

Experiment 1A

Equilibrium Potentials Potential Steps Away from Equilibrium

Experiment Overview

In electrochemical systems, the first thing one always needs to know is the potential at which no current flows (*i.e.* the [open circuit potential](#) or the [equilibrium potential](#), where $I=0$). The equilibrium potential is analogous to the point on a map that says, "You Are Here." For an electrochemical system with a single reversible reaction, equilibrium potentials can be predicted accurately using the [Nernst Equation](#). Once the equilibrium potential is known, the effects of changing the potential can be predicted; if the potential of the electrode is set positive of the equilibrium potential then an oxidation reaction will occur on the electrode, whereas setting the electrode potential negative of equilibrium will cause a reduction reaction to occur. Whenever the potential of an electrode is changed, it takes time to reestablish equilibrium. Experiment 1A will allow you to assess the validity of the Nernst Equation at equilibrium, and the [Cottrell Equation](#) for the transient behavior of the system when the potential is stepped from equilibrium to a potential far from equilibrium.

Background Theory

Under ideal conditions when there is no current flow, the potential of an electrode is given by the [Nernst Equation](#)

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\prod_i a_i^{s_i} \right), \quad (1)$$

where E is the equilibrium potential measured relative to a particular reference electrode, E° is the standard state potential measured relative to the same reference electrode, $R=8.314$ J/mol-K, T is absolute temperature (K), n is the number of electrons transferred in reaction, $F=96486$ C/mol e^- , \prod_i is the product operator ($\prod_i a_i^{s_i} = a_1^{s_1} * a_2^{s_2} * a_3^{s_3} \dots$), a_i is the activity of species i ($=1$ for species in standard state and $\approx c_i$ for dilute ions in solution), and s_i is the stoichiometric coefficient for species i (+ for products, - for reactants). Equation (1) can be used to predict how changes in electrolyte concentration will affect the potential of an electrode, provided the reaction occurring on the electrode surface is known.

When an electrode is stepped from the equilibrium potential to a potential away from equilibrium, a current flows. If the potential is stepped far from equilibrium, then the current that flows through the system normally will be dictated by the rate that reactants can be transported from the bulk solution to the interface where they are consumed. In a stagnant electrolyte with very high conductivity, the rate reactants move is limited solely by diffusion through solution. Figure 1 schematically shows the concentration profile as a reactant is consumed (at the diffusion

limited rate) on a planar electrode immersed in a stagnant electrolyte. At short times, only reactant very near the electrode is depleted, but as time progresses an ever thickening depletion layer forms. Reactant from the bulk solution has to diffuse across this depleted layer to react at the surface, so as time progresses the rate of reaction decreases because the rate that reactant can reach the electrode decreases.

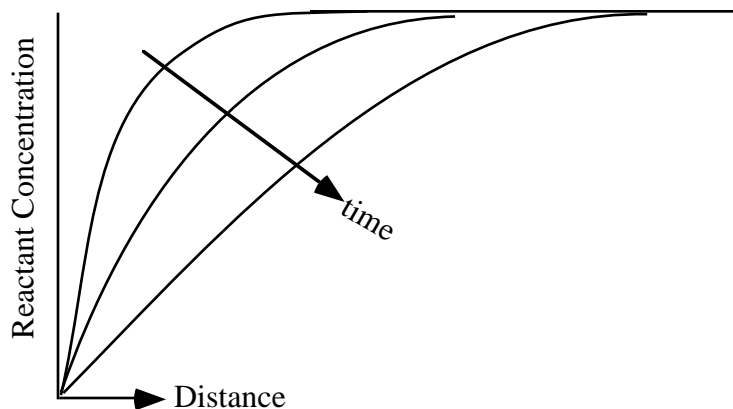


Figure 1. Evolution of concentration profiles in a quiescent electrolyte next to an electrode whose potential is stepped far from equilibrium.

The [diffusion limited current](#) under these conditions is described by the [Cottrell equation](#)

$$I(t) = \frac{nFAD^{1/2}C^*}{\pi^{1/2}t^{1/2}} \quad , \quad (2)$$

where $I(t)$ is the time varying current, A is the electrode area ($=0.7854 \text{ cm}^2$ in this experiment), D is the reactant species diffusivity (cm^2/s), C^* is the bulk composition of reactant (mole/cm^3), $\pi=3.14159$, and t is time (s).

Experimental Procedure

Both experiments will use electrolytes made from FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ and $1 \text{ M H}_2\text{SO}_4$. The potential determining reaction is



where the sulfuric acid acts as an inert component that raises the conductivity of the electrolyte to the point where we don't need to worry about voltage changes due to a resistive electrolyte (sulfuric acid is called the [supporting electrolyte](#)).

A series of solutions with different concentrations of Fe^{+2} and Fe^{+3} will be used to test the validity of the Nernst Equation. A saturated calomel electrode (SCE) will serve as the reference electrode for all of the experiments. The experiment involves immersing a platinum (inert)

electrode in each solution and recording the potential of the platinum relative to the SCE. Analysis will require plotting the measured potentials using axes suggested by the form of Eq. (1), *i.e.* E vs. $\ln[c_{\text{Fe}^{+3}}/c_{\text{Fe}^{+2}}]$, and comparing the results to values predicted by Eq. (1).

Given below are operating procedures for getting started with the experiment. **You should always be prepared to modify the instrument settings and experimental conditions to improve the results you get. Don't hesitate to "play around" and figure out how the instruments work. You will have plenty of time with this experiment.** If you are concerned that you might break something, or don't understand the interplay between instrument and experiment, then ask for assistance.

EQUILIBRIUM POTENTIAL MEASUREMENTS USING A DIGITAL VOLTMETER (DVM)

- (1) Carefully immerse Pt and SCE electrodes in electrolyte of interest, making sure to keep Pt electrode from hitting sides or bottom of cell.
- (2) Set DVM to measure Volts D.C.
- (3) Connect Pt working electrode to the red (+) terminal of the DVM
- (4) Connect SCE to the black (common or -) terminal of the DVM
- (5) Record voltage
- (6) Remove electrodes, rinse with deionized water, and gently pat dry.
- (7) Repeat steps (1) through (6) for each electrolyte of interest.

The diffusion limited current induced by making a potential step far away from equilibrium will be performed using a 0.7854 cm^2 electrode immersed in an unmixed beaker containing 20 mM Fe^{+3} and 10 mM Fe^{+2} . The electrode should be placed in the unstirred beaker and allowed to sit undisturbed for a few minutes so the solution is truly quiescent. The potential step experiment will be operated under computer control. Once current vs. time data is acquired, you should analyze the data by plotting I vs. $t^{-1/2}$ to see if Cottrellian behavior is observed during any portion of the transient period. Also, from the slope of the plot, you should determine the diffusion coefficient for the diffusion limited reactant.

As before, when following the experimental recipe given below, you might need to modify the instrument settings for best results.

POTENTIAL STEP EXPERIMENTS USING THE PAR 173 POTENTIOSTAT UNDER COMPUTER CONTROL

- (1) Carefully immerse Pt working electrode, a Pt counter electrode, and SCE in electrolyte of interest, making sure to keep working electrode from hitting sides or bottom of cell.
- (2) Select DUMMY CELL
- (3) Connect the Platinum working electrode to the Working Electrode lead (Green)

- (4) Connect the saturated calomel electrode (SCE) to the Reference Electrode lead
- (5) Connect the Platinum counter electrode to the Counter Electrode lead (Red)
- (6) Set the OPERATING MODE switch to NULL
- (7) Set METER knob to POTENTIAL, with the inner knob set to 1.
- (8) Select EXT. CELL
- (9) Push the button labeled A.
- (10) Switch the APPLIED POTENTIAL channel A toggle to +
- (11) Adjust the channel A potentiometer until the meter is nulled (reads 0). This should be very close to the value you get using a DVM in the first part of this experiment.
- (12) Select DUMMY CELL
- (13) Set the OPERATING MODE switch to CONTR. E
- (14) Set CURRENT FOLLOWER to 1 mA
- (15) Toggle the left-most EXT.SIG. INPUT switch to ON.
- (16) On computer screen, set CONTROL TYPE = Potentiostat, set DISK CURRENT CONVERTER = 1 mA/V, set SWEEP TYPE to Square Wave, set SWEEP MAXIMUM = 0, set SWEEP MINIMUM = -500, set CV SWEEP RATE = 50, and set NUMBER OF CYCLES =1.
- (17) Select EXT. CELL (Button A should still be pushed, and the equilibrium potential should still be dialed up on the Channel A potentiometer)
- (18) Run the Computer Program
- (19) After 20 s, the data will be plotted on the to the right of the screen (scroll there). Make sure not too much of the Current vs. time data was either off-scale or recorded with too low resolution. If either was true, you need to change the CURRENT FOLLOWER setting on the potentiostat and the CURRENT CONVERTER in software to match it. Also, make sure the current near the beginning of the time trace is close to zero. If not, you need to tweak the Channel A potentiometer to make it zero (if the initial current is positive, make the potentiometer setting smaller...vice versa if the initial current is negative) Keep adjusting until the initial current is close to zero.
- (20) Select DUMMY CELL
- (21) If all is well, repeat items (7)–(11) but set SWEEP MINIMUM = +500 on the computer screen before running program.