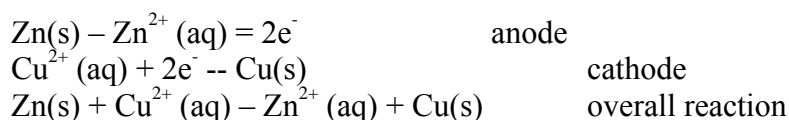


VOLTAIC CELLS

Introduction

An electrochemical reaction is a chemical reaction that involves reduction and oxidation (a redox reaction). The energy released in a spontaneous redox reaction can be used to do electrical work. This is accomplished using a voltaic (or galvanic) cell, a device in which the transfer of electrons occurs through an external pathway rather than directly between reactants. A spontaneous redox reaction takes place when a strip of zinc is put into a solution containing copper sulfate. The reaction is $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$. Carrying out the reaction in this way, however, will not permit the obtaining of useful electrical energy. Instead, a zinc strip is placed into a solution of zinc sulfate in one container. A copper strip is placed into a solution of copper sulfate in another container. An electrical conducting wire is connected between the zinc and copper strips. A salt bridge containing an electrolyte capable of maintaining charge balance in each solution is placed between the two solutions. A voltmeter can be placed in the circuit to measure the potential generated in the reaction. Zinc is oxidized to Zn^{2+} in one compartment. The zinc strip is called the anode electrode. Cu^{2+} is reduced to copper in the other compartment. The copper strip is called the cathode electrode. The electrons lost by the zinc to form Zn^{2+} travel from the anode through the external circuit to the cathode and are picked up by Cu^{2+} ions as they form copper atoms on the electrode.

The electrochemical reaction can be represented as two half-reactions:



If all the components of the cell are in their standard states (with $[\text{Zn}^{2+}] = 1.0 \text{ M}$ and $[\text{Cu}^{2+}] = 1.0 \text{ M}$), the cell is called a standard cell. The voltage generated by the standard cell is called the standard cell potential (E°). It is convenient to have a shorthand mechanism for designating voltaic cells. The standard zinc-copper cell can be written as



In this designation the anode or oxidation half-cell is represented on the left side and the cathode or reduction half-cell is represented on the right side. The electrodes in the two half-reactions are electrically connected using a salt bridge represented by two vertical lines. The cell electrodes are represented at the two ends in this notation. A single vertical line shows the phase boundary between the solid electrode and the electrolyte solution in each half-cell.

Pre-Lab Problem: What is the cell potential in a Zn/Cu cell that has a $[\text{Zn}^{2+}]$ of 0.10 M in the Zn half-cell and a $[\text{Cu}^{2+}]$ of 0.010 M in the Cu half-cell?

I. Standard Cells

Six standard voltaic cells will be set up and the potential generated by each will be measured. However, instead of setting up the half-cells in beakers, they will be set up on a piece of filter paper. The half-cells are established by placing three drops of 1.0 M NaNO_3

Procedure:

Obtain a disk of filter paper. Place three drops of 1.0 M CuSO_4 solution at the top of the filter paper (at 12 o' clock). Put a strip of copper in contact with the CuSO_4 solution. Place three drops of 1.0 M $\text{Pb}(\text{NO}_3)_2$ solution on the right side of the filter paper (at 3 o' clock). Put a piece of lead in contact with the $\text{Pb}(\text{NO}_3)_2$ solution. Transfer three drops of 1.0 M AgNO_3 solution to the bottom of the filter

paper (at 6 o' clock). Put a piece of silver in contact with the AgNO_3 solution. Transfer three drops of 1.0 M ZnSO_4 solution to the left side of the filter paper (at 9 o' clock). Put a zinc strip in contact with the ZnSO_4 solution. Put two drops of 1.0 M NaNO_3 in the center of the filter paper to serve as the salt bridge. Draw a diagram of the filter paper and the placement of the solutions and the metal electrodes.

Turn the voltmeter on to the 2 volts DC range. Place the leads of the voltmeter successively on the Cu and Pb strips to measure the potentials of the Cu/Pb, Cu/Ag, Pb/Zn, and Ag/Zn standard voltaic cells, respectively. If you get a negative potential, switch the leads on the metals so that you get a positive potential. The metal which you connect to the black lead of the voltmeter to get a positive reading is the anode electrode of the cell. Record the potentials for each of the cells on the data sheet, and compare them to the literature values.

II. Nonstandard Cells

If one or more of the components of a voltaic cell is not in its standard state, the cell is not a standard cell. The potential that is expected to be generated in such a cell can be calculated from the Nernst equation, $E = E^\circ - \frac{(0.0592)}{n} \log Q$.

In this equation, E° is the standard cell potential, E is the cell potential, n is the number of electrons transferred in the reaction, and Q is the reaction quotient.

Procedure:

Obtain a filter paper disk and put three drops of 1.0 M AgNO_3 solution. Transfer three drops of 0.010 M CuSO_4 to the right side of the filter paper (at 3 o' clock). Set a strip of copper on the CuSO_4 solution. Place three drops of 0.010 M $\text{Pb}(\text{NO}_3)_2$ solution at the bottom of the filter paper (at 6 o' clock). Put a piece of lead in contact with the $\text{Pb}(\text{NO}_3)_2$ solution. Put two drops of 1.0 M NaNO_3 solution in the center of the filter paper. Press the leads of the voltmeter onto the metal strips and measure the potentials of the Ag/Cu and Ag/Pb nonstandard voltaic cells. Record the values of the potentials on the data sheet. Calculate values for the potentials expected using the Nernst equation.

III. Concentration Cell

A concentration cell is a voltaic cell in which the anode and cathode compartments are the same except that the concentrations of species present are different. For ex., silver concentration contains a silver electrode in contact with a silver nitrate solution of a certain concentration in one compartment, and a silver electrode in contact with a silver nitrate solution of a different concentration in the other compartment. The half-cell potential generated in each of the half-cells is given by the Nernst equation,

$$E = E^\circ - \frac{(0.0592)}{n} \log [\text{Ag}^+]$$

The potential of the concentration cell is the difference between the two half-cell potentials $E^\circ_{\text{Ag}} - (.0592/1) \log [\text{Ag}^+]_{\text{conc.}} - (E^\circ_{\text{Ag}} - (.0592/1) \log [\text{Ag}^+]_{\text{dilute}})$ OR $E^\circ_{\text{cell}} - (.0592 \log [\text{Ag}^+]_{\text{conc.}} / [\text{Ag}^+]_{\text{dilute}})$

Procedure: Use a disk of filter paper, and put three drops of 1.0 M silver nitrate on it. Place a piece of silver in contact with the 1.0 M silver nitration solution. Transfer three drops or 0.010 silver nitrate to a different spot on the filter paper. Put a piece of Ag on the 0.010 M silver nitrate solution. Add 2 drops of 1.0 M sodium nitrate between the other two solutions. Press the leads of the voltmeter against the 2 silver strips, and measure the potential of the cell. Record the value of the potential on the data sheet and calculate the expected values of the potential from the Nernst Equation.

Data Sheet: Standard Cells

Voltaic Cell	Experimental Potential (V)	Literature Value (V)
$\text{Pb(s)} \text{Pb}^{+2}(1.0\text{M}) \text{Cu}^{+2}(1.0\text{M}) \text{Cu(s)}$		0.47 V
$\text{Cu(s)} \text{Cu}^{+2}(1.0\text{M}) \text{Ag}^{+1}(1.0\text{M}) \text{Ag(s)}$		0.46 V
$\text{Zn(s)} \text{Zn}^{+2}(1.0\text{M}) \text{Cu}^{+2}(1.0\text{M}) \text{Cu(s)}$		1.10 V
$\text{Pb(s)} \text{Pb}^{+2}(1.0\text{M}) \text{Ag}^{+1}(1.0\text{M}) \text{Ag(s)}$		0.93 V
$\text{Zn(s)} \text{Zn}^{+2}(1.0\text{M}) \text{Pb}^{+2}(1.0\text{M}) \text{Pb(s)}$		0.63 V
$\text{Zn(s)} \text{Zn}^{+2}(1.0\text{M}) \text{Ag}^{+1}(1.0\text{M}) \text{Ag(s)}$		1.56 V

Nonstandard Cells

Voltaic Cell	Experimental Potential (Volts)	Literature Value (Volts)
$\text{Cu(s)} \text{Cu}^{+2}(0.010\text{M}) \text{Ag}^{+1}(1.0\text{M}) \text{Ag(s)}$		0.52 V
$\text{Pb(s)} \text{Pb}^{+2}(0.010\text{M}) \text{Ag}^{+1}(1.0\text{M}) \text{Ag(s)}$		0.99 V

Concentration Cells

Voltaic Cell	Experimental Potential (V)	Literature Value (V)
$\text{Ag(s)} \text{Ag}^{+}(1.0\text{M}) \text{Ag}^{+}(0.010\text{M}) \text{Ag(s)}$		0.118 V

Discussion:

1. Why would you expect no potential to be generated between two half-cells in this experiment until the sodium nitrate solution migrates to a point where it overlaps both of the half cell solutions?
2. Discuss some possible sources of error that could account for the differences in the experimental values of the cell potentials you obtained and the literature values.

Resources:

Conclusion: