizes how the instructor may promote some of the student conceptions due to the lack of subject knowledge and misleading explanations and representations found in textbooks.</td>
</tr>
<tr>
<td>Instructor expectations from the teaching sequence</td>
<td>Emphasizes the accuracy in the explanations about the scientific models and theories used to introduce the electrochemical concepts.</td>
<td>Emphasizes the need for coherent connection between the concepts in an explicit fashion.</td>
</tr>
<tr>
<td>Use of teaching resources (e.g.; textbooks)</td>
<td>Acknowledges the errors in general chemistry textbooks when explaining the concepts.</td>
<td>Uses the general chemistry textbook as the primary instructional source, not realizing that figures and statements found in textbooks are possible sources of students’ conceptions.</td>
</tr>
</tbody>
</table>

Each instructor related to the teaching sequence according to their own experience. For participant B, the development of the electrochemistry teaching sequence was a learning experience in terms of the subject knowledge, whereas for participant A the development of the teaching sequence became an evaluation of the fundamental concepts required for the understanding of the electrochemical concepts and the educational needs (e.g., connection...
among concepts) for translating these concepts to students. The resulting electrochemistry teaching sequence fulfils each of the instructors’ expectations in terms of the scientific content, educational expectations (address students conceptions), design (coherent and explicit) and the educational activities provided.

In conclusion, an electrochemistry teaching sequence was developed taking into consideration how to most effectively address students’ conceptions in electrochemistry and shifting the pedagogical emphasis from a quantitative approach to a more profound and conceptually connected approach. The proposed teaching sequence have shown to address instructors’ consciousness about the teaching of electrochemistry resulting in an educational tool that fulfills instructors’ expectations about electrochemistry instruction.

5.2. Conclusions

An exhaustive examination of the literature revealed the difficulties experienced by students and instructors around the world understanding the topic of electrochemistry. A revision of fourteen general chemistry textbooks including three of the most popular ones, facilitated understanding the traditional approach in electrochemistry instruction. The identified sources of conceptions and understanding of the traditional approach allowed contributing knowledge to the development of the instructional material (teaching sequence). Thirteen modules were developed and major contributions for conceptual change included: a conceptual approach based on Gibbs free energy, addressing conceptions about the electrochemical process and developing educational activities to engage the students during the learning process.
The theoretical framework chosen, “Two Worlds”, facilitated the translation of core concepts from discipline-specific models and theories (Marcus theory and DOS) into a context that makes explicit the electrochemical process to general chemistry students. The approach for the design of the teaching sequence (section 3.2.1) guided the reconstruction of the electrochemistry curriculum through a coherent and unambiguous connection between the concepts of redox reactions and electric circuits using terminology, representations and analogies as teaching tools.

The electrochemistry teaching sequence was evaluated using a phenomenographic approach to assess chemistry instructors’ consciousness with regards to the teaching of electrochemistry. This approach allowed for the development of an electrochemistry teaching sequence through a continuous modification of the modules until instructors’ expectations were fulfilled. A phenomenographic analysis revealed four categories of qualitative variation in instructors’ consciousness: subject knowledge, recognizing students’ conceptions, instructors’ expectations for the teaching sequence and use of teaching resources.

5.3. Proposed future work

The proposed electrochemistry sequence has shown to serve as a tool to evaluate instructors’ consciousness about the teaching of electrochemistry using a phenomenographic approach. However, this work is limited to the evaluation of two chemistry instructors; therefore, an in-depth investigation including a greater population of instructors is appropriate. In addition, the significance of instructors’ expertise on the teaching of electrochemistry should be further investigated\(^1\). Field testing the electrochemistry sequence
with students from different levels (i.e. high school, undergraduate, graduate) could provide insight into the effectiveness of this sequence to mitigate or eliminate students’ conceptions in electrochemistry that have proven to be persistent through different cultures and academic levels.

**Implementation and assessment**

The electrochemistry teaching sequence developed in this work has a strong potential to benefit students and instructors as it provides coherent and explicit scientific explanations of the fundamental concepts involved in the electrochemical process. The feasibility of the teaching sequence in facilitating conceptual change among students and instructors needs to be validated. An assessment tool needs to be designed to measure the persistence of the reported electrochemistry conceptions after an implementation of the teaching sequence is conducted. Moreover, the effectiveness of the teaching sequence in bridging the gap between students’ conceptions and the intended knowledge during electrochemistry instruction needs to be investigated.

In addition, the teaching sequence can serve as research tool to investigate: students cognitive pathways in connecting models and theories to the real world\(^4\), the benefits of using representations from discipline-specific models and theories during instruction in promoting expert-like modeling practice among students\(^2,3,4\), and the effectiveness of educational activities at engaging and motivating the students during the learning process\(^4\).
REFERENCES


APPENDICES

Appendix A. Electrochemical series activity ................................................................. 141
Appendix B. Gibbs free energy of the electrochemical process ................................. 143
Appendix C. Reference electrode ............................................................................. 148
Appendix D. Interfacial equilibrium ......................................................................... 150
Appendix E. Electrodes ............................................................................................. 153
Appendix F. The external circuit .............................................................................. 156
Appendix G. Relating redox reactions and electric circuits ..................................... 158
Appendix H. Nernst Equation ................................................................................... 161
References .................................................................................................................. 165
Appendix A. Electrochemical series activity

Purpose:

Describe the relative redox activity (easy of oxidation) of chemical species by constructing thermodynamic cycles and comparing the standard enthalpy change (ΔH°) values of the oxidation reactions.

Questions:

1. List all physical processes involved in the oxidation of Na metal.
   \[ \text{Na} \,(s) \rightarrow \text{Na}^+ \,(aq) + \text{e}^- \]

2. Write the reactions that describe each of the physical processes listed in the answer to question 1.

3. List the types of energies required for each reaction.

4. Construct a diagram connecting the reactions identified in question 2 to describe the oxidation of Na \,(s). Label the reactions with their corresponding energies.

5. What is the physical meaning of the sign in the enthalpy values?

6. How can one use these individual energy values to determine the total enthalpy change (ΔH°) for the oxidation reaction? Determine ΔH° using tabulated values\(^1\,\,2\).

7. Construct a diagram (thermodynamic cycle) and determine ΔH° for the oxidation of each the following redox couples:
   a. \( \text{Zn} \,(s)/\text{Zn}^{2+} \,(aq) \)
   b. \( \text{Cu} 
   \,(s)/\text{Cu}^{2+} \,(aq) \)
c. $\text{Pt}_\text{aq}/\text{Pt}^{2+}\text{aq}$

d. $\text{F}^-\text{aq}/\text{F}_2\text{g}$

e. $\text{Fe}^{2+}\text{aq}/\text{Fe}^{3+}\text{aq}$

f. $\text{Cl}^-\text{aq}/\frac{1}{2}\text{Cl}_2\text{g}$

8. Order the metals Zn, Cu and Pt according to their relative activity (from the most active to least active metal).

9. According to the results above, can you explain the use of Pt as an inert metal electrode?
Appendix B. Gibbs free energy of the electrochemical process

Purpose:

Describe the electrochemical process in terms of the standard Gibbs free energy of the electron(s) transferred in a redox half-reaction ($G^\circ_{e\text{ redox}}$).

Questions:

Part I. Gibbs free energy curves

1. Determine the standard Gibbs free energy change ($\Delta G^\circ$) for the following oxidation process (using tabulated values$^{1,2}$):

$$\text{H}_2(1\text{atm}) \rightarrow \text{H}^+(1.0\text{M}) + e^- \text{ (vac)}$$

2. Determine the standard Gibbs free energy change ($\Delta G^\circ$) for the following oxidation process using the reaction above as a reference:

$$\text{Fe}^{2+}(0.01\text{M}) \rightarrow \text{Fe}^{3+}(0.01\text{M}) + e^- \text{ (vac)}$$

3. For the following redox half-reaction: $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$

   a. Construct a representation describing the equilibrium between reactants and products.

   b. Label the Gibbs free energy of the reduced species, oxidized species and the electron transferred in the representation.

   c. Determine $G^\circ_{e\text{ redox}}$ using tabulated values$^3$.

4. Construct a representation of Gibbs free energy and define $G^\circ_{e\text{ redox}}$ for the redox half-reaction above.
5. How well do the $\Delta G^\circ$ and $G^\circ_{e, \text{redox}}$ values for the redox half-reaction determined in parts 2 and 3c compare?

6. Based on your observations, can you define $\Delta G^\circ$ for a redox process?

**Part II. Density of states model**

Figure 1B represents the density of states model for the following redox reaction:

$$\text{MnO}_4^{-}\,(3.0\,\text{mM}) + 8\text{H}^+\,(3.0\,\text{M}) + 5\text{[Fe(CN)]}_6^{4+}\,(3.0\,\text{mM}) \rightarrow 5\text{Fe}[(\text{CN})_6]^{3-}\,(3.0\,\text{mM}) + \text{Mn}^{2+}\,(3.0\,\text{mM}) + 4\text{H}_2\text{O} \,(l)$$

![Figure 1B: Distribution of electron energy states for two redox half–reactions and the energy states available for electron transfer between the two redox half-reactions.](image)

Answer the following question using the representation above:

1. Identify the density of states for reduced and oxidized species in the redox reaction.
2. Determine the \( G_e^{\text{redox}} \) value for each half-reaction.

3. Identify the Fermi levels in the representation.

4. Determine \( \Delta G^\circ \) and describe the spontaneous electron transfer between the redox half-reactions.

**Part III. Measuring the cell potential (\( E_{\text{cell}} \))**

**Experiment:**

Construct the following electrochemical cell:

![Diagram of electrochemical cell](image)

**Procedure:**

Safety note: Students should wear gloves and work in the hood during the experiment.
1. Prepare 1.0 mM solutions of each of the following compounds: K₄Fe(CN)₆ and K₃Fe(CN)₆.

2. Transfer 30 mL of each of the solutions to a 100 mL beaker.

3. Prepare a 0.01 M solution of KMnO₄.

Safety Note: The following stock solutions (part 4 and 5) should be prepared by the instructor in the hood and wearing gloves.

4. Prepare a 6.0 M solution of H₂SO₄.

5. Prepare a 1.0 mM stock solution of acidic KMnO₄ by transferring 10 mL of 0.01 M KMnO₄ and 50 mL of 6.0 M H₂SO₄ to a 100 mL volumetric flask (fill to the mark with deionized water).

6. Transfer 30 mL of the KMnO₄ stock solution to a 100 mL beaker.

7. Insert a platinum electrode into each of the beakers (half-cells).

8. Prepare the salt bridge by soaking filter paper in a 1.0 M KCl solution.

9. Connect both half-cells (beakers prepared in parts 2 and 6) using the filter paper as shown in Figure 2B.

10. Connect the electrochemical cell to the voltmeter according to Figure 2B. Read the potential.

Questions:

1. Using the measured standard cell potential (E°cell), determine ΔG° as follows:

   \[ \Delta G° = -nF E°_{cell} \]

2. Compare the ΔG° values determined in parts I and II, and III.
3. What does the $E^{\circ}_{\text{cell}}$ value represent in the electrochemical process?
Appendix C. Reference electrode

Purpose:

Determine the absolute standard redox potential ($E^\circ_{\text{ox/red}}$) for a redox half-reaction using the standard hydrogen electrode (SHE) as a reference.

Questions:

The standard hydrogen electrode (SHE) reaction is as follows:

$$\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+_{(aq)} + 2\text{e}^- \quad E^\circ = 0$$

1. Using thermodynamic values, calculate $E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}}$ for the following redox half-reaction using SHE as a reference as shown in Figure 1C:

$$\text{Fe}^{2+}_{(a=1)} \rightleftharpoons \text{Fe}^{3+}_{(a=1)} + \text{e}^-$$

Where $E^\circ_{\text{cell}} = E^\circ_{\text{ox/red}} - E_{\text{SHE}}$

2. Compare the calculated $E^\circ_{\text{ox/red}}$ with values reported in tables\(^4\).
Figure 1C: Electrochemical cell comprised of a redox half-cell at standard conditions connected to SHE. \( \text{H}_2 \text{ (latm)} \) is bubbled through the solution containing Pt wire immersed in \( \text{H}^+(a=1) \) solution so that dissolved \( \text{H}^+ \) is in equilibrium with \( \text{H}_2\text{ (latm)} \). (Figure was modified from the reference)\(^5\).
Appendix D. Interfacial equilibrium

Purpose:

Describe the interactions between an inert metal electrode and redox species in solution in a redox half-cell.

Questions:

1. Describe the analogies between the metal electrode and redox solution for each of the concepts in Table 1D.

Table 1D: Comparison between redox solutions and metal electrodes with regard to electronic states.

<table>
<thead>
<tr>
<th>Concept</th>
<th>Redox solution</th>
<th>Metal electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of electronic states</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron-occupied states</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron-vacant states</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fermi level</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gibbs energy at the Fermi level</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Construct a representation describing the interfacial equilibrium between a Pt metal electrode and the following redox species in solution according to the density of states model:

\[ \text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^- \]

Experiment:

Construct the following electrochemical cell:
Procedure:

Safety note: Students should wear gloves and work in the hood during the experiment.

1. Prepare 1.0 mM solutions of each of the following redox compounds: $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$.

2. Transfer 30 mL of each of the solutions to a 100 mL beaker.

3. Prepare a 0.01 M solution of KMnO$_4$.

Safety note: The following stock solutions should be prepared by the instructor in the hood and wearing gloves.


Figure 1D: Electrochemical cell connected to a voltmeter.
5. Prepare a 1.0 mM stock solution of acidic KMnO₄ by transferring 10 mL of 0.01 M KMnO₄ and 50 mL of 6.0 M H₂SO₄ to a 100 mL volumetric flask (fill to the mark with deionized water).

6. Transfer 30 mL of the KMnO₄ stock solution to a 100 mL beaker.

7. Insert a platinum electrode into each of the beakers (half-cells).

8. Prepare the salt bridge by soaking filter paper into a 1.0 M KCl solution.

9. Connect both half-cells (beakers prepared in parts 2 and 6) using the filter paper as shown in Figure 1D.

10. Connect the electrochemical cell to the voltmeter according to Figure 1D. Read the potential.

11. Replace the Pt electrode with a Au metal electrode. Read the potential.

Questions:

1. Construct a representation describing the spontaneity of the electrochemical process that would initially take place if the voltmeter was replaced with a resistive load that allowed current through the circuit in the electrochemical cell using the density of electronic states model.

2. Compare E_{cell} values obtained when using Pt and Au metal electrodes.

3. Based on your observations, what is the function of an inert electrode in the electrochemical process?
Appendix E: Electrodes

Purpose:

Describe the function of active and inert electrodes in the electrochemical process.

Experiment:

Part I. Active electrodes

Construct an electrochemical cell for the following redox reaction:

\[ 2\text{Ag}^{+}_{(0.01\text{M})} + \text{Zn}_{(s)} \rightarrow 2\text{Ag}_{(s)} + \text{Zn}^{2+}_{(0.01\text{M})} \]

Procedure:

1. Prepare 0.01 M solutions of each of the following redox compounds: AgNO₃ and ZnSO₄.
2. Transfer 20 mL of the AgNO₃ solution to a 100 mL beaker and 20 mL of the ZnSO₄ solution to another 100 mL beaker.
3. Insert a Ag metal electrode into the beaker containing the AgNO₃ solution and a Zn metal electrode into the beaker containing the ZnSO₄ solution.
4. Prepare the salt bridge by soaking a piece of filter paper in a 1.0 M NaNO₃ solution.
5. Connect both half-cells (beakers prepared in parts 2 and 3) using the salt bridge.
6. Connect the electrochemical cell to the voltmeter according to electrochemical conventions. Read the potential.
7. Replace the Ag electrode with a Pt electrode. Record your observations.
Part II: Inert Electrodes

Construct an electrochemical cell for the following redox reaction:

\[ 2[\text{Fe(CN)}_6]^{3-}_{(0.01\text{M})} + \text{Zn}_{(s)} \rightarrow 2[\text{Fe(CN)}_6]^{4+}_{(0.01\text{M})} + \text{Zn}^{2+}_{(s)} \]

Procedure:

1. Prepare 0.01 M solutions of each of the following redox compounds: \( K_4\text{Fe(CN)}_6 \) and \( K_3\text{Fe(CN)}_6 \).
2. Transfer 10 mL of each solution into a 100 mL beaker and insert a Ag metal electrode into the solution.
3. Prepare the salt bridge by soaking a piece of filter paper into a 1.0 M NaNO\(_3\) solution.
4. Connect the \( K_4\text{Fe(CN)}_6 / K_3\text{Fe(CN)}_6 \) redox half-cell to the Zn/Zn\(^{2+}\) half-cell prepared in part I using the salt bridge.
5. Connect the electrochemical cell to the voltmeter according to electrochemical conventions. Read the potential.
6. Replace the Ag electrode with a Pt electrode. Record your observations.
7. Now, replace the Pt electrode with Au electrode. Record your observations.

Questions:

1. Compare the cell potentials observed for the electrochemical cells in part I when replacing Ag with Pt in the half-cell containing AgNO\(_3\) solution. Explain
2. Compare the cell potential observed for the electrochemical cells in part II upon replacing Ag with Pt and Au electrodes in the half-cell containing $K_4Fe(CN)_6$ / $K_3Fe(CN)_6$ solution. Explain.

3. According to your observations, describe the function of the Ag electrode in the electrochemical cells in part I and II.
Appendix F: The external circuit

Purpose:

Describe the function of the electrical components of the electrochemical cell by constructing the basic circuit of a voltmeter and determining resistance, current and voltage in the electrochemical cell.

Experiment:

1. Using a 10 MΩ resistor and an ammeter, construct the basic circuit of a voltmeter according to Figure 1F. Hint: Connect the resistor in series to one end of the ammeter using an alligator clip.

![Figure 1F: Basic circuit of a voltmeter.]

2. Construct an electrochemical cell for the following redox reaction:

   \[ \text{Zn}(s) + \text{Cu}^{2+}_{(0.1M)} \rightarrow \text{Zn}^{2+}_{(0.1M)} + \text{Cu}(s) \]
3. Connect the electrochemical cell to the voltmeter circuit according to electrochemical conventions. Record the ammeter reading.

4. Determine the potential of the electrochemical cell using Ohm’s Law.

5. Replace the resistor in the voltmeter circuit with a 100 Ω resistor. Record the ammeter reading. Determine cell potential.

6. According to your observations, can you describe the relation between the resistance of the external circuit and the measured current in the electrochemical cell?
Appendix G: Relating redox reactions and electric circuits

Purpose:

Determine the electrical conditions required (resistance and current) for accurately measuring $E_{\text{cell}}$ under interfacial equilibrium and relate those conditions to the electron transfer occurring in the electrochemical cell.

Experiment:

1. Construct an electrochemical cell for the following redox reaction:

$$\text{Zn}_\text{(s)} + \text{Cu}^{2+}_{(0.1\text{M})} \rightarrow \text{Zn}^{2+}_{(0.1\text{M})} + \text{Cu}_\text{(s)}$$

2. Connect the electrochemical cell to a voltmeter according to electrochemical conventions.

3. Connect a 150 $\Omega$ resistor between the two leads of the electrochemical cell as shown in Figure 1G. Measure $E_{\text{cell}}$. Hint: Use alligator clips to connect the resistor to the cell and voltmeter.
Figure 1G: Electrochemical cell connected to a voltmeter and resistor.

4. Replace the resistor according to the resistance values listed in Table 1G. Measure $E_{\text{cell}}$ for each of the resistance values.

Table 1G: Experimental results.

<table>
<thead>
<tr>
<th>Resistance (Ω)</th>
<th>Measured $E_{\text{cell}}$ (V)</th>
<th>Calculated current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5. Calculate the electric current in the electrochemical cell for each resistance value by applying Ohm’s law.

6. Graph resistance versus voltage.

7. Graph current versus voltage.

Questions:

Questions 1 and 2 refer to the graphs constructed during the experimental section.

1. Describe $E_{\text{cell}}$ as resistance changes in the electrochemical cell.

2. Describe $E_{\text{cell}}$ as the electric current changes in the electrochemical cell.

3. Describe the resistance and current when the cell approaches the $E_{\text{cell}}^\circ$ value of the redox reaction.

4. According to your observations, what are the electrical conditions (current and resistance) required in order to measure $E_{\text{cell}}^\circ$ using a voltmeter?

5. Construct a representation of an electrochemical cell describing the electrochemical process occurring when connected to a voltmeter (e.g., electron transfer, equilibrium).
Appendix H: Nernst Equation

Purpose:

Differentiate between $E_{\text{cell}}$ and $E^\circ_{\text{cell}}$ by describing Gibbs free energy changes ($\Delta G$) resulting from changes in redox species concentration in a concentration cell.

Part I: Density of electronic states model

1. Calculate $G^\circ_e$ for the redox half-reactions using tabulated values.$^3$

   
   
   \[
   \text{[Fe(CN)\textsubscript{6}]^{4-}_{(0.01M)} \rightleftharpoons [Fe(CN)\textsubscript{6}]^{3-}_{(0.01M)} + e^-}
   \]

2. Calculate the density of states (D) for each redox species in the concentration cell ([Fe(CN)\textsubscript{6}]^{4-} and Fe(CN)\textsubscript{6}^{3-}) as G changes using the following equations:

   \[
   D_{\text{(occupied)}} = C_{\text{Red}} \cdot \exp \left[ \frac{-(G - G^\circ + \lambda)^2}{4\lambda kT} \right]
   \]

   \[
   D_{\text{(occupied)}} = C_{\text{Ox}} \cdot \exp \left[ \frac{-(G - G^\circ + \lambda)^2}{4\lambda kT} \right]
   \]

where $G^\circ$ is equal to the $G^\circ_e$ of the redox half-reaction, $C_{\text{Red}}$ and $C_{\text{Ox}}$ are analytical concentrations of reduced and oxidized species, respectively, $k$ is the Boltzmann constant (1.3806 x 10^-23 J/K), $T$ is temperature in Kelvin and $\lambda$ is the reorganization energy. Hints: 1. Set $\lambda$ equal to 4.1 x10^4 J/mol in order to be able to identify the intersection points in the graph. 2. Determine D for a range of G values (e.g., from 1.0x10^5 J/mol to -1.5x10^5 J/mol).

3. Graph G versus D for each redox half-reaction in the concentration cell in Figure 1H. Hint: Construct one graph for each half-cell by plotting G values on the y-axis versus the calculated D values for the oxidized and reduced species on the x-axis.
4. Identify the Fermi levels of each half cell represented in the graphs.

5. By performing graphical analysis, determine $G$ and $G^\circ$ values for each half-cell.

6. Using both graphs, determine $\Delta G^\circ$ and $\Delta G$ values for the redox reaction in the concentration cell.

**Part II: Gibbs free energy**

For the following redox reaction:

$$[\text{Fe(CN)}_6]^{4-} \stackrel{0.1\text{M}}{\rightleftharpoons} [\text{Fe(CN)}_6]^{3-} + e^-$$

1. Determine $\Delta G$ according to the following equation:

$$\Delta G = \Delta G^\circ + RT \ln[Q]$$

where $R$ is the gas constant (8.314472 J/K·mol), $T$ is temperature in Kelvins, and $Q$ is the reaction quotient:

$$Q = \frac{[\text{Ox}_1] \cdot [\text{Red}_2]}{[\text{Red}_2] \cdot [\text{Ox}_2]}$$

**Part III: Construct a concentration cell**

**Experimental Procedure:**

Construct the following concentration cell:
1. Prepare the following solutions: 0.1M of $\text{K}_4\text{Fe(CN)}_6$, 0.1M of $\text{K}_3\text{Fe(CN)}_6$ and 0.01 M of $\text{K}_3\text{Fe(CN)}_6$.

2. Construct the redox half-cells as follow:

<table>
<thead>
<tr>
<th>Beaker 1</th>
<th>10 mL of 0.1 M $\text{K}_4\text{Fe(CN)}_6$</th>
<th>10 mL of 0.1 M $\text{K}_3\text{Fe(CN)}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beaker 2</td>
<td>10 mL of 0.1 M of $\text{K}_4\text{Fe(CN)}_6$</td>
<td>10 mL of 0.01 M $\text{K}_3\text{Fe(CN)}_6$</td>
</tr>
</tbody>
</table>

3. Insert a Pt electrode into each of the beakers.

4. Prepare the salt bridge by soaking a piece of filter paper into a 1.0 M KCl solution.

5. Connect both redox half-cells using the salt bridge as shown in Figure 1H.

6. Connect the electrochemical cell to the voltmeter as shown. Measure the potential.
7. Determine $\Delta G$ from the measured $E_{\text{cell}}$ value as follows:

$$\Delta G = -nF E_{\text{cell}}$$

**Part IV: Nernst equation**

1. Calculate $E_{\text{cell}}$ for the concentration cell in Part III using the Nernst equation.

2. Determine $\Delta G$ from the calculated $E_{\text{cell}}$ value as follows:

$$\Delta G = -nF E_{\text{cell}}$$

**Questions:**

1. Are the $\Delta G$ values obtained in Parts I, II, III and IV comparable?

2. According to your observations, how does the position of the Fermi level relate to changes in redox species concentration?

3. Explain the significance of the $\Delta G^\circ$ and $E^\circ_{\text{cell}}$ values obtained for the concentration cell.

4. Describe the differences between $E^\circ_{\text{cell}}$ and $E_{\text{cell}}$.

5. Describe the physical meaning of the Nernst equation.
REFERENCES


