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DEVELOPMENT OF A MATHEMATICAL MODEL FOR GALVANIC CELLS

by

JOSHUA JOHNSON

(Under the Direction of Fernando Rios)

ABSTRACT

It is possible to utilize principles of equilibrium thermodynamics to model the voltage a battery renders as it powers a load in time and discharges. Similarly, consideration of the internal chemistry inside a battery or galvanic cell, enables modeling thereof. This paper builds upon these principles and presents a derivation of the Nernst equation that utilizes this result to model discharge curves in time for different types of batteries. The Nernst equation relates chemical activity of the reagents inside a battery to the open circuit voltage rendered by the system. By combining the Nernst equation with Faraday's laws of electrolysis, it is possible to obtain realistic battery models. Such models can reproduce discharge behavior, such as voltage rendered vs. time, under a particular electrical load. The results from this work demonstrate that the model matches real battery discharge behavior rather closely and provides insights into battery operation and how to best utilize such. The use of the model will allow the development of more efficient intelligent battery chargers and for superior energy control systems to be developed, which would manage batteries utilized for energy storage. In summary, the research herein starts at first principles and builds upon itself until a model is presented capable of describing the behavior of galvanic cells, or batteries, as these operate in time. This paper then develops and applies the model aforementioned and ends by discussing future avenues for development and room for possible advancement.

INDEX WORDS: Battery, Battery models, Chemical activity, Discharge curves, Equilibrium thermodynamics, Faraday's laws of electrolysis, Galvanic cell, Nernst equation, Open circuit voltage

DEVELOPMENT OF A MATHEMATICAL MODEL FOR GALVANIC CELLS

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MASTER OF SCIENCE

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by

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DEDICATION

This paper is dedicated to the many teachers who have guided my education who are too numerous to list explicitly, Neil Stewart Peddersen, Charles Bleichner, Edward Thelen, Dr. Fernando Rios, and Dr. Rocio Alba-Flores. The author is eternally grateful for the contributions made on his behalf by these individuals.

Neil Peddersen, whose informal instruction assisted me greatly throughout my early interest in electronics, is ultimately responsible for my enduring interest in electronics and science at large. Although he has been gone for some eleven years, he is missed greatly and his dedication to his community and peers is remembered by the author and cherished.

Charles Bleichner was an electrical engineer of merit who graduated in 1939 and served his country throughout the second world war through his work in military electronics and radar. His work in electronics and the manufacture of electron tubes for General Electric was equally remarkable. His discussions with the author many years ago further inspired a career path in electronics and electrical engineering.

This work is also dedicated to Edward Thelen. A remarkable engineer, volunteer at The Computer History Museum, and friend - Mr. Thelen greatly assisted the author through the generous advice and wisdom he so kindly shared. His work has been an inspiration for many.

This work is, last but certainly not least, dedicated to Dr. Fernando Rios-Gutierrez and Dr. Rocio Alba-Flores. They have helped the author greatly with their generous time and assistance. I am forever grateful to them for their dedication and passion - in education, engineering, and life. The author is profoundly indebted to these faculty members, and others, for their continued support and assistance over the last years.

It is with the greatest happiness that this work could be written and come to be. Such would have been an impossibility without the efforts of those listed above, and others not mentioned. Thank you all for your work and time which has ultimately rendered this research paper possible.

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The author also acknowledges his parents for their great care and help. Thank you so very much for your years of helping me pursue a graduate degree. Your care and efforts have helped me continue my education as few in my family historically have been able to do so. I am forever indebted.

As a final acknowledgement, the author would like to acknowledge the many nameless scientists who may be forgotten - but whose contributions live on through the present. The dedication of many such pioneering scientists has proven an inspiration to the author.

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CHAPTER 1

INTRODUCTION

1.1 Purpose of this research

This work attempts to render a mathematical model of battery behavior. For the design of control systems, a model of the "plant" is required to design the controller to precision. The "plant" is the system under control, whose operation is manipulated to render a desired state or outcome. If it is possible to mathematically describe battery operation in time, then work along these lines could be undertaken and controllers customized for batteries themselves. Accordingly, the work herein investigates the internal workings of batteries, or "galvanic cells" as they are often called. This paper attempts to develop a comprehensive model of a battery in mathematical terms. Moreover, this work has immediate practical applications and merit due to the increased use of batteries as means of energy storage. A more effective utilization of such devices is perhaps possible if the behavior of the battery can be mathematically understood and predicted. In brief, the work herein has sought to render such a model capable of utility in this way.

1.2 How this Research Is Original

It is explained to every electrical engineering student how a battery behaves like an ideal voltage source in series with an internal resistance [9]. The author has found such a simple model of battery behavior rather crude and simplified to an extent that it is lacking. This work is original in that it tries to supersede such a primitive understanding and develop a mathematically rigorous model of the battery. Such a model would provide useful information that previous instruction and study did not render. Among the insights sought is a model of the terminal voltage rendered by a battery as it is discharged in time. This information is critical to the engineer in that it is required to properly utilize batteries as means of energy storage. The research and efforts herein aspire to bridge a divide between chemistry and electrical engineering to understand the inner workings of a battery further than previously possible.

CHAPTER 2

LITERATURE REVIEW AND ELECTROCHEMISTRY BACKGROUND

2.1 Chemical Fundamentals of Galvanic Cells

Batteries are called “galvanic cells” or “voltaic cells” in the field of chemistry where they are studied – after Luigi Galvani and Alessandro Volta who developed the first batteries about the year 1800 [1]. Since the invention of such early apparatus, batteries have grown in complexity and improved in their performance. Such electrochemical devices as batteries are somewhat difficult to study from the perspective of the electrical engineer due to the significance of the chemical reactions involved and their mechanics - pertaining to how, exactly, a battery generates a voltage. A study of the chemical background required to understand battery operation is presented herein. First, some fundamental definitions and terms must be defined and introduced.

2.1.1 Introductory Material

Galvanic cells or batteries operate by means of chemical changes or reactions – namely those that involve electron transfer. Such electron transfer chemical reactions are called “oxidation reduction reactions”. These reactions in chemistry involve the exchange of electrons between reagents as the reaction progresses [2]. They can be caused by electricity (electrolysis of water into its constituents, say) or can render electricity (as in batteries, where the electron transfer is due to connection with an external circuit). Oxidation and reduction processes are always coupled. One occurs with the other due to conservation of charge.

Electrochemistry and the oxidation – reduction processes studied by this area have many practical uses, in addition to the storage battery. A list of processes made possible by electrochemistry includes:

Applications of Oxidation – Reduction Reactions and Electrochemistry [2]*:*

1. Manufacture of metals, aluminum, magnesium, and others.
2. Batteries, energy storage.
3. The biological cell and its reactions – esp. neurons and how they operate via ion channels.
4. Chemical measurements, indirectly (pH, say).

Of course, given that chemical energy can be converted to electrical energy, the inverse processes is also possible and is useful in certain industries [2,3].

Such systems that convert electrical energy into chemical energy (or equivalently yield desired chemical changes) are called “electrolytic cells”, and these devices allow chemicals to be broken up into pure elements by the influence of an electrical current that causes such chemical changes to transpire. In such a way, electrical energy works to drive a non-spontaneous chemical reaction in electrolytic processes [2,3].

Terminology for the components of a galvanic cell is standardized across literature. Oxidation reactions occur at a metal surface called the anode. Reduction occurs at a similar metal surface called the cathode [1,2]. “An Ox and a Red Cat” is a phrase that helps one recall this. These terms are set, of course, for the discharge process.

A battery at its core consists of the cathode and anode metals immersed in some liquid solution or paste. This intermediate solution is called the “electrolyte” and must contain charged species, or ions. These ions, in solution, can move and have electric charge on them. In a battery or electrolytic cell, electrons themselves do not move through the solution (they cannot, see chapter three). The ions must be mobile for conduction to transpire or for a useful battery to generate an appreciable current. Electrical conduction through mobile ions in a solution is called electrolytic conduction [4].

Oxidation – reduction reactions are unique in their transferring electric charge between chemical species. A very basic reaction is shown below. Notice that electrons appear in the chemical equations as products or reagents. This fact explains, partially, the ability of a battery to render electrical energy from that in chemical form. Take into consideration the electrolysis of common table salt (sodium chloride, or NaCl). It can be rendered molten and be converted into its base elements via electrolysis facilitated by an electric current. The term "Redox" is used commonly to refer to oxidation - reduction reactions.

Example Redox (oxidation reduction) reaction – electrolysis of NaCl:

a) $2Na^{+}(l) + 2e^{-} \rightarrow 2Na(l)$ [Cathode, this is reduction, or gain of electrons.]

b) $2Cl^{-}(l) \rightarrow Cl_2(g) + 2e^{-}$ [Anode, this is oxidation, or loss of electrons.]

---

c) $2Na^{+}(l) + 2Cl^{-}(l) + 2e^{-} \rightarrow 2Na(l) + Cl_2(g) + 2e^{-}$ [Electrons cancel, these go through the external circuit.]

Chemical Equation 1. Electrolysis of Table Salt. Reactions "a" and "b" sum to render "c".

The entire reaction (sum) is called the “cell reaction”. In short, this reaction shows that NaCl can be broken up from this ionic salt into the base elements of chlorine and sodium if an appropriate electric current is applied. Typical battery chemistry runs like this, but in reverse. A chemical reaction occurs and the spontaneous electron transfer may be employed to drive power to an external circuit [1,2,3].

One may wonder why a battery requires an electrolyte solution. The electrolyte serves, almost always, as a chemical reagent that facilitates the desired oxidation – reduction reaction. It also serves other nuanced purposes. The battery electrolyte balances charge around the electrodes and enables the conductivity of the solution and therefore the battery itself [3].

Electrolysis and galvanic reactions would be impossible without this “conductive” agent. Charges would build up and become “stuck” at the electrodes. A current (either applied or generated) would then be impossible.

2.1.2 Relationships between Current and Chemical Change

Measurements of electrical current and time can be used to calculate the amount of chemical change during electrolysis (or inside a battery) [3]. Faraday (British pioneering scientist) first determined such relationships in the 1830s. In short, chemical change in an electrochemical cell is proportional to the total charge that such a device has had passed through it. Charge past a point in a wire is the integral of current in time, or simply current multiplied by time for the case of nearly constant electric currents [5].

Some fundamental constants and equations for predicting chemical changes based on current and time are introduced below. Notice that a constant has been defined and called "Faraday's constant" which is the charge of a mole of electrons. This is equivalent to the charge held by Avogadro's number of electrons (since Avogadro's number of molecules is 1 mole, by definition). With this constant known, chemical changes can be predicted in electrolytic cells [5]. Similarly, if one knew the charge that a battery facilitated through a circuit, then the chemical change involved in the battery could be estimated to precision. In short, the following definitions apply and allow electrolytic processes to be understood in terms of the electricity applied and the chemical changes rendered.

- 1 Faraday = 1 F = charge of 1 mol of e^-, named after the above scientist. (Charge of Avogadro’s number of electrons, or 6.022×10^{23} of them).
- 1 Faraday (1 mol of electrons) has a charge of nearly 96,485 Coulombs.

Basic electrical definitions can be manipulated to render the equation for total charge past a point in a wire. This work renders [2]:

Eq. 1. *Q(past a point in a wire, Coulombs) = I(Amperes) x t(seconds) (for constant currents.)*

This simple formula, and the known Faraday constant, allow interesting calculations to be performed.

2.1.3 Calculations based on Faraday's Laws

Electrolysis may be predicted, or the quantities of chemicals rendered calculated, with Faraday's discovery that I (electric current) is proportional to the chemical changes rendered [2,3,5]. The chemical change is also proportional to the time that a current is applied. These two "laws" allow calculations to be executed which relate electrical current to the resulting chemical action that such renders. Michael Faraday arguably founded electrochemistry as a science with the discovery of these "laws" in the 1830's.

This material is best understood in terms of a simple example. One elementary one is given below.

For example:

Copper is deposited from ionic form (in solution) to the plate of an electrolytic cell (the cathode where it is reduced out of solution). 2.00 Amperes runs through the solution for 20 minutes. The copper comes from a solution of $CuSO_4$ (copper II sulfate), which has dissolved into ions.

The weight of plated copper (taken from the solution by chemical change and bonded to the cathode) may be found as below:

- 20 minutes x 60 seconds per minute = 1200 seconds, total.
- 1200 seconds x (2.0 Coulomb / second) = 2400 Coulombs, total.

Division by the Faraday constant renders moles of electrons, total:

- 2400 ÷ 96,500 = 0.0249 Faradays of Charge, total.

The chemical reaction is required as known to go further. It is:

Reduction of Copper: Cu^{2+} (inside solution) + $2e^-$ → Cu (solid, at cathode)

Chemical Equation 2. Reduction of Copper (II) Ion.

Thus, one mol of copper being extracted requires two moles of electrons to be run through such a system and the reverse is true in the case of a battery using this reaction.

This above work may be combined to yield (using the molar mass of copper from the periodic chart):

- 0.0249 ~~Faraday~~ x (1 ~~mol Cu~~ / 2 ~~Faraday~~) x (63.5 g Cu / ~~mol Cu~~) = 0.791 grams of copper is plated or removed from ionic form in solution.

This demonstrates a fundamental problem in electrochemistry. A battery roughly shows this situation in reverse. Battery installments must have greater mass for larger ampere hour provisions to be rendered. This is due to the above mathematics. The charge a battery forces through a circuit comes from chemicals inside the battery. Such chemical species have a certain valance number of electrons per ion. More current for greater time intervals implies more total charge is required [5]. Such a situation requires more chemicals to render the charge necessary. Thankfully, Faraday's constant is large – but despite this fact batteries will have to increase in their bulk in order to render greater currents for longer times. This is further studied latter in this chapter.

2.1.4 Electrochemistry of the Galvanic Cell

Spontaneous electron transfer must take place through an external circuit in a battery [2]. The chemical reactions, although spontaneous, are otherwise similar to those in electrolysis cells. One species loses electrons (is oxidized), and these travel to another metal species that gains electrons (is reduced). The charge flow must occur through an external circuit and this is how batteries may deliver electrical energy from chemical energy.

The oxidation and reduction processes, by themselves, are called "half -reactions" inside a battery. Often, these two half reactions occur in separate containers / places in a battery. The energy change is not lost as heat (which would occur if the chemicals were put together and reacted directly with each other), but becomes an electric current [2,3]. This is only possible by such separation and even modern batteries contain such a geometry allowing for this aspect [1].

The study of modern batteries is difficult due to many factors [1]. Some reactions are non-stoichiometric and often non – ideal effects (pertaining to reaction kinetics, diffusion, and "liquid junction potentials") are encountered. To begin the study of galvanic cells, a simpler example is considered. It involves a known oxidation and reduction reaction and is easy to set up in the laboratory to be observed and experimented with. Moreover, this simple galvanic cell demonstrates principles and rules that apply to *all other galvanic cells.* As such, this system is considered first below. It is called the "Daniel cell" (after another prominent 19th century chemist) and proves useful for educational purposes [2].

2.1.5 The Daniel Cell – A Simple Battery

The Daniel cell is a simple apparatus. Silver nitrate and a silver bar are placed in a beaker by themselves. Copper nitrate and a copper bar are set by themselves in another beaker [3]. A “porous bridge” or “salt bridge” connects the two and is filled with cotton and a potassium chloride / water solution. This system was developed in 1845 and constitutes the “Daniel Cell” – one of the first practical batteries [1]. Its chemistry can be explained simply as below. The chemical action is simple and easy to understand.

Two coupled processes transpire. The result is:

$Ag^+(aq) + e^- \rightarrow Ag(s)$ [Reduction at the cathode. Silver moves from solution to the silver electrode.]

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ [Oxidation at the anode. Copper moves from the electrode into the solution.]

Chemical Equation 3. The coupled reactions of the Daniel Cell.

The first reaction must take place twice as rapidly as the second, so that charge is balanced between these coupled processes [2].

The electrons in the equations travel through the external circuit, setup between the electrodes. Notice that the ions in solution exist because silver nitrate dissociates into nitrate and silver ions when mixed with water [3].

Notice that with the Daniel cell and other batteries the anode is negative, and the cathode is positive. Ion exchange occurs in the salt bridge between the half – cells. Such is, again, required for a current to flow over a time interval [6]. Cations (positive ions) move towards the cathode. Anions (negative ions) move towards the anode.

2.1.6 Alternate Chemistry used in the Daniel Cell

Daniel cells varied in their construction between two chemistries. Silver is rather weak in its ability as an electrode. Often, zinc was used in place of it in the simple Daniel cell [2]. Sulfate can be substituted for nitrate, with no changes, as well [2].

Thus, zinc can be the oxidized metal in a battery (Zinc's use was common in the 19th century. Nearly every battery used a zinc anode until the 1920’s.) [1]. Copper can be reduced. The resulting chemistry is:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (Oxidation = loss of electrons “OIL”.) → **Oxidation is Loss of electrons.**

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (Reduction = gain of electrons “RIG”.) → **Reduction is Gain of electrons.**

Chemical Equation 4. Alternate chemistry used in the Daniel Cell

Notice that in either situation two different metals must be employed. In general, the two half cells must use different metals or at least different electrolytes or chemicals [6]. Such a difference is required for oxidation to occur in one place and reduction in another. These reactions render a battery’s voltage [6]. Two identical half cells yield a voltage of zero, in all instances. This leads to the observations stated below.

- Crucial fact in Electrochemistry: The voltage across the electrodes of a galvanic cell can be attributed to the difference in the tendencies of the two half – cells to undergo reduction. This is caused by utilization of dissimilar metals (the copper and zinc) or differences in chemical species inside the half – cells themselves [2, 6].
- Cell voltage depends on the composition of the electrodes, the electrolyte in the battery, and the concentration of the ions in each half – cell [6]. Such principles are explained below and further in the third chapter of this work.

Thankfully, many chemists worked on electrochemistry in the 19th and early 20th centuries [1]. These individuals determined that battery EMF (or terminal voltage) can be predicted. The introduction to such work is given in the section below.

2.1.7 Standard Cell Potentials, EMF predictions

Standard electrode reactions are tabulated. Each metal or chemical species that can be reduced has an associated potential difference (voltage) that it can contribute in a battery chemistry (or, sometimes, requires – taking away voltage from a battery’s potential difference) [2,3,6]. Such a table of known electrodes and their reduction reactions is called the “standard reduction potential table”.

This is explained below and is an integral data set for predicting battery EMF under open circuit conditions. Such values only hold under standard temperature and pressure (that is, 20° Celsius nearly and 1 Atm. of pressure) [6]. The concentrations of liquid solutes are held at 1 Mol / Liter [6].

It is hard to extend such theory to non – ideal conditions that deviate from these. This task is left to the next chapter, which explains the chemical thermodynamics of galvanic cells and how open circuit EMF is related to chemical and physical parameters.

The standard reduction potential is represented by E^o_{cell}. Such is, again, the measured potential of the half - cell in question when ion concentrations are 1.00 M / L, the temperature is 20° Centigrade, and gases involved (if any) are at 1 Atm. of pressure.

Standard cell (also called standard reduction) potentials are not above a few volts [2,3,6]. They are less than five volts for each known species as of 2021. There is one question left open here that needs elucidated and answered. To achieve a voltage measurement, a reference must be taken at will. A voltmeter has two leads after all and a standard half-cell only has one terminal.

What reference is used for half – cells? Such would act as another terminal for the voltmeter and would allow potential differences to be measured.

A standard half-cell was determined and arbitrarily assigned a potential of zero volts. Such is the “Standard Hydrogen Electrode”, detailed latter [1,6]. This standard allows relative potentials to be taken. Only potential differences matter, and as such the standard is not entirely important [1].

In short, each half – reaction has a potential which tabulates the “desire” of that half – reaction to run spontaneously as a *reduction reaction*. If the process strongly favors *oxidation,* then this potential would be large and negative. Standard cell voltages are positive for reduction and negative for oxidation [2,3]. Changing the sign thereof changes the direction of the reaction [6].

In general, it approximately holds, under standard conditions:

Eq. 2. $E^o_{cell} = \text{Standard reduction potential}_{\text{(substance reduced)}} - \text{Standard reduction potential}_{\text{(substance oxidized)}}$

A difference in tabulated half – cell potentials, in this manner, allows for estimates of galvanic cell open circuit potential difference [1,2,3,6]. Of course, such only holds true at standard conditions, under which the values were measured [1,6]. This process is best illustrated with an example. The Daniel cell, mentioned above, is an excellent example of how such tabulated values are useful. The relevant work would follow as thus.

2.1.7.1 Determining the EMF of the Silver - Copper Cell (The Daniel Cell)

The net chemical change inside the Daniel cell would be:

$2Ag^{+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ [Total cell reaction.]

Silver is reduced. Copper is oxidized.

The two reduction half reactions are:

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ Greater tendency to become reduced. (Would actually reduce silver.)

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ Lesser tendency for reduction. Is oxidized in actual system (this reaction "goes backwards").

Ergo the theoretical potential difference, under open circuit conditions, can be found using tabulated "standard reduction potential" values for the species involved. Substituting such values into the difference would render:

$E^{o}_{cell} = E^{o}_{Ag+} + E^{o}_{Cu2+}$ = 0.80 – 0.34 = 0.46 Volts. [Using tabulated reduction potential values.]

Notice that the copper reaction's potential is negative since this reaction is run as an oxidation. Both silver and copper favor reduction, but silver more so. Thus, silver is reduced here, and copper is oxidized.

Each metal has its own propensity, which can be determined by studying the standard reduction table. Zinc likes to be oxidized, as does lithium, potassium, etc [6]. Some non-metals greatly favor reduction. Again, per convention, the SHE (standard hydrogen) electrode is defined as being indifferent. It's standard EMF is, to reiterate, set arbitrarily as "0". The values tabulated in the "standard reduction table" (rendered below) allow numerical figures to be had which show the alternate behavior of differing metals and electrodes.

In brief, reduction potentials (tabulated) can be used to predict the standard cell potential of batteries and to further predict overall cell reactions in galvanic cells [3]. This is proven, experimentally, latter in this work.

2.1.7.2 The Lead – Acid Battery

The above theory leads to practical results when applied to the lead – acid battery, used to start cars and for some energy storage. Such a battery is described below.

Lead and lead dioxide are used in a sulfuric acid electrolyte in a car's lead – acid battery. The half – reactions are:

$PbO_2(s) + 4H^{+}(aq) + SO_4^{2-}(aq) + 2e^{-} \rightarrow PbSO_4(s) + 2H_2O$ [Reduction potential = 1.69 Volts.]

$PbSO_4(s) + 2e^{-} \rightarrow Pb(s) + SO_4^{2-}(aq)$ [Reduction potential = -0.36 Volts.]

Chemical Equation 5. Chemical reactions undertaken inside Lead-Acid Battery.

The reaction with the highest reduction potential undergoes reduction in reality (at the cathode). Thus, the first reaction is reduction. The second reaction is oxidation, which takes place at the anode.

The overall cell reaction can be found by adding the reactions above and canceling the electrons. This obtains:

$PbO_2(s) + 4H^{+}(aq) + 2SO_4^{2-}(aq) + Pb(s)^{-} \rightarrow 2PbSO_4(s) + 2H_2O$

Chemical Equation 6. Net reaction, Lead-Acid Battery

This reaction, again, takes place in lead – acid storage batteries, which are used to start cars, run golf carts, etc. The second reaction (above the one here) runs in reverse. Hence, lead sulfate is a product and not a reagent.

Notice that the open circuit potential difference can be predicted by standard reduction potential values:

V(produced, nominally) = Potential of substance reduced – Potential of substance oxidized

= 1.69 – (-0.36) = 2.05 Volts.

The lead - acid battery in a car has six identical cells. These are wired in series. Thus, the total voltage rendered by the series combination adds between cells. It holds accordingly that a well charged lead acid battery, with six cells wired in series, has an open circuit potential of about:

2.05 Volts per cell x 6 cells in series = 12.30 volts, or nearly.

Such work, as written, shows the relationship between *electrical engineering and chemistry.* Chemical knowledge predicts the potential per cell. Electrical knowledge concludes that voltages add together when cells (batteries) are wired in series. Both types of information are required to render the above result of 12.30 volts, full charge. Very close potentials to this are observed in real – world lead acid batteries.

2.1.8 Summary of Electrochemistry, Figures

The above work has introduced the fundamentals of battery chemistry in brief, although most practical systems are not as simple as those shown here [1]. Two general observations can be concluded and are stated below.

General Rule I: The half – reaction having the more positive reduction potential always undergoes reduction [1,6]. The other half-reaction involved is forced to undergo oxidation. This holds even if the reaction does not take place in a galvanic cell (battery) [3]. Oxidation is reduction that *runs in reverse.*

General Rule II: Further, any functioning galvanic cell has a measured cell potential of a positive value. If such a potential were negative, the process would be non-spontaneous (it requires energy to occur and does not render free energy – such as an electrolytic cell) [5,6].

Oxidation and reduction are coupled chemical changes that allow electron transfer during chemical reactions. Batteries work upon such chemistry. Standard reduction potential tables can be employed to estimate battery open circuit voltages, at least given the reagents inside the battery are set under standard chemical conditions [1,6]. Batteries function, essentially, because some chemical species favor reduction more so than others. This difference in the affinity of chemicals to “capture” electrons is what, in short, makes energy storage and generation inside a battery possible [1,6].

To complete this introductory section, figures are presented below that show the Daniel cell (as would be seen on a laboratory bench) and the construction of the standard hydrogen electrode. A table of standard reduction potentials, for reference, is also reproduced here.

Galvanic cell and reactions considered earlier:

Daniel Cell Example: →

$2Ag^{+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ [Total cell reaction.]

Silver is reduced. Copper is oxidized.

The two reduction half reactions are:

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ **Greater tendency to become reduced. Is actually reduced in reality.**

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ **Lesser tendency for reduction. Is oxidized in actual system. (Runs in reverse).**

Ergo,

$E^{o}_{cell} = E^{o}_{Ag+} + E^{o}_{Cu2+}$ = 0.80 – 0.34 = 0.46 Volts. [Using tabulated reduction potential values and taking a difference.] Notice that this value is observed in experiments.

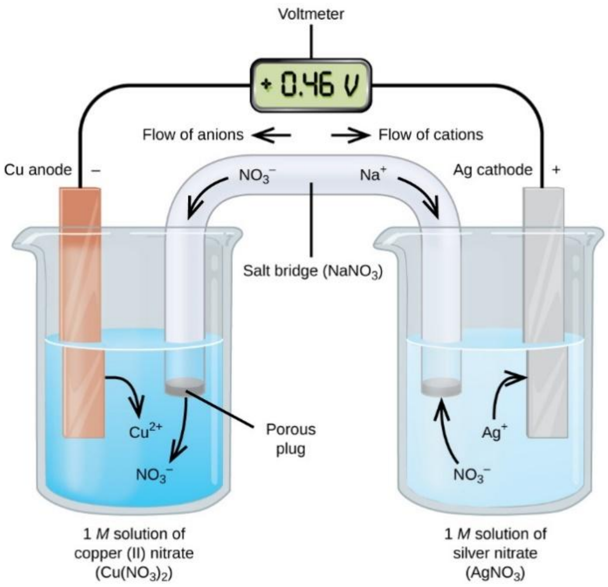


Figure 1. The Daniel Cell, realized.

From "Chemistry", by P. Flowers and K. Theopold, 2021, https://opentextbc.ca/chemistry/chapter/17-2-galvanic-cells/

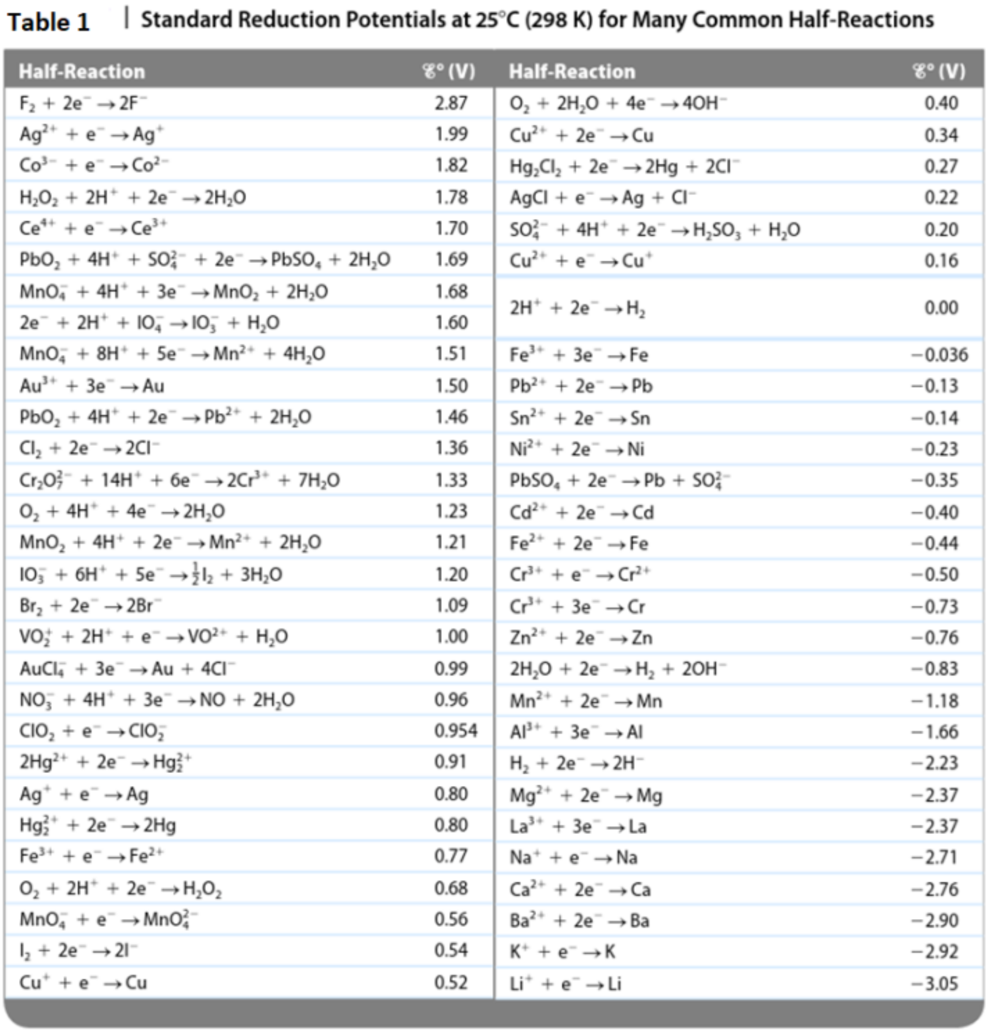


Table 1 | **Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions**

Half-Reaction	$\mathcal{E}^\circ$ (V)	Half-Reaction	$\mathcal{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60		
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$Ag^+ + e^- \rightarrow Ag$	0.80	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Na^+ + e^- \rightarrow Na$	−2.71
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$K^+ + e^- \rightarrow K$	−2.92
$Cu^+ + e^- \rightarrow Cu$	0.52	$Li^+ + e^- \rightarrow Li$	−3.05

Table 1. Standard Reduction Potentials [2].

2.1.9 The Standard Hydrogen Electrode

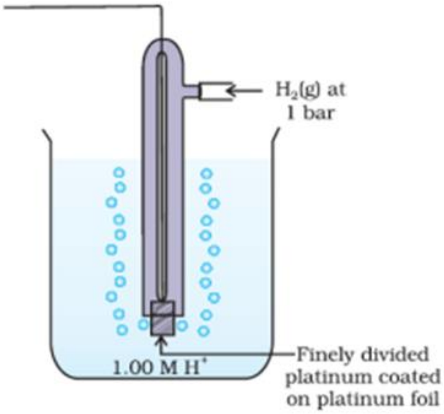


Figure 2. The Standard Hydrogen Electrode [2].

The above electrode of platinum with 1 bar hydrogen gas sparged over it is defined to have a potential of zero volts ("generated" by it). Other standard half cells (those in the above table) are measured against this one, as mentioned [1]. The “salt bridge” of the other cell would make contact with the electrolyte of this standard cell. Such a salt bridge allows for ionic conduction (dissociated ions to move) between half cells, without allowing electrolytes to mix [6]. The differing electrolytes may react directly with each other, and the redox reaction may not be able to occur. The salt – bridge (seen in earlier figures) is a tool that allows for precise measurements and the avoidance of such an undesired effect [6].

The standard hydrogen electrode is rather dangerous. It operates only when hydrogen gas (highly flammable and sometimes explosive!) is bubbled or sparged over the platinum electrode (immersed itself in some acid). Over the long-time intervals required for experimental measurements, the hydrogen could accumulate and explode. The author could have rendered a means of obtaining hydrogen, but the risk was seen to outweigh the benefits. An alternative existed and was chosen.

For the experiments involving reduction potentials below, a copper cathode in copper (II) sulfate was used. Given that the copper sulfate was at a "standard concentration", the potential of this "reference cell" was known from existing tabulations. Other half-reactions could be tested against this reference - with the benefits of not having to worry about hydrogen, obtaining that reagent, etc.

2.1.10 Battery limitations as understood via Faraday’s Electrolysis Laws

Large storage batteries would require a large quantity of mass, as the electric charge transferred as a current by a battery comes from the oxidation of some material (a reactive metal, like lithium perhaps). Since I x t is related to mass, this may prove a limit or concern for large storage batteries. More lithium would require greater cost. An example highlighting such an issue is below.

A lithium-ion battery oxidizes lithium and renders a current of 1 ampere for 3 hours. How much lithium (mass of the metal itself) must be moved into solution as an ion (and therefore exist inside the battery’s anode beforehand) for this current to be supplied?

Faraday’s law for electrolysis yields the answer as:

1 Ampere = 1 C / Sec. → Hence, [1 C / Sec] x [3600 Sec / hr.] x [3 hr.] = 10,800 Coulombs of charge must be supplied.

The oxidation of lithium, chemically, would be:

$$\mathrm{Li(s)} \rightarrow \mathrm{Li^{+}(in\ solution)} + e^{-}$$

Chemical Equation 7. Oxidation of Lithium

The above is the reaction for lithium to be oxidized and to yield the electrons for the current required to flow. 96,500 C of charge is a mole of electrons. Thus,

10,800 C / 96,500 C = 0.112 Mol of e^-

This implies that 0.112 Mol of lithium is oxidized and is now in solution in the battery. The weight of this metal would be:

0.112 Mol x (6.941 grams / Mol) = 0.78 grams of lithium.

Sadly, it appears that current x time supplied to a system by a battery has a linear relationship with the mass required for the battery.

So, 10 amperes for the same three hours would require some 7.8 grams of lithium to enter solution. 100 amperes for the same three hours would require some 78.0 grams of lithium to enter solution. Et – cetera. *Larger storage batteries would have to be heavier.* The above figures are rather extremely idealistic. Multiple fold more of the lithium metal may be required in practice (the electrodes cannot completely dissolve!) [1].

Although the masses calculated here are not extremely large, powering entire towns or cities with galvanic cells (perhaps as energy storage devices used alongside renewable energy or intermittent power) would require a large amount of material by the effect mentioned above. Therefore, it may prove of utility to research battery chemistries involving affordable materials – as such large storage batteries would require literally tons of the metal reagents (or other chemicals) necessary.

2.2 Listing of Current, Commercial Battery Chemistries

Batteries fall into two broad classes: the primary and secondary cells. Primary batteries are used once and cannot be recharged. Secondary cells, more significant today, do allow recharging [1]. This paper focuses mainly on secondary batteries, sometimes called storage batteries. To give the reader a frame of reference, common battery chemistries are mentioned below. There are, of course, hundreds of reaction schemes that exist [6]. These have proven the most common and popular.

2.2.1 Chemical reactions for a set of batteries, in use today

I. The Lead Acid Battery, used in Automobiles, Boats, Campers, Etc.

This battery is a secondary cell, it can be recharged.

Cathode Reaction: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$

Anode Reaction: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

These reactions are coupled. When they are reversed, the sulfuric acid is converted to hydrogen ions and sulfate ions. These are used in both reactions as reagents (reactants). Hence the system is "clever" in this way.

Moreover, a lead acid battery can be recharged (restoring the reagents) via a current being forced opposite the direction it supplies one (technically this process is electrolysis).

II. The Zinc – Carbon Dry Cell, used for decades as the "D" battery for flashlights, radios, etc.

This battery is cheap, but always has a short shelf life due to spontaneous self - discharge. Accordingly, it is rarely used anymore. It was the workhorse of many devices years ago [1].

The chemical reactions are:

Cathode Reaction: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Anode Reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Chemical Equation 8. Reactions of the Zinc-Carbon Dry Cell.

Sadly, this battery is absolutely not rechargeable. Attempts that try this fail, as the zinc cannot be restored easily at the anode. Zinc can react with water or acids and bases to render zinc ion (in solution) and hydrogen gas. However, Zn^{2+} does not readily react with hydrogen gas - which could reverse the process. Hence, this chemistry is non – reversible under ordinary conditions.

III. The Alkaline Cell, which replaced the Zinc-Carbon Cell in most applications today [1].

It has a longer shelf life and comparable cost. The reactions are:

Cathode Reaction: (Similar to II, above) $2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

Anode Reaction: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O + 2e^-$

Chemical Equation 9. Reactions of the Alkaline Cell.

Notice how a product (hydroxide) from the cathode reaction is a reagent in the anode reaction. This is a common theme in clever battery chemical reactions. This battery chemistry was developed in the 1950's and worked well for that era (EG. Use in portable radios) [1]. This type of battery is not typically rechargeable, sadly. Some types may be recharged, but these are more expensive and operate under greater pressures than possible by the primary (single use) type.

IV. The Nickel – Cadmium Cell (NiCad battery), a common "legacy" rechargeable battery that predated the lithium-ion type of battery by about 30 years.

The chemistry of this secondary cell involves the reactions below.

Cathode Reaction: $2e^- + NiO_2(s) + 2H_2O \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$

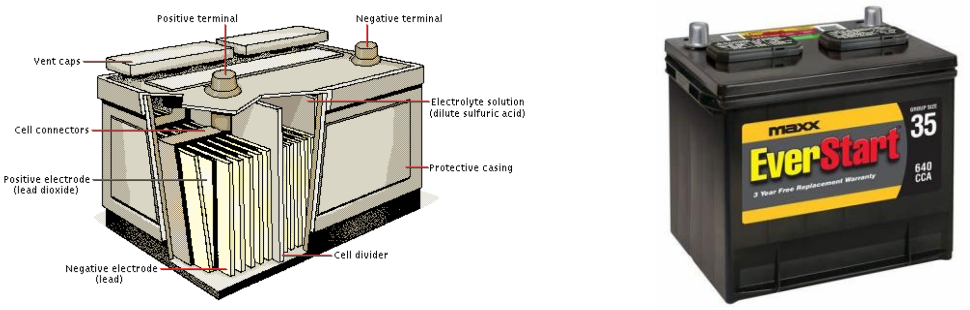
Anode Reaction: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Chemical Equation 10. Reactions of the Nickel-Cadmium Cell.

This battery is rechargeable but is not as popular as it once was because it uses cadmium which is toxic to life. This battery was probably the favorite for small electronics before the lithium-ion battery was developed in the 1990s.

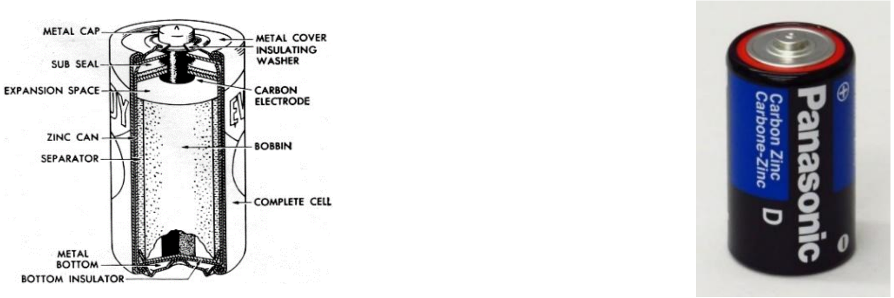
All the cells mentioned in this section have been used and seen commonly in daily life [1,6]. To allow the reader to connect the names with the battery's appearances, images of each type are reproduced below. Moreover, cross section diagrams (detailing internal construction of each) are provided. These figures give a deeper perspective on how different schemes have been used over time to combine the two metal electrodes and the chemical solution into a congruent package. Just as with capacitors, many different design styles exist – with each having its own benefits and drawbacks [1].

2.2.2 Pictures of Common Cells, their Internal Construction



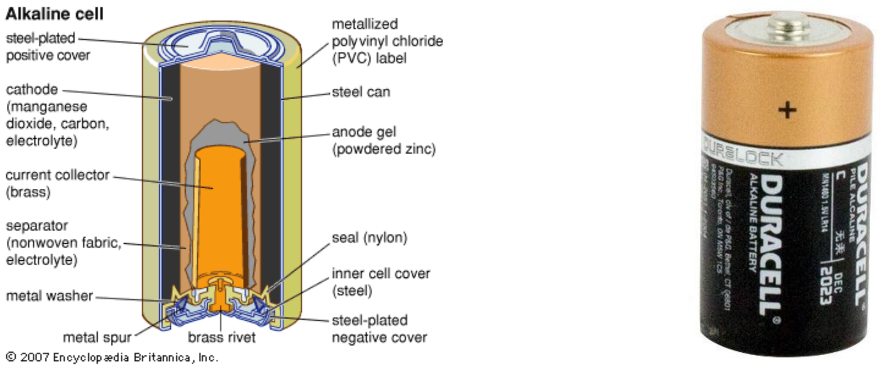
A. Internal Construction B. External Appearance

Figure 3. The Lead – Acid Storage Battery.



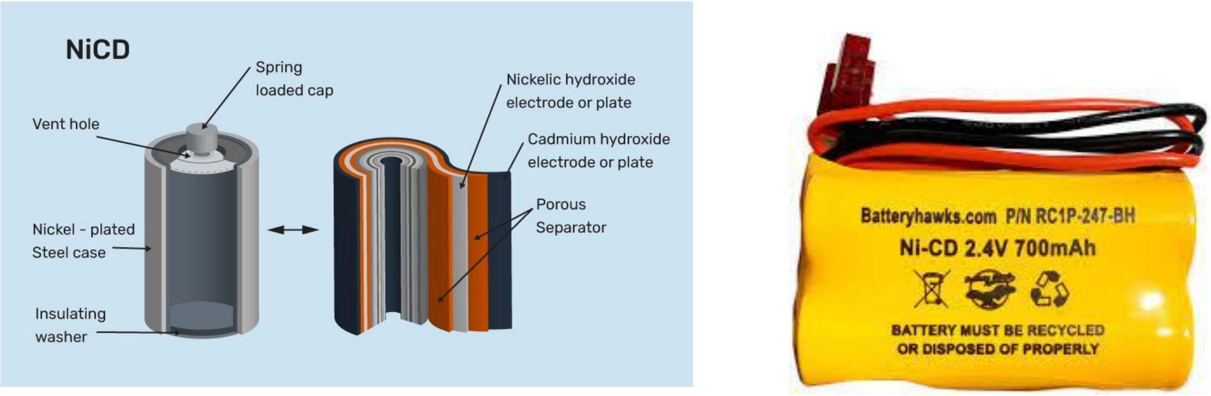
A. Internal Construction B. External Appearance

Figure 4. The Carbon – Zinc Dry Cell.



A. Internal Construction B. External Appearance

Figure 5. The Alkaline Cell / Alkaline Battery.



A. Internal Construction B. External Appearance

Figure 6. The NiCad Battery / Nickel Cadmium Cell.

2.2.3 Notes and Comments

A recent trend in battery composition is using alkali metals (lithium, sodium, etc.) and sometimes alkaline earth metals (typically magnesium). These metals, although they have their chemical issues, are different from the ones used in batteries in the 19th and much of the 20th centuries. Batteries of the 1960s and before primarily used zinc or lead as the anode [1]. The Nickel-Cadmium cell was used between that era and now [6]. It appears that the 21st century will use batteries with the above alkali metals in them. One concern of great merit is that the periodic chart only has so many metals. Perhaps development of futuristic “meta-materials” will help this problem, but the number of known metal elements is finite. Upon studying chemistry and battery reaction schemes, it appears harder to develop cathode materials than ones used for the anode [1]. Perhaps progress could be undertaken along these lines in the future, as the energy density of a battery is contingent on both cathodic and anodic species [1,6].

2.3 Experimental measurements of reduction potentials

To investigate the theory presented above, two experiments were performed. These attempted to measure reduction potentials by setting up galvanic cells and taking measurements of these devices. It is possible to re-create the entire standard reduction potential table by this process [1,2,3]. The measurements obtained suggest that the standard reduction potential table is correct – although it is rather difficult to obtain potentials exactly as high as this table records. The standard reduction table appears to be an "upper limit" and it requires great chemical precision to obtain voltages exactly as large as the table lists. The experiments performed are listed below.

1. Copper Sulfate and Zinc Sulfate Battery – First Experiment (The Daniel Cell):

Anodic Reaction: $Zn \rightarrow Zn^{2+} + 2e^-$ $E^0 = 0.76$

Cathodic Reaction: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = 0.34$

Sum of Reactions: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $E^0_{Cell} = 1.10$ Volts

In the battery described here, zinc moves from the anode electrode into the solution as an ion. Copper moves out of the solution and collects *on the cathode itself*. The chemical process proceeds in this direction, yielding a current as the electrons move charge through an external circuit. The open circuit voltage is the sum of the reduction potentials, shown as E^0_{Cell} above. This is about 1.10 volts for 1 M / Liter concentration and standard conditions. This cell was constructed with 1M / L concentrations and standard conditions, and an open circuit voltage of 1.040 Volt was observed. This agrees with the theory here very closely. Notice that the anode has 1 M/L zinc sulfate as its solution. The cathode has 1 M/L copper (II) sulfate as its solution. The percentage error observed in the author's determination of E^0_{zinc} is only 8.5%. This is decent for chemical measurements.

The standard potential of zinc metal being reduced can be determined by taking a difference:

E^0_{Cell} (actual) = 1.040 = 0.34 - (X)
Where 0.34 is the potential (tabulated) of the copper - copper(II) sulfate "reference cell" (mentioned earlier, that replaced the SHE for these experiments).
Ergo, X = - 0.70 (the potential of zinc as it is being reduced – the sign is reversed for oxidation). Zinc's reduction potential is quoted as -0.76 volts. This would be 0.76 volts if run in reverse as an oxidation reaction (as the "anodic reaction" above shows). The obtained value of 0.70 is very

close to that of 0.76. Hence, standard reduction potentials can be checked or obtained initially by careful experiment – as conducted here.

Notice that in any battery, one metal is oxidized or looses electrons. Another is reduced, and gains electrons. These processes are immutably linked and one cannot occur without the other occurring somehow. Hence, the need for the copper "standard half-cell" mentioned. The potential of this half – cell had to be set at 0.34 volts for the zinc reduction potential to be found.

The standard reduction potentials, mentioned several times here, remain the same. They do not vary with electrode size or the number of times the reaction transpires with its various molecules. Charge must be balanced between the oxidation and reduction process – thus one must multiply the half-reactions until a common multiple is seen and the electrons gained in reduction equal the electrons lost in oxidation between the reaction's metals. However, this alters charge but *never* the standard potentials. These values are determined by the metals used or reactions run, not the scale at which they are run [1,6]. The "scale" at which the reactions are run is a factor which determines the current possible [1,5,6].

In batteries, electron flow comes from the anode (where electrons are stripped from some metal atoms or material) and flows to the cathode (where these electrons join some compound and allow "reduction" to occur). Overall, this process explains how batteries can generate electric currents.

Ionic flow inside the electrolyte balances charge flow and forms the internal resistance which loses some electrical energy as heat [1,6]. Such chemical information justifies the "equivalent" resistance term used to model batteries in electrical engineering. Battery modeling, in greater detail, is described in the following chapters.

A final note on battery chemistry is in order, however. Battery electrodes must be made of *conducting* solid substances. This limits the choices of materials employed. Sometimes, platinum electrodes can be used with non – conducting reactions. However, platinum is incredibly expensive and therefore this method is seldom employed outside of the laboratory.

2. Copper Sulfate and Iron / Salt Battery – Second Experiment:

   The reduction potential of iron being reduced can be found, within some error, by another experiment. In this case, another half – cell was used in place of the zinc / zinc-sulfate one. This half – cell used an iron electrode and a potassium chloride (1 M/L) electrolyte. The reaction is thought to proceed as below.

Cathodic Reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu$	with $E^0 = 0.34$ Volt.
Anodic Reaction: $Fe \rightarrow Fe^{2+} + 2e^{-}$	with $E^0 = 0.44$ Volt

Net Reaction (Sum): $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$, with $E^0_{Cell} = 0.78$ Volt

Chemical Equation 11. Theoretical Reaction of an Iron-Copper Cell.

The reduction of copper out of solution and the oxidation of iron into solution can render a current in a battery. The open circuit voltage of the battery is tabulated at around 0.78 Volt, theoretically. This is based on the standard reduction potential difference.

This cell was constructed with the 1 M/L copper (II) sulfate and copper cathode reference cell. The anode half – cell took more time to develop. It was found that 1M/L KCl worked as an electrolyte of merit. (Zinc sulfate, initially used, worked very poorly.) Iron was the anode, so the above reaction would hold. Wrought iron of almost pure nature was employed as it was more pure in its iron content than other substances, like galvanized pipe or stainless-steel parts. The open circuit voltage reached a value of 0.650 volts when measured with a high impedance voltmeter. A difference renders the reduction potential of iron.

0.650 = 0.34 – (X) = Actual copper – iron cell voltage.

(X) = reduction potential of Iron, as measured in the laboratory = -0.31 volts.

The actual reduction potential of Iron(II) into iron(solid) is around -0.44 volts. This is an error of 29%, but such errors are typical in chemistry work and result from purity concerns and side reactions. Both existed in the experiments performed herein.

2.3.1 Interpretation of the experiments performed

These experiments with galvanic cells show that zinc has the lowest reduction potential of the three metals. It oxidizes the easiest. Second is iron, which also readily undergoes oxidation. Last is copper, as the cathode in both cases. Copper “desires” reduction. Thus, this trend shown in the standard reduction table can be reproduced in the laboratory from experimental results with physical experiments. The different properties of various metals render some better cathodes (will undergo reduction) or anodes (metals that like to be oxidized) [1,2,3,6].

Lithium and potassium are the metals that “prefer” oxidation the most. Their reduction potential is nearly -3 volts in each case. On the opposing end, silver and cobalt prefer reduction most of the metals that exist.

Sadly, the best oxidizing agent (or the substance that “prefers” reduction of itself the strongest) is fluorine gas as it becomes individual fluoride ions. Since this substance is a gas at ambient temperatures and pressure (and never more than a liquid unless at *very extreme (low) temperatures*) it may be unsuited to any employment in a battery. Fluorine is also extremely dangerous. If it were somehow possible, it would make the best-known cathodic species. A "lithium-fluoride" battery would have a single cell potential of nearly 5.91 volts. A typical flashlight battery only has 1 1/2 volts, single cell, for comparison.

In conclusion, the chemistry of the battery directly allows prediction of its voltage (open circuit). Such chemistry gives insight into decent material choices (lithium or sodium anodes, say) and the electrical properties that material choice alters (namely voltage, indirectly current). Further analysis and work along these lines is documented in the next chapter – where equilibrium thermodynamics is introduced, and it is shown that open circuit battery voltage is contingent upon reagent concentrations and temperature. The standard reduction potential values, therefore, only hold for such standard conditions that these were taken at [1,6]. Investigation of physical chemistry, and its pertinence to galvanic cells, is the topic of the next chapter – which allows further analysis of batteries (and their workings) in the quantitative realm. Figures of the experimental apparatus utilized in this section are given for reference below.

a) Entire Apparatus: Half – Cells (Jars) and Salt Bridge with 1M KCl Solution.

b) Salt – Bridge and electrodes as taken from service in testing the chemistry. Cotton in the salt bridge tubes slows diffusion inside it.

c) The Zinc anode consisted of a zinc – plated bracket connected as shown. It proved suitable and gave a decent measurement of the reduction potential of zinc.

d) The “standard” copper – copper (II) sulfate cell. Copper pipe (pure) was used as the cathode. A laboratory thermometer ensured the temperature was near 25^{o} C when the measurements were taken.

Figure 7. Images of Experimental Apparatus and Chemicals Employed.

CHAPTER 3
THERMODYNAMIC THEORY

3.1 Introduction

The battery is a vessel in which oxidation – reduction reactions occur. These allow conversion between chemical and electrical energy (and vice versa for secondary batteries which can be recharged). In a battery, the anode is where *oxidation* takes place. The cathode is where *reduction* takes place. Oxidation is the loss of electrons from a chemical species. Reduction is the gain of electrons to a chemical species. In a battery, discharging, the anode has a "-"charge and the cathode has a "+" charge. To maintain the balance of electric charge in a battery, conduction must take place within the metal electrodes (cathode and anode). The electrolyte in which the electrodes react must be conductive to maintain a flow of current (this is called "ionic conduction" whereby charged chemical species are mobile and allow a current to flow – which is distinct from electron flow in a wire) [4].

Such material gives a partial description of a battery's workings but leaves the quantitative character of battery operation left with little to go on. This chapter goes deeper into the theory and thermodynamics of the battery in general – explaining quantitatively how such a system generates an EMF and how such depends upon the inner materials involved. This work will allow determination of a battery's relative charge level from chemical parameters, will prove integral in developing an understanding of battery chemistry and action, and is utilized directly to model battery behavior in time.

3.2 Electrochemical Theory

During the use of a battery (or its discharge), two coupled chemical reactions take place. These can be written, in general form, as:

At the anode ("-" electrode):

$$\gamma\ (Reduced\ species)_B \rightarrow\ \delta\ (Oxidized\ species)_B + me^-$$

At the cathode ("+" electrode):

$$\beta\ (Oxidized\ species)_A + n\, e^-\ \rightarrow \alpha\ (Reduced\ species)_A$$

Chemical Equation 12. General Oxidation - Reduction Reaction [5].

The Greek letters of γ, δ, α, and β are simply the stochiometric coefficients of the chemical reactions at hand. Species "A" is ultimately reduced, and species "B" is ultimately oxidized. Typically, these reagents are metals and metal ions, or related metal compounds.

Materials commonly utilized in batteries have changed over time – allowing incremental improvements in battery life [1]. In the 19th century, zinc was the anode metal of choice, nearly universally. Latter, lead and cadmium were used as anode materials. Today, lithium (with its great desire to undergo oxidation) is used as an excellent anode material. Other possible anode materials of interest are sodium, potassium, and magnesium. These may be somewhat lower than lithium in certain metrics or better than it, but lithium is rare, and research is underway to find more economical alternatives. For example, household storage of electrical energy may be more practical using sodium than lithium compounds, despite the weight of the former. Sodium costs less and offers comparable performance [6].

Oxidation – reduction reactions are always coupled. It is impossible for oxidation to occur without reduction transpiring, and vice – versa. Moreover, metallic elements towards the left of the periodic table make excellent anodes. Non – metallic elements towards the right of the periodic table make excellent cathodes. This trend can be attributed to differences in electro-negativity of the elements in these columns [6]. Moreover, a battery works based on *the affinity for electron transfer between different metal compounds or elements* [6]. Such transfer is forced through an external circuit connection, and hence chemical energy is transferred directly to electrical energy. Thus the utility of such systems.

3.3 Fundamental Thermodynamic Theory

Thermodynamics and energy transfer must be understood to appreciate battery operation and behavior. It is best to begin at the beginning of this science and develop into a congruent theory.

In the 17th and early 18th century, Newtonian mechanics was introduced. Newton gave us equations such as force = mass x acceleration and work = force x distance. The steam engine was invented around this timeframe and the expansion of steam (a gas) was put to work. Some interesting mathematics was figured then that relates to batteries. This includes the work done by a gas and the "work – energy theorem" [6]. These are explained below in turn.

3.3.1 Work done on a Particle in one direction

Since work = force x distance, at the limit of the infinitesimal:

Eq. 3. dw

So, for a non – infinitesimal amount of distance traversed:

$$\textbf{Eq. 4.}\ Work\ (total) = \int_{x(start)}^{x(stop)} F(x)dx$$

Notice that work is energy, measured in joules. The above follows in one – dimension from standard calculus. Power is the *rate of work*. Power can be written as the derivative of work with respect to time. Power is measured in *watts*.

$$\textbf{Eq. 5.}\ P = \frac{dW}{dt}$$

Now, this case can be generalized to three dimensions of motion. A force can be resolved into x, y, and z components. This can move a particle some distance in all x, y, and z directions. The general differential would therefore be:

$$\textbf{Eq. 6.}\ dw(three\ dimensions) = F_x dx + F_y dy + F_z dz$$

What is the relationship between work, force, and kinetic energy? Kinetic energy results from work. What is the expression for K.E.? The following mathematics gives a proof of the "Work – Energy Theorem", a critical conclusion of Newtonian Physics – even 250 years later.

3.3.2 The Work – Energy Theorem, its Proof

For a body or particle that has work done on it, in all three dimensions (general case) [6]:

$$\textbf{Eq. 7.}\ W = \int_{x(start)}^{x(stop)} F(x)dx + \int_{y(start)}^{y(stop)} F(y)dy + \int_{z(start)}^{z(stop)} F(z)dz$$

Now, force is the product of mass and acceleration. It can be stated that [6]:

$$\textbf{Eq. 8.}\ F_x = ma_x = m\frac{dv_x}{dt} = m\frac{dv_x}{dx}\frac{dx}{dt} = mv_x\frac{dv_x}{dx}$$

This follows simply by the chain rule and basic mathematics.

This allows the work – energy equations to be re-written in a form that involves the initial and final velocities (not the positions) [6]. Such would follow as:

$$\textbf{Eq. 9. a.}\ Work = \int_{V_x(start)}^{V_x(end)} mv_x dv_x + \int_{V_y(start)}^{V_y(end)} mv_y dv_y + \int_{V_z(start)}^{V_z(end)} mv_z dv_z$$

The fundamental theorem of calculus can be utilized to evaluate the indefinite integrals. Such would obtain (executing all three in tandem):

Eq. 9. b. $Work = \frac{1}{2}m\left[V_x(end)^2 + V_y(end)^2 + V_z(end)^2\right] - \frac{1}{2}m\left[V_x(start)^2 + V_y(start)^2 + V_z(start)^2\right]$

Notice that this equation explains how the equation "K.E. = (1/2) x m x v^2" is derived [6]. If the starting velocity is zero in all components, then the expression would be reduced to:

Eq. 9. c. $Work = \frac{1}{2}m\left[V_x(final)^2 + V_y(final)^2 + V_z(final)^2\right] = K.E.$

This work alludes to the statement that:

Eq. 9. d. $Work\ (done\ or\ utilized) = K.E._{final} - K.E._{initial} = \Delta K.E.$

This is the work – energy theorem. There are two main types of energy – kinetic (of motion) and potential (based on position and electric / magnetic / gravitational fields). Both are involved in batteries (the kinetic energy of the electron, indirectly, and the energy of "chemical potential"). Kinetic energy and potential energy, summed together, render the mechanical energy of a system [6]. In short, it is the energy of a body's motion and its energy of potential. Energy is conserved, of course. It can be transferred, but neither created nor destroyed [6].

3.3.3 Thermodynamics of Gases, PV Work

Thermodynamics is largely based on gases and their pressure, volume, and temperature changes. Pressure is defined as force / area involved. Such could be the area of a piston in a cylinder. Now, it is true that [6]:

$$dW_{on\ system\ or\ by\ system} = F_x dx$$

for a single axis. This can be generalized, in the case of a gas, to the below expression [6].

Eq. 10. a. $dW_{on\ system\ or\ by\ system} = F_x dx = Pressure \times Area \times dx = -P\,dV$

This is true since force is equal to pressure multiplied by area. Notice that the negative sign is added by convention and the "dV" term is added since Area multiplied by dx is the volume differential in rectangular coordinates. It holds that:

Eq. 10. b. $W_{reversible} = -\int_1^2 PdV$

This equation is the expression of the work done by a pressure or volume change on a gas. Such would apply to squeezing a balloon (altering pressure and volume), or a piston moving to expand or compress a gas. Notice that the expression here is the area under the P-V diagram for a gas.

Strictly, the equation above is path – dependent and is a line integral [6]. Also, pressure is a function of temperature and volume – this can be enumerated by the "ideal gas law", as will follow shortly.

3.3.4 Cases considered of PV Work

I. A piston in a cylinder of area "A" moves from position x(initial) to x(final). What is the work done by the piston moving to decrease the volume the gas occupies (such as occurs in an air compressor)?

It is true that, roughly, pressure x volume = n x R x Absolute temperature [2,6]. This is the "ideal gas law", and it has been known since the 19th century.

Notice that it is true that:

$$\textbf{Eq. 11. } P = \frac{nRT}{V}$$

So, a change in pressure implies a change in volume. If, conversely, volume and temperature are known (at a given gas quantity) – then pressure can be computed. Pressure is, again, the quotient of force and area. Recalling the formula for P-V work, it can be stated that [6]:

$$\textbf{Eq. 12. a. } W_{reversible} = -\int_1^2 PdV = -\int_1^2 \frac{nRT}{V}dV = -nRT\left[\ln\left(V(final)\right) - \ln\left(V(initial)\right)\right]$$

Since volume is equal to area times the distance from the "end" of the cylinder (where the gas's pressure diverges to infinity), the above result can be "restated" as (via logarithm rules):

$$\textbf{Eq. 12. b. } W_{reversible} = -nRT\left[\ln\left(V(final)\right) - \ln\left(V(initial)\right)\right] = -nRT\left[\ln\left(\frac{V(final)}{V(initial)}\right)\right]$$

And,

$$\textbf{Eq. 12. c. } W_{reversible} = -nRT\left[\ln\left(\frac{V(final)}{V(initial)}\right)\right] = -nRT\left[\ln\left(\frac{\cancel{A\times} X_{pos\,final}}{\cancel{A\times} X_{pos\,initial}}\right)\right] = -nRT\left[\ln\left(\frac{X_{fin.}}{X_{init.}}\right)\right]$$

Thus, when a piston moves from x(initial) to x(final), the work done is the above expression. Of course, the pressure changes and the volume changes when this work is done. Both are considered here. However, the area of the cylinder is fixed, and the quantity of gas is also. Ergo, the expression above is valid for the case of a cylinder and piston (such as in a steam engine, etc.). Notice that n is the number of moles of gas, R is the universal gas constant, and T is the Kelvin (or absolute) temperature of the gas. This derivation assumes that the temperature of the gas is constant. The above solved for the PV work involving a volume change. A pressure change's work can be solved analogously [6]. This follows as the case below:

II. Imagine that instead of a volume change being predominant (as in case "I" above), a pressure change is the dominant factor at hand. Such could happen when a balloon is squeezed or if more molecules of gas were added to a system. If a pressure change is the dominant disturbance to the ideal gas - piston system, it holds that:

Volume may be solved from the ideal gas law as:

$$V = \frac{nRT}{P}$$

Ergo,

Eq. 13. $W_{reversible} = -\int_1^2 PdV = -\int_1^2 V\,dP$

This holds since you can integrate a function both ways. The area is equivalent in both circumstances under the P-V curve [6].

Further mathematical manipulation may render:

Eq. 14. a. $W_{reversible} = -\int_1^2 PdV = -\int_1^2 \frac{nRT}{P} dP = -nRT\int_{p(init)}^{p(final)} \frac{1}{P} dP$

Evaluation of the rightmost integral obtains:

Eq. 14. b. $W_{reversible} = -nRT\int_{p(init)}^{p(final)} \frac{1}{P} dP = -nRT\left[\ln(\frac{p(final)}{p(initial)})\right]$

This equation is very significant. Why? Its right-hand form appears as a term in "the Nernst Equation" which *predicts the voltage (open circuit) of a battery in general (non – constant) conditions*. Ergo, it is important to understand where this term comes from analytically. Notice that this equation would solve the energy added to a balloon by squeezing it (increasing pressure, decreasing volume, all the while T remains nearly constant as does the quantity of gas). It holds that concentration discrepancies behave (chemically) similar to pressure differences [1,6]. Moreover, gaseous reagents in certain laboratory cells, when considered in Nernst's equation, *do obey the term above, summed with the other energies at hand* [1]. This effect is explained further in this paper, but ultimately it is contingent on the above result involving PV work.

3.3.5 Notes on Heat and Specific Heats

Heat is a temperature disparity between two bodies that leads to energy transfer as a transference of temperature from the hotter to the cooler body. In short, temperature is molecular kinetic energy (thus the information on K.E. mentioned earlier). When two bodies are placed in contact, at dissimilar temperatures, the kinetic energy of the warmer one decreases and leads to the K.E. of the cooler one to increase [6]. This is heat transfer in brief. Heat is energy flow as "flow" of temperature. It only occurs from hotter bodies to cooler ones (this is the second law of thermodynamics) [6].

A simple equation for heat flow is (at equilibrium):

Eq.15. a. $m_2C_2(T_2 - T_{fin.}) = m_1C_1(T_{fin.} - T_1) = q\ (flow\ of\ heat)$

This equation models the situation of hot body "two" being placed next to cooler body "one" [6]. After some time to establish equilibrium, body one is warmer and body two is cooler. This is heat flow as modeled by this equation.

The "C" terms are specific heats, which are coefficients that reflect the temperature / energy relationship for different materials [6]. It is easier to heat metal than wood due to differences in "C" between these materials, for example. The "m" terms are the masses of the bodies. It is harder to heat larger bodies than smaller ones. "T", of course, represents the temperatures involved. Strictly speaking, the specific heat is a function of temperature.

Ergo, it holds that total heat transfer (energy transferred as heat) would be [6]:

Eq. 15. b. $q_{p,fixed\ total} = m\int_{T1}^{T2} C_p(T)dT$

Here $C_p(T)$ is a function for specific heat, contingent upon temperature.

3.3.6 Fundamental Thermodynamic Definitions

Some basic definitions are in order for one to understand thermodynamics. The energy of a system (in total) is the sum of its kinetic energy, potential energy, and "internal energy" caused by things like temperature and internal effects (residual chemical energy) [6]. Notice that the K.E. and potential energy (caused by external fields) are often zero. This leads to the system's total energy being equal to its internal energy (chemical potential and heat energy).

The equations obeyed by a body thermodynamically are as follows [6]:

Eq. 16. $E_{total,\ of\ a\ body} = K.E. + P.E. + E_{internal}$

K.E. is “kinetic energy” (energy of motion). P.E. is “potential energy” (from electric or gravitational fields). What is “$E_{internal}$”? It is the result of chemical potential energy and temperature of the system (heat energy at one time imparted to it). The equation for it is [6]:

Eq. 17. a. $E_{internal} = U.$

Eq. 17. b. $\Delta U = q + W = heat\ energy\ change + Work\ energy\ change.$

Notice that energy is conserved [6].

Ergo,

Eq. 18. $\Delta E_{system} + \Delta E_{surroundings} = 0$

This is the first law of thermodynamics. A sign convention is obeyed that a “+” energy is energy sent into a system. “-“ energy values are indicative of energy sent from a system [6]. A battery or galvanic cell would obey this rule entirely, of course.

3.3.7 Thermodynamic State Functions

Two state functions are commonly used in thermodynamics: internal energy and enthalpy [6]. These are defined as follows below.

Heat and work are not state functions. They depend on the path or process that a system takes, and not simply the initial and final states of the system. This makes calculations using these metrics difficult. Enthalpy and internal energy are state functions and can be figured solely based on the initial and final states of the system [6]. Between two points, the enthalpy and internal energy changes are the same – irrespective of the path taken.

Internal energy is the sum of heat and work added to or done by a system:

$$dU = dq + dw$$

Internal energy changes only are affected by the initial and final states of the system. Ergo, the change in internal energy can be written as:

$$\Delta U = U_{final} - U_{initial}$$

Notice that for a cyclical process (EG. An ideal battery that can be recharged and discharged infinitely many times at 100% efficiency), it holds that:

ΔU (entire process completed) = 0

Now, internal energy takes into account heat and work done on or by a system. It does not account for pressure volume changes and the energy effects that these can render. A function called "enthalpy" does account for such pressure – volume work, as well as work done on or by the system. It is defined as:

$$\textbf{Eq. 19. } H = Enthalpy = U + PV = q + w + (PV\ work)$$

Notice that internal energy is measured and used for constant *volume* processes. Enthalpy is used for constant *pressure* processes. Notice that chemical reactions facilitate enthalpy changes [6].

Consider a process that happens at a constant pressure. Take a change in energy due a volume change at constant pressure. Heat may change also. The mathematics would be:

$$\textbf{Eq. 20. a. } \Delta U = internal\ energy\ change = U_{final} - U_{initial} = q + w = q_{p\ fix} - \int_{Vinit}^{Vfinal} PdV$$

And,

$$\textbf{Eq. 20. b. } \Delta U = U_{final} - U_{initial} = q_{p\ fixed} - P(V_{final} - V_{initial})$$

It is possible to write the heat change as below by transposing the above as:

$$\textbf{Eq. 20. c. } q\ change_{p\ fixed} = U_{final} - U_{initial} + P(V_{final} - V_{initial})$$

Notice that the heat change is equal to the change in internal energy plus the work the gas or system does via PV work. In other words, heat energy added (from chemical reactions) is converted into internal energy in other forms and useful work. This is what this equation represents. It may represent two gases reacting to render a change in potential energy (chemical or internal energy that is) and useful work via a volume change at a nearly constant pressure. The heat energy change drives both and this is the meaning of this equation. However, using internal energy also requires the volume and pressure information to reckon the total heat energy change required to impart both. There is a better way. Enthalpy figures can be used to determine the total heat energy change in a system [6].

Note: The above equation may apply to a cylinder at a constant (nearly) pressure from a large boiler. It may expand a piston/gas volume against air pressure and do work. This is the P-V term. The remainder of the heat energy from burning fuel is lost or rendered less useful (although it still exists) as "internal energy" of the steam itself. Such a situation makes the above equation make sense – where it is otherwise vague and hard to determine its significance physically. Thermodynamics was developed to explain the operation of the *steam engine*. It did so and lead to improved versions.

It is possible to combine the initial and final terms of the above equation to render:

Eq. 20. d. $q\ change_{p\ fixed} = \left(U_{final} + PV_{final}\right) - \ (U_{initial} + PV_{initial}) = \ H_{final} - \ H_{initial}$

Ergo, enthalpy differences for a reaction yield the total energy it can render as heat, both to modify internal energy or drive a piston through PV work [6]. Enthalpy is therefore a more powerful metric than “internal energy” alone. It is also true that:

Eq. 20. e. $\Delta H = \ \Delta U + P\Delta V = q$

For solids and liquids, the P-V change is tiny. Most of the enthalpy change is the internal energy change.

For these media, it is very nearly true that:

Eq. 20. f. $\Delta H \ \approx \ \Delta U \ \approx \ q\ released$

This completes the fundamental definitions of U, H, and q (internal energy, enthalpy, and heat flow respectively).

3.3.8 Further Notes on Heat Flow

A more formal expression for heat flow is, considering specific heat as a function (which it is, varying slightly with temperature):

$$q_{p\ fixed} = mass\ \times \int_{Tinitial}^{Tfinal} C_p(T)dT\ \ \approx mass\ \times C_{average} \times \Delta T$$

Notice that “C” indicates a specific heat here. T is absolute temperature. Often the specific heat function is not known, and an "average" value for "C" is employed [6].

Again, for liquids and solids, PV work is minimal. V is nearly constant, and P is constant. PV work is only significant for gases and similar situations. For the case of a solid (such as an electrode in a battery):

$\mathrm{U} = \mathrm{m} \times C_p \times \Delta T + W(on\ solid\ by\ chemical\ reactions\ say) = heat + work$

Thus, the internal energy term takes into account something of a battery’s action. A battery’s electrodes convert some chemical energy into electrical energy. Some is lost as heat. This is the significance of the work herein – as per conservation of energy.

3.3.9 Basic Thermodynamic Definitions

Some terminology applies to thermodynamic processes which is not used in common English. These terms are best elucidated and defined so that if they are encountered, they are understood.

- Isothermal processes occur at a constant temperature.
- Adiabatic processes involve no heat transfer.

A battery is possibly isothermal if operated lightly. It is not adiabatic, or it may overheat if no heat could be dissipated under heavy load.

- Isobaric processes transpire under constant pressure.
- Isochoric processes take place under a constant volume.

Some batteries are not isobaric, yet modern dry cells are more or less isochoric. Their volume is fixed by their container and there is no expansion.

3.4 Chemical Thermodynamics

Chemical reactions facilitate enthalpy changes. Accordingly, the theory presented above may apply to such systems. Such application allows for energy changes to be considered mathematically [1,6].

3.4.1 Chemical Equilibrium and Chemical Potential

Chemical reactions can be explained in terms of the "chemical potential" (μ) of the various reagents that compose the mixture that is undergoing the reaction. At equilibrium, since total chemical potential (a metric of the ability to do work) is null, it is reasonable to state the obvious statement [6]:

Eq. 21. $\sum_i V_i \mu_i = 0$

Here the "v" coefficient denotes the amount of each reagent with chemical potential of "μ", these are summed across the composition of the mixture. When this sum is zero, there is no work that the solution can do. Ergo, its composition is static, and the solution has reached chemical equilibrium (a state where chemical reactions favor no change and run in both directions at the same rate) [6].

Chemical potentials are contingent upon the species at play chemically and the "inherent" energy carried by such. They are also contingent upon the possible PV work that the chemical species may perform or otherwise alter somehow. Chemical potential therefore depends on standard chemical measurements and by some formula that depends on pressure and temperature [6]. The ideal gas law allows the following formulas and results to be obtained. Chemical potential varies with changes in conditions, as below (considering the case of differing pressures):

Eq. 22. a. $\mu(T, P_2) - \mu(T, P_1) = change\ in\ PV\ work\ by\ P\ change$

The right hand side can be evaluated by the following differential equation (assume isothermal process):

Eq. 22. b. $\int_{init}^{final} d\mu = \int_{init}^{final} \frac{nRT}{P} dP = \bar{V} dP$

Assuming a constant temperature process, the change in pressure affects the chemical potential as described by this integral above. Typically, for standard chemical tables, n = 1 Mole. Ergo, the "n" term can be omitted from the work above. Notice that this integral is a *remarkably similar result to that obtained in the previous section*, above (EG. PV work integrated, case of a pressure change). The work may follow as:

Eq. 22. c. $change\ in\ PV\ work\ by\ P\ change = \int_{init}^{final} \frac{RT}{P} dP = RT[\ln(P\_final) - \ln(P\_initial)] = RT \times ln\left[\frac{P_{final}}{P_{initial}}\right]$

Now that the change in PV work is known, the original difference can be rewritten as:

$$\textbf{Eq. 22. d. } \mu(T, P_2) - \mu(T, P_1) = RT \times ln\left[\frac{P_{final}}{P_{initial}}\right]$$

Now if the chemical potential of the T, P_1 term is the standard tabulated value (at 25° Celsius and 1 Atm.), then the above result can be rewritten as:

$$\textbf{Eq. 22. e. } \mu(T, P_2) = \mu^o(T, P_1) + RT \times ln\left[\frac{P_{final}}{P^o}\right]$$

The term with the “o” superscript, here, denotes a standard chemical potential value at 25° Celsius and 1 Atm. of pressure. The equation above relates non – standard pressures / conditions and their associated chemical potentials to tabulated values under controlled conditions.

This is a fundamental result and is therefore important, as it is used to derive the Nernst equation – which describes a battery’s voltage output quantitatively when it has various non-standard concentrations of internal reagents, products formed, etc. [1,6].

3.4.2 Notes on Chemical Potential

Chemical potential is free energy that can be done by a chemical in solution or by its inherent energy (potential energy that may be liberated). Chemical potential is therefore a measure of something called Gibb’s free energy [6].

Thus (via the “Gibb’s equation”):

$$\textbf{Eq. 23. } \mu_{chemical\ species} = \bar{G} = \bar{H} - T\bar{S} = Enthalpy\ Work - Entropy\ Losses$$

This is, of course, true since the right-hand side is the “Gibbs Free Energy Equation” (proven latter in this work). The temperature and entropy term (“S” term) can be eliminated if the system is at constant temperature (is isothermal). When no entropy change is manifest, the Gibb’s free energy is equivalent to the enthalpy change.

3.4.3 Theory of Chemical Equilibrium

The equilibrium criteria essentially means that the chemical mixture or reaction has no free energy for any process to transpire. This situation is analogous to a moment arm or lever under perfect balance whereby no further changes occur. Mathematically, this can be written by stating the “scaled sum of chemical potentials is zero” [6]. The chemical potentials are scaled insofar as the various reagents (or products) are present, that is, their molar quantities present in the mixture. Ergo:

$$\sum_i V_i \mu_i = 0$$

Substituting in the general form of chemical potential, considering the PV effects:

Eq. 24. a. $\sum_i V_i \left[\mu^o(T, P^o) + RT\ ln\left[\frac{P_i}{P^o}\right]\right] = 0$

This result can be used to obtain reaction equilibrium constants mathematically. Reaction equilibrium constants are important metrics in chemistry that relate how a reaction "tends" towards reaching completion (where all / part of the reagents are transformed into products) [6]. Technically speaking, the equilibrium constant is the value of the reaction quotient (defined latter) at equilibrium (after the chemical reaction "stops" and obtains a steady state). Such useful constants can be rendered from molar (standard) values of Gibb’s free energy for reactions. The derivation for such a result can be obtained using work such as the above.

It follows that [6]:

Eq. 24. b. $\sum_i V_i \mu^o(T, P^o) + RT \sum_i V_i\ ln\left[\frac{P_i}{P^o}\right] = 0$

This holds at equilibrium. The summation of the left term is the “molar Gibb’s energy” of the chemical mixture or reaction system at standard temperature and pressure. The right summation takes into account non-standard conditions (EG. Pressure differentials from standard temperature and pressure conditions).

Thus, it holds that:

Eq. 24. c. $\Delta G_T^o = \sum_i V_i \mu^o(T, P^o)$

Now, the above two results can be combined to render (at equilibrium):

Eq. 24. d. $\sum_i V_i \mu^o(T, P^o) = -RT \sum_i V_i\ ln\left[\frac{P_{i,equilibrium}}{P^o}\right] = \Delta G_T^o$

Now, the above equation can be used to determine the equilibrium constant (K_p^o), which can be found from the Gibb’s free energy and the remainder of the terms.

The work would follow as (using logarithm rules):

Eq. 24. e. $\Delta G_T^o = -RT \sum_i V_i \, ln\left[\frac{P_{i,equiilibrium}}{P^o}\right] = -RT \times ln\left[\prod_i \left[\frac{P_{i,equiilibrium}}{P^o}\right]^{V_i}\right] = -RT \times ln(K_p^o)$

The highlighted term is called “K_p^o”, it is the equilibrium constant for the chemical reaction. This constant is a product of pressures or concentrations (used with liquids and their reactions) which are present under equilibrium conditions - or when the reaction is complete. The above work allows the solution to the equilibrium constant as:

Eq. 24. f. $K_p^o = e^{\frac{\Delta G_T^o}{-RT}}$

This is a major result that may prove useful in chemical work and physical chemistry. The equilibrium constant is related to Gibb’s free energy and vice versa.

Therefore, if one is known, the other can be figured (given the conditions at hand for equilibrium, etc.) Battery chemistries must strongly favor equilibrium, and they do for all commercial units, since this relation holds. Reactions that favor completion towards rendering products are more useful in galvanic cells compared with reactions that do not favor completion and therefore render less energy (by the above relationship) [1,6].

3.4.4 Notes on Entropy, Enthalpy, and Free Energy

Some more information is required to have the material to derive the Nernst equation, which predicts battery voltage as a function of chemical constants and known concentrations, pressures, etc. The remaining information pertains to entropy, free energy, and enthalpy. In short, it is true that [2]:

Eq. 25. a. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

The total entropy change of any process is the universe’s entropy change. It is the total (sum) of the system’s entropy change and the surroundings entropy change. This makes sense based on intuition.

By definition, the change in entropy of a system’s surroundings may be stated as [2]:

Eq. 25. b. $\Delta S_{surroundings} = -\frac{q\ (or\ heat\ dissipated)}{Temperature\ of\ Surroundings\ (K)}$

Notice that entropy is positive for exothermic processes and is negative for endothermic ones. The numerator of this fraction is an enthalpy change (heat change), and the definition here applies at pressure and temperature being held as constant [2].

The entropy change of the universe and the Gibb's free energy changes are related [2]. This can be shown by mathematics as follows below and recalling basic definitions.

Gibb's free energy equation is stated as (taking this as a definition):

$$G = H - TS$$

Notice that G is the Gibb's free energy, H is the enthalpy change, T is surrounding temperature, and S is entropy. Division of this equation by -T would render:

Eq. 25. c. $\frac{\Delta G}{-T} = \frac{\Delta H}{-T} - \frac{T\Delta S}{-T}$

Which is equivalent to:

Eq. 25. d. $\frac{\Delta G}{-T} = \frac{\Delta H}{-T} + \Delta S$

Notice that the left-hand term is the universe's entropy change, the rightmost term is the system's entropy change. The enthalpy change over temperature term (middle term) is the surrounding's change in entropy. This proves the earlier intuitive result [2].

Thus, the Gibb's free energy equation comes from and can be reduced to the total entropy sum that relates universal entropy increase to that of the system and its surroundings.

3.4.5 Fundamental Reaction Variables, Chemical Reaction Rules

Entropy changes in chemical reactions obey:

Eq. 26. a. $\Delta S^{o}_{reaction,total} = \sum S^{o}_{products} - \sum S^{o}_{reactants}$

The total entropy change of a chemical reaction is the standard entropy of the products (summed over all total products) minus the standard entropy of all reactants involved (summed over all of the reactants involved) [6]. Such "o" superscripts indicate standard values, as tabulated in chemical manuals.

Enthalpy changes in chemical reactions obey a similar rule. It is true that (directly analogous to the above) [6]:

Eq. 26. b. $\Delta H^{o}_{reaction,total} = \sum \Delta H^{o}_{formation,\ products} - \sum \Delta H^{o}_{formation,\ reactants}$

The total enthalpy change of a chemical reaction is the difference between the enthalpies of formation of the products (summed over all of them) and the reactants (summed over all of these).

Because enthalpies and entropy data obey these two rules, and the Gibb's equation holds, it stands to write that free energy values obey a similar rule. They do, and it remains true that:

Eq. 26. c. $\Delta G^{o}_{reaction,total} = \sum \Delta G^{o}_{formation,\ products} - \sum \Delta G^{o}_{formation,\ reactants}$

Notice that, again, "G" is free energy, "H" is enthalpy, and "S" is entropy, always, in the equations above and in those that follow.

3.4.6 Fundamental Equations of Electrochemistry and The Electrochemical Potential

It holds that one mole (Avogadro's number) of electrons has a charge which is known. This charge is called "Faraday's constant" and has a value of 96,485 Coulombs. Since the value of this is known, it follows that the charge of n_i moles of an ion can be computed:

Eq. 27. $Q_i(that\ is, charge\ total\ of\ ion\ species) = z_i \mathcal{F} n_i$

Where z is the valance of the ion or its charge. Script f is the Faraday constant. Since charge is the integral of current (or current times time for constant current figures), battery ion transfer can be found from current measurements, ion valence values, and known time intervals. This was first mentioned in the previous chapter. This equation can be "rearranged" to solve for moles of ion transferred or valence charge.

A battery must consist of two electrodes (metals typically) and at least one phase (between them and reacting with them – called the "electrolyte") that is an electrical conductor, but which is not a metal or similar electronic conductor. Typically, liquid solutions that contain ions and sometimes molten salts are used as electrolytes [1]. Many are chemical pastes today [1]. Any attempt to use an electronic conductor (or metal) as an electrolyte would "short out" the two electrodes and no useful potential difference or current could be extracted from such a battery [6].

The expression for internal energy of an electrochemical system, including a battery, must be rewritten. It must consider the electric potential and the chemical potential. Such can be written, for the general chemical species "a", as:

Eq. 28. a. $dU^{a} = TdS^{a} - PdV^{a} + \mu_j^{a} dn_j^{a} + \phi^{a} dQ_j^{a}$

An electrochemical system's internal energy must consider the entropic term, the pressure – volume term, the chemical potential, and the electric potential (listed on the right-hand side in this order, respectively).

Notice that “ϕ” is a potential in volts (“a” and “j” are subscripts or indices). The earlier results may be substituted into this equation to render:

Eq. 28. b. $dQ_j^a = z_j * F * dn_j^a$

Therefore:

Eq. 28. c. $dU^a = TdS^a - PdV^a + \mu_j^a dn_j^a + \phi^a[z_j * F * dn_j^a]$

Factoring obtains the equivalency that [6]:

Eq. 28. d. $dU^a = TdS^a - PdV^a + [\mu_j^a + \phi^a z_j F]dn_j^a$

The boxed term replaces the chemical potential with a more accurate “electrochemical potential” term that includes both chemical potential (aforementioned) and the molar electrostatic potential energy inherent with a non-zero potential difference being involved (EG. a voltage).

The term for electrochemical potential replaces chemical potential in the equilibrium condition for galvanic cells and other electrochemical systems. Thus, it is proper to state [6]:

Eq. 28. e. $\widetilde{\mu_j^a} = electrochemical\ potential = \mu_j^a + z_j F \varphi^a$

Notice that F is Faraday’s constant here.

For closed electrochemical systems (such as a battery), at equilibrium, it holds that:

Eq. 29. a. $\sum_i v_i \widetilde{\mu_i^a} = 0$

This is the reaction equilibrium criteria, which is the same formula as earlier – given that the chemical potential is replaced by the total potential available – or the “electrochemical potential” term introduced above. When reaction potentials are matched between reagents and products, the situation is at equilibrium and no observed chemical activity can transpire. The “v” term in the above summation denotes the stoichiometric coefficients of the reagents and products involved (thus scaling their respective electrochemical potential values).

Substitution of the appropriate variables into the above summation renders [6]:

Eq. 29. b. $\sum_i v_i \widetilde{\mu_i^a} = \sum_i v_i \, [\mu_i^a + z_i F \varphi^a] = 0$

Rearrangement of terms yields:

Eq. 29. c. $\sum_i v_i \mu_i^a = -\sum_i v_i z_i F \varphi^a = -nFE$

Here "E" is the potential difference a battery renders. The chemical potential (and the battery's setup) must be in the "standard state" for such a formula to work (tables are recorded under such conditions, as mentioned in the previous chapter). Notice that the middle summation turns into the rightmost term since E is a potential difference and theta is an *absolute potential*.

This result may be tested. For a simple battery called the "Daniel cell" (mentioned in the previous chapter), zinc is oxidized, and copper is reduced. In brief the chemical equation is:

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

The copper is reduced from copper sulfate to metal copper at the cathode. The zinc moves from a zinc metal electrode into solution (which happens to be zinc sulfate).

The net process has two electrons transferred for each reaction (ergo n = 2 for the process). The standard state potential difference (at open circuit) can be solved for as:

Eq. 29. d. $\sum_i v_i \mu_i^a = -nFE = \Delta G_T^o$

Or:

Eq. 29. e. $\frac{\sum_i v_i \mu_i^a}{-nF} = E\ (open\ circuit\ at\ standard\ state)$

Here, "standard state" indicates concentrations of 1 Mol / L and gas pressures of 1 Atm. (where applicable). The sum of chemical potentials alone is the Gibbs free energy for the reaction, which is converted into electrical energy. The appropriate work (for the Daniel cell) renders:

$$\frac{-\mu(Cu^{2+})+\mu(Zn^{2+})}{-2(96,485)} = \frac{-65.52\frac{kJ}{mol}-147.03\frac{kJ}{mol}}{-2(96,485)} = E\ (open\ circuit\ at\ standard\ state) = 1.101 \text{ Volts}$$

This relation explains how chemical potential may be sent to electrical potential (more accurately *balanced* by electrical potential at equilibrium) [6]. The standard voltage of a Daniel cell is very nearly 1.10 volts, which nicely verifies the above work. Notice that metals in solid states do not contribute to the sum of chemical potentials. Also, reagents subtract from the summation (copper ions) while products add to the summation (zinc ions in this case).

This work has allowed quantitative predictions of cell EMF values under standard state chemical conditions. This ties the last chapter's material (standard reduction potentials) into the inherent thermodynamics (namely, by the above equation). Such is interesting, but of little practical use – since as a battery is drained or as temperatures vary – such standard conditions are hardly constant and rarely persist anywhere. The next section of this paper explains how the "Nernst equation" is derived and how it allows for quantitative predictions of cell EMF, even under such non – ideal conditions.

3.4.7 Derivation of the Nernst Equation for Electrochemical Cells

It is shown above that:

Eq. 30. a. $\sum_i V_i \mu^o(T, P^o) = -RT \sum_i V_i \, ln \left[\frac{P_{i,equiilibrium}}{P^o}\right] = \Delta G_T^o$

This equation, put into simple English, would read:

"Total Potential Change Possible (or "ΔG_T^o") = Energy taken by Maximum Pressure Change (right term)"

Under non-standard (STP) conditions, the total free energy change would be (by the above rules and deductive logic):

Eq. 30. b. $G = Free\ Energy\ Total = \ \Delta G_T^o + \ RT \sum_i V_i \, ln \left[\frac{P_{i,equiilibrium}}{P^o}\right]$

Thus, the free energy available (total) is that possible by the standard chemical values (the tabulated "ΔG_T^o") and the conditions regarding PV work (the rightmost term). The standard free energy is that at 1 Atm. and 25° Celsius, the other term accounts for non – standard conditions.

It is known that for electrical systems, the total energy that is rendered or used is obtained by an equation of the form:

Eq. 30. c. $Energy\ Used = I \ \times V \ \times t = power \ \times time$

Assume that for a time current is held constant and recall that the ampere is measured in Coulombs / second. Thus, for an electric circuit, total energy used is:

$$Energy\ Used = Q \ \times V = Coulombs \ \times \ \frac{Joules}{Coulomb} = Q(total\ past\ a\ point) \times Potetial\ Difference.$$

Eq. 30. d.

This holds since I x t (for fixed I) is equal to Q or total charge past a point in a circuit.

Thus, it is possible to state that:

Eq. 30. e. $Work_{\max\ possible} = \ \Delta \mathrm{G} = \ -\mathrm{nF}\mathcal{E}_{cell} = moles\ of\ charge \ \times \ charge\ per\ mol \ \times$ $standard\ Potential\ diff.$

Ergo, since the Gibb's Free Energy would be equated to the above term in the case of a battery or galvanic cell [6]:

$$\textbf{Eq. 30. f.}\ -\mathrm{nF}\mathcal{E}_{cell} = \Delta G_T^o + RT\sum_i V_i\, ln\left[\frac{P_{i,equiilibrium}}{P^o}\right]$$

The remaining energy available is that initially possible due to the reaction (ΔG_T^o) less the term caused by the concentration or pressure differential or disparity (the "RT" and summation term above).

Now, the reaction energy possible can be written in terms of the standard potential (see above work on standard state EMF calculations). The equation can be rewritten as [6]:

$$\textbf{Eq. 30. g.}\ -\mathrm{nF}\mathcal{E}_{cell,\ actual} = -nF\mathcal{E}_{standard}^o + RT\sum_i V_i\, ln\left[\frac{P_{i,equiilibrium}}{P^o}\right]$$

This is true since:

$$\Delta G_T^o = -nF\mathcal{E}_{standard}^o$$

Where n is the number of moles of electrons in the current that a battery renders, F is the Faraday constant (charge per mole of electrons or about 96,000 Coulombs), and the "E standard" term is the standard reduction potential difference of the metals or reagents in the battery (as detailed in the last chapter).

The equation can be rewritten in equivalent terms as (dividing all present by "-nF"):

$$\textbf{Eq. 31.a.}\ \mathcal{E}_{cell,\ actual} = \mathcal{E}_{standard}^o - \frac{RT}{nF}\sum_i V_i\, ln\left[\frac{P_{i,equiilibrium}}{P^o}\right]$$

This is the Nernst equation, that represents the EMF (voltage) rendered by a battery – when it is not under standard conditions and temperature.

The Nernst equation shows the character of the EMF rendered by a battery. It depends on the intrinsic reduction potential differences and the concentration or pressure differences that affect or skew the chemical reaction(s) involved. The summation is the reaction quotient for the chemical reaction. The Nernst equation can be restated as a simpler result [6]:

$$\textbf{Eq. 31. b.}\ \mathcal{E}_{cell,\ actual} = \mathcal{E}_{standard}^o - \frac{RT}{nF}\ln(Q)$$

This holds since "Q", or the reaction quotient, is equivalent to:

$$\textbf{Eq. 32.}\ Q = \prod_i \left[\frac{P_{i,equiilibrium}}{P^o}\right]^{V_i} = \prod_i \left[\frac{C_{i,equiilibrium}}{C^o}\right]^{V_i}$$

The "Q" value is taken as the above product over all "i" gases involved. V_i is the stoichiometric coefficient of each gas molecule involved. P^o is the standard state (1 Atm.) at which the gases were present when the standard EMF was recorded. For liquids, concentrations are used (Molarity values) [1,6]. The standard state of reagents / products (used in standard EMF tables) is 1 Mole / Liter in such cases. The rest of the theory remains essentially the same, replacing gas partial pressures with concentrations in the above reaction quotient [6]. The gaseous reaction quotient is the middle term. The liquid reaction quotient is the rightmost term, where "C" is a concentration value in M / L. Notice that C^o would be 1 M / L in practice.

Remember that the product of the inner arguments taken inside one natural logarithm is equivalent to the sum of the logarithms of each argument taken individually. This explains how the summation of many logarithm terms can be condensed into a single product, as is rendered above for “Q”.

When the reaction quotient or “Q” is equal to the equilibrium constant “K” for a given battery's chemical reaction, the voltage is zero as the reaction is at equilibrium given this situation. In such a state of equilibrium, the battery’s voltage is zero because the cell may perform no more useful work (the chemicals are “spent”).

Using standard conditions (assuming a room temperature of 20° Celsius) and substituting values for “R” (universal gas constant) and the Faraday constant “F”, the Nernst equation can be reduced to [6]:

Eq. 31. c. $$\mathcal{E}_{cell,\ actual} = \mathcal{E}^{o}_{standard} - \frac{0.0592}{n}\ln(Q)$$

This holds at temperatures of near 20° Celsius. Remember that “n” is the number of moles of electrons transferred per mole of reaction occurring. Q is, as mentioned earlier, the reaction quotient for the system.

3.4.8 Refinements of the Nernst Equation, Method to determine equilibrium constants, and notes on chemical activity

The above remark yields an insight into determining reaction equilibrium constants for galvanic cells. When the value for Q is K (the reaction equilibrium constant), then the EMF yielded is zero [1,6]. Copying the Nernst equation and substituting yields:

Eq. 33. a. $$0 = \mathcal{E}^{o}_{standard} - \frac{RT}{nF}\ln(K)$$

Hence,

Eq. 33. b. $$\mathcal{E}^{o}_{standard} = \frac{RT}{nF}\ln(K)$$

So,

$$\textbf{Eq. 33. c. } \frac{nF\mathcal{E}^{o}_{standard}}{RT} = \ln(K)$$

And finally,

$$\textbf{Eq. 33. d. } e^{\frac{nF\mathcal{E}^{o}_{standard}}{RT}} = K$$

Thus, the reaction equilibrium constant can be determined for an electrochemical reaction given the standard EMF value. The above formula shows the work required and all practical batteries have reactions that strongly favor products over reagents (the value for K is typically very large).

Notice that liquids and concentrated solutions do not behave as ideally as gases (for which the Nernst equation was derived to apply). The Nernst equation still works within excellent accuracy, given a concept called “chemical activity” is introduced. In short, the molarity of a solute must be multiplied by a coefficient to determine an “effective” concentration in the liquid [6]. The liquids (water and such solvents) involved act to reduce molecule movement and so such activity coefficients are nearly always below unity. In short, when the Nernst equation is used with liquid solutions or liquid chemistry, the following should be substituted for each concentration put into the formula:

$$\textbf{Eq. 34. } activity\ (effective\ concentration\ used\ in\ Nernst\ eqn.) = \gamma_i \times m_i$$

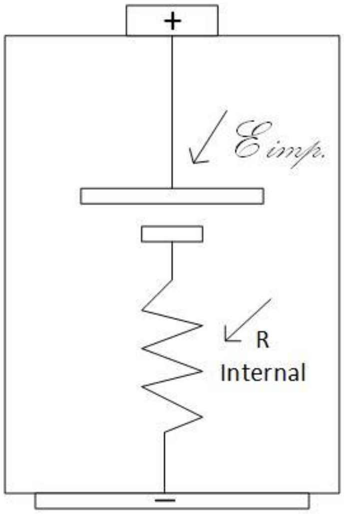
Here gamma is the activity coefficient (tabulated values are used). M is the molarity of the solute in some solvent. The “activity” value is put inside the reaction quotient of the Nernst equation. Such a “correction” allows the Nernst equation to accurately predict EMF values for galvanic cells that employ liquid states and solutions therein. More is mentioned on the effect of chemical activity in the next chapter.

3.4.9 Model of the Battery, Suitable for Electrical Engineers

Combination of information above and analysis thereof leads to a superior battery model for the electrical engineer to employ. Such would effectively be an imperfect voltage source (with a variable voltage set by the Nernst Equation and dependent on chemical properties of the battery), and a series resistance that models the limited conduction of the ions in the electrolyte. An image of such a battery model (schematic) is shown below for clarity. How such a model can be employed and utilized practically is explained hereafter.

Note: A battery roughly works like an imperfect EMF source that has a voltage that falls with decreasing reagent concentrations and increasing product concentrations. The inverse is also true. It also has an “inherent” internal resistance that accounts for imperfect ionic conduction within the battery’s electrolyte.

Although there are other imperfect effects and side reactions (some are partially detailed in the next chapter), and losses to consider, these are believed to be the most dominant ones inside a battery. The figure below represents the model detailed herein.



Model of the Battery, Consisting of Two Major Parts:

1. The series resistance is due to the imperfect conduction through the electrolyte. It is tabulated and can be found experimentally as:
   R(internal) = V(open circuit) / I(short circuit).
2. The imperfect EMF is set by the internal chemistry and concentrations of the reagents. The term $\mathcal{E}_{\text{imperfect}}$ is set by the Nernst equation. However, the concentrations vary (decreasing reagents and increasing products) as the battery is used. The ideal EMF must be updated during use for this reason.

Figure 8. Model of the battery as a Component – Accounting for Chemical Parameters Inside of It.

3.4.10 Instance of a Battery Model, its significance in modeling the Lithium-Ion Battery

The following algorithm can be used to predict battery behavior in time. Each step requires multiple calculations, but when these are done the terminal voltage and series current can be determined as the battery discharges. The initial conditions are taken as known. Notice: this model would work best with small currents and a slow discharge. More rapid discharge conditions may lead to further losses than predicted here and increase the “irreversibility” involved thermodynamically. This model is based on equilibrium thermodynamics, which involves small changes to a system in time. Great stress on a battery would take more modeling to accurately predict electrical ramifications thereof [1].

An improved battery model, as built upon piece by piece to this point, would work by the steps below:

Step I. Determine the EMF of the dependent (imperfect source), $\mathcal{E}_{\text{imperfect}}$, from the concentrations and status of the reagents and products in the battery. The Nernst equation (derived and explained above) is evaluated in this step.

Step II. The load is assumed to have a known resistance for at least a small time interval. The current flowing through the battery would then be:

$$I_{through\ battery} = \frac{\mathcal{E}_{imperfect}}{R_{internal} + R_{of\ the\ load}}$$

Step III. The current flowing implies that electrons which pass through the external circuit come from and are returned to chemical reagents inside the battery / galvanic cell [6]. Ergo, current alters the concentration of the reagents and products inside the battery. This can be modeled via Faraday's Laws of Electrolysis [3]. Next, one would update reagent and product concentrations with such calculations and return to step I. Continuation of this process would transpire until battery voltage falls to zero or the battery is disconnected from its load. This algorithm allows calculations (approximate) of a battery's output current and voltage vs. time.

The process above can be run to model battery behavior. Parameters and other work will change between different batteries, as size and chemistry particulars may vary. Step III may be hard to visualize or understand, but it is known that about 96,000 coulombs is the charge of 1 mole of electrons (6.022 x 10^{23} of them). Thus, although the mathematics for steps I and II is already explained, and step III may seem difficult – but it is not. This step was partially explained in the previous chapter.

For example, the buildup of lithium in solution when it acts as an anode would run something as follows. The chemical reaction would be:

$$Li(solid) \rightarrow Li^{+}\ (inside\ solution) + e^{-}\ (sent\ through\ external\ circuit)$$

Now, this is a simple chemical process. More advanced ones would take place in reality, but these work along the same principles. A current flows. The charge comes from or returns to chemical agents or species inside the battery. There is a relationship between charge total past a point and chemical changes per Faraday's electrolysis laws [2,3]. The mathematics would run, for lithium ionizing and entering an electrolyte solution:

Eq. 35. a. $I_{average,momentary} \times \Delta t = Q_{flowed\ past\ a\ point,momentary}$

Then,

Eq. 35. b. $\frac{Q_{flowed\ past\ a\ point,momentary}}{96{,}485\ Coulombs} = moles\ of\ Li\ entering\ solution_{during\ \Delta t}$

So,

Eq. 35. c. *Total lithium in solution = total lithium ions already in solution + moles of Li entering solution*

Now, this process would show reagents decreasing in time and products increasing in time during the use of a battery to render a current. Such would alter the reaction quotient (as mentioned before) and the algorithm would continue back to step I after altering the chemical states by this process. Of course, this step would have to be more advanced in a real battery, but the details can be worked out and the mathematics holds.

Thus, an “Engineer’s Model of a Battery” can be deduced form work involving fundamental chemistry, thermodynamics, and other physical concerns (the internal resistance, say). Mathematical analysis continues in the next chapter and experiments are performed to evaluate the work herein. The Nernst equation is investigated experimentally in the next chapter as well, and ionic conductivity is investigated due to its significance as a limiting factor. Finally, the battery model mentioned above is experimentally compared with the discharge of actual batteries and conclusions are drawn.

CHAPTER 4

COMPARISON OF THEORY TO EXPERIMENTAL DATA, RESULTS AND CONCLUSIONS

4.1 Introduction

The previous two chapters have introduced fundamental chemical principles illustrating how batteries work and how they generate a potential difference. In brief, this action can be reiterated as follows.

Chemical reactions occur at the threshold between metal electrodes and a liquid solution that both electrodes are immersed in. In one reaction, electrons are lost. The other occurs to capture or “grab” electrons from the first. In short, these electrons move through an external circuit – or a system of electronic components and wires that connect both metal electrodes. Useful work is done using the energy rendered. The rate at which these coupled reactions occur are linked, as charge is conserved. Such chemical processes, involving electron transfer during chemical changes, are “oxidation – reduction reactions”. Galvanic cells (batteries) operate upon such chemical reactions that allow conversion of chemical energy into energy electrical in form.

The previous two chapters placed this theory on firm footing. To investigate the validity of such work in practice, two experiments were conducted and are documented in this chapter. One experiment sought to investigate how the Nernst equation models open circuit EMF, namely the accuracy of this model and how it functions in the laboratory to predict experimental results. The second experiment herein worked to investigate how ionic conductors, or mobile ions in solution, pass a current. In a liquid or paste electrolyte solution, where mobile ions conduct a current (not electrons), is the conduction ohmic? Literature implies that with the exception of surface effects at electrodes, ionic conduction is essentially ohmic in character. This is put to the test, as ionic conductivity partially determines the “internal resistance” of a battery, and this term appears in the model introduced in the previous chapter.

Finally, in the conclusion of this chapter, actual alkaline cells (“D” batteries) were discharged. Such allows voltage information to be taken in time. This set of data is compared with theoretical calculations done by a MATLAB program – which implements the model derived in the previous chapter. Such work attempts to relate theory with direct practical use. In so doing, un-ideal effects are encountered (chemical activity, irreversible thermodynamic effects, the “electrical double layer”, liquid junction potentials, etc.) [1,6]. Such effects and further theory thereof are partially explained in this chapter and investigation of such details continues into the next chapter. It is hoped that such comparison between theory and practical reality provides greater insight into battery operation, predictions thereof, and – through such work – a better ability to control such.

In short, the entirety of the work in this thesis attempts to elucidate a battery's inner workings on a chemical and thermodynamic basis. The results of this analysis and research could then be directly employed to realize a control system which is "inspired" in its topology and methods by the chemical and thermodynamic principles encountered in detailed study of battery operation. The whole of such investigation, it is hoped, will enable the future development of a control system which accounts for real phenomena occurring inside batteries under its control. It is believed that such an advance will have direct benefits in prediction accuracy and control of battery operation in time.

4.1.1 Notes on Electrolyte Conductivity – Which relates to battery internal resistance

According to [5] ionic conductivities can be modeled analogously to how resistances / resistivity is treated in metals – given that concentrations and temperature are held as constants. The mathematics for this would follow as [4,5]:

$$\textbf{Eq. 36. a. } Resistance = \rho \frac{Length}{Area\ (cross\ section)}$$

Here ρ is a constant that depends on the species that is ionized in a liquid or solvent. It is a "specific resistivity" which can be related to a "specific conductivity" per the equation below.

$$\textbf{Eq. 36. b. } \rho = \frac{1}{Ꝁ}$$

Here Ꝁ is the specific conductivity. For a liquid with several ionic species, the specific conductivity is approximately stated as [5]:

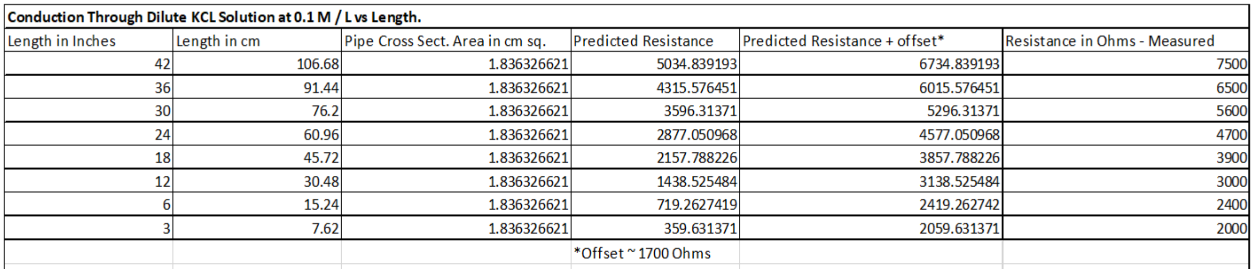
$$\textbf{Eq. 36. c. } Ꝁ = \sum_i c_i z_i \lambda_i$$

Here c is the concentration, z is the valance, and lambda is the "equivalent conductivity" (tabulated). Of course, KCL and KVL (Kirchhoff's laws) are valid in a battery as anywhere.

4.1.2 Experiments on Ionic Conduction

Electrolytes and ionic solutions are seldom worked with in electrical engineering. Accordingly, these types of conductors merit their own investigation from an electrical viewpoint. Do liquid electrolytes obey Ohm's law – even approximately or under controlled conditions? To investigate this, the following experiment was performed.

A pipe was filled with a 0.1 mole / liter potassium chloride solution. The pipe had a known length and constant cross-sectional area. Two rubber stoppers with stainless steel screws as contacts held the liquid inside the pipe and allowed for electrical contact with the liquid / electrolyte solution. The solvent was distilled water, as to be entirely pure from other salts besides from the potassium chloride intentionally added. The resistance was measured for the system, the liquid was then drained. The pipe was cut to a shorter length and the electrolyte was added again at the same dilution. The apparatus was set up equivalently, and resistance was measured this way over various lengths of the pipe filled with the same electrolyte solution. This experiment is very similar to how Ohm's law was determined in the 1820's by Georg Ohm. The difference is that Ohm used metal conductors and the instance here uses a length of an ionic solution. The results for this experiment are tabulated below.



Conduction Through Dilute KCL Solution at 0.1 M / L vs Length.

Length in Inches	Length in cm	Pipe Cross Sect. Area in cm sq.	Predicted Resistance	Predicted Resistance + offset*	Resistance in Ohms - Measured
42	106.68	1.836326621	5034.839193	6734.839193	7500
36	91.44	1.836326621	4315.576451	6015.576451	6500
30	76.2	1.836326621	3596.31371	5296.31371	5600
24	60.96	1.836326621	2877.050968	4577.050968	4700
18	45.72	1.836326621	2157.788226	3857.788226	3900
12	30.48	1.836326621	1438.525484	3138.525484	3000
6	15.24	1.836326621	719.2627419	2419.262742	2400
3	7.62	1.836326621	359.631371	2059.631371	2000
			*Offset ~ 1700 Ohms		

Table 2. Resistance of a column of a potassium chloride solution vs. length of the column.

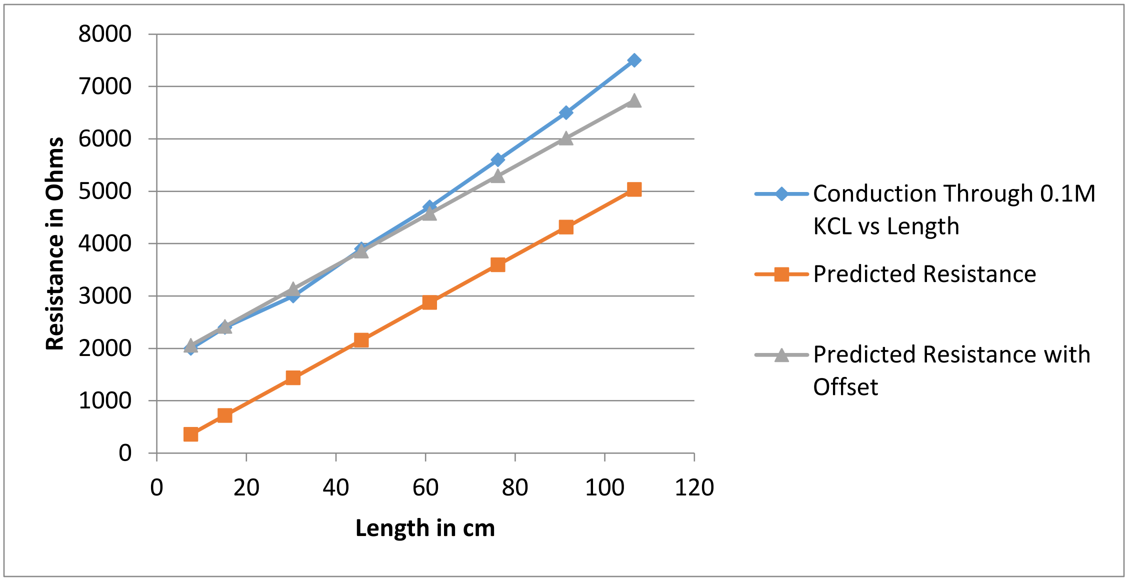


Figure 9. Resistance of a column of KCl solution (0.1 M/L) vs. length of the column.

Upon examination of the above plots, notice that the above conductivity equations can be solved using the appropriate tabulated values [4,5]. This renders the orange line shown in the above figure. The actual resistance is about 1700 Ω higher than the orange curve. In effect, this “offset” remains constant over the data set as measured. The grey curve is the same as the orange one, shifted by this offset of 1700 Ω.

An interpretation of these odd results is as follows. The metal – liquid junction somehow renders a resistance of 1700 Ω. Although identical (and relatively inert) stainless steel terminals were used at the metal – liquid junction, some surface effect here acts to impede the flow of current. This is most likely not back EMF (generated by redox reactions as in a battery) because the metals are identical as is the solution [6]. Thus, the galvanic potential should be zero. Possibly, water molecules are polarized near the terminals due to the voltage applied by the ohmmeter when the resistance was measured. This polarization of water most likely behaves like an electrical double layer or barrier [1]. Such accounts for the offset qualitatively.

When this un-ideality is considered, the KCl solution does behave in an Ohmic sense. The resistance increases linearly with length, as the plot shows. Although this experiment was devised to measure resistance in an ionic solution, batteries (which always contain some ionic electrolyte [1]) have similar behavior in their internal resistances. Some of the internal resistance in a battery is due to length between the electrodes (in the Ohmic sense). The rest is somehow related to the liquid – electrode interface and the “offset” that this junction renders. Exactly how this junction renders a resistance merits further work [1,6]. However, in the large picture, ionic solutions behave very approximately like resistances. Such justifies the use of “internal resistance” terms in battery models. An image of the apparatus, involved in the above experiment, is shown below for reference. The pipe was cut into shorter lengths, as explained, as the experiment progressed.

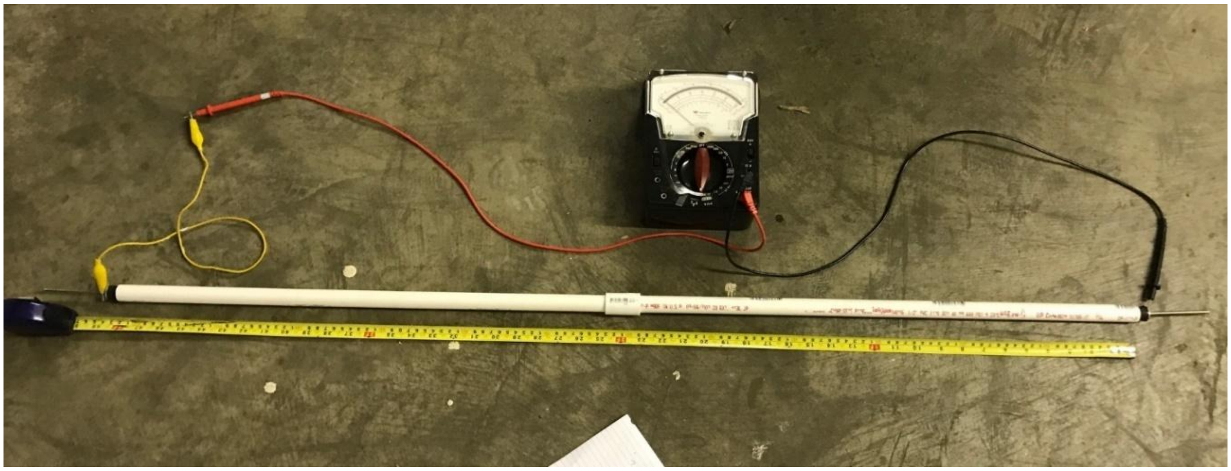


Figure 10. Experimental apparatus for the above ionic conductivity experiment. The pipe contained 0.1 M / L potassium chloride, in distilled water. The meter measured the resistance.

One final note is in order. The concentration of 0.1 M / L was not used in the above equations for conductivity by itself. In concentrated solutions, the concentration behaves un-ideally. It must be multiplied by a factor called the “activity” to render the “effective” concentration – or the concentration *which it acts like, if it were ideal.* The activity coefficients used here were read from the *Handbook of Chemistry and Physics* [8], where such are tabulated. This “activity” effect is a non-ideality which is considered further latter on. To get the precision of the above, it must be taken into account, however. The activity coefficient is required because *not all of the salt or ionic compound dissolves*. Multiplication by a factor corrects for this. The activity of 0.1 M / L potassium chloride in water is 0.77. Thus, the solution behaves like ideal 0.077 M / L potassium chloride, fully dissolved, in solution.

4.1.3 Ionic Velocities and Calculations Thereof

In electrolyte solutions, mobile ions transfer electric current. Since this is the case, the “average” velocity of any ion can be found mathematically. In short, ions in a solution may migrate slowly or “drift” between electrodes immersed in the solution (due to the electric field present [4]). In effect, the ions move very slowly. Because there are so many of them, and because electric *field* moves extremely rapidly, there is no appreciable delay between when an EMF is put across the cell and the resulting current that is set into motion (in the case of charging a battery – perhaps). If the average speed of an ion is “s” in a given direction, then it holds that:

$$\textbf{Eq. 37. a. } s \times \Delta t \times A = volume\ of\ charge\ moved$$

Here, “s” is the average motion of a charge carrying ion (or its velocity). Delta t is a small time increment over which the charge carriers may flow. “A” is a hypothetical area, crossed by the charge carrier ions during their transit. The above expression relates the charge velocity ("s") and the electrode area ("A") to the volume over which the charges would have moved. All charges (inside this volume, hypothetical, of dimensions A (area) by s x dt) would possibly collide with an electrode which is not more than “s * dt” away from this rectangle (that is, area “A”).

The total charge within this volume (which would constitute the current flowing electrolytically) would be:

$$\textbf{Eq. 37. b. } v\ \times C\ \times\ N_A = ions\ per\ unit\ volume\ of\ electrolyte\ soln.$$

Here “v” is the number of ions per molecule (of the solute added). C is the concentration of the solute molecules (in moles per Liter). The constant “N_A” relates moles to the *number of molecules present* (a very large number). In short, multiplication of these two expressions renders “volume of charge moved” times “charges per volume”. Such is equivalent to:

$$\textbf{Eq. 37. c. } number\ of\ ions\ past\ rectangle\ \text{"a"} = s \times \Delta t \times A\ \times (v\ \times C\ \times\ N_A)$$

Since this is the number of charges moving past a surface, it constitutes an electric current. The ion flux in motion would be nearly:

$$\textbf{Eq. 37. d. } J\ (Ion\ flux) = \frac{s \times \cancel{\Delta t \times A} \times (v \times C \times N_A)}{\cancel{\Delta t\ A}} = s \times (v\ \times C\ \times\ N_A)$$

Multiplication by charge per ion renders charge per unit time and unit area. This is “charge flux” or “current density”. The mathematics would read:

$$\textbf{Eq. 37. e. } J(Charge\ Flux) = (ze)[\, s \times (v\ \times C\ \times\ N_A)]$$

Here “z” is the valance charge of the ion species in question, “e” is the fundamental unit of electric charge (electron’s charge in Coulombs), s is the average drift velocity of ions moving, v is the number of ions per molecules of solute (which has a concentration of “C”). N_A is the Avogadro number. Notice that e times Avogadro’s constant is equivalent to Faraday’s constant (charge per mole of electrons). This observation allows simplification of the above work.

It follows that:

$$\textbf{Eq. 37. f. } J(Charge\ Flux) = (z\cancel{e})[\,s \times (v\ \times C\ \times \cancel{N_A})] = zFsvC$$

It is known that drift speed of an ion in solution, under an electric field, can be written to approximation as [4]:

$$\textbf{Eq. 37. g. } s = \ \mu E$$

Here "µ" is the mobility. "E" is the electric field.

Substitution obtains:

$$\textbf{Eq. 37. h. } J(Charge\ Flux) = zFsvC = zFvC(\mu E)$$

The above result is the approximate quantity of charge that flows per unit time and area via ion migration in an electrolyte solution (due to an electric field). Multiplication by “A” or the area of the electrodes would obtain:

$$\textbf{Eq. 37. i. } I(electric\ current) = \ zFvC(\mu E)A$$

It is true that E (or the electric field) is nearly equal to the potential difference divided by the length of the cell (the length between electrodes) [6]. Such is equivalent to the “length” mentioned during the section on conductivity. Since E ~ V / length, it is possible to write:

$$\textbf{Eq. 37. j. } I = \ zFvC\mu A\frac{V(across)}{length}$$

However, it was shown earlier that:

$$\textbf{Eq. 37. k. } I = \frac{V(across)}{R} = G\ \times V(across) = \frac{\kappa \times A}{length}V(across)$$

The above results come from rearranging the work introduced in describing electrolyte conductivity. The above two equations solve for the same thing, the current flowing through the electrolyte. These can therefore be set equal to each other and simplified further as:

$$\textbf{Eq. 37. l. } zFvC\mu\cancel{A}\frac{V(\cancel{across})}{\cancel{length}} = \frac{\kappa \times A}{\cancel{length}}\cancel{V(across)}$$

The above effectively solves for “kappa” or the specific conductivity of an ion species in solution. It is:

$$\textbf{Eq. 37. m. } \kappa = \ zFvC\mu$$

This must be divided by ion concentration, whose total is equal to vC (the number of ions per solute molecule times the concentration of the solute molecules). This correction obtains the desired molar conductivity.

It is:

$$\textbf{Eq. 37. n. } \lambda = \frac{K}{vC} = zF\mu$$

This listed result is confirmed by referenced sources [4]. In short, once kappa is known the molar conductivity can be found (lambda here). From here, the original "s" variable can be determined. This is the average ion velocity. The average ion velocity under the influence of an electric field would be:

$$\textbf{Eq. 37. o. } s = \mu E = \frac{\lambda}{zF} \times \frac{V(across)}{length}$$

The above result is obtained from back substitution after lambda is known from the other variables. Lambda is the molar conductivity, z is the ion valance, F is Faraday's constant. V(across) / length (length between two electrodes in a cell) is a close approximation to the electric field inside the solution. Overall, the above manipulation allows one to dead – reckon ion drift velocities from physical parameters and quantities. To gain some insights, we can calculate the drift velocity of the ions in the potassium chloride test solutions mentioned above. It holds that the drift velocities of the ions involved are very small, and it would take hours for them to move, on average, a centimeter. However, because there are so many ions, their net effect is to drive a large current [4]. The tabulated calculations are:

Voltage (Ohmmeter applied) (Volts)	Lambda (Cl-)	Lambda (K+)	Length of Ion Channel (M)	Velocity (Cl-) (M/S)	Velocity (K+) (M/S)
22.5	0.007635	0.00735	1.0668	1.66897E-06	1.60667E-06
22.5	0.007635	0.00735	0.9144	1.94713E-06	1.87445E-06
22.5	0.007635	0.00735	0.762	2.33656E-06	2.24934E-06
22.5	0.007635	0.00735	0.6096	2.9207E-06	2.81167E-06
22.5	0.007635	0.00735	0.4572	3.89427E-06	3.7489E-06
22.5	0.007635	0.00735	0.3048	5.8414E-06	5.62335E-06
22.5	0.007635	0.00735	0.1524	1.16828E-05	1.12467E-05

Table 3. Ion Velocities (M/S), calculated, for migrating ions under the influence of an electric field.

The above calculations are telling. Inside a battery, many ions are moving to facilitate charge transfer. It is impossible to see solvated ions, so their relative motion is not apparent. However, currents flow inside batteries because many ions move - or drift - but very slowly [4]. This sluggish motion is undergone when a battery renders a current (the current flows through the electrolyte, as is required). Although batteries give "instantaneous" currents when connected to a circuit, these currents actually move rather slowly in the electrolyte itself. The charge carriers move at speeds on the order of those listed in table 3.

4.1.4 Experimental Verification of The Nernst Equation

The above work gives some information into why a battery has an internal resistance. Ions in solution move slowly under an electric field. Some of this motion is lost as heat and most of a battery's current - through the electrolyte itself - is composed of ions moving of great multitude yet very slowly. Voltage is lost in making the ions move. Hence, internal resistance exists.

The Nernst equation, which relates open circuit cell EMF to chemical concentrations inside the cell, was derived and detailed in the last chapter. It can be put to the test of experiment, and the measured results compared with those calculated theoretically.

Regular batteries are sold with reagents of unknown concentration. Disassembling them and reassembling them will not alter the concentrations predictably. Therefore, a galvanic cell has to be made anew in the laboratory and have its component solutions manipulated explicitly. This was done using a Daniel cell and by ensuring the concentration of a half – cell's solution was altered incrementally. The EMF of the cell was taken for each differing concentration. The results of such work (along with recording temperature and using de-ionized water in the solutions) allowed for experimental insight into the accuracy of the Nernst equation in practice.

A Daniel cell was constructed with two half – cells connected by a salt – bridge. The first half – cell was held as fixed. It was composed of 1 mole / liter zinc sulfate in pure water. The electrode was zinc, in contact with the solution. This cell was left alone throughout the entire experiment.

The second cell consisted of copper (II) sulfate in various concentrations with a copper electrode. The solvent was, of course, water. The two cells were held in electrical contact by a salt bridge. In practice, this was a string wet with a 0.1 M / L potassium chloride solution. By altering the copper sulfate's concentration, various EMF values were manifest. These were recorded with a high – impedance voltmeter. The experiment gave several concentration and EMF values. These are tabulated, as below.

Nernst Model for Data Taken	Zn2+ (Mol)	Cu2+ (Mol) - CORRECTED	Voltage Predicted	Voltage Measured	Percent Error (%)
	1	0.047	1.06247686	1.053	0.891959211
	1	0.016	1.048618641	1.05	0.131731333
	1	0.0105	1.043201518	1.043	0.019317263
	1	0.0041	1.031107416	1.029	0.204383723
	1	0.00074	1.009088621	1.02	1.081310276

Table 4. Daniel cell voltage values for various copper sulfate concentrations in that respective half-cell. The Nernst equation may predict these EMF values. This is shown in the "Voltage Predicted" column. The zinc sulfate half-cell was held at constant concentration, and acted as a reference during the experiment.

The average temperature throughout the experiment was 25 degrees Celsius. This value and the constants required may be used to evaluate the Nernst equation at each copper sulfate concentration. The results render a plot like that show below. Notice that the *activity* of copper sulfate is what matters. This value is determined by multiplying the copper sulfate molarity (concentration) by activity coefficients (tabulated). Such renders the *activity* of the copper sulfate in solution. This is why “corrected” is written over the column for copper 2+ in the above table – to signify that this column is the effective concentration, not the molarity alone. This is, in short, what “activity” means.

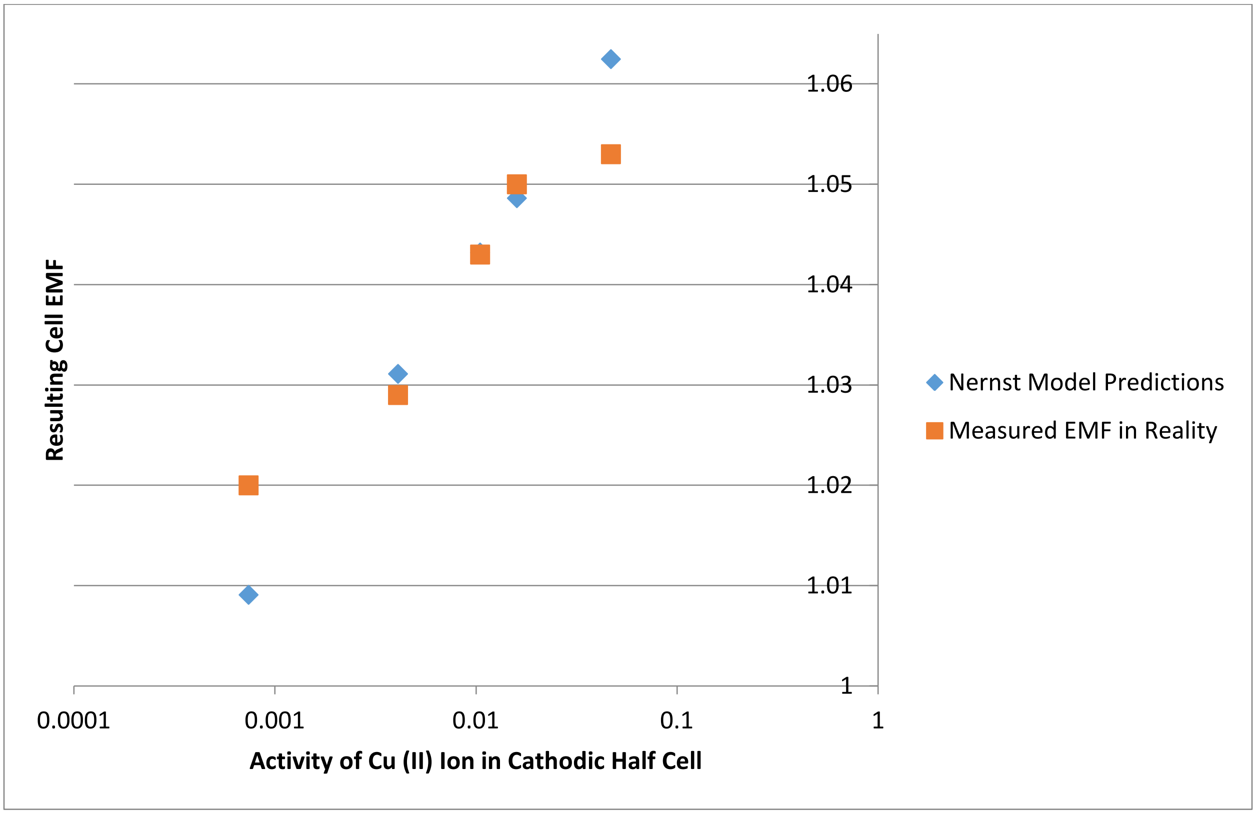


Figure 11. Nernst equation predictions (blue) for cell EMF vs. experimental measurements (orange). The activity (effective concentration) of copper II sulfate is on the horizontal axis. The cell voltage is on the vertical axis. Notice that the Nernst equation does predict open circuit EMF rather accurately.

The above plot shows that the Nernst equation does predict battery open circuit voltage rather well for various electrolyte concentrations. This equation has some discrepancy at the extreme ends of the concentration range, but these samples pushed the limits of the equipment involved. In short, this work was a success, and it shows that the Nernst model works to predict open circuit cell EMF when concentrations and chemical species are known.

The Nernst equation can be demonstrated by laboratory measurements. Such measurements show that it yields behavior as seen in the lab and in practice. A battery is thought to die because the concentrations become very skewed as reagents are spent and products form.

When reagents run completely out, the logarithm term becomes large as the logarithm of a value near zero is approaching negative infinity. Calculations involving the Nernst equation with low reagent concentrations show that the cell EMF would approach zero as the reagents were depleted and their activities converged towards zero. This explains, theoretically, why a battery “dies” and presents a voltmeter with a potential of near zero volts after it has been used extensively and its reagents are spent.

4.2 Mathematical Modeling of Battery Discharging

In short, this and the subsequent chapters have worked to investigate the inner operation of the battery. Once a firm grasp of such principles is at hand, a battery can be modeled appropriately. From the particulars of such modeling work, an effective control system could be developed and optimized. In brief, this is the whole of the purpose of this thesis. Once the “transfer function” of a battery is known, based upon chemical principles as detailed herein, then appropriate techniques can be applied to model the behavior thereof and control the charging / discharging thereof to obtain the greatest utility and efficiency. This is the philosophic approach taken in this work, moving from the “bottom” of basic principles upwards towards the desired goal. This goal is, of course, a mathematical model of battery operation.

Of course, the opposite approach could have been chosen. One could work from battery discharge data and other information and attempt to work backwards to grasp the mechanism (that is, how a battery functions in detail) which is at hand. Of course, this approach simply would take too long and is far too prone to error for a single person to effectively implement and write a thesis about. However, a compromise is reached as empirical data is compared with the model that has been derived and justified. This work is drawn up below.

To test the work here, a proper battery test subject had to be chosen. The author understands that lithium-ion batteries are prone to explosion and overheating if disassembled or mishandled. For this reason, and because it may prove insightful to disassemble the battery experimental subjects to see their internal structure, alkaline (manganese dioxide: zinc) batteries were used as test subjects. The “D” alkaline battery was the choice decided upon. These were bought “fully charged” (as they are primary cells) and discharged across a 3Ω load. The voltage across the load was plotted vs. time by chart recorder. This process was done for many different brands of alkaline cell to get a “ballpark” of how the discharge behavior appears graphically. The data is shown below.

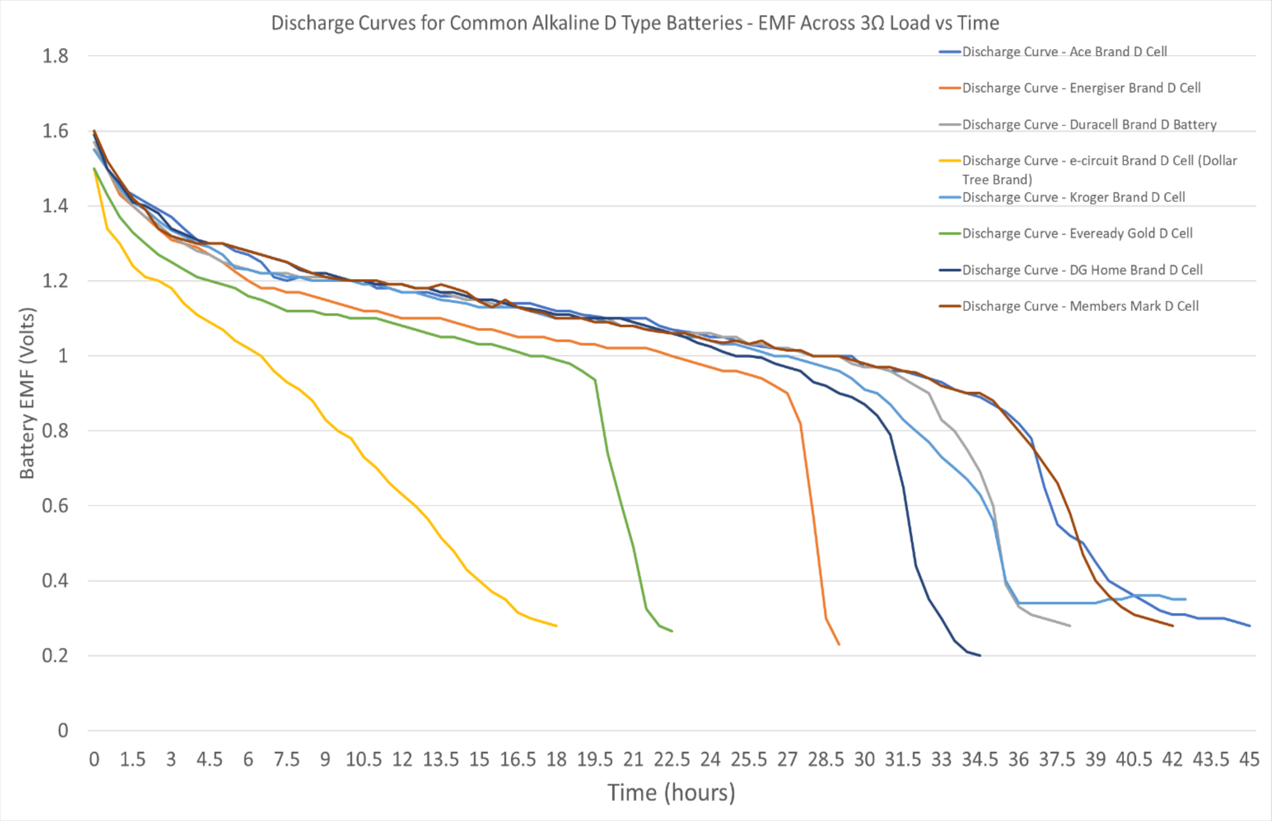


Figure 12. Voltage rendered by various "D" alkaline batteries vs. time, as these were discharged across a 3Ω load. Eight brands were tried in total. The curves appear to approach a "limit", believed to be the "ideal" behavior of such cells.

The figure above shows the voltage rendered by alkaline D batteries vs. time as these were used to drive a current through a 3Ω load. Some contenders performed very poorly (EG. E – Circuit, Eveready Gold, etc.). The "most ideal" ones consisted of the curves which extended furthest to the right – of which the Ace Hardware brand and Members Mark Brand performed the best. In short, the initiative here is to see if these curves can be reproduced mathematically – through utilization of the theory presented. This is investigated below.

First, the algorithm devised was presented in the previous chapter. It was written as a list of steps but would be better presented as a flowchart which could be implemented by use of a MATLAB program. The flow chart for the battery model is given on the next page and subsequent description of this follows.

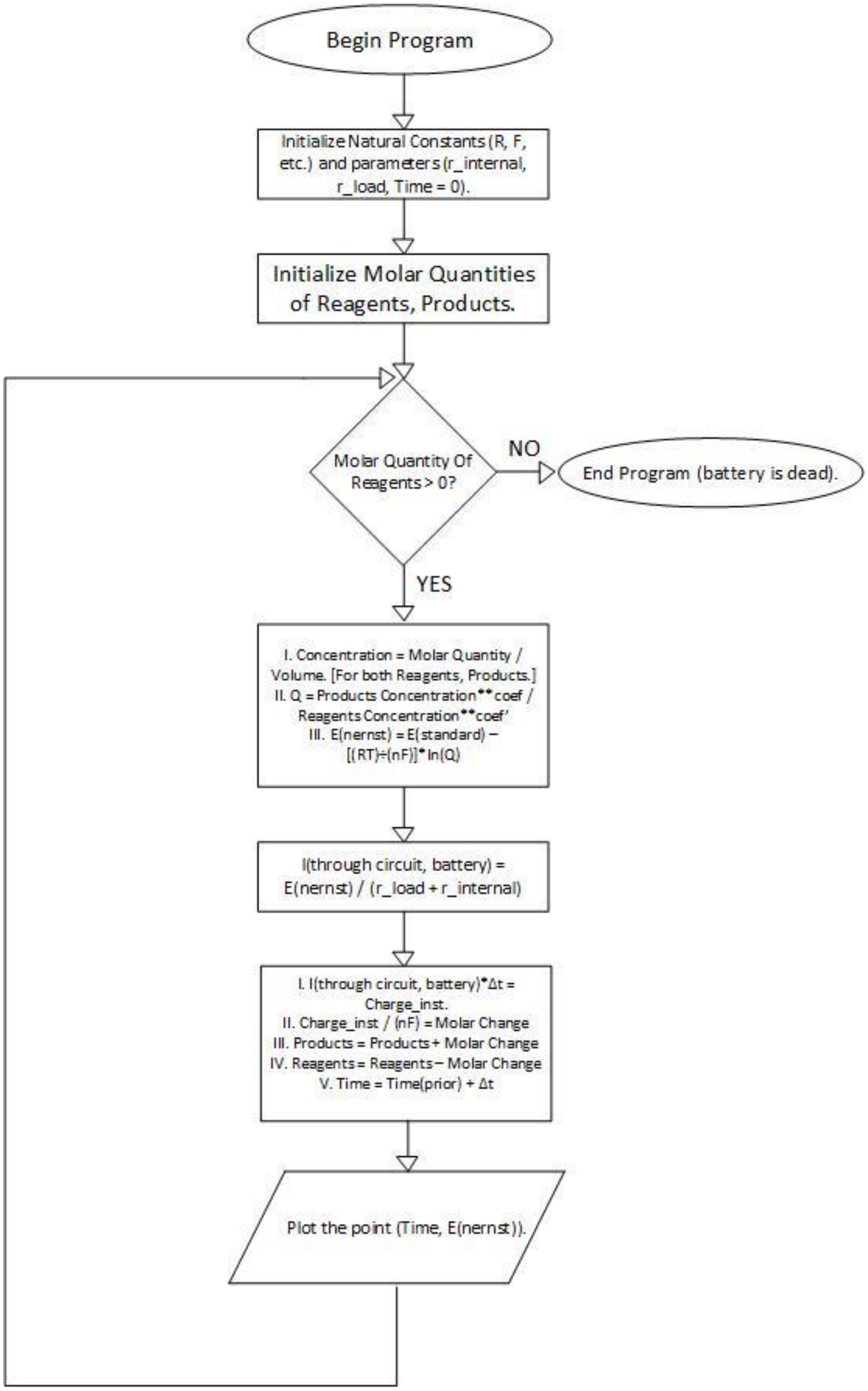


Figure 13. Flow chart of the algorithm to model battery discharge behavior. This was introduced in the second chapter and is written in complete form above. This process was implemented in MATLAB based upon this diagram.

First, the results will be mentioned from this programming work. Latter, the limitations will be mentioned in detail – along with the particulars of such. A MATLAB program was written based upon the above work. It appears to render behavior which is comparable with reality. However, this model is somewhat optimistic as it does not account for the electrical "double layer" that the electrodes form inside the battery [1]. However, the model does show the correct qualitative shape when juxtaposed with real data taken in the laboratory.

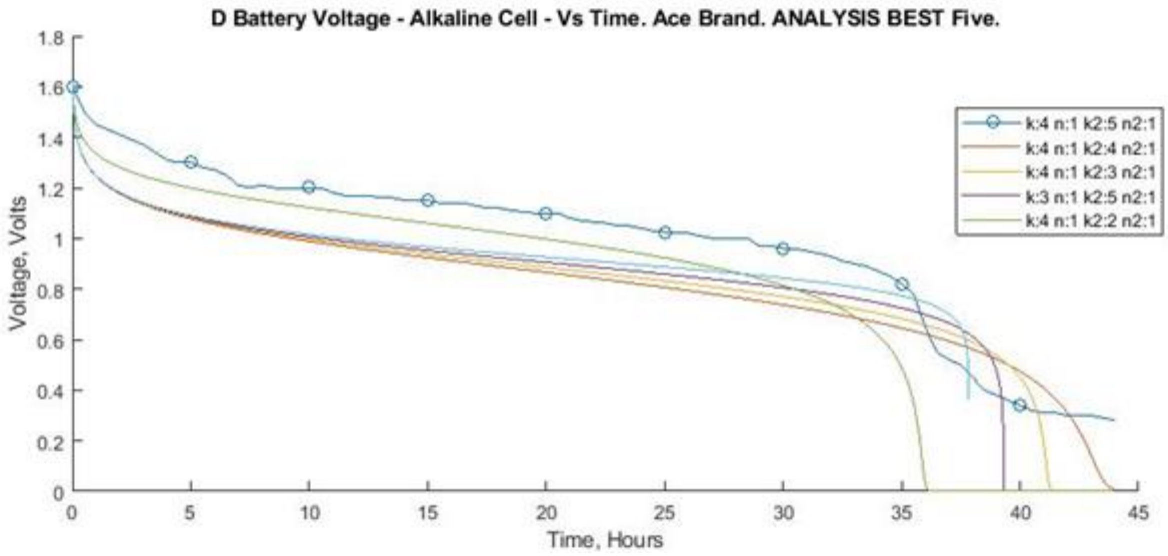


Figure 14. Computer model results of battery discharge voltage vs. time. Five possible models are presented (this is explained below). The blue curve with the "o" marks upon it is the ace hardware "D" battery's discharge curve. This originally was shown in figure 12, above.

The MATLAB program written based upon chapter two's model and the flow chart given above rendered figure 14. The curves rendered in fig. 14 appear to approximate actual battery discharge over time. This is quite a coincidence and must be more than such in terms of the natural phenomena occurring. This work has succeeded, in this way, in modeling part of battery function, and in a manner that may prove of utility to the electrical engineer.

However, one may wonder why several curves are present. This is because the alkaline manganese dioxide : zinc chemistry in alkaline batteries (the "D" cells used in this work) is not fully understood. The zinc half cell reacts by oxidizing zinc, as usual.

The manganese dioxide half – cell is far less understood. The manganese dioxide undergoes many different reactions and through several steps as it does so [1]. This makes the modeling much more difficult than simple batteries, like the aforementioned Daniel cell. The curves above attempt to model this situation despite this issue – how this was undergone is explained below. First, more information on the alkaline manganese dioxide : zinc system is required. Such a system is still heavily utilized in primary batteries today, in contrast to the Daniel cell which used an alternate chemistry [1].

4.2.1 The Manganese Dioxide : Zinc System

The alkaline cell obeys the chemical equation, overall:

$$2Zn + 3MnO_2 \rightarrow Mn_3O_4 + 2ZnO$$

All reactants and products are solids. It may appear that the Nernst equation can not be applied. However, the battery does have a diminishing potential with use [1]. This holds even if a high – impedance voltmeter makes the readings. This means or implies the concentration of something is changing and the Nernst equation can model the EMF's drop, somehow, with use of the battery. The electrolytes are pastes with KOH (potassium hydroxide) as their liquid "solvent". Inside these pastes are small particles of manganese dioxide (near the cathode) and zinc (near the anode).

The manganese dioxide and manganese oxides inside alkaline batteries are a generic black paste. Before and after use they appear the same as a homogeneous and un-insightful black powder [1]. Moreover, their chemistry is complicated and sometimes non-stoichiometric [1]. Much research was done in the last fifty years to elucidate the chemistry of the manganese dioxide in an alkaline cell. Such work led to conclusions, summarized below, found by other researchers [1].

The manganese dioxide roughly undergoes the following steps as the battery is discharged [1]:

I. MnO_2 becomes $MnO_{1.7}$ through reduction.
II. $MnO_{1.7}$ becomes $MnO_{1.5}$ through another step of reduction.
III. Finally, $MnO_{1.5}$ is reduced to $MnO_{1.33}$ through a final reduction process.

Notice that $MnO_{1.33}$ is the same as Mn_3O_4. This appears in the above reaction (final manganese product). Hence the reaction is not one step, but many. There is some disagreement in the steps [1], but the list above shows the general consensus.

The two steps above may be combined as:

MnO_2 becomes $MnO_{1.5}$ through two steps of reduction.

The charge on manganese in manganese dioxide is 4+. The charge on manganese in $MnO_{1.5}$ would be 3+. Notice that $MnO_{1.5}$ is equivalent to Mn_2O_3. The two reactions (step I and II) above may be combined and written as a proper chemical equation [1]. This would read:

$MnO_2 + H_2O + e^- \text{-->} Mn\,OOH + OH^-$

Chemical Equation 13. Partial reaction of Manganese Cathode, Theoretical [1].

MnOOH dissociates, rendering Mn^{3+} in solution inside the manganese dioxide paste.

The water molecule (and others involved in intermediate steps – not shown) come from and return to KOH and water. Writing the Nernst equation for this limiting reaction would render a form such as:

$$\textbf{Eq. 38. } E = E^o - \frac{RT}{F} ln\left[\frac{Mn^{+3}}{Mn^{+4}}\right]$$

The Mn^{+4} resides in the reagent MnO_2. The chemistry of manganese is very complicated, and as a result various models were tried to match reality with the computer model introduced here.

4.2.2 Utilization of Least Squared Error Techniques

The program did not know the chemical reaction going on inside the alkaline cell. The net reaction does not influence the Nernst equation, because the products are solids that do not contribute to the Nernst equation [6]. Only liquid and gaseous phases contribute to this natural law [1,6]. Some intermediate steps (such as those involving manganese, mentioned above [1]) take place. Since this is not entirely understood [1,6], various parameters were “tried out”. For each set of parameters, the model (mentioned in the above flowchart) was run. The squared error between the model and reality was found for each set of parameters on a data point by data point basis. The error was summed up over the entire dataset as the difference between theory and reality that was squared. The five instances with the least squared error totals were listed in the above figure. Such a "regression" tactic was employed to determine, by programming, models that come close to describing the discharge behavior of the alkaline batteries in time. This allows modeling, despite certain unknowns.

The issue involved is that the reaction is not known in the limiting step(s) that leads to EMF decreasing with use [1]. Accordingly, the general reaction was assumed to be of the form:

$K_2[\text{reagent}] + n_2e^- \rightarrow X\ [\text{solid product}]$

$X[\text{solid reagent}] + ne^- \rightarrow K\ [\text{product}]$

Chemical Equation 14. General reaction form, assumed for the alkaline cell model.

This would have a general reaction quotient, Q, of:

$$\textbf{Eq. 39. } Q = \frac{[product]^K}{[reagent]^{K_2}}$$

This expression would be fed into the Nernst equation. The values of n and n_2 would relate the electron transfer and would also appear in a modified Nernst equation (see the appendices for the details). Overall, the computer program tried many different values for the K coefficients and n coefficients. The “K” coefficients are stoichiometric coefficients. The “n” coefficients are the electrons transferred per reaction.

It is known that stoichiometric coefficients are seldom greater than 5 [3]. Electrons transferred per reaction never really exceeds four [2]. This leads to some *5 x 5 x 4 x 4* (or 400) combinations of possibilities for a simple reaction and product form of the reaction quotient. It may have several limiting products and reagents (Q may be more complicated than shown above), but it is physically impossible to narrow down the possibilities by computation alone (due to exponentially increasing time required to run the model for each situation).

The best curves, with the least accumulated squared error against the actual discharge curves, were shown in the above figure. “K” is preferred as near 4. Both “n” coefficients are near “1”. K2 is preferred as near 3,4, or 5. This information can perhaps relate to the exact chemistry [1], but the author is not sure which reaction(s) leads to these coefficients being favored.

4.2.3 Manual fitting of the model to the experimental results

It is possible to manipulate the parameters of the numerical model manually. Such allows for manual fitting of curves, other than the aforementioned squared error techniques. These plots are interesting, and some are extremely close to reproducing the original behavior of the discharge curves obtained from experiment. One such example is listed below.

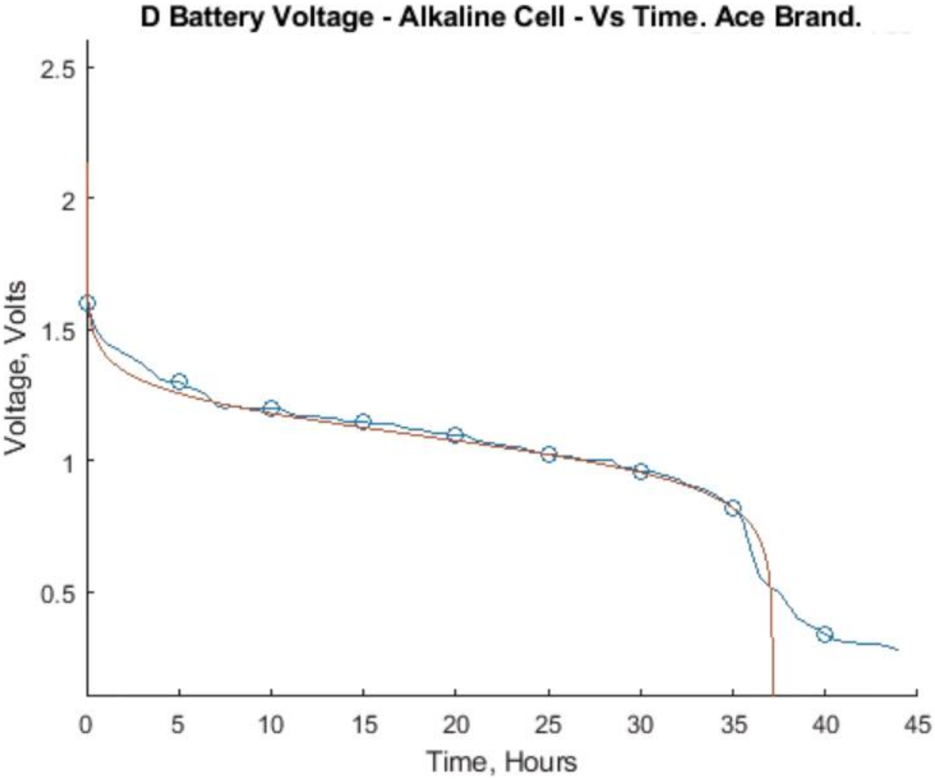


Figure 15. Manually adjusting the parameters of the model presented herein allows for close agreement with experimental results. This curve comes extremely close to reproducing the discharge curve in time. The parameters were: $k = k_2 = n_2 = 1$ and $n = 0.285$.

The chemical significance of this above model is not fully understood by the author. Perhaps gas pressure (H_2 generated during battery operation via unintentional electrolysis of water - which is inside the KOH electrolyte) builds up inside the sealed zinc can which the battery is composed of. Either way, a value of n being 0.285 does not match physical reality in an obvious manner because n should be an integral multiple (of electrons transferred per reaction). This odd value may be a result of some inefficiency that is yet to be considered [1].

However, the above model comes extremely close to predicting reality. Correction factors added to the Nernst equation may allow a better model of battery discharge curves. The source of such necessity is not known, but possibilities include pressure or temperature gradients inside the battery, chemical impurities, and other possibilities. However, the Nernst equation can be utilized as a valuable tool. Combined with electrical laws and manipulated, a model of battery discharge in time can be contrived. This model allows the voltage vs. time curves of real batteries to be predicted. The above plot shows wonderful agreement with reality. Such an observation leads to another question, as of yet unanswered but important: Can the system, solved numerically and described by figure 15, be reduced to an ODE or system of differential equations? Can this system be solved analytically (not just numerically)? What would this analysis reveal regarding the nature of battery function in time?

4.2.4 Conversion from a numerical, iterative process into a system of differential equations

The algorithm presented and utilized for the above figures can be turned into an equivalent differential equation. It is possible, perhaps that this system can be solved analytically. Such analytical solutions may be useful to the engineer or battery chemist. The process is straightforward, but the differential equations form a first order, non-linear system of two equations. The work would follow as below. Some simplifications are made to render a comprehensible system.

The EMF rendered by a battery would take the form:

$$\textbf{Eq. 40. a. } E = E^{o} - \frac{RT}{nF} \ln \left(\frac{Product}{Reagent}\right)$$

The variables have their traditional meaning. "Product" is the product concentration. "Reagent" is the reagent's concentration. Both of these would be in mole / liter units. Let's replace these words with "P" and "R", respectively.

In an instant, the change in charge, or current flowing, would be (nearly):

$$\textbf{Eq. 40. b. } \frac{dQ}{dt} = \frac{E}{R_{load} + r_{internal}}$$

The most obvious differential equation system is formed as follows. Charge flow is related to chemical changes inside a battery. The change in chemical quantities involved would take the form of:

$$\textbf{Eq. 40. c. } \frac{dProduct\ Ammount}{dt} = \frac{dQ}{dt} * \frac{1}{nF} = \frac{E}{(R_{load} + r_{internal})nF}$$

and, analogously,

$$\textbf{Eq. 40. d. } \frac{dReagent\ Ammount}{dt} = \frac{dQ}{dt} * \frac{1}{nF} = \frac{-E}{(R_{load} + r_{internal})nF}$$

However, to make a consistent equation, "concentration" has to be related to "amount" per the above reasoning. The relationship would be:

$$\textbf{Eq. 40. e. } \frac{dConcentration}{dt} = \frac{dAmmount}{dt} * \frac{1}{volume\ of\ half{-}cell}$$

This assumes a homogeneous phase, as did the earlier work.

Combination of these results renders the differential equation system. For the sake of rendering a form which is "solvable", the desired variable is understood to be the *concentration* not the *amount*. The desired solutions are two functions, P(t) and R(t), which would represent the concentrations of the products (increasing during discharge) and reagents (decreasing during discharge) - as these change in time. Notice that plugging P(t) and R(t) into the Nernst equation would directly determine the voltage as a function of time (after these functions are solved for and are known).

The system of equations would be:

$$\textbf{Eq. 40. f. } \frac{dP(t)}{dt} = \frac{E}{(R_{load}+r_{internal})nFV} = \frac{E^o - \frac{RT}{nF}\ln\left(\frac{Product}{Reagent}\right)}{(R_{load}+r_{internal})nFV}$$

and,

$$\textbf{Eq. 40. g. } \frac{dR(t)}{dt} = \frac{-E}{(R_{load}+r_{internal})nFV} = \frac{-\left[E^o - \frac{RT}{nF}\ln\left(\frac{Product}{Reagent}\right)\right]}{(R_{load}+r_{internal})nFV}$$

This is a first order system of non-linear differential equations. Simplifications can be taken as:

$$\textbf{Eq. 40. h. } \frac{dP(t)}{dt} = \frac{E^o - \frac{RT}{nF}\ln\left(\frac{Product}{Reagent}\right)}{(R_{load}+r_{internal})nFV} = \frac{E^o}{(R_{load}+r_{internal})nFV} - \frac{\frac{RT}{nF}\ln\left(\frac{Product}{Reagent}\right)}{(R_{load}+r_{internal})nFV}$$

and,

$$\textbf{Eq. 40. i. } \frac{dR(t)}{dt} = \frac{-\left[E^o - \frac{RT}{nF}\ln\left(\frac{Product}{Reagent}\right)\right]}{(R_{load}+r_{internal})nFV} = \frac{-E^o}{(R_{load}+r_{internal})nFV} + \frac{\frac{RT}{nF}\ln\left(\frac{Product}{Reagent}\right)}{(R_{load}+r_{internal})nFV}$$

Simplification can continue as:

$$\textbf{Eq. 40. j. } \frac{dP(t)}{dt} = \frac{E^o}{(R_{load}+r_{internal})nFV} - \frac{RT\ln\left(\frac{P(t)}{R(t)}\right)}{(R_{load}+r_{internal})(nF)^2V}$$

And,

$$\textbf{Eq. 40. k. } \frac{dR(t)}{dt} = \frac{-E^o}{(R_{load}+r_{internal})nFV} + \frac{RT\ln\left(\frac{P(t)}{R(t)}\right)}{(R_{load}+r_{internal})(nF)^2V}$$

Now the final system is at hand. For the sake of simplicity, the terms can be grouped. Notice the similarity between the two systems. Substitution simplifies things greatly. Introduce two new variables. These can be called "C" and "D":

$$\textbf{Eq. 40. l. } C = \frac{E^o}{(R_{load}+r_{internal})nFV}$$

and, also,

Eq. 40. m. $D = -\frac{RT}{(R_{load}+r_{internal})(nF)^2V}$

These terms are constants. Notice that "V" is the "volume" of the half - cells of the battery (the anodic and cathodic compartments of the battery wherein the chemicals reside).

The above system can be written very simply, using these constants, as:

Eq. 40. n. $\frac{dP(t)}{dt} = C + D\ln\left(\frac{P(t)}{R(t)}\right)$

And,

Eq. 40. o. $\frac{dR(t)}{dt} = -C - D\ln\left(\frac{P(t)}{R(t)}\right)$

This is the final system. Solved with initial conditions, it is expected to render curves such as the computer model above did. However, it is non-linear. No obvious or common solution method exists for this system because of the logarithm term and the quotient inside of that. However, it is possible to make simplifications and reach certain interesting conclusions.

It is possible to consider the case of a battery where the products are solids and do not affect the reaction. This would eliminate the first of the above equations. It turns out that the single differential equation that results is entirely possible to solve. The solution can then be compared with real data and the numerical algorithm which should agree with it. This would work as follows below.

Modifying the equations to remove the product's influence would obtain:

Eq. 40. p. $\frac{dR(t)}{dt} = -C - D\ln(R(t))$

Here, define "D" as the negative of the constant "D" defined above. Redefine D to be:

Eq. 40. q. $D = \frac{RT}{(R_{load}+r_{internal})(nF)^2V}$

The equation above is a separable differential equation. It can be separated and solved as:

Eq. 40. r. $\frac{dR(t)}{-C-D\ln(R(t))} = dt$

This can be integrated to obtain:

Eq. 40. s. $\int \frac{dR(t)}{-C-D\ln(R(t))} = \int dt$

The left integral is very hard to simplify. However, it can be reduced to a known function. U-substitution is utilized, twice, to render the final form. The mathematical manipulation required is drawn up below:

First, the "-" sign may be distributed outside of the integral. The right integral may be solved.

Eq. 40. t. $-\int \frac{dR(t)}{C+D\ln\,(R(t))} = t$

Now, the first u-substitution may be implemented.

Set U equal to ln(R(t)). This implies that:

$$u = \ln\big(R(t)\big) \rightarrow \frac{du}{dR} = \frac{1}{R(t)} \rightarrow dR = R(t)du$$

Also, R(t) itself is equal to e^u, by fundamental definitions. Application of these substitutions obtains:

Eq. 40. u. $-\int \frac{e^u du}{C+D\mathrm{u}} = t$

This integral is simpler, but unfortunately also has no anti-derivative.

Performing u substitution again obtains a form which is simplified as far as possible. To maintain intelligibility, "v" will be used instead of using "u" again in the substitution. The substitution work follows as:

$$V = \ln(R) + C/D = u + C/D$$

Notice how ln(R) is the previous substitution, or "u". This explains the above manipulation.

Now, it holds true that:

$$dV = du$$

Using standard integration rules obtains:

Eq. 40. v. $-\frac{e^{-C/D}}{D}\int \frac{e^{u+C/D}du}{\frac{C}{D}+\mathrm{u}} = t$

Notice how the front multiplier corrects for the adjustments made inside the integral. This is a valid manipulation and the substitution would render:

Eq. 40. w. $-\frac{e^{-C/D}}{D}\int \frac{e^V dV}{V} = t$

The integral above is the furthest this can be reduced. It is called the "exponential integral" and is not an elementary function. It can be represented as "Ei(x)", where "x" is its argument. Thus, the above differential equation would reduce to:

Eq. 40. x. $-\frac{e^{-\frac{C}{D}}}{D}Ei(V) = t$

Now, the substitution for "V" can be "reversed" to obtain the final solution. This would be:

Eq. 40. y. I. $-\frac{e^{-\frac{C}{D}}}{D}Ei(\ln(R(t)) + \frac{C}{D}) = t$

The final result is, adding the constant of integration:

Eq. 40. y. II. $-\frac{e^{-\frac{C}{D}}}{D}Ei(\ln(R(t)) + \frac{C}{D}) + K_{const.of\ integration} = t$

The above result can be confirmed by wolfram or similar software.

This is the furthest the solution can go. It is the inverse function of the desired result. If a function existed such as the "inverse exponential integral function", then the following could be stated:

Eq. 40. z. I. $-\frac{e^{-\frac{C}{D}}}{D}Ei\left(\ln\left(R(t)\right) + \frac{C}{D}\right) = t - K_{const.of\ integration}$

Multiplication renders:

Eq. 40. z. II. $Ei\left(\ln\left(R(t)\right) + \frac{C}{D}\right) = \frac{-D}{e^{-\frac{C}{D}}}(t - K_{const.of\ integration})$

Using "Ei^{-1}" to represent the inverse function of the exponential integral:

Eq. 40. z. III. $\left(\ln\left(R(t)\right) + \frac{C}{D}\right) = Ei^{-1}\left(\frac{-D}{e^{-\frac{C}{D}}}(t - K_{const.of\ integration})\right)$

Perform subtraction to render:

Eq. 40. z. IV. $\ln\left(R(t)\right) = Ei^{-1}\left(\frac{-D}{e^{-\frac{C}{D}}}(t - K_{const.of\ integration})\right) - \frac{C}{D}$

Finally, the antilogarithm is taken:

Eq. 40. z. V. $R(t) = e^{Ei^{-1}\left(\frac{-D}{e^{-\frac{C}{D}}}(t - K_{const.of\ integration})\right) - \frac{C}{D}}$

This is the desired solution. The two-equation system may be too difficult to solve completely, but the reduced system of a single equation can be solved, and the solution is listed above. The exponential integral is a monotonic function, so it is believed that an inverse function exists. The constants listed above would be substituted for "C" and "D". Notice that the simplified treatment here did not mention the exponent on the reagent's concentration. This would be taken outside of the logarithm and merged with the "D" term via traditional logarithm rules. Notice that "K" is an integration constant, set when the formula is used.

Now, it remains to be shown that this analytic solution is equivalent to the algorithm presented earlier in the results it renders. The inverse function "Ei^{-1}" is not a function on MATLAB. Accordingly, a subroutine could be written to solve for this. However, another approach exists.

It is possible to create an array of concentration values (for the reagent itself). The array would start at the initial concentration and have equally spaced values until a value very close to zero was reached. The battery is dead when the reagent approaches a limiting value of zero. The inverse function would then render *what time these concentration values were obtained during discharge*. By transposing the coordinates on the plot, the equivalent solution can be plotted. This is true because plotting points of the form (x,y) renders the inverse function of points plotted in the order (*y*,*x*). In short, a MATLAB program was written which did exactly this. Moreover, the resulting plot can be juxtaposed against the original model - and comparison can be accomplished. For the system of a single reagent alone (the product's concentration is not significant), both of these should agree exactly if the above work is correct.

This comparison process was executed, and the aforementioned agreement was found precisely. In short, the previous model which was "tuned" to model the discharge behavior of the D alkaline cell was modified to neglect the chemical product's influence on the voltage discharge. The numerical algorithm was then compared in its results to the analytic solution of the non-linear equation which describes the same behavior. These two curves agree exactly, and this implies that the non-linear equation was solved appropriately. The figure taken from MATLAB is reproduced below.

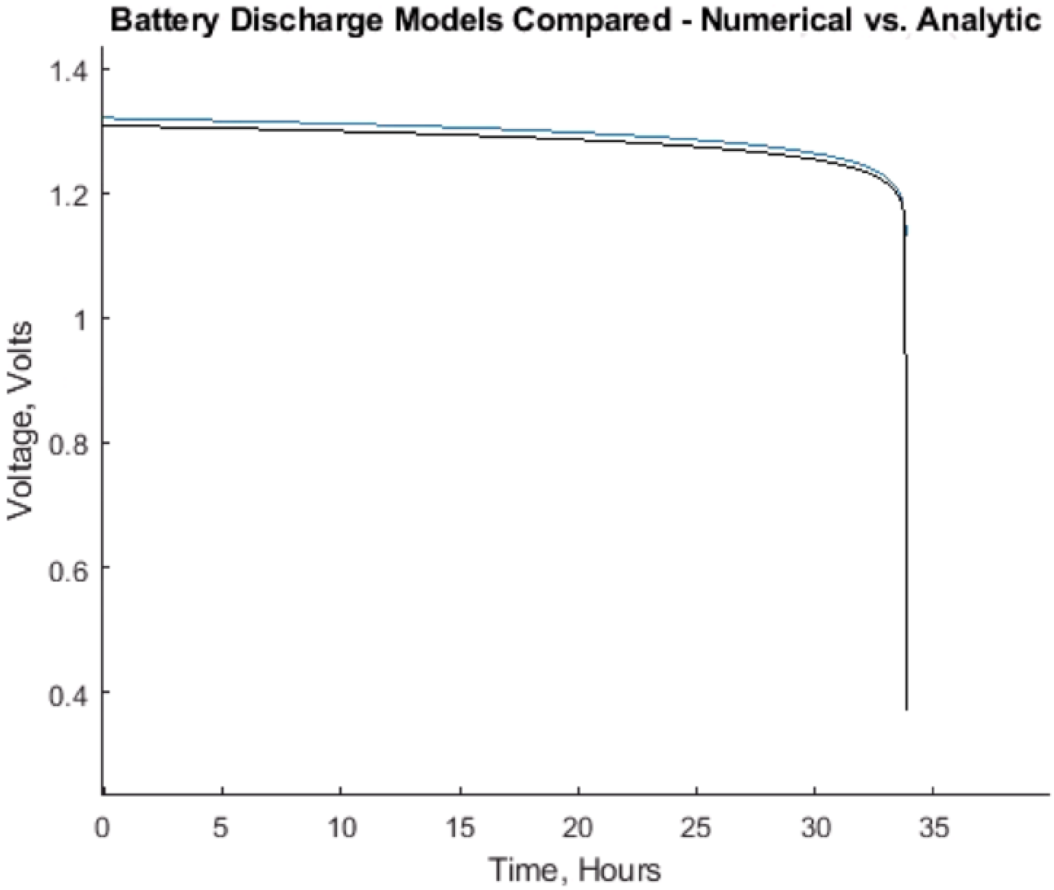


Figure 16. Agreement between numerical and analytic models.

The black curve (analytical solution of the above differential equation system) matches exactly the blue curve (numerical solution to the same system). The blue curve was drawn 10mV higher than it actually is, otherwise it would be entirely covered by the black trace and not visible. Such implies that the solution to the simplified system is correct.

The above work implies an interesting observation. Initial decreases in battery voltage, immediately after a load is applied upon a full charge, are due to chemical reactions rendering *product species*. Removing the "product" species term in the model removes the initial "dip" in battery voltage. The final decline of voltage to zero, upon discharge, is caused by chemical reagents becoming depleted. The figure above justifies these inferences as the product term has been removed, yet the concentration of the reagent alone explains the final decline of the battery's EMF as the device is discharged. Thus, it appears that initial voltage decline is due to products forming around the electrodes. The final decline is ascribed to an exhaustion of chemical reagents.

Certain batteries have a "flat discharge behavior" which resembles the above figure more so than the alkaline battery data plotted earlier. Perhaps in these instances one could apply the reduced model to some accuracy. For instance, lithium iron phosphate batteries ("LFP" batteries) have a very flat discharge curve. A typical plot is given below. The simplified model here can reproduce such a discharge behavior. LFP batteries are being considered for use in electric vehicles and for general energy storage. These batteries are known for their stability and the fact that they do not utilize cobalt [7]. Accordingly, their utilization may prove greater in the future. Sadly, LFP batteries have a high internal resistance - but this drawback is partially "made up" by the benefits of this interesting cell. The computer model introduced for the alkaline battery was modified to model an LFP cell (a type 18650 cell made by LithiumWerks, serial number APR18650M1B). The results are consistent with reality and show that in certain instances, the products formed may be neglected and the simplified equation utilized.

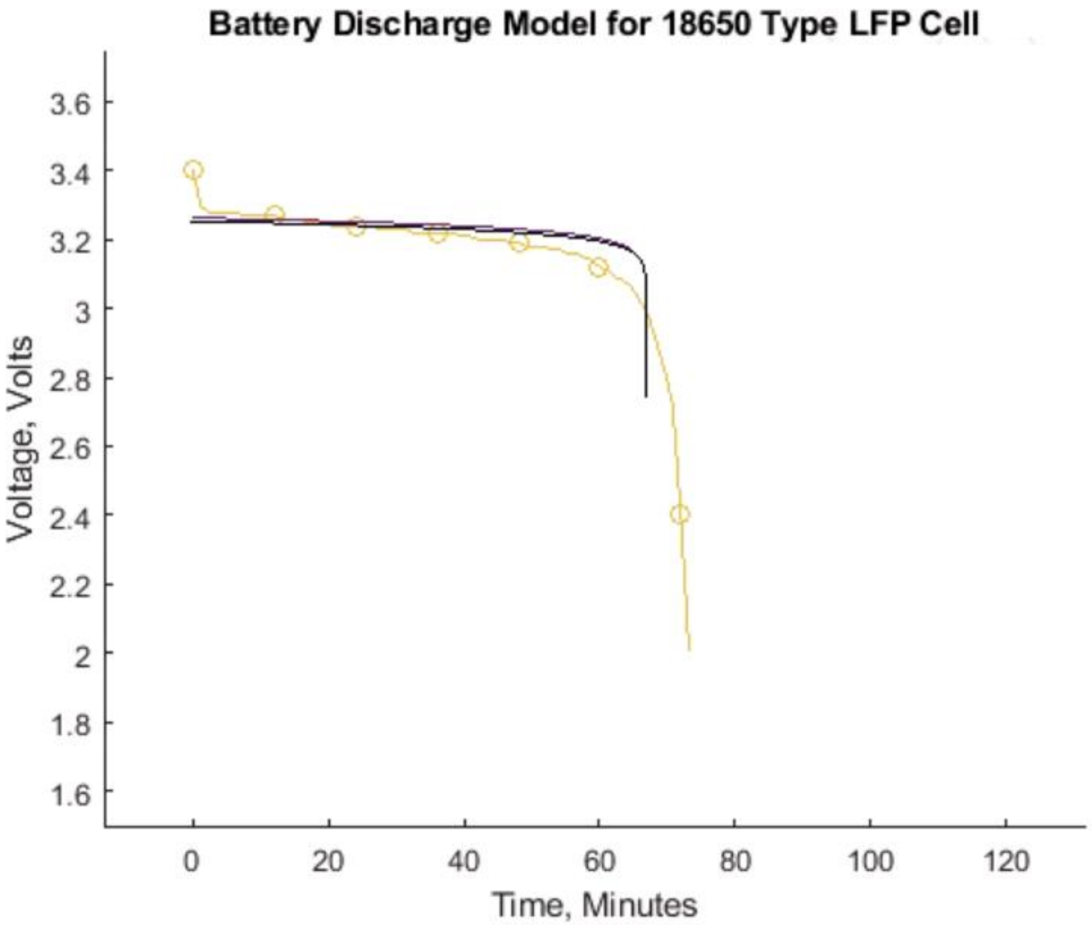


Figure 17. Model of Type 18650 LFP battery vs. real discharge behavior. The black curve is the simplified differential equation model. The yellow curve is discharge voltage vs. time. Notice how the voltage approaches zero rapidly as the chemical reagents are exhausted.

The above model assumes an internal resistance of about 12.6 mΩ, taken from the unit's datasheet. The load in question here would draw 1.2 amperes from the battery. 3.00Ω, close to this load, was used in the modeling. The model fits the data with a value of E^o set to 3.21 volts (near reality). The volume of each half cell was approximated as being half the volume of the battery canister (again, with measures taken from the datasheet and division being performed). The only factor set "empirically", without being taken from a datasheet or calculated from such literature, is the chemical reagent's concentration as an initial condition. The model fits the curves, as shown above, when the reagent concentration is initially set to be some 5.20 Moles / Liter. This value is entirely possible chemically.

On an interesting side note, the chemical reactions in the LFP battery are well understood. This stands in direct contrast to the alkaline cells mentioned earlier.

The chemistry in the LFP cell runs as follows, during the discharge process:

Chemical reaction at the Cathode (positive terminal):

$$Li^+ + C_6 + e^- \rightarrow LiC_6$$

Chemical reaction at the Anode (negative terminal):

$$LiFePO_4 \rightarrow FePO_4 + \ Li^+ + e^-$$

Chemical Equation 15. Reactions occurring inside an LFP Type Battery.

The stoichiometric coefficients are "1" in these reactions. It is also a 1 electron process (n = 1). The Nernst equation in the computer model program (and the terms for the differential equation model) were set up to account for such. The chemical reagent that is being depleted appears to be $LiFePO_4$, or lithium iron phosphate. Notice that the flat discharge curve allowed for the products (LiC_6, iron phosphate) to be neglected. This lead to some deviance with reality, but surprisingly little.

This work shows how this paper's model may be applied to multiple types of battery. It is just required that certain parameters are known in advance. These include the internal resistance, the standard voltage (E^o), the temperature of the system, the chemical reaction obeyed, and an estimate of the concentration of the chemical species involved in the system. In the work above, the concentration of the reagent species was not known initially. However, after the model was fitted to the data, a reasonable and possible concentration value was obtained.

In conclusion, mathematical models of battery discharge in time are possible and can model behavior as seen in the laboratory. It remains a shame, however, that battery datasheets are sparse in detail (especially regarding the internal workings and chemistry). If datasheets gave the reagents employed and their particulars, then the estimation work here would not be required and more precise work would be possible. It remains a detriment to the field that some datasheets, even for common batteries, do not even contain discharge curves for different loads!

4.2.5 Application of the Above Work to Robotics

Many have wondered whether the theory presented herein has any practical use or may be utilized to avail in "real-world" situations. The discharge experiments employed here dissipated power through an Ohmic load. One question, of merit, is whether the theory presented herein can be employed to assist in modeling battery behavior in real life systems. That is, even when the battery is being discharged across a variable resistance or something more complicated - such as servomotors inside a robotic system. In short, it is certainly possible to apply the work to real life systems - and an example follows for the case of a "simple" robot.

Although it is beyond the scope of this paper's work, it is possible to make a simple three-wheeled robot that uses IR reflection photo-sensors and fuzzy logic to follow a tape line around a path or curve. If the curve is closed, the robot will endlessly move around the path and dissipate energy. Of course, the question is whether the material herein can be used to model this situation. To investigate this question, a line following robot was outfitted with an SD card writer and display which would record battery voltage points in time. One data point was taken each 30 seconds and displayed on a local LCD and recorded to a file on an SD card. The robot and its onboard "chart recorder" are shown below. One observation is apparent, the battery discharge curve looks very similar to those determined by earlier experiments and theory. One possible concern is the "noise" which is manifest on the dataset. This is caused, mostly, by the fact that the robot has to continually turn servomotors on and off in order to follow the line to precision (that is, to turn or correct its course). This leads to a variable load and a variable battery EMF based upon the Ohmic drop varying across the internal resistance of the cell. For this experiment, an alkaline "9-volt" battery was used as the power source for the servomotors. See the dataset in the figure below.

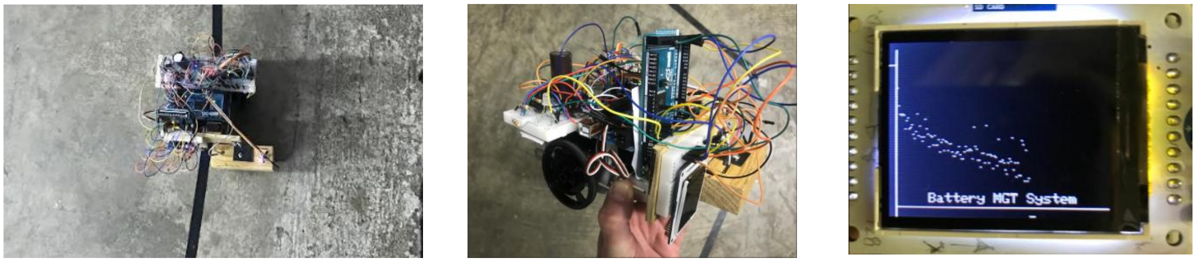


Figure 18. Line following robot (leftmost and middle figures). It dissipates energy by continually moving around a tape line on the floor. Outfitted with a data logger, it can plot voltage vs. time (right figure). The data was sent to an SD card for future analysis on MATLAB.

The robot appears to render a discharge curve similar to those already discussed, such as those in fig. 12. It is possible to model the battery discharge of this robot, given a few simplifying assumptions. First, since the robot runs along the same path over and over, it is assumed that it behaves as if it has some sort of "average load". In practice, ammeters and voltmeters can be used to determine such a behavior in real-time. Here, manual multi-meters were used for this purpose. It was determined that at 9 volts, the servomotors utilize some 287.5 mA of current, on average. Since the servomotors turn on and off rapidly, an average has to be used here. In reality, precision measurements can avoid such. However, the model works out in this case also. Since the voltage powering the servomotors is near 9 volts, the average resistance the servomotors act as is some 31.30Ω. The MATLAB programs mentioned, like the one in the appendix, can be utilized to model this situation. In short, the results of this work are shown below.

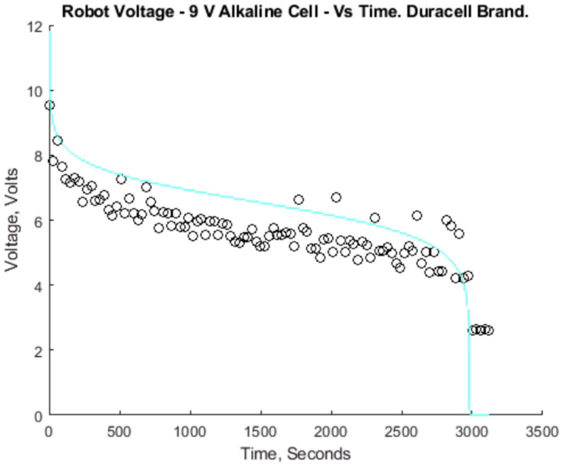


Figure 19. Voltage data vs. Time for Line Following Robot. The model (blue line) is superimposed upon the scatter plot of voltage values. Notice the agreement that is apparent.

Since this is a 9V battery, with six 1.5 volt cells wired in series, the Nernst voltage model has to be multiplied by six to account for this difference. The internal construction uses the same materials as the alkaline cell - so the chemistry particulars remain the same. The internal resistance of a 9V battery is larger since it is tinier and has less surface area on its electrodes. The model seems to suggest a value of nearly 6Ω or so. The cyan curve does show agreement with the shape and behavior of the dataset. Thus, it appears that the battery modeling conducted herein can be applied, in modified form, to loads other than resistors. These appear to include the servomotors utilized in the aforementioned line following robot. The general agreement seen in the graphs presented is striking, and hints that a battery really does obey thermodynamic models - to a rather interesting degree.

4.2.6 Conclusions

The above work and this paper at large have shown the development of a useful battery model. The model is able to predict and reproduce discharge voltage vs. time for a number of useful systems. In this way, the work detailed in this paper has proven successful. The mathematical manipulation was rigorous and time consuming. It would be interesting to see a microcontroller programmed to run this model in time - and report the predictions calculated against measured battery behavior. Such comparisons would allow empirical factors to be added so that agreement could be achieved.

It is believed, although not investigated, that such a control system would offer greater flexibility to users of battery powered systems. If a battery's operation and charge level in time could be predicted, and it seems it can, then the user can be informed on the status of such. This would allow such individuals to work around this information - and possibly avoid the unpleasant experience of having to deal with equipment that quits working due to a dead battery. The work above appears promising, and it is believed that this model could be taken further and ultimately implemented in consumer products.

4.3 On Chemical Effects Seen in Batteries

The work presented in this paper has tried to be comprehensive, reliable, and to cover the dominant mechanics which transpires inside a galvanic cell. However, it is impossible to include every effect involved in a single model - especially if this model is to be comprehensible by the engineer. Accordingly, effects only partially considered or left not fully explained are elucidated below.

There are many effects that occur inside batteries, in addition to the main thermodynamic work mentioned in detail here. These include the effects of chemical activity [1,6], over-potential [1], and diffusion [1,6]. These effects are considered in more complicated battery models, but the complexity of these models prohibits any easy understanding of such work - especially by electrical engineers and others perhaps unfamiliar with advanced chemistry.

To render this work comprehensive and rounded, such chemical effects are detailed below - with some thought as to how these may be integrated into the battery model introduced. Of course, introducing these terms into the model would render a system of differential equations most certainly impossible to solve by hand or analytic methods. Computer models exist which account for these terms. It is remotely possible that the two - equation, non-linear differential equation system mentioned earlier could be solved in terms of mathematical operators. However, systems much beyond this in complexity would be impossible to analyze by hand. This is a great misfortune, as such analysis would perhaps prove insightful into battery operation and engineering of systems which utilize such.

4.3.1 On Chemical Activities

Chemical activity has been mentioned earlier in this chapter. In short, solutes in a solvent often behave as if they had a lesser concentration than they really do [1,6]. This is caused by a myriad of intermolecular effects and must be corrected for in many real world systems [1,6]. Texts that treat the inner workings of a battery must mention and explain chemical activity [1]. The concept of chemical activity was introduced long ago when gaseous phases were considered. It has since been extended to liquid solutions and pastes - such as are commonly used in batteries today.

Chemical activity is related closely to the concept of fugacity. When a gas is at a low pressure, it tends to behave "ideally" and the ideal gas law holds very accurately [1]. As a gas is compressed, intermolecular forces begin to take effect as the molecules become closer together. This causes behavior to skew from the ideal predictions. Gas "fugacity" attempts to correct for such a deviation, as it is used in physical chemistry.

Take the example of chemical potential:

$$\mu_i = \mu_i^0 + RTln(f_i)$$

For a gaseous phase, the chemical potential changes when the mixture is at a different pressure than the standard state. The standard state has the "0" superscript. "f_i" is the fugacity term that resides inside the logarithm term. This changes the standard state chemical potential of the ith component of a gas to its measured value.

Notice that in the low pressure limit, as the total gas pressure falls towards zero, fugacity becomes equal to the partial pressure of the i^{th} component of the gas [1]. Similarly, at vanishing concentrations of a solute in a solvent, the activity becomes equal to nearly the concentration [1]. Thus, for a gas:

$$\frac{f_i}{partial\ pressure_i} \rightarrow 1\ as\ pressure_{total\ of\ system} \rightarrow 0$$

Remember that chemical potential is the change in Gibb's free energy with respect to the number of moles of reagent present. This definition assumes temperature and pressure are fixed. When they vary, the above thermodynamic equation is used to adjust the standard values. The reason this is so is partially elucidated in the previous chapters. Moreover, standard chemical potentials are taken at 1 atmosphere in practice (regular air pressure).

For very dilute solutions, the activity of a solute may be approximated by the molarity it has. In an ideal world, activities would be set equal to actual concentrations. For the reasoning above (which extends in an analogous fashion to the liquid phase), this is not possible [1,6]. Using concentrations alone to approximate activities leads to great errors in a great many practical situations [1]. This explains the corrections made earlier in this chapter.

Introduction of a coefficient which translates concentration values to activity values helps with this situation. Such values are determined experimentally and are tabulated in books on chemical data. In short:

$$\gamma_i = activity\ coefficient = \frac{activity_{ith\ component}}{concentration_{ith\ component}}$$

Thus, this equation can be re-arranged to render:

$$\gamma_i(concentration) = \ activity$$

The activity value obtained behaves as an "effective" concentration. Such a value would be put into the Nernst equation, to obtain EMF predictions based upon the status of chemical reagents inside a galvanic cell.

Thus, the effect of intermolecular forces and un-ideality thereof can be partially taken into account. Moreover, this was required for accuracy when the Nernst equation was tested experimentally earlier in this chapter. The model presented here can be modified by including activity terms. Such would be required for the most precise work in practice.

Activity coefficients are determined almost exclusively experimentally, especially for chaotic situations when concentrations are large and intermolecular forces are too complicated to model on a theoretical basis [1].

On a final note, the chemical potential equation for liquid solutes would be written as:

$$\mu_i = \mu_i^0 + RTln(a_i)$$

Here "a_i" is the activity at hand. Notice that if the activity is unity (at low pressures and standard states), the logarithm term is zero. The chemical potential is then the standard, tabulated value alone. Activity was introduced in liquid solutions *directly analogously* to fugacity - which is used for gaseous phase work. In summary, the influence of chemical activity is the first esoteric chemical effect that must be considered. It is best visualized as an "effective concentration" - even if the actual concentration is different from this value [6].

4.3.2 On Overpotential

Overpotential is a result of electrode losses inside a battery [1,7]. Chemical reactions inside a battery occur primarily on the plane surfaces of electrodes. This "interface" is significant in its operation and the inefficiency thereof. There is usually a lost potential difference between the electrode and the solution it is immersed in. This is, put in its simplest terms, overpotential. The metal electrode may alter the local concentration near itself also. This leads to a situation termed the "ionic double-layer".

In the ionic double layer, solvent molecules may surround solute molecules. Such interferes with solute molecules and their interaction (desired) with the metal electrodes [1]. This situation is described as a "Helmholtz layer" and this "layer" rests adjacent to electrode surfaces [1,6]. The ions that constitute the Helmholtz layer are typically opposite in charge to the charge on the electrode itself. Helmholtz layers are very thin. They are less than 10^{-7} centimeters in most instances [1]. The Helmholtz layer is partially responsible for overpotential. Surface effects at the electrode and interactions with solvent molecules also lead to overpotential.

In short, batteries have two types of losses. When a current is drawn from a battery, the Nernst voltage is larger (slightly) than the terminal voltage recorded. This is due to two causes:

I. Ohmic losses through the imperfect ionic conductor electrolyte [1]. This is considered in the model detailed in this work. The approximate resistance of the electrolyte is equal to the open circuit voltage divided by the short circuit current. Ionic conduction was considered earlier, and experiments were performed to investigate such an effect.

II. Losses associated with interfaces - namely the electrode's interface with the electrolyte it is immersed in or otherwise in contact with [1]. This source of losses is much more difficult in its operation and the understanding thereof.

The second cause above is the overpotential effect mentioned earlier. Overpotential is sometimes called overvoltage. It is an undesirable effect that exists in primary and secondary cells [1, 7]. In effect, it is a loss that is due to the electrode’s interface with the electrolyte phase.

Overpotential is defined as [1]:

Eq. 41. $\eta = EMF_{actual,measured} - EMF_{nernst,predicted} = overpotential$

In short, the overpotential is rather small for almost all battery types (on the order of 120mV) [1]. However, as a current is drawn it remains true that there is some slight deviation from thermodynamic predictions. This is caused, in large part, by irreversible effects occurring inside the battery. Three types of overpotential exist. In practice their total effect is “summed” and leads to the deviation mentioned above [1]. These three types of overpotential are:

I. Concentration overpotential – the concentration of reagents and products is different near the electrode than in the bulk solution. This skews the potential obtained somewhat [1].

II. Activation overpotential – The limiting step in the chemical reaction involved sometimes leads to an energy barrier and energy losses thereof. This effect is caused by limitations involving reaction kinetics. In theory, catalysis could lower the significance and magnitude of this form of overpotential [1].

III. Ohmic overpotential – Even when the bulk IR drop of the electrolyte is considered, some residual IR drop may remain. This is thought to be due to poor conducing films that sometimes develop on electrode surfaces as time progresses [1,5].

These three effects can be considered in more advanced battery models. The model in this paper takes into account, partially, types I and III. Activation overpotential is more difficult to analyze as it requires a knowledge of chemical kinetics and statistical mechanics to model and understand [1].

Concentration overpotential can be modeled by adding multiplier terms to the Nernst equation. In short, this type of work attempts to explain voltage differences in terms of the electrode's presence altering local concentrations. The concentration terms in the Nernst equation, which are strictly speaking activity values for the chemicals involved, only matter as these are realized *at the surface of the metal* *electrodes*. It is possible for the electrode to alter local concentration values [1]. The EMF observed will then deviate somewhat from the value predicted, using the bulk solution properties. One way to model this situation was found in literature [1].

For a simple reaction of the form:

$$bB \rightarrow vV^{+s} + ne^{-}$$

The concentration overpotential can be calculated by means of the equation [1]:

Eq. 42. a. $\eta_{concentration} = EMF_{actual} - EMF_{predicted} = \frac{RT}{nF} ln\left[\frac{(a_{V+s})^{v}}{(a_{V+s})_{at\ electrode}{}^{v}} \frac{(a_B)_{at\ electrode}{}^{b}}{(a_B)^{b}}\right]$

Notice that the activity values in the above equation are meant to be the bulk-phase quantities, except where "at electrode" is mentioned in the subscript. The above equation can be confirmed as true by solving the Nernst equation, twice, and subtracting as shown.

The work would follow as:

$$\eta_{concentration} = \left[E^{o} - \frac{RT}{nF} ln\left[\frac{(a_{V+s})_{at\ electrode}{}^{v}}{(a_B)_{at\ electrode}{}^{b}}\right]\right] - \left[E^{o} - \frac{RT}{nF} ln\left[\frac{(a_{V+s})^{v}}{(a_B)^{b}}\right]\right]$$

$$= \frac{RT}{nF} ln\left[\frac{(a_{V+s})^{v}}{(a_{V+s})_{at\ electrode}{}^{v}} \frac{(a_B)_{at\ electrode}{}^{b}}{(a_B)^{b}}\right]$$

Eq. 42. b.

The conclusion, mentioned above, is drawn because the logarithm difference can be rendered a logarithm of the quotient of the same arguments. In other words, Log(a) - Log(b) = Log(a/b).

The model in this paper partially considers concentration overpotential since the Nernst equation model is fitted to empirical data. It is interesting to note that diffusion is the principal mass transport process involved in batteries (see the next section) [1]. The diffusion process may alter the effect of concentration overpotential when diffusion limits the rate at which reagents move towards electrodes and products move away from these interfaces.

Activation overpotential is a result of chemical kinetics. Certain chemical reactions require energy to become started. Catalysis and applications thereof can lower this "activation energy" requirement. The specifics of such reactions and the activation energy barrier involved may depart from classical mechanics and enter the quantum realm [1]. Put rather simply, chemical reactions take place in sequential steps. Often a single step can involve an energy barrier which must be overcome for the reaction to proceed [1]. This barrier can lead to slight deviations from thermodynamic predictions, although the remaining factors to overpotential (I and III on the list above) are far more significant in their contribution than activation overpotential.

Activation overpotential is described by the Tafel equation and roughly increases in proportion to the logarithm of the current that the battery is producing [1]. In this manner, activation overpotential is more significant for large currents than smaller ones. In addition to being caused by the energy barrier, as aforementioned, another notable fact exists regarding activation overpotential. The potential lost in this way appears to be integral in speeding up a chemical reaction (inside a battery) or being useful in "forcing" a chemical reaction to favor completion to products, say [1]. Some reactions favor both forward and reverse directions. In some instances, activation overpotential is spent when this potential increases the rate of the reaction as it proceeds in a particular direction.

To conclude, activation overpotential is perhaps one of the most complicated effects that occurs inside a battery. Although nearly always less than ~120 mV or so, activation overpotential requires a knowledge of chemical kinetics and quantum mechanics to properly explain. Even this rigorous study has its limits. Activation overpotential is only understood when the entire chemical reaction occurring inside a battery is completely detailed in all of its steps [1]. In the case of the alkaline zinc:manganese dioxide cell, it would prove difficult to impossible to model activation overpotential - since the chemistry is not entirely understood for this system [1].

Ohmic overpotential effectively is what remains of the overpotential when activation overpotential and concentration overpotential have been considered and accounted for. This form of loss is due to oxide layers that sometimes form on metal electrodes. One form of ohmic overpotential is an oxide layer that sometimes forms in older "D" alkaline cells.

These cells have a zinc anode. If left for years, unused, sometimes an oxide layer forms on the pure zinc metal "can". Many oxides and other chemical impurities similarly act to interfere with current flow. The leads to a potential drop when a current is flowing. Such a form of overpotential is considered in this paper's work through the "internal resistance" term. It is believed that this term, or the effective resistance in series with a battery's emf, partially accounts for such non-ideal effects. As evidence to this, older cells typically have larger values of internal resistance.

4.3.4 On Diffusion

Diffusion limits the rate at which chemical species come in contact with electrodes in a battery. Thus, this process proves a significant limitation in certain instances [1]. Diffusion obeys Fick's first and second laws inside a battery. It can be mathematically described in terms of these known equations. In real batteries, the geometry is rather complicated, and the situation is inherently three dimensional. Modeling of the exact diffusion process is, for all practical purposes, rather difficult.

Diffusion effectively can limit current density inside a galvanic cell. Such happens when reagents reaching an electrode are limited in doing so by the diffusion process. The maximum current density is then limited by such a transport step, as the reaction exceeding such a rate would lead to reagents running out at an electrode's surface [1]. Such a situation can be described mathematically. However, for real batteries, the coefficients for the diffusion equation are not known to much accuracy. Worse yet, the diffusion equation in a useful form is a complicated partial differential equation. Finally, in the case of diffusing products, the chemical kinetics of the process involved must be understood. These effects combined effectively make mathematical modeling of diffusion impractical for alkaline batteries. Accordingly, one weak point of this paper's model is its not considering diffusion. Diffusion has a far greater effect on chemical reagents used inside a battery compared with chemical products formed. Its effect is believed to be minor, at least for common batteries in use. Diffusion, in practice, proves a greater limitation for fuel cells, as compared with batteries [1].

It would not prove impossible to model diffusion between two planar electrodes. However, the instance where diffusion matters most is inside the cathode of the alkaline battery or inside the porous electrodes involved in the lithium-ion battery. Both of these situations involve electrodes with microscopic pores, whose dimensions are not known to precision. The modeling of diffusion is, for this reason, left to others. Works such as [1] and [6] describe the mechanics of diffusion.

CHAPTER 5

CONCLUSIONS

It is possible to model alkaline batteries using computer programs written based upon work in chemical thermodynamics. This work is left open ended as the exact chemical reaction inside the alkaline cell is not well understood. Possibilities have been discussed and various methods employed to model this chemical process - which must obey fundamental thermodynamic laws [1,6]. Models reflecting actual behavior have been documented in this paper.

It is believed that the material herein could be put to practical use in industry. Many consumers care about battery management systems so that personal electronics do not inadvertently run out of energy. This situation is of greater importance when considering the case of all electric vehicles. Moreover, the information presented here may be useful in designing a control system for the charging and use of a battery - as such a controller would have metrics which are believed to reflect physical phenomena occurring inside the battery. Empirical data can describe battery operation. The work here goes further and attempts to explain it. Finally, it may be possible to write the algorithm presented as a differential equation system which has an analytic (closed form) solution. Such would allow further numerical investigation and analytic solutions for curves such as shown in fig. 14. These solutions, although not found in this work, are believed to somehow involve the exponential integral function.

Finally, it is a shame that energy storage devices are not commonly mentioned in courses for electrical engineers. With the possible exception of the capacitor, devices of energy storage are not considered very often. This work, it is hoped, can act as a springboard or "prototype" which will facilitate its readers to further study the areas of electrochemistry, thermodynamics, and the physics of galvanic cells. With the background presented here, there are many avenues for improvement and refinement. Such avenues hold promises for practical developments, which in time will hopefully allow galvanic cells to be utilized to their fullest potential and to the greatest utility by society and humanity at large.

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APPENDIX

SAMPLE MATLAB PROGRAM UTILIZED FOR BATTERY MODELING

```
% Battery Modeling Program
% Josh Johnson, Georgia Southern University, 9-16-2021
% First Version

% Define constants:
R = 8.314; % J mol^-1 K^-1 Units, Universal gas constant.
T = 298.15; % Kelvin equivalent of room temperature.
F = 96485.00; % The Faraday Constant, charge of mol of e-.

% Nominal Potential of Alkaline Cell:
E_standard = 1.20 + (1/20)*0.5; % Volts (make this the initial OC voltage)...

% Internal Resistance, Approximate:
R_int = 1/40.00; % Ohms

% Load Impedance, set in experiment:
R_load = 2.9; % Ohms


% Parameters, known, are above. Enter Known measurements into array
% for comparing actual discharge, vs modeled one (will be on same plot).

% Use the "most ideal" instance - The "Ace Hardware" Battery:

v_t_actual = [1.6, 1.5, 1.45, 1.43,
1.41,1.39,1.37,1.34,1.31,1.3,1.3,1.28,1.27,1.25,1.21,1.2,1.21,1.2,1.2,1.2,1.2,1.2,1.18,1.17,1.17,1.17,1.16,...
1.16,1.15,1.15,1.15,1.14,1.14,1.14,1.13,1.12,1.12,1.11,1.105,1.1,1.1,1.1,1.08,1.07,1.065,1.06,1.05,1.05,1.04,1.03,1.025,1.02,1.02,1.01,1,1,1,...
1,0.97,0.97,0.96,0.96,0.95,0.94,0.93,0.91,0.9,0.89,0.87,0.85,0.82,0.78,0.65,0.55,0.52,0.5,0.45,0.4,0.38,0.36,0.34,0.32,0.31,0.31,0.3,0.3,0.3,0.29,0.28];


t = 0:1:88;
t = t * 0.5;
length(t);
length(v_t_actual);

hold on;
legStr = {'Measured Values'};
% Plot Measured Data.
plot(t,v_t_actual, '-o','MarkerIndices',1:10:length(v_t_actual))
title('D Battery Voltage - Alkaline Cell - Vs Time. Ace Brand.')
xlabel('Time, Hours')
ylabel('Voltage, Volts')

% Now the model must be run, compared to actual results.

% Consider a single term in the Nernst Equation -

% Theory -
```

```
% Some product builds up. This leads to Nernst voltage to fall.

% Product starts at "zero" mass and "zero" concentration (low value).

% The model would work as follows -

volumeChamber = (1.51^2 * 3.14159 * 5.7 * 0.5 / 1000.00); % Volume of half - cell, approx. (L)

differential = 0.10; % Differential is 1/10th second.

k2 = 1; % Reagent.
n = 1; % Reagent.

        Error = 0;
        voltageOutputModel = [];
        timeArray = [];
        concentrationReagent = 27.20; % Large Ammount (Mol/L). - Reagent
      for i = 0:differential:(60*60*45)
        E_nernst = E_standard - ((R*T) / (n*F))*log(1 / concentrationReagent);
        I_through = E_nernst / (R_int + R_load);
        molesChange = (I_through * differential) / (n*F);
        molesChangeReagent = (I_through * differential) / (n*F);
        concentrationReagent = ((concentrationReagent*volumeChamber - molesChange) / volumeChamber);
        if mod(i,100) == 0
            voltageOutputModel = [voltageOutputModel, E_nernst];
            timeArray = [timeArray, (i / 3600.00)];
        end
        if(concentrationReagent < 0)
          break;
        end
      end
      plot(timeArray, voltageOutputModel);
      hold on;
% Try to solve analytically. Compare to see if solution correct (agrees).\/
D = -(R*T / ((n*F)*(n*F)*((R_int + R_load))));
C = E_standard / (n*F*((R_int + R_load)))-D*log(volumeChamber)-D*log(volumeChamber);
Error = 0;
    voltageOutputModel = [];
    timeArray = [];
    concentrationReagent = 27.20; % Large Ammount (Mol/L). - Reagent

for iterator = concentrationReagent*volumeChamber:-0.001:0
  time = (-exp(-C/D)/D)*ei(log(iterator) + (C/D));
  E_nernst = E_standard - ((R*T) / (n*F))*log(volumeChamber / iterator);

     voltageOutputModel = [voltageOutputModel, E_nernst];
     timeArray = [timeArray, (time/(3600.00)) + 40.00];

end

plot(timeArray, voltageOutputModel, 'k');
```