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**Understanding Galvanic Cells and Electrochemistry**

**INTRODUCTION**

A reduction-oxidation (redox) reaction involves the transferring of electrons from the reducing agent to the oxidizing agent. Each reduction and oxidation half reaction has a standard reduction potential that when combined into an overall balanced reaction can contribute to an overall standard reduction potential for the redox reaction. A table of the half-cell standard reduction potentials used in this experiment is listed in Table 1 below.

Reduction Half-Reaction	E° values (V)
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn}(\text{s})$	-0.76

Table 1: Half-reactions and their corresponding electric potentials.

A Galvanic Cell can harness the electrons transferred by splitting up the half-reactions into separate cells and requiring the electrons to pass through a wire. This flow of electrons is electricity! – and has a corresponding electric potential (voltage).<sup>1</sup>

This experiment seeks to become familiar with Galvanic Cells in their construction, mechanisms for electron transfer, and influences that different ion concentrations can have on a cell's potential. The following Nernst Equation is a helpful tool that can help relate the cell potential with the measured potential and the concentration of different redox ions:

$$\text{Nernst} \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0592}{n}\right) * \text{Log}(Q) \quad \text{Eq.1}$$

where  $E_{\text{cell}}$  is the cell potential,  $E^{\circ}_{\text{cell}}$  is the cell potential at standard values,  $n$  is the number of moles of electrons transferred, and  $Q$  is the fraction in evaluating equilibrium positions of reactions. Since Galvanic Cells are essentially batteries, one part of this experiment was devoted to understanding how a large amount of time (or large shifting of ion concentrations) affects the voltage of a cell. This is important for understanding how batteries work and why they cannot work forever.

This experiment also tackled the challenge of determining an unknown half-reaction potential with the vanadium half-reaction. Since half-reaction potentials cannot be measured directly, this is an important step in the understanding of how half-reactions are calculated from an overall cell reaction.

By reacting the unknown vanadium half-reaction with a known half-reaction of silver, an overall  $E_{\text{cell}}$  could be measured. By finding the overall  $E_{\text{cell}}$ , the standard reduction potential for vanadium could be found from the Nernst Equation and Equation 2 below.<sup>2</sup>

$$E_{\text{cell}}^0 = E_{\text{oxidation}} + E_{\text{reduction}} \quad \text{Eq. 2}$$

## **METHODS**

### *Galvanic Cells Construction*

The experiment was performed according to C118 Laboratory Handouts, Indiana University.<sup>1</sup> The electrochemical cell was assembled from a vial containing a 2.0M ammonium nitrate salt bridge solution, two medicine droppers which contained the various ion solutions, the corresponding metals which served as electrodes, and a voltmeter. Cotton plugs were pushed into the tips of the medicine droppers to keep the solutions from draining into the ammonium nitrate solution. The ammonium nitrate solution was changed periodically as some solution from the half-cell diffused through the cotton plug.

### *Galvanic Cell Measurements*

Five different electrochemical cell reactions with varying ion components were performed and voltages were recorded. For the first trial, an electrode containing 0.10 M copper sulfate and a copper wire, and another electrode containing 0.10 M zinc sulfate and a zinc wire was assembled. The cell notation can be seen below:



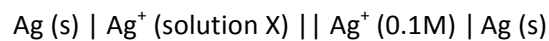
where zinc is the anode and copper is the cathode. The two electrodes were placed in the ammonium nitrate salt-bridge solution and a potential reading was measured. The cell notations for the following four reactions are shown below:



\*This reaction simulated the use of a battery over time therefore has unbalanced ion concentrations.

### *Concentration Cells*

Five concentration cells were constructed and used to create a calibration curve that was used to determine an unknown concentration of silver ion. Each cell was prepared by using 0.1 M  $\text{Ag}^+$  ion solution, while the other cell was constructed using a specific silver concentration. Each silver concentration was diluted by a factor of 10 and the values for the solutions in increasing diluteness were  $1.0 \cdot 10^{-1}$  M  $\text{Ag}^+$ ,  $1.0 \cdot 10^{-2}$  M  $\text{Ag}^+$ ,  $1.0 \cdot 10^{-3}$  M  $\text{Ag}^+$ ,  $1.0 \cdot 10^{-4}$  M  $\text{Ag}^+$ , and  $1.0 \cdot 10^{-5}$  M  $\text{Ag}^+$ . Potential values for each reaction were recorded. The cell notation for each reaction was as follows:



### *Determining $\text{VO}_2^+/\text{VO}^{2+}$ HALF-REACTION POTENTIAL*

A half-reaction potential for vanadium was found by constructing a Galvanic Cell with the following cell notation:

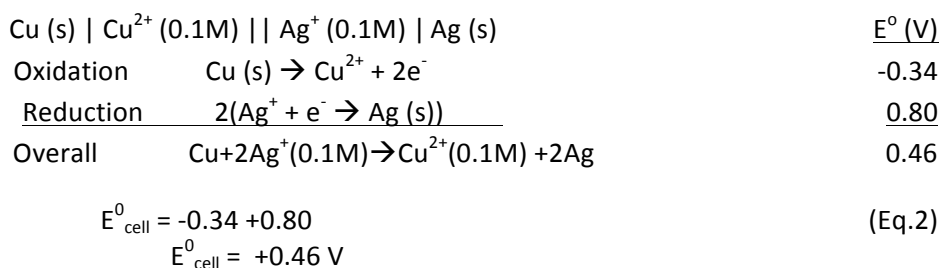


The overall cell potential was measured and the half-cell reduction for vanadium was determined by using Equation 1 and 2. The solution for the cathode portion of the cell was prepared by mixing equal volumes of the two 0.05M vanadium solutions provided to reach a final concentration of 0.1M. Since a vanadium metal was not available, a carbon electrode was used as a spot for reduction and as an electrical conductor to the external circuit.<sup>1</sup>

## RESULTS

### Galvanic Cells

Four Galvanic Cells were constructed with various oxidizing and reducing agents. Their standard reduction potential ( $E^{\circ}_{\text{cell}}$ ), expected reduction potential ( $E_{\text{cell}}$ ) based on concentration values, and the measured voltage of the cell are represented below. A fifth Galvanic Cell was constructed in an effort to simulate the use of a battery over time. Table 1 below shows the findings of each Galvanic Cell trial. An example calculation for an overall balanced redox reaction and  $E_{\text{cell}}$  determination is displayed by the copper and silver redox reaction below:



To determine the predicted potential of the cell based on the concentrations used ( $E_{\text{cell}}$ ), the Nernst Equation (Eq. 1) was used.

$$\begin{aligned}
 E_{\text{cell}} &= 0.46\text{V} - \frac{0.0592}{2e^-} * \text{Log} \left( \frac{(0.1\text{M})}{(0.1\text{M})^2} \right) \\
 E_{\text{cell}} &= 0.43 \text{ V}
 \end{aligned}$$

Trial #	Overall Reaction	$E^{\circ}_{\text{cell}}$ (V)	$E_{\text{cell}}$ (V) (based on concentrations)	$E_{\text{cell}}$ (V) measured	Difference between $E_{\text{cell-expected}}$ and $E_{\text{cell-measured}}$ (V)
1	$\text{Zn} + \text{Cu}^{2+} \text{ (0.1M)} \rightarrow \text{Zn}^{2+} \text{ (0.1M)} + \text{Cu}$	1.1	1.1	1.092	0.008
2	$\text{Cd} + \text{Cu}^{2+} \text{ (0.1M)} \rightarrow \text{Cd}^{2+} \text{ (0.1M)} + \text{Cu}$	0.74	0.74	0.653	0.087
3	$\text{Pb} + \text{Cu}^{2+} \text{ (0.1M)} \rightarrow \text{Pb}^{2+} \text{ (0.1M)} + \text{Cu}$	0.47	0.47	0.483	0.013
4	$\text{Cu} + 2\text{Ag}^+ \text{ (0.1M)} \rightarrow \text{Cu}^{2+} \text{ (0.1M)} + 2\text{Ag}$	0.46	0.43	0.286	0.144
5	$\text{Zn} + \text{Cu}^{2+} \text{ (0.1M)} \rightarrow \text{Zn}^{2+} \text{ (1.0M)} + \text{Cu}$	1.1	1.041	1.076	0.035

Table 1: Overall Balanced Reactions and Their Corresponding Electric Potentials.

### Concentration Cells

An unknown concentration of silver ion was determined by plotting increasingly dilute solutions of silver ion solution and its corresponding electric potential in mV. A plot representing these findings is represented in Figure 1 below. As represented, the graph shows a positive linear regression and has an  $R^2$  value of 0.8738, indicating a fairly stable correlation between decreasing ion concentration and electric potential.

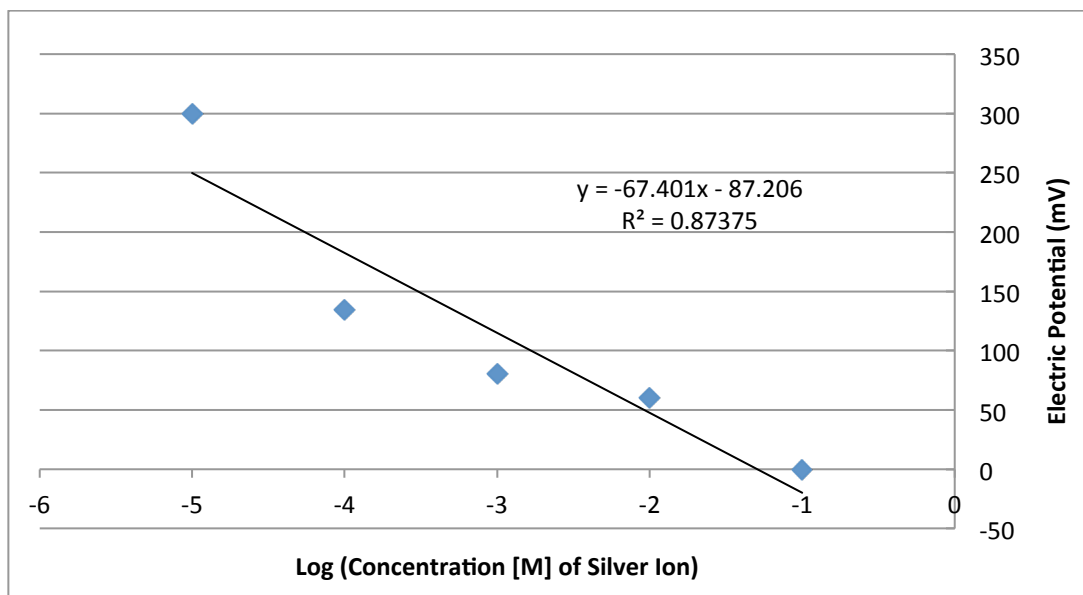


Figure 1: Electric Potential vs Concentration Calibration Curve

Using the measured potential (176 mV) of the unknown silver concentration, it was possible to use the linear equation to determine the Molarity of the unknown:

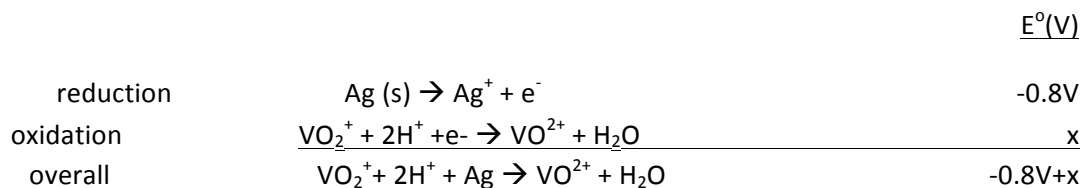
$$\begin{aligned} 176 \text{ mV} &= -67.401(x) - 87.206 \\ x &= -3.905 \text{ M} \\ \mathbf{10^{(-3.905)} = 1.244 \cdot 10^{-4} \text{ M} = [\text{Ag}^+]} \end{aligned}$$

Another method for calculating the unknown silver concentration could be found from using the Nernst Equation (Equation 1):

$$\begin{aligned} 0.176 \text{ V} &= 0 \text{ V} - \frac{0.0592}{1e-} \cdot \text{Log}\left(\frac{[\text{Ag}]}{[0.1 \text{ M}]}\right) \\ \mathbf{[\text{Ag}^+] = 1.06 \cdot 10^{-4} \text{ M}} \end{aligned}$$

### $VO_2^+/VO^{2+}$ Half-Reaction Potential

An unknown half-reaction potential for  $VO_2^+/VO^{2+}$  was determined by making a redox solution with the known half-reaction potential of  $Ag^+$  and measuring the overall potential of the cell. The cell notation can be found in the methods section.



The measured value of  $E_{cell}$  in lab was 0.285 V. In order to obtain the  $E_{cell}^{\circ}$  half-reaction potential for vanadium, the Nernst equation must be used to relate the measured value to true standard reduction potential,  $E_{cell}^{\circ}$ .

$$0.285 V = E_{cell}^{\circ} - \frac{0.0592}{1e^-} \cdot \log\left(\frac{[0.05M][0.1M]}{[1.0065M][0.05M]}\right) \quad (\text{Eq. 1})$$
$$E_{cell}^{\circ} = 0.2256V$$

By obtaining the  $E_{cell}^{\circ}$ , it was then possible to determine the unknown half-reaction potential for vanadium by using Equation 2:

$$0.2256V = -0.8V + x \quad (\text{Eq. 2})$$
$$x = E^{\circ} \text{ vanadium half-reaction} = +1.0256V$$

## DISCUSSION

By accurately constructing various Galvanic Cells and measuring the cell potentials, a stronger understanding for redox and electrochemistry was established. It was observed that altering the concentrations of anode or cathode concentrations changed the overall cell potential. The magnitude of this change in potential could be derived theoretically from the Nernst Equation. It was also concluded that electrodes of the same solution at the same concentrations provide zero voltage, as in concentration cells. Only upon changing the concentration of these concentration cells did a change in voltage occur.

With each Galvanic Cell trials, an  $E_{cell}^{\circ}$  was calculated based on the standard-reduction potentials of the ions being used. Using the Nernst Equation and the cell's ion concentrations, an expected  $E_{cell}$  value was also calculated. Often, as with the trials of #1, #2, and #3, the  $E_{cell}^{\circ}$  and expected  $E_{cell}$  were the

same. This was due to the identical reactants/products concentrations used in the cells. The expected  $E_{\text{cell}}$  values and the measured  $E_{\text{cell}}$  values with a volt-meter were similar. The least similar value occurred in trial #3 when the difference between the expected and measured potential was 0.144 V. The next furthest difference between expected and measured potential occurred in trial #2 and had a difference of 0.087V. Overall, the expected values and the measured values were fairly close, with the closest expected and observed value occurring in trial #1 and was only 0.008V apart. Although the measured cell potentials and theoretical values were close, none of them were perfect. This is most likely due to sources of error in the experiment. There were certain aspects of this experiment that were hard to control, such as the accuracy of the voltmeter. After every reading, the voltmeter would waver above or below the measured reading and never really settled on a set voltage. This required some estimation for the real measured potential. It was also hard to control for ions from the electrodes not leaking into the ammonium nitrate salt bridge solution. The leaking of ions could have interfered with the salt bridges ability to put electrolytes into the correct cathode/anode solution. It's also possible that the metal electrodes were not sanded enough which wouldn't provide for an accurate voltage reading. Some of the metals were oxidized and needed sanding to uncover their pure metal form. Overall, the measured readings were fairly close and the sources of error seemed to have a minimal effect. In future experimental designs, it would be beneficial to use closed electrode cells with pure metals and a salt bridge that connected each half cell externally rather than internally (such as using a piece of bologna rather than an ammonium nitrate solution).

The fifth trial was used to demonstrate how a battery gets used over time. This was done by increasing the concentration of products. Since a battery is basically a Galvanic Cell, after a long period of time the reactants get used up, oxidized, and more products are formed. This results in a higher concentration of products and is what this cell is meant to simulate. For this experiment, the battery was meant to simulate trial #1 over a long period of time. Using the Nernst Equation and general thinking, it was expected that the cell potential in the battery would drop. This is supported by our measured  $E_{\text{cell}}$  from trial #1 to trial #5 where it can be seen that the cell potential dropped from 1.092V to 1.076V due to a shift in ion concentration to the products side.

Two methods for determining an unknown silver concentration was used. One involved using concentration cells of decreasing levels of concentration, measuring the cell potential, and constructing a calibration curve. The other involved using the measured cell voltage and plugging it into the Nernst Equation in order to determine the theoretical concentration. Of these two methods, the latter seemed

to be the most accurate. As seen in Figure 1, the  $R^2$  value for the calibration curve was only 0.8738. Although this is a fairly stable relationship, the theoretical relationship should be exactly linear and have an even stronger  $R^2$  value. Using the Nernst Equation, it was possible to plug in the measured potential value and determine a concentration based on the theoretical  $E^\circ_{\text{cell}}$  value and other known silver concentration, rather than relying on five other data points each with their own possible sources of error. Sources of error from the concentration cells could have come from not replenishing the ammonium nitrate solution as frequently as needed and the fluctuating accuracy of the voltmeter. Although these sources of error may not have skewed the data too much, it might have made the calibration curve slightly stronger.

The measured overall cell potential for the vanadium half reaction was 0.285V. However, this value represents the measured potential rather than the standard cell potential. A standard cell potential is necessary to determine the missing half-reaction potential of vanadium. By using the Nernst Equation, the half-cell potential for vanadium was +1.0256V, which was slightly above the value range calculated in the previous experiment of 0.94V-0.97V. This could be due to either an inaccuracy in the voltmeter reading, or an inaccuracy in the qualitative analysis from the previous vanadium experiment. Interestingly, another group found the overall cell potential reading to be 0.209V, which would have given a vanadium standard half-reaction potential of 0.95V, which would have been in the range calculated from last week. Because of this finding, it is more likely that the vanadium half-reaction finding in this experiment is not correct due to a miss-read by the volt-meter.



## **REFERENCES**

1. Burdge, Julia R. *Chemistry*. New York: McGraw-Hill Higher Education, 2010; pg. 818-841.
2. Robinson, J.K., (2012). C118 Laboratory Handouts, Principles of Chemistry and Biochemistry II, Indiana University.