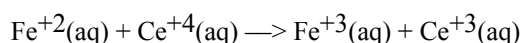
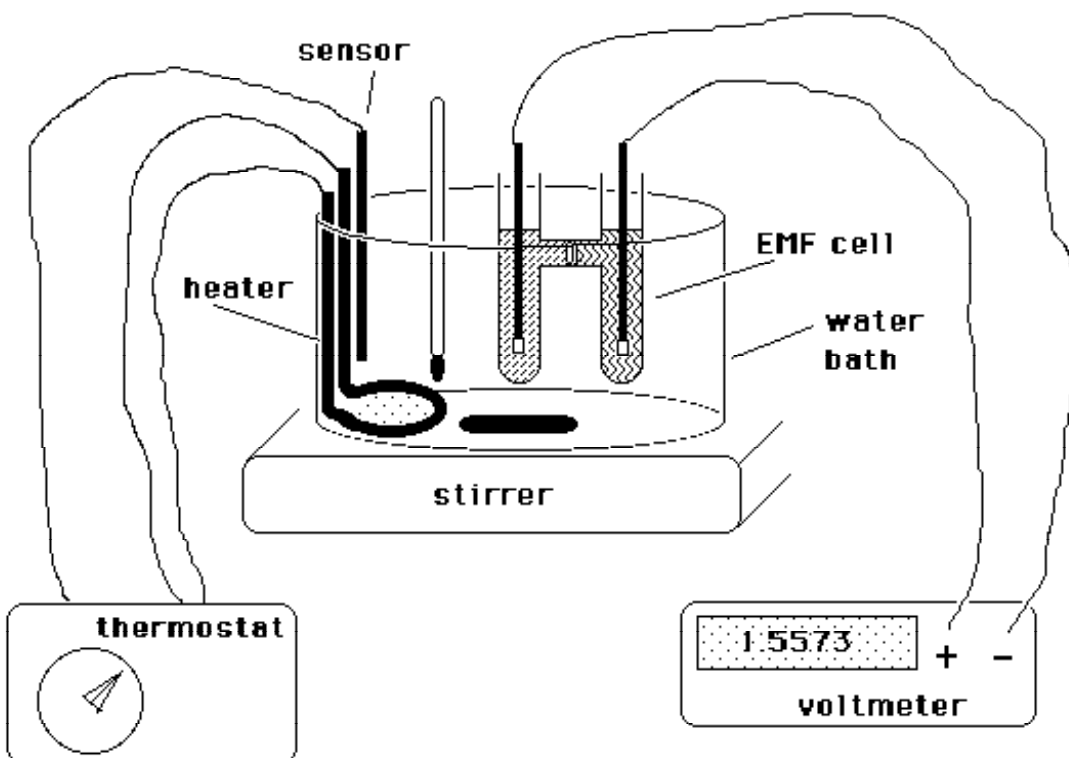


Part I. In this experiment you will determine the cell potential at several temperatures for the reaction:



The standard value E° can be obtained at a given temperature from the Nernst equation. ΔG° can be then be obtained from: $\Delta G^\circ = -nFE^\circ$. From the temperature coefficient of the standard cell potential, it is possible, using a modified form of the Gibbs-Helmholtz equation, to calculate the entropy change, ΔS° (see below), and the standard enthalpy change, Then ΔH° can be obtained from: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.



Two special pieces of apparatus are needed: a water bath which can be maintained at a constant temperature and adjusted to various temperatures, and a device for high-precision measurement of the electrical potential. The usual method for the latter is to use a potentiometer circuit, which uses an adjustable voltage to counteract or "balance" the voltage of the electrochemical cell system. Under these conditions, the chemical reaction is "reversible" because a slight shift in the opposing voltage from the potentiometer will allow electron transfer either as written or in the reverse direction. (This assumes that the electrode electron transfer processes are themselves reversible.) When the (measured) potentiometer voltage exactly equals and balances the cell voltage, the system is then reversible, and no current flows. Modern digital voltmeters also have a high enough resistance (impedance) to measure the cell voltage under negligible current flow conditions, so that for our purposes, we will assume that such a voltmeter will measure the "reversible" voltage. The error introduced by this assumption is negligible in cases where one is measuring voltages to 4 decimal places. It can become significant for more precise measurements. In this experiment, voltages will be measured to 4 decimal places with a high-impedance voltmeter.

A special "H" cell will be available in the laboratory. It contains a fritted glass disc to separate the two half cells. The liquid levels on each side of the cell should be the same; otherwise, hydrostatic pressure will gradually force some mixing of the two half-cell contents. A fresh cell system should be set up as described below, and then data should be collected at a series of temperatures between about 25°C and 45°C all in one day. It will take about 2 hours to obtain the necessary readings once the system is set up.

The following stock solutions are required (each needs to be made up in 0.500 M H₂SO₄): 0.0100 M Ce(SO₄)₂, 0.0100 M FeSO₄, 0.0050 M Ce₂(SO₄)₃, and 0.0050 M Fe₂(SO₄)₃. The solutions are to be made up quantitatively, but even with careful weighing and volumetric work, there are some problems of instability and the reagents are of uncertain purity. *Time saving hint: Make up a 500 mL solution of 0.500 M sulfuric acid. Then weigh out the required amounts of both the ceric and cerous salts into a 100 mL volumetric flask. Dilute the mixture to 100 mL using the 0.500 M sulfuric solution. Carry out the same procedure with the ferric and ferrous salts. It would be a good idea to deoxygenate the remaining sulfuric acid solution before using it in this second step in order to minimize oxidation of dissolved ferrous ion.* This method of preparation makes the entire solution needed for each half cell. 100 mL will be plenty of material because the H cell requires no more than 20 mL for rinsing and filling each cell leg. Make sure the H cell is clean and dry. Also make sure you have Pt electrodes ready to mount in the two cells. The electrodes should be clean, shiny platinum, and they should be stored in the appropriate half-cell solutions between experiments. Pour the appropriate solutions into the two sides of the cell and adjust the volume to produce equal heights on each side.

Adjust the constant temperature bath to the lowest temperature which can be maintained (probably around 23°C). Clamp the cell in place in the bath. Be sure there is good circulation in the bath and that the cell is in good thermal contact with the bath. Start taking readings of the cell, recorded to 0.1 mV, and continue until the cell has reached thermal equilibrium and the potential is stable for at least 10 minutes. Record all cell potentials and times directly in your notebook. Also record the temperature (to 0.01°C). When you are satisfied that you have a reliable potential for the cell, raise the bath temperature approximately 4°C and determine the cell potential in the same way as before. Continue to a maximum T of about 45°C. Note that you do not need to spend time getting the temperatures adjusted exactly to the desired values. Set the thermoregulator approximately, then record the actual temperature.

Before proceeding further, it is necessary to calculate E° from each of the measured E values. Use the Nernst equation. Include activity coefficients calculated from the Davies equation (Table attached) or the extended Debye-Huckel formula. (You will need to determine the ionic strength of each solution. Under the conditions of this experiment, H₂SO₄ dissociates into HSO₄⁻ and H⁺, but HSO₄⁻ (bisulfate or hydrogen sulfate) does not undergo significant further dissociation. You can use this information in calculating ionic strengths, and if you like, you can readily check the assumption that bisulfate does not dissociate significantly.)

Plot E° versus temperature and obtain the slope. You will probably want to use a computer program to do this, although hand-drawn graphs on good graph paper also give excellent results. If you do hand-drawn graphs, be sure to choose coordinate values which spread the data out both directions on the graph paper. Please note that for error analysis, you want both the equation of the curve and the uncertainty estimates for the curve parameters. A program like StatView does not provide these parameters, although it will give a good slope and intercept and a nice-looking graph. For a better analysis which includes error estimates, use the LSquare EXCEL program on the Macs. If the line is curved at all, note this in the report, but use the linear analysis procedure. From the least-squares line, calculate the potential and

ΔG° at 25°C. Then calculate ΔS° using the relationship: $\Delta S^\circ = nF \left. \frac{\partial E^\circ}{\partial T} \right)_p$ and finally, calculate ΔH° . (You might also

try plotting E°/T vs. 1/T. The slope of this graph equals - $\Delta H^\circ/nF$ (see derivation at the end of this document). Does one method have an advantage over the other? With good data, it works well to use both kinds of graphs.)

The discussion in the report should include:

1. The equations which relate E to ΔG , ΔH , and ΔS . Derive these relationships if you can.
2. Discussion with appropriate calculation of the importance of ideal vs. non-ideal effects. (What does application of the Davies or extended Debye-Huckel limiting equation to your conditions suggest about the importance of non-ideal effects, and about the likely validity of your non-ideal corrections?)
3. Discussion of the differences between standard values and actual values.
4. Comparison of your values with literature values where available.
5. Include a good graph of your data. Discuss the linearity or non-linearity of your results.

6. Error analysis: use the uncertainty in the slope to calculate an uncertainty in ΔS° . Use the uncertainty in slope and intercept to calculate the uncertainty in ΔG° at 25 °C. For ΔH° , you may use either the uncertainties in ΔG° and ΔS° to get the uncertainty, or the uncertainty in the slope of the E/T vs 1/T plot. (For error analysis, it is strongly recommended that you use a spreadsheet program such as EXCEL. Turn in a printout of the spreadsheet with the report.)
7. Turn in the "activity problem" near the end of this document.

Helmholtz equation and voltage, and the E/T vs. 1/T plot:

The Helmholtz equation is $\frac{\partial(\Delta G/T)}{\partial T} = -\frac{\Delta H}{T^2}$: where the " ∂ " implies a derivative under constant pressure conditions.

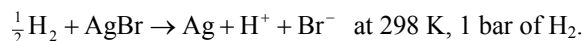
Substituting $\Delta G = -nFE$, we get: $\frac{\partial(E/T)}{\partial T} = \frac{\Delta H}{nFT^2}$ which may be rearranged to: $\partial(E/T) = \frac{\Delta H}{nF} \frac{\partial T}{T^2} = -\frac{\Delta H}{nF} \partial(1/T)$

With leads to: $\frac{\partial(E/T)}{\partial(1/T)} = -\frac{\Delta H}{nF}$

This is the rationale for plotting E/T vs 1/T to obtain a value of ΔH from the slope.

Part II. Using voltage data to test Debye-Huckel (DH) ideas.

In the Ce/Fe lab, the ionic strengths are rather high and there are unknown "junction potentials" across the salt bridge. This makes it impractical to use this cell for testing theoretical ideas about ion activity. However, much work has done with carefully selected cell systems under very dilute conditions to establish both the validity of Debye-Huckel models and the E° values tabulated in many sources. As an example, we will look at the analysis of the the reaction:



The Nernst equation at 25 °C, including activity coefficients, is:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT \ln 10}{nF} \log_{10} Q = E^\circ - \frac{RT \ln 10}{1F} \log_{10} \frac{a_{\text{H}^+} a_{\text{Br}^-}}{P_{\text{H}_2}} = E^\circ - 0.05916 \log_{10} \frac{a_{\text{H}^+} a_{\text{Br}^-}}{P_{\text{H}_2}}$$

(The base 10 log form is the version commonly found in most chemistry, biochemistry and physiology textbooks outside physical chemistry.)

Using $a = \gamma m$ and $\log \gamma_i = \frac{-0.509 z_i^2 \sqrt{\mu}}{1 + \alpha_i \sqrt{\mu} / 305}$ (Debye-Huckel) with ionic strength $\mu = \frac{1}{2} \sum_{\text{all ions}} m_i Z_i^2 \approx \frac{1}{2} \sum_{\text{all ions}} M_i Z_i^2$ we

have:

$$E = E^\circ - 0.05916 \log_{10} a_{\text{H}^+} a_{\text{Br}^-} = E^\circ - 0.05916 \log_{10} \gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{Br}^-} m_{\text{Br}^-} = E^\circ - 0.05916 \log_{10} m_{\text{HBr}}^2 - 0.05916 \log_{10} \gamma_{\text{H}^+} \gamma_{\text{Br}^-}$$

At very low ionic strengths, the denominator of the DH formula is close to 1 and the formula approaches the DH

Limiting Law: $\log \gamma_i = \frac{-0.509 z_i^2 \sqrt{\mu}}{1 + \alpha_i \sqrt{\mu} / 305} \approx -0.509 z_i^2 \sqrt{\mu}$ Note that since H^+ and Br^- have the same value of Z^2 , they will

both have the same activity coefficient value under very dilute conditions. This is often called the "mean activity coefficient" and will be given by: $\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{\mu} + bm$ where the bm term is a small empirical correction for hydrated ion volume effects.

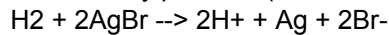
Note also that for a 1:1 electrolyte such as HBr, the ionic strength $\mu = \frac{1}{2}(m_{H^+} + m_{Cl^-}) = m_{HCl}$

Using these last expressions in the formula for E above, we have:

$$E = E^\circ - 0.1183 \log_{10} m_{HBr} - 0.1183 \log_{10} \gamma_{\pm} = E^\circ - 0.1183 \log_{10} m_{HBr} + 0.1183(0.509)(1)\sqrt{m} - 0.1183bm$$

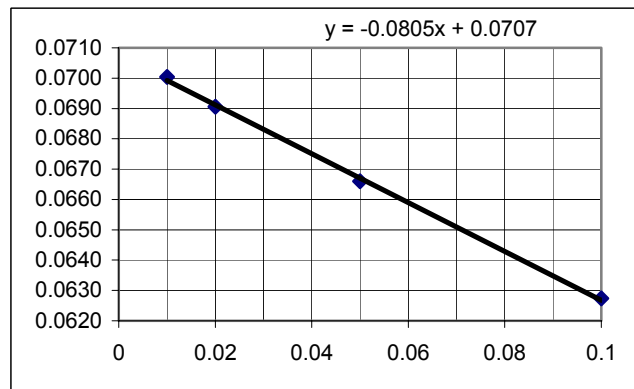
Rearranging, we have: $E + 0.1183 \log_{10} m_{HBr} - .0602m^{1/2} = E' = E^\circ - 0.1183bm$ This equation is used with the following data to make the plot shown:

EMF activity problem (7.23 from Daniels and Alberty)



| m | E exp | E' |
|------|--------|--------|
| 0.01 | 0.3127 | 0.0700 |
| 0.02 | 0.2786 | 0.0691 |
| 0.05 | 0.2340 | 0.0666 |
| 0.1 | 0.2001 | 0.0627 |

intercept = $E^\circ = 0.0707$ V



Because the H/H⁺ half reaction standard value is set to 0.000 by definition, the resulting E° is the negative of the standard reduction voltage for Ag/AgBr. This is how most of the tabulated values have been determined!

Finally if you sketch a standard picture of this battery with a salt bridge, you can then see that the salt bridge is not needed! With no salt bridge, the measured voltages are due solely to the chemical reactions. If salt bridges are required, there are always small voltage changes across the solution/salt bridge boundaries and these prevent making precise measurements of standard values.

Problem (Turn this in as part of this lab)

Here is some data for the similar reaction: $\frac{1}{2}H_2 + AgCl \rightarrow Ag + H^+ + Cl^-$

| | | | | | |
|-----------|---------|---------|----------|---------|---------|
| m HCl | 0.00322 | 0.00562 | 0.009138 | 0.02563 | 0.1238 |
| E (volts) | 0.52053 | 0.49257 | 0.4686 | 0.41824 | 0.34199 |

- sketch a picture of the emf cell that corresponds to this reaction. Explain why a salt bridge is unnecessary for this system.
- Using the DH Limiting Law, make a plot that can be used to determine the E° value of this system under standard conditions. (very similar to the example!)
- Compare the standard voltage value with that found in a typical textbook source (give the reference!)

Davies equation and values: $\log_{10} \gamma_z = Z^2 \left(\frac{-0.509\sqrt{\mu}}{1+\sqrt{\mu}} + 0.15\mu \right)$

Where μ = ionic strength and γ_z = activity coefficient for an ion of charge Z

Davies equation results for various charges

| Ionic Strength (μ) | γ for Z = ± 1 | γ for Z = ± 2 | γ for Z = ± 3 | γ for Z = ± 4 |
|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 0.00001 | 0.9963 | 0.9853 | 0.9673 | 0.9427 |
| 0.00002 | 0.9948 | 0.9794 | 0.9542 | 0.9200 |
| 0.00003 | 0.9936 | 0.9748 | 0.9442 | 0.9030 |
| 0.00004 | 0.9927 | 0.9710 | 0.9360 | 0.8890 |
| 0.00005 | 0.9918 | 0.9677 | 0.9288 | 0.8769 |
| 0.00006 | 0.9911 | 0.9647 | 0.9223 | 0.8661 |
| 0.00007 | 0.9903 | 0.9619 | 0.9164 | 0.8562 |
| 0.00008 | 0.9897 | 0.9594 | 0.9110 | 0.8472 |
| 0.00009 | 0.9891 | 0.9570 | 0.9059 | 0.8388 |
| 0.0001 | 0.9885 | 0.9548 | 0.9011 | 0.8310 |
| 0.0002 | 0.9839 | 0.9370 | 0.8638 | 0.7707 |
| 0.0003 | 0.9803 | 0.9237 | 0.8364 | 0.7279 |
| 0.0004 | 0.9774 | 0.9127 | 0.8142 | 0.6939 |
| 0.0005 | 0.9749 | 0.9032 | 0.7952 | 0.6654 |
| 0.0006 | 0.9726 | 0.8947 | 0.7785 | 0.6408 |
| 0.0007 | 0.9705 | 0.8870 | 0.7636 | 0.6191 |
| 0.0008 | 0.9685 | 0.8800 | 0.7500 | 0.5997 |
| 0.0009 | 0.9667 | 0.8735 | 0.7375 | 0.5820 |
| 0.001 | 0.9650 | 0.8673 | 0.7260 | 0.5659 |
| 0.002 | 0.9517 | 0.8204 | 0.6406 | 0.4531 |
| 0.003 | 0.9419 | 0.7872 | 0.5837 | 0.3840 |
| 0.004 | 0.9339 | 0.7608 | 0.5406 | 0.3351 |
| 0.005 | 0.9271 | 0.7388 | 0.5061 | 0.2980 |
| 0.006 | 0.9211 | 0.7198 | 0.4773 | 0.2685 |
| 0.007 | 0.9157 | 0.7031 | 0.4527 | 0.2444 |
| 0.008 | 0.9108 | 0.6881 | 0.4312 | 0.2242 |
| 0.009 | 0.9062 | 0.6745 | 0.4123 | 0.2070 |
| 0.01 | 0.9020 | 0.6621 | 0.3954 | 0.1921 |
| 0.02 | 0.8708 | 0.5751 | 0.2880 | 0.1094 |
| 0.03 | 0.8499 | 0.5217 | 0.2313 | 0.0741 |
| 0.04 | 0.8340 | 0.4838 | 0.1952 | 0.0548 |
| 0.05 | 0.8213 | 0.4549 | 0.1700 | 0.0428 |
| 0.06 | 0.8107 | 0.4319 | 0.1512 | 0.0348 |
| 0.07 | 0.8017 | 0.4131 | 0.1368 | 0.0291 |
| 0.08 | 0.7939 | 0.3973 | 0.1253 | 0.0249 |
| 0.09 | 0.7871 | 0.3838 | 0.1160 | 0.0217 |
| 0.1 | 0.7811 | 0.3723 | 0.1082 | 0.0192 |
| 0.2 | 0.7460 | 0.3096 | 0.0715 | 0.0092 |
| 0.3 | 0.7326 | 0.2881 | 0.0608 | 0.0069 |