Electrochemistry: batteries, thermodynamics, and cell potentials

You are encouraged to read the following sections in Tro (3rd ed.) to prepare for this experiment: Sec 18.3 – 18.5 covering electrochemical cells and standard reduction voltages, and Sec 18.8 on electrolysis.

Electrochemistry (oxidation/reduction or redox) is a branch of thermodynamics involving reactions in which electrons are transferred from one reactant to the other. The *potential* (*E*) for these electrons to be transferred is measured in volts (1 V = 1 J/C). A volt represents two important thermodynamic concepts: 1) the likelihood that the electrons will be transferred and 2) the amount of energy transferred per amount of charge that moves. The concepts of moving electrons and energy are central to many processes including solar panels and photosynthesis. Sunlight striking a panel forces electrons to move. This charge movement is the electrical current the panel supplies. Sunlight striking a leaf promotes electrons in chlorophyll to become "high energy electrons." These high energy electrons have great potential to be transferred and consequently sufficient energy to do the difficult work of splitting water to make the oxygen that we breathe.

Standard cell potentials (Textbook, section 18.4)
Typical of thermodynamics, *E* is a state function, so that *E* values represent the difference in potential between two states, reactants and products. Because redox reactions can be broken into two separate oxidation and reduction half-reactions, this allows potentials for individual half reactions to be measured relative to any properly defined standard. Thermodynamic standards are usually chosen for their moderate energetics (neither extremely reactive or unreactive) and for the common nature of the reagents involved. In this way the standard hydrogen electron (SHE) is the established thermodynamic standard such that the following half reaction has a defined standard voltage of zero:

$$\text{SHE:} \quad 2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^o = 0.00 \text{ V} \qquad ([H^+] = 1 \text{ M}, P(H_2) = 1 \text{ atm}, T = 25 \text{ }^oC)$$

Take a minute to review the table of standard reduction potentials (Table 18.1, p 873) and see that SHE is in the middle of the listed values (moderate energetics), and that protons (H^+) are a common component of several of the half reactions listed.

The conditions necessary for the SHE half-reaction are not always practical; tanks of flammable hydrogen gas are needed. Therefore, it is often the case that another half reaction is used as a surrogate for SHE. Any stable half reaction will do for this purpose. In this experiment, the nickel (II) reduction half reaction will serve as the standard, so that all other half reactions will have their voltage measured against $Ni(s)|Ni^{2+}(aq)$. The following two tables demonstrate the arbitrary choice of standard. On the left, SHE is the standard. On the right $Ag^+(aq)|Ag(s)$ is the standard. Note that while the absolute *E* values may change, the *relative ordering and relative E values remain fixed*, a consequence of the inherent reactivity of the elements involved. The measured potential (relative to the surrogate) can be corrected to the value relative to SHE.

Half Reaction	E (V)
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80

Half Reaction	E (V)
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-1.20
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	-0.80
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0

Temperature dependence of *E* (Textbook, section 18.5)
Equation 1 reminds us that *E* values, like free energies, are temperature dependent. You may remember that measuring ΔG as a function of temperature allowed the determination of enthalpy and entropy values for the KNO_3 solubility. Equation 1 represents key thermodynamic relationships at a given temperature.

$$\Delta G^o = -nFE^o = \Delta H^o - T\Delta S^o \qquad\qquad [1]$$

At two different temperatures one obtains

$$-nFE_{cold} = \Delta H^o - T_{cold}\Delta S^o \qquad\qquad -nFE_{hot}{}^o = \Delta H^o - T_{hot}\Delta S^o \qquad\qquad [2]$$

Solving each expression in [2] for ΔH^o (assuming enthalpy nearly T independent) one obtains

$$T_{cold}\Delta S^o - nFE_{cold} = \Delta H^o = T_{hot}\Delta S^o - nFE_{hot} \qquad\qquad [3]$$

Equation [3] rearranges to give

$$[T_{cold} - T_{hot}]\Delta S^o = nFE_{cold} - nFE_{hot} \qquad\qquad \text{and}$$

$$\Delta S^o = \frac{nF[E_{cold} - E_{hot}]}{[T_{cold} - T_{hot}]} \qquad\qquad [4]$$

Expression [4] indicates that ΔS^o can be determined from measuring E at two different temperatures. One can then use this entropy change to solve for ΔH^o using either expression in Equation [2].

Measuring voltages using our voltmeters
Consider the Cd/Ni reaction shown below and the two component half reactions.

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad\qquad E(Cd^{2+}|Cd))$$
$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^- \qquad\qquad E(Ni|Ni^{2+})$$

$$\overline{Cd^{2+}(aq) + Ni(s) \rightarrow Cd(s) + Ni^{2+}(aq) \qquad\qquad E_{total} = E(Cd^{2+}|Cd) + E(Ni|Ni^{2+})}$$
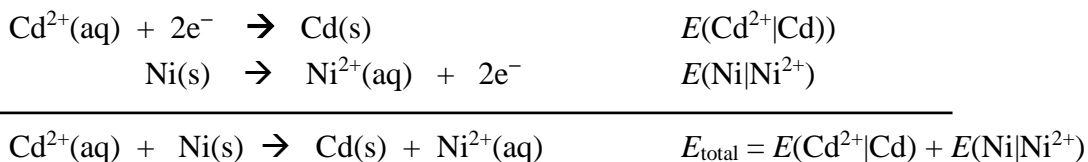
E_{total} will be the value measured on the voltmeter display if the cadmium is connected to the cathode of the meter (reduction) and the nickel is connected to the anode of the meter (oxidation). If the nickel half cell is assigned as the standard for the day, this makes $E(Ni) = 0$ for that measurement so that the meter reading becomes $E(Cd)$ ($E_{total} = E(Cd) + 0$). If Cd is connected to the cathode, this reading is therefore the $Cd^{2+}(aq)|Cd(s)$ reduction voltage. See the images of our volt meters on the next page identifying their anode and cathode connections.

If the meter connections are reversed, the same potential is measured but with the opposite sign, because now the system would be equipped to observe E for the reverse reaction

$$Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+}(aq) + Ni(s)$$
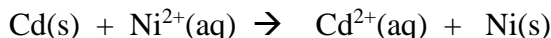
Electrolysis: forcing nonspontaneous redox processes to occur (Textbook, section 18.8)
Reactant favored processes (ΔG + or E -) can be forced to occur with an external source of energy like a wall outlet or a battery. A schematic of a battery is shown at right. A wire connecting the terminals allows the spontaneous flow of electrons from the anode of the battery (-) to the cathode (+). This setup shorts out the battery, discharging its energy, and no useful work is done. If this wire is severed and each end connected to graphite electrodes, the system is now equipped to force a non-spontaneous electrolysis reaction to occur (far right). The battery remains the driving force for this process, but now the anode of the battery can force electrons to be consumed (forced reduction) and the battery's cathode can forcibly remove electrons (forced oxidation) in the electrolysis portion.
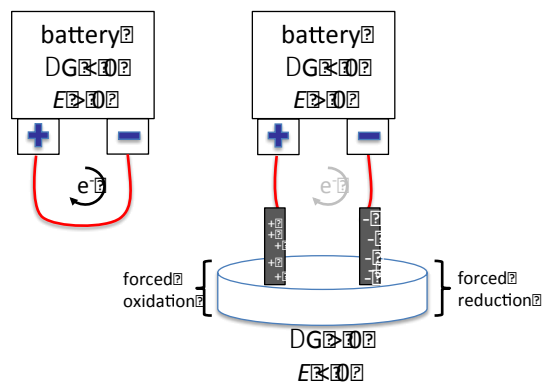
You will use a 9 V battery as an energy source and will electrolyze KI(aq) in this experiment.

Table 1. Materials to be used in this experiment

Metal ion solutions	Metals	Other solutions	Other equipment
0.01 M $NiSO_4(aq)$ 0.01 M $CuSO_4(aq)$ 0.01 M $ZnCl_2(aq)$ 0.5 M $KNO_3(aq)$ shared sat'd $K_2Cr_2O_7(aq)$ (2 drops)	strips of Ni Cu Zn	isopropanol(aq) (10 drops) 0.1 M HCl(aq) (1 drop) 0.1 M KI(aq) phenolphthalein indicator	voltmeters with alligator leads ice bath two graphite electrodes 9 V battery at least three 50 mL beakers

Safety
- Wear departmentally approved eyewear while doing this experiment
- Metal ion and acid solutions are caustic irritants. Handle with care and clean up spills promptly.
- Dichromate ion is a cancer suspect. Use only necessary amounts and dispose of waste accordingly.
- Isopropanol and acetone are both flammable liquids. Do not use open flames.

General procedural notes:

1. Salt bridges will be made using filter paper cut in strips that have been soaked in 0.5 M $KNO_3(aq)$. For convenience, beakers of KNO_3 will be shared across a bench. Use a fresh salt bridge for each cell assembly. Old salt bridges can be discarded in the trash.

2. Metal surfaces should be polished with steel wool or similar mild abrasive to ensure the metal and not layers of metal oxide are in contact with salt solutions.

3. We have two different style voltmeters for use in today's experiment. Use the plug connectors to interface with the meters. For connections to metal half-cells, use alligator clip leads to connect from the meter cables to the metal of interest (make sure there is a good connection with the alligator clip leads).
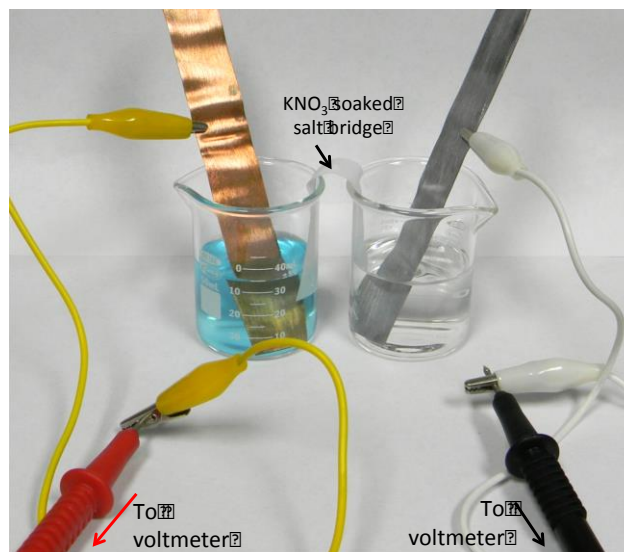

$V \overline{}$

Use the Volts DC setting in the 2 V range.

Be sure and TURN OFF the meters when you are finished.

COM = anode terminal

V = cathode terminal

KNO_3 soaked salt bridge

To voltmeter

To voltmeter

Procedural Steps, Results and Observations

I. Measuring standard reduction potentials for a voltaic cell

Fill three different 50 mL beakers one with 20 mL 0.01 M Cu^{2+}, one with 20 mL of 0.01 M Ni^{2+}, and the third with 20 mL of Zn^{2+} solution. Beaker markings are sufficient precision here. Place a piece of each metal in its respective metal ion solution. Be careful to prevent beakers tipping and spilling. Connect the nickel electrode to the anode (black or – for a voltaic cell). Connect the copper cell and the zinc cell each in turn to the cathode (red or + for a voltaic cell) of the voltmeter. Close the circuit between the nickel cell and the cell being studied by draping a salt bridge between the two beaker cells being tested. Save each metal/ion solution half cell for the next part of the procedure. Used salt bridges can be discarded in the trash.

I.1 Measured potentials relative to $Ni^{2+}|Ni$

Reduction Half Reaction	E(V)
$Ni^{2+}(aq)|Ni(s)$	0
$Cu^{2+}(aq)|Cu(s)$	
$Zn^{2+}(aq)|Zn(s)$	

I.2 Corrected potentials relative to SHE

Reduction Half Reaction	E^{o}(V)
$Ni^{2+}(aq)|Ni(s)$	-0.23
$Cu^{2+}(aq)|Cu(s)$	
$Zn^{2+}(aq)|Zn(s)$	

Use your measured half-cell potentials from Table I.1 above to determine the overall potential for the reaction: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$. Show your work.

II. Temperature dependent potentials

Record the potential of a cell at room temperature made using your Zn & Cu half cells from part I. Do this with the copper connected to the cathode (red or + for a voltaic cell) and Zn to the anode (black or – for a voltaic cell). Record the room temperature using a thermometer.   Next carefully place your $Zn(s)| Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$ assembly into a large ice bath. Add a fresh salt bridge across the two cells. Place a thermometer in the bath. Allow the system to sit in the bath long enough to reach thermal equilibrium. Record the stable cold voltage of this cell and the cold temperature of this cell.

Temp. (^{o}C)	Temp. (K)	E(V)
room temp		

(a) Consider the cell-voltmeter connections Cu (cathode) and Zn (anode). Write the corresponding overall reaction being monitored by the voltmeter in this part of the experiment.

(b) Determine the entropy change for this reaction using Equation 4. Show your work and give units.

$$\Delta S^{o} = \text{_____}$$

(c) Determine the enthalpy change for this reaction using Equation 3. Show your work and give units.

$$\Delta H^{o} = \text{_____}$$

III. Reaction of an alcohol with dichromate ion

Place 10 drops of rubbing alcohol (aqueous isopropyl alcohol) into a small test tube. Add to this mixture, 2 drops of saturated $K_2Cr_2O_7(aq)$.

(a) Note initial colors of reagent mixtures and any immediate color changes that occur when the dichromate contacts the alcohol.

(b) Add 1 drop of 0.1 M HCl to your test-tube mixture. Gently shake the mixture (without spilling) to ensure the contents are mixed. Note the time that the acid was added and monitor the mixture. Record any observations and evidence of chemical changes. Dispose of this reaction mixture in the container identified by your instructor.

IV. Electrolysis of KI(aq)

Fill a plastic petri dish approximately half-way with KI(aq). Add three drops of phenolphthalein indicator. Gently swirl the dish (without spilling) to ensure the indicator is thoroughly dispersed. Place the dish on a piece of white paper to improve color contrast for your observations. Connect using alligator leads: one graphite electrode to the + battery terminal (serving as the anode in an electrolysis) and a second to the – battery terminal (serving as the cathode in an electrolysis). Without allowing them touch, place the (+) connected electrode and (-) connected electrode into the petri-dish solution.

(a) At the (+) electrode, record any observations and evidence of chemical changes.

(b) At the (-) electrode, record any observations and evidence of chemical changes.

(c) After a minute of electrolysis, remove the (+) electrode and slide it along a piece of white paper. What did you observe?

(d) Test the same with the (-) electrode. Contrast your observations with this electrode to the observation above in (c).

When finished, this solution may be washed down the drain with followed by plenty of water. Wash your graphite electrodes with soap and water to remove residual products coating their surfaces.

Postlab Questions

1. The table below summarizes voltages relative to SHE (from Table 18.1). These same potentials can be corrected to their value relative to the saturated calomel electrode (SCE). SCE has a voltage that is +0.244 V vs SHE at 25 °C. Complete the left-hand column of the table by giving the potentials for each half reaction corrected relative to SCE.

Half Reaction	E (V vs SCE)	E^o (V vs SHE)
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$		-0.45
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$		0.34
$Ag^+(aq) + e^- \rightarrow Ag(s)$		0.80

2. The image at right shows one of our voltmeters connected to a typical AA battery. One would use this to test the amount of life left in a battery.

(a) What should the meter read (???) with the connection shown and a new battery?

(b) What should the meter read (???) if the connections were reversed?

(c) Identify two reasons that batteries go dead, forcing you to buy new or recharge.

(d) Which of your reasons in (c) is remedied when batteries are recharged?

3. Thermodynamics of the copper/zinc cell

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

(a) Use the standard thermodynamic values from the table at right to determine the standard entropy change for the reaction above.

Species	ΔH_f^o (kJ/mol)	S^o (J/mol·K)
Cu(s)	0	33
Cu^{2+}(aq)	64.9	-98
Zn(s)	0	42
Zn^{2+}(aq)	153.4	109

(b) How does your value in (a) compare to your experimentally determined value in Section II?

(c) Use the standard thermodynamic values from the table to determine the standard enthalpy change for the reaction above.

(d) How does your value in (c) compare to your experimentally determined value in Section II?

(e) Is this reaction predicted to be product or reactant favored under standard conditions? Did your experimentally determined voltage support this? Explain.

4. For Experiment III, the reaction involves the conversion of dichromate ion to chromium(III) aqueous. At the same time, isopropyl alcohol (C_3H_8O) is converted to acetone (C_3H_6O).

(a) Write the balanced half reaction (acidic conditions) involving dichromate ion. Is this process oxidation or reduction?

(b) Write the balanced half reaction (acidic conditions) involving isopropyl alcohol. Is this process oxidation or reduction?

(c) Combine your two half reactions from (a) and (b) to arrive at the overall reaction. Is this reaction predicted to more or less product favored at increasingly lower pH?

(d) The image it right shows a commercial product one can exhale into to test one's blood alcohol (ethyl alcohol) level. Suggest a reason that the crystals in the package are initially yellow.

5. These questions deal with the electrolysis of KI(aq). Consult Table 18.1 for relevant half reactions.

(a) Consider your observations at the (+) electrode. Write the balanced half-reaction responsible for these observations, give the E^o value (from Table 18.1) for this half reaction. Explain how your observations are consistent with this half reaction.

(b) Consider your observations at the (-) electrode. Write the balanced half-reaction responsible for these observations, give the E^o value for this half reaction. Explain how your observations are consistent with this half reaction.

(c) Combine your two half reactions to arrive at the overall electrolysis occurring. Is this process predicted to be more or less product favored at lower pH?

Pre-lab Questions

1. Work carefully Examples 18.4, 5, and 6 from your lecture text.

2. The table at right is similar to Table 18.1 in that it tabulates standard reduction voltages of half reactions, but in this case the half reactions involve organic molecules important in biochemistry. Note here that the standard conditions are biochemically standard conditions ($E^{o'}$) where T = 25 °C but $[H^+] = 10^{-7}$ M (much less acidic than the $[H^+]$ = 1 M in Table 18.1).

(a) Identify the strongest reducing agent from this table.

(b) Identify the strongest oxidizing agent from this table.

(c) Compare the E^o for the oxygen half reaction to the same half reaction in Table 18.1. Under which conditions, high pH or low pH is oxygen a stronger oxidizing agent?

Oxidized form		Reduced form	$E^{o'}$(V)
Glutahione (oxidized) + 2e⁻	→	Glutathione (reduced)	-0.23
Fumarate + 2e⁻	→	Succinate	0.03
Ubiquinone (oxidized) + 2e⁻	→	Ubiquinone (reduced)	0.10
½ O₂ + 2H⁺ + + 2e⁻	→	H₂O	0.82

3. When you are recharging your cell-phone battery, is this an example of a nonspontaneous or a spontaneous redox reaction? Explain.

4. Use information from Table 18.1 and Appendix II.B to answer the following questions dealing with the reaction:

$$Al(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + \tfrac{3}{2}H_2(g)$$
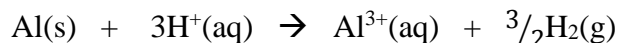
(a) Use half-cell potentials from Table 18.1 to determine the standard potential for this reaction. Is aluminum predicted to react with acids under standard conditions?

(b) Use information from Appendix II.B to determine the standard free energy change for the reaction above.

(c) Now clear fractions for this reaction to give $2Al(s)$ + $6H^+(aq)$ → $2Al^{3+}(aq)$ + $3H_2(g)$.

i) Determine ΔG^o for this altered version of the reaction using your answer in (b).

ii) Now calculate E^o for this altered reaction using your ΔG^o and the relation between these two thermodynamic quantities.

(d) When one multiplies a reaction by a factor to clear fractions what happens to…

      i) …the moles of electrons transferred?

      ii) …the grams of reactant(s) consumed?

      iii) …the moles of product(s) produced?

      iv) …the free energy change for the reaction?

      v) …the potential for the reaction?