# Chapter 10: Electrochemistry

Elon Musk, an innovator in the field of harnessing renewable sources to generate electric power see a huge potential for electric cars to change the way Americans drive.

Selling an electric sports car creates an opportunity to fundamentally change the way America drives.

* Elon Musk

I've actually made a prediction that within 30 years a majority of new cars made in the United States will be electric. And I don't mean hybrid, I mean fully electric.

* Elon Musk

Given the importance of energy production (and in particular, production from renewable sources) alluded to by Richard Smalley in his address to the United States Congress (see Chapter 1), Elon Musk’s vision seems well-aligned with Smalley’s priority.

The generation and consumption of electrical energy and how it is harnessed to do work in the universe lends itself very nicely to discussion within the framework of thermodynamics. In this chapter, we will use some of the tills we have developed to relate electrochemical processes to thermodynamic variables, and to frame discussions of a few important topics.



## Electricity

Electricity has been known for some time. Ancient Egyptians, for example, referred to electric fish in the Nile River as early as 2750 BC (Moller & Kramer, 1991). In 1600, William Gilbert studied what would later be seen to be electrostatic attraction, by creating static charges rubbing amber (Stewart, 2001). And Benjamin Franklin’s famous experiment (although it is actually uncertain if he performed the experiment) of attaching a metal key to a kite string occurred in 1752, and showed that lightening is an electrical phenomenon (Uman, 1987).

One of the biggest breakthroughs in the study of electricity as a chemical phenomenon was made by Alessandro Volta, who in 1799 showed that electricity could be generated by stacking copper and zinc disks submerged in sulfuric acid (Routledge, 1881). The reactions that Volta produced in his **voltaic pile** included both **oxidation** and **reduction** processes that could be considered as **half-reactions**. The half-reactions can be classified as **oxidation** (the loss of electrons) which happens at the **anode** and **reduction** (the gain of electrons) which occurs at the **cathode**. Those half reactions were

Figure 1. Alessandro Volta (1745-1827)

Zn 🡪 Zn2+ + 2 e- (anode)

2 H+ + 2 e- 🡪 H2 (cathode)

The propensity of zinc to oxidize coupled with that of hydrogen to reduce creates a potential energy difference between the electrodes at which these processes occur. And like any potential energy difference, it can create a force which can be used to do work. In this case, the work is that of pushing electrons through a circuit. The work of such a process can be calculated by integrating

where E is the potential energy difference, and dQ is an infinitesimal amount of charge carried through the circuit. The infinitesimal amount of charge carried through the circuit can be expressed as

where e is the charge carried on one electron (1.6 x 10-19 C) and dN is the infinitesimal change in the number of electrons. Thus, if the potential energy difference is constant

But since the number of electrons carried through a circuit is an enormous number, it would be far more convenient to express this in terms of the number of moles of electrons carried through the circuit. Noting that the number of moles (n) is given by

and that the charge carried by one mole of electrons is given by

where F has the magnitude of one Faraday (or the total charge carried by one mole of electrons.) The Faraday is named after Michael Faraday (1791-1867) (Doc, 2014), a British physicist who is credited with inventing the electric motor, among other accomplishments.

Putting the pieces together, the total electrical work accomplished by pushing n moles of electrons through a circuit with a potential difference E, is

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| **Example**: A current of 2.00 ampere is passed through an electroplating cell containing an initial concentration of silver of [Ag+] = 1.00 M to electroplate silver metal onto a spoon. If the current is passed through the cell for a time period of 15 min, what mass of silver will be deposited onto the spoon?  **Solution**: Since 1 ampere x 1 second = 1 coulomb, and 96484 coulomb = the charge carried by 1 mole of electrons |

### The connection to G

Recall that in addition to being used as a criterion for spontaneity, G also indicated the maximum amount of non p-V work a system could produce at constant temperature and pressure. And since we is non p-V work, it seems like a natural fit that

If all of the reactants and products in the electrochemical cell are in their standard states, it follows that

where Eo is the **standard cell potential**. Noting that the molar Gibbs function change can be expressed in terms of the reaction quotient Q by

it follows that

Dividing by –nF yields

which is the **Nernst equation**. This relationship allows one to calculate the cell potential of a electrochemical cell as a function of the specific activities of the reactants and products. In the Nernst equation, n is the number of electrons transferred per reaction equivalent. For the specific reaction harnessed by Volta in his original battery, Eo = 0.763 V (at 25 oC) and n = 2. So if the Zn2+ and H+ ions are at a concentration that gives them unit activity, and the H2 gas is at a partial pressure that gives it unit fugacity,

## Half Cells and Standard Reduction Potentials

Zn 🡪 Zn2+ + 2e- Eoxo = 0.763 V

2 H+ + 2 e- 🡪 H2 Eredo = 0.000 V

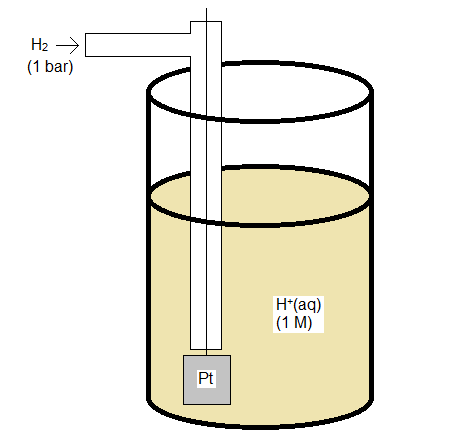
Much like G itself, E can only be measured as a difference, so a convention is used to set a zero to the scale. Toward this end, convention sets the reduction potential of the standard hydrogen electrode (SHE) to 0.00 V.

### Standard Hydrogen Electrode

The standard hydrogen electrode is constructed so that H2 gas flows over an inert electrode made of platinum, and can interact with an acid solution which provides H+ for the half reaction

2 H+(aq) + 2 e- 🡪 H2(g)

Both H+ and H2 need to have unit activity (or fugacity), which if the solution and gas behave ideally means a concentration of 1 M and a pressure of 1 bar.



## Electrochemical Cells

Standard reduction potentials can be measured relative to the convention of setting the reduction potential of the **Standard Hydrogen Electrode** (SHE) to zero. A number of values are shown in the table below. Several more standard reduction potentials are available in (Bratsch, 1989).

|  |  |
| --- | --- |
| Reduction Half Reaction | Eo (V) |
| F2 + 2 e- 🡪 2 F- | 2.87 |
| MnO4- + 8 H+ 🡪 Mn2+ + 4 H2O | 1.51 |
| Au3+ + 3 e- 🡪 Au | 1.50 |
| Cl2 + 2 e- 🡪 2 Cl- | 1.360 |
| Tl3+ + 3 e- 🡪 Tl | 1.211 |
| Br2 + 2 e- 🡪 2 Br- | 1.065 |
| Hg2+ + 2 e- 🡪 Hg | 0.854 |
| Ag+ + e- 🡪 Ag | 0.799 |
| Hg22+ + 2 e- 🡪 2 Hg | 0.790 |
| Fe3+ + e- 🡪 Fe2+ | 0.771 |
| Hg2SO4 + 2 e- 🡪 2 Hg + SO42- | 0.615 |
| I2 + 2 e- 🡪 2 I- | 0.536 |
| Cu+ + e- 🡪 Cu | 0.521 |
| Cu2+ + 2 e- 🡪 Cu | 0.337 |
| HgCl2 + 2 ee 🡪 Hg + 2 Cl-‑ | 0.268 |
| AgCl + e- 🡪 Ag + Cl- | 0.222 |
| Sn4+ + 2 e- 🡪 Sn2+ | 0.15 |
| AgBr + e- 🡪 Ag + Br- | 0.071 |
| 2 H+ + 2 e- 🡪 H2 | **0.000** |
| Pb2+ + 2 e- 🡪 Pb | -0.126 |
| Sn2+ + 2 e- 🡪 Sn | -0.136 |
| AgI + e- 🡪 Ag + I- | -0.152 |
| CuI + e- 🡪 Cu + I- | -0.185 |
| Ni2+ + 2 e- 🡪 Ni | -0.250 |
| Tl+ + e- 🡪 Tl | -0.34 |
| PbSO4 + 2 e- 🡪 Pb + SO42- | -0.355 |
| Fe2+ + 2 e- 🡪 Fe | -0.440 |
| Zn2+ + 2 e- 🡪 Zn | -0.763 |
| Sn(OH)62- + 2 e- 🡪 HSnO2 + 3 OH- + H2O | -0.90 |
| Al3+ + 3 e- 🡪 Al | -1.66 |
| Mg2+ + 2 e- 🡪 Mg | -2.37 |
| Na+ + e- 🡪 Na | -2.714 |
| Li+ + e- 🡪 Li | -3.045 |

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| **Example**:  Which pair of reactants will produce a spontaneous reaction if everything is present in its standard state at 25 oC?  Fe + Cu2+ or Fe2+ + Cu  **Solution**:  The species with the higher standard reduction potential will force the other to oxidize.  From the table,  Cu2+ + 2 e- 🡪 Cu 0.337 V  Fe2+ + 2 e- 🡪 Fe -0.440 V  So the iron half-reaction will flip (so that iron is oxidizing) and the spontaneous reaction under standard conditions will be  Cu2+ + Fe 🡪 Cu + Fe2+ Eo = 0.777 V |

### Calculating Cell Potentials

Using values measured relative to the SHE, it is fairly easy to calculate the standard cell potential of a given reaction. For example, consider the reaction

2 Ag+(aq) + Cu(s) 🡪 2 Ag(s) + Cu2+(aq)

Before calculating the cell potential, we should review a few definitions. The anode half reaction, which is defined by the half-reaction in which oxidation occurs, is

Cu(s) 🡪 Cu2+(aq) + 2 e-

And the cathode half-reaction, defined as the half-reaction in which reduction takes place, is

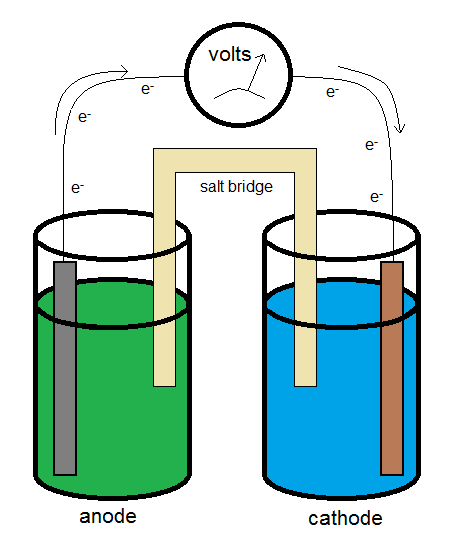
Ag+(aq) + e- 🡪 Ag(s)

Using **standard cell notation**, the conditions (such as the concentrations of the ions in solution) can be represented. In the standard cell notation, the anode is on the left-hand side, and the cathode on the right. The two are typically separated by a **salt bridge**, which is designated by a double vertical line. A single vertical line indicates a phase boundary. Hence for the reaction above, if the silver ions are at a concentration of 0.500 M, and the copper (II) ions are at a concentration of 0.100 M, the standard cell notation would be

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| **Example**:  Calculate the cell potential at 25 oC for the cell indicated by  Cu(s) | Cu2+(aq, 0.100 M) || Ag+ (aq, 0.500 M) | Ag(s)  **Solution**:  In order to calculate the cell potential (E), the standard cell potential must first be obtained. The standard cell potential at 25 oC is given by  And for a cell at non-standard conditions, such as those indicated above, the Nernst equation can be used to calculate the cell potential. At 25 oC, The cell potential is given by  Noting that 1 J/C = 1 V, |

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| **Example**:  Calculate the cell potential at 25 oC for the cell defined by  Ni(s) | Ni2+ (aq, 0.500 M) || Cu(s) | Cu2+(aq, 0.100 M)  **Solution**:  We will use the Nernst equation. First, we need to determine Eo. Using the table below, it is apparent that  Cu2 + 2 e- 🡪 Cu Eo = 0.337 V  Ni2+ + 2 e- 🡪 Ni Eo = -0.250 V  So copper, having the larger reduction potential will be the cathode half-reaction while forcing nickel to oxidize, making it the anode. So Eo for the cell will be given by  And the cell potential is then given by |

### Measuring the Voltage



A typical galvanic electrochemical cell can be constructed similar to what is shown in the diagram above. The electrons flow from the anode (the electron source) to the cathode (the electron sink.) The salt bridge allows for the flow of ions to complete the circuit while minimizing the introduction of a junction potential.

## Entropy

The Gibbs function is related to entropy through its temperature dependence

A similar relationship can be derived for the temperature variance of Eo.

Consider the following data for the Daniel Cell (Buckbeei, Surdzial, & Metz, 1969) which is defined by the following reaction

Zn(s) + Cu2+(aq) ↔ Zn2+(aq) + Cu(s)

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| --- | --- |
| T (oC) | Eo (V) |
| 0 | 1.1028 |
| 10 | 1.0971 |
| 20 | 1.0929 |
| 25 | 1.0913 |
| 30 | 1.0901 |
| 40 | 1.0887 |

From a fit of the data to a quadratic function, the temperature dependence of over the measured temperature range is easily established.

So, at 298 K,

So the entropy change is calculated by

The standard entropy change for the Daniel cell reaction at 25 oC is

.

The standard entropies of formation for the species involved in the Daniel cell are

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| **Species** | **Sfo (J mol-1 K-1)** |
| Zn(s) | 33.150 |
| Zn2+(aq) | -112.1 |
| Cu(s) | 41.63 |
| Cu2+(aq) | -99.6 |

It is the negative entropy change that leads to an increase in standard cell potential at lower temperatures. For a reaction such as

Pb(s) + 2 H+(aq) 🡪 Pb2+(aq) + H2(g)

which has a large increase in entropy (due to the production of a gas-phase product), the standard cell potential decreases with decreasing temperature. As this is the reaction used in most car batteries, it explains why it can be difficult to start ones car on a very cold winter morning. The topic of temperature dependence of several standard cell potentials is reported and discussed by Bratsch (Bratsch, 1989).

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| **Example**: Consider the redox reaction which is used to generate electricity in most car batteries:  Given the following data  2 H+ + 2 e 🡪 H2 0.0 V  Pb2+ + 2 e 🡪 Pb -0.126 V   |  |  | | --- | --- | | Species | Sfo (J mol-1 K-1) | | H+(aq) | 0 | | H2(g) | 130.684 | | Pb2+(aq) | 10.5 | | Pb(s) | 68.81 |  1. Calculate the standard cell potential (Eo) at 25 oC, 2. the standard reaction entropy (Srxno) at 25 oC, 3. and the standard cell potential at 0 oC.   **Solution**: The target reaction can be generated by adding the data reactions (with the lead half-reaction flipped):   |  |  | | --- | --- | | 2 H+ + 2 e 🡪 H2 | 0 V | | Pb 🡪 Pb2+ + 2 e | 0.126 V | | 2 H+ + Pb 🡪 Pb2+ + H2 | 0.126 V |   The entropy change is given by  Since  It follows that at constant pressure  So, if the entropy change is constant over the temperature interval, the change to the standard cell potential is given by  So  And |

## Concentration Cells

The generation of an electrostatic potential difference is dependent on the creation of a difference in chemical potential between two half-cells. One important manner in which this can be created is by creating a concentration difference. Using the Nernst equation, the potential difference for a concentration cell (one in which both half-cells involve the same half-reaction) can be expressed

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| **Example**:  Calculate the cell potential (at 25 oC) for the concentration cell defined by  Cu(s) | Cu2+ (aq, 0.00100 M) || Cu2+ (aq, 0.100 M) + Cu(s)  **Solution**:  Since the oxidation and reduction half-reactions are the same,  The cell potential at 25 oC is calculated using the Nernst equation:  Substituting the values from the problem: |

## Applications to Equilibrium

Since the standard cell potential, Eo, is directly related to the stand Gibbs function change

It follows that the standard cell potential will also be related to an equilibrium constant describing a redox reaction. The relationship between Go and K is given by

So, it follows that

At 298 K, this can be transformed similarly to the Nernst equation

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| **Example**: Based in the standard reduction potentials  Cu2+ + 2 e 🡪 Cu 0.337 V  Zn2+ + 2 e 🡪 Zn -0.763 V  Calculate the value of the equilibrium constant for the reaction  **Solution**: The standard cell potential, Eo, for the reaction is  The equilibrium constant can be calculated from the relationship  So |

### Solubility

Electrochemical measurements can be used to calculate solubility products (Ksp) based on measurements where one of the solid electrodes is the salt of the compound for which the Ksp value is desired.

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| **Example**: Based on the following data  PbSO4 + 2 e- 🡪 Pb + SO42- -0.355 V  Pb2+ + 2 e 🡪 Pb -0.126 V  calculate Ksp for PbSO4(s) at 25 oC.  **Solution**: The target reaction is that for the dissociation of AgBr(s):  This can be generated from the half reactions by flipping the second half reaction and adding.  PbSO4 + 2 e- 🡪 Pb + SO42- -0.355 V  Pb 🡪 Pb2+ + 2 e 0.126 V  PbSO4 🡪 Pb2+ + SO42- -0.229 V  And since  We see that |

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# Vocabulary and Concepts

anode 232, 237

cathode 232, 237

concentration cell 243

half-reactions 232

Nernst equation 234

oxidation 232

reduction 232

salt bridge 237

standard cell notation 237

standard cell potential 233

Standard Hydrogen Electrode 235

voltaic pile 232

# Learning Objectives

Upon successful completion of this chapter, a student will be able to

1. Articulate and utilize the connection between Go and Eo for oxidation-reduction reactions.
2. Define the terms *anode*, *cathode*, *half-cell*, *standard reduction potential*, and other terms found in the “Vocabulary and Concepts” section.
3. Connect the temperature dependence of standard cell potential to entropy changes.
4. Utilize the connections between standard cell potential and equilibrium constants to calculate equilibrium constants and concentrations from electrochemical daya, and vice versa.

# Problems

1. Silver is electroplated onto a spoon by suspending the spoon in a 1.00 M solution of AgNO3 and passing a 2.00 amp current through it for 15.0 min. What mass of silver is deposited on the spoon?
2. Calculate the standard cell potential for the reaction
3. The following data can be found in a table of standard reduction potentials at 25 oC:

Sn4+ + 2 e 🡪 Sn2+ 0.15 V

Sn2+ + 2 e 🡪 Sn -0.136 V

From these data, Calculate the standard reduction potential for the half-cell

Sn4+ + 4 e 🡪 Sn ? V

1. From a table of standard reduction potentials at 25 oC, the following is found:

Cu2+ + 2 e 🡪 Cu 0.337 V

Zn2+ + 2 e 🡪 Zn -0.763 V

From these data, calculate the cell potential for the cell constructed as

1. A Daniel cell is constructed

and the cell potential is measured to be 1.05 V. Calculate the concentration of Cu2+ ions in the cathode half-cell.

1. Given the following standard reduction potentials, calculate the value of Ksp for AgI.

AgI + e- 🡪 Ag + I- -0.152 V

Ag+ + e 🡪 Ag 0.799 V

1. Ksp for PbCl2(s) is 1.8 x 10-4 M3. Based on this, and the standard reduction potential

Pb2+ + 2 e 🡪 Pb -0.126 V

calculate the standard reduction potential for

PbCl2 + 2 e 🡪 Pb + 2 Cl- ?

1. At 25 oC, Kf = 8.9 x 102 M-1 for the complexation reaction

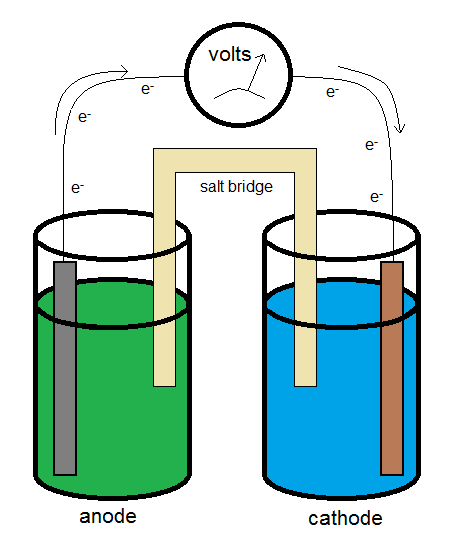
Given that the standard reduction potential at 25 oC

Fe3+ + 3 e 🡪 Fe 0.771 V

determine the standard reduction potential for the half-reaction

FeSCN2+ + 3 e 🡪 Fe + SCN- ? V

1. Ni2+ Ions complex with EDTA by the reaction



Kf for this complex formation equilibrium is 3.6 x 1018 M-1. A half-cell is prepared to be 0.100 M in Ni2+ and 1.00 M in EDTA. Its standard reduction potential is measured relative to a copper half-cell, in which [Cu2+] = 1.00 M. The standard reduction potentials for the bare-ion reductions are

Cu2+ + 2 e 🡪 Cu 0.337 V

Ni2+ + 2 e 🡪 Ni -0.250 V

From these data, calculate the cell potential once the complexation reaction of N2+ with EDTA has reached equilibrium.

1. Consider the redox reaction

Given the following data

Mg2+ + 2 e 🡪 Mg -2.37 V

Li+ + e 🡪 Li -3.045 V

|  |  |
| --- | --- |
| Species | Sfo (J mol-1 K-1) |
| Mg2+(aq) | -138.1 |
| Mg(s) | 32.68 |
| Li+(aq) | 13.4 |
| Li(s) | 29.12 |

1. Calculate the standard cell potential (Eo) at 25 oC,
2. the standard reaction entropy (Srxno) at 25 oC,
3. and the standard cell potential at 37 oC.