

## CHAPTER 1: INTRODUCTION

In this book, we will look at some of the fun analytical things that electrochemists have done and are currently doing. We start with inorganic electrochemistry which allows us to briefly examine electron transfer kinetics for compounds that are relatively free of coupled chemical reactions. We next move to organic systems to develop a strategy for recognizing electroactive groups in organic chemistry. We will discuss strategies for beating out coupled chemical reactions. In Chapter Six we examine the parallels of photochemical and electrochemical methods of adding energy to the system, primarily as an introduction for Chapter Seven, which focusses on the biological photo-stimulated vectorial electron transfer system of photosynthesis and on vectorial electron transfer in respiration. This latter chapter, in turn, serves as an introduction to Chapter Eight, which looks at the synthetic design of vectorial electron transfer systems by electrochemists.

### A. ELECTROCHEMISTRY: ADDING ENERGY TO A SYSTEM

Electrochemists can, and often do, apply energy to a solution in the form of an electrode potential and subsequently measure currents (Volt  $\rightarrow$  am  $\rightarrow$  metry):

$$\Delta G = -nFE \quad [1.1]$$

where  $\Delta G$  is the energy applied in joules (Joules are equivalent to coulomb-volts),  $F$  is the faraday constant in coulombs,  $9.64846 \times 10^4$  C/eq,  $E$  is the applied voltage (V), and  $n$  is the number of equivalents (electrons/mole) in a reduction reaction:



This process is analogous to the application of energy to solution in the form of light:



for the process:



where the distribution of molecules in the excited state is described by the Boltzmann equation:

$$N^* = N^0 \exp(-\Delta G/kT) \quad [1.5]$$

where  $N^*$  is the number of molecules in an excited state,  $N^0$  is the number of molecules in the ground state,  $\Delta G$  is the difference in energy between the ground state and the excited state (equation 1.3),  $k$  ( $1.381 \times 10^{-23}$  J/K) is the Boltzmann constant, and  $T$ , is the absolute temperature.

Similar concepts apply in electrochemistry. In electrochemistry, an electrode consisting of some charge conducting material is placed into a conductive media. A second electrode is connected through a voltage (energy) source (Figure 1.1). Before  $\Delta G$  (energy) is applied at the electrode surface, the solution is in equilibrium with a Boltzmann-like distribution of ions in the oxidized and reduced state:

$$[\text{Red}] = [\text{Ox}] \exp(-\Delta G_{\text{soln,equilibrium}}/RT) \quad [1.6]$$

where  $R$  is the molar gas constant ( $8.314$  J/K-mol) and  $\Delta G_{\text{soln,equilibrium}}$  refers to the free energy of the solution in its equilibrium state. This equation is more familiar to electrochemists in the rearranged form:

$$\ln \{[\text{Red}]/[\text{Ox}]\} = -\Delta G_{\text{soln, eq}}/RT \quad [1.7]$$

$$nFE_{\text{soln, eq}}/RT = \ln \{[\text{Red}]/[\text{Ox}]\} \quad [1.8]$$

$$E_{\text{soln, eq}} = \frac{RT}{nF} \ln \left\{ \frac{[\text{Red}]}{[\text{Ox}]} \right\} \quad [1.9]$$

where a standard state,  $E^\circ$ , is given to the condition  $[\text{Red}] = [\text{Ox}]$ :

$$E_{\text{soln, eq}} = E^\circ - \frac{RT}{nF} \ln \left\{ \frac{[\text{Red}]}{[\text{Ox}]} \right\} \quad [1.10]$$

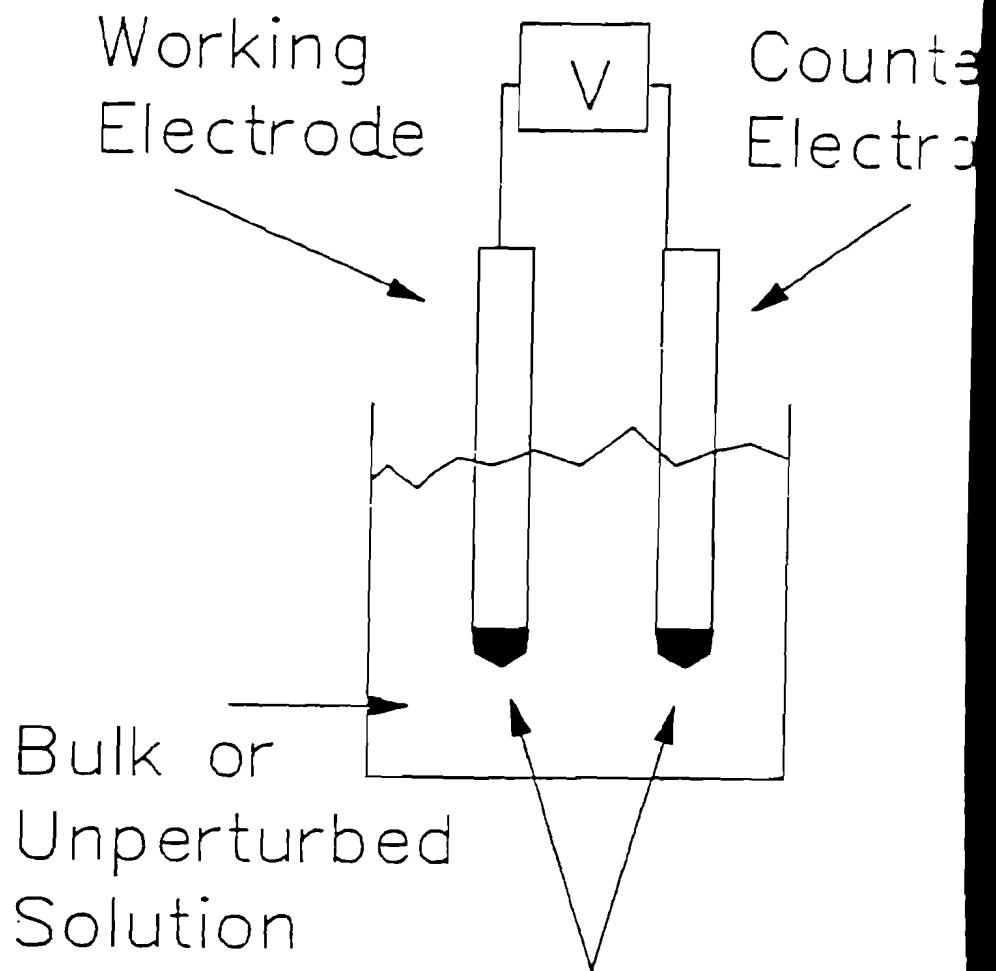
Equation [1.10] is the Nernst equation and is written with a negative sign for a reduction equation [1.2]. The sign convention is fixed and can be memorized as, "you never want to see a red ox". The meaning of the standard reduction potential can be remembered as thinking that electrons flow from region of high negative charge (negative values of  $E^\circ$ ) to regions of low negative charge (positive values of  $E^\circ$ ).

When a potential is applied at the electrode surface, a region near the electrode is perturbed, different from the remainder of the solution (Figure 1.1). This region experiences a different free energy:

$$\Delta G_{\text{surf}} = -nFE_{\text{surf}} \quad [1.11]$$

Because the potential at the surface has been perturbed, the Boltzmann-like ratio of oxidized to reduced ions must change. The change in state is accompanied by a flow of electrons to or from the electrode depending on whether potential at the electrode surface,  $E_{\text{surf}}$  is larger than or less than the potential of the bulk solution,  $E_{\text{soln}}$ .

The system now consists of two different regions (heterogeneity): that near the surface with  $[\text{Red}_{\text{surf}}]$  and  $[\text{Ox}_{\text{surf}}]$  and



## Perturbed Solution

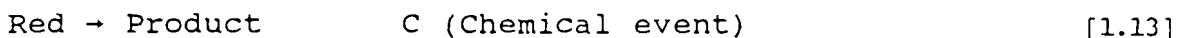
1.1. A diagram of an electrochemical two electrode cell containing an electrolyte solution with a redox active species  $O$  present in the solution. Two electrodes are immersed in solution and connected via a voltage source,  $\Delta V$ . The total potential drop is experienced primarily at the interfaces between the electrodes and solution, creating a heterogeneous system (interface + bulk). In general, three electrode cells are often used where the third electrode is a reference electrode.

that away from the surface (bulk) with  $[Red_{bulk}]$  and  $[Ox_{bulk}]$ . The presence of the two different concentration regimes results in a diffusion layer,  $\delta x$ , across which, at a negatively poised electrode, for example, oxidized species flow toward the electrode and reduced species flow away from the electrode.

Because the applied electrode potential results in this nonequilibrium condition, voltammetric techniques, most beloved by electrochemists, are kinetic techniques and have all the advantages and disadvantages of other kinetic techniques. In the first place, because of the heterogeneous nature of the electrochemical perturbation, all currents measured must be interpreted in light of diffusion equations. This is unlike many spectroscopic techniques where the entire solution similarly is perturbed.

A second consideration for electrochemists is the rate of the actual electron transfer event. One must worry whether the reduction reaction is fast enough (reversible) to keep up with the growth of the diffusion layer. If not, the diffusion currents must be interpreted with the additional factor of slow electron transfer kinetics as an electron is transferred to or from the electrode surface to the solution species. This is usually not a consideration for photochemists due to the very rapid time scale of the photochemical event.

A third consideration for electrochemists is the lability of the reduced species generated at the electrode surface. If so, then the currents require an additional interpretation in terms of coupled chemical reactions:



This is not often a problem in analytical applications of spectroscopy. The photochemical event often involves a transition from a  $\pi$  to a  $\pi'$  orbital, in which no bond breakage take place. With the dissipation of energy through collisional transfer or re-radiation, the original electronic ground state can again be obtained

These three differences: heterogeneity of the solution, time scale of the primary event (absorption of light, transfer of an electron), and the coupling of chemical processes, give rise to the strengths and weaknesses of electrochemical voltammetric methods for analytical applications.

We will occasionally make reference to the type of technique employed in the measurements and so next briefly survey a few select methods.

#### B. POTENTIAL SWEEP: CYCLIC VOLTAMMETRY

Consider our electrochemical cell (Figure 1.1). We will start with a solution initially rich in the oxidized form of an electroactive compound so that  $E_{\text{soln},\text{eq}}$  is positive (see equation 1.10). (All of our examples are for reduction reactions, however the same concepts apply equally well to oxidations reactions.) Next, we add energy to the system via applied electrode potential.

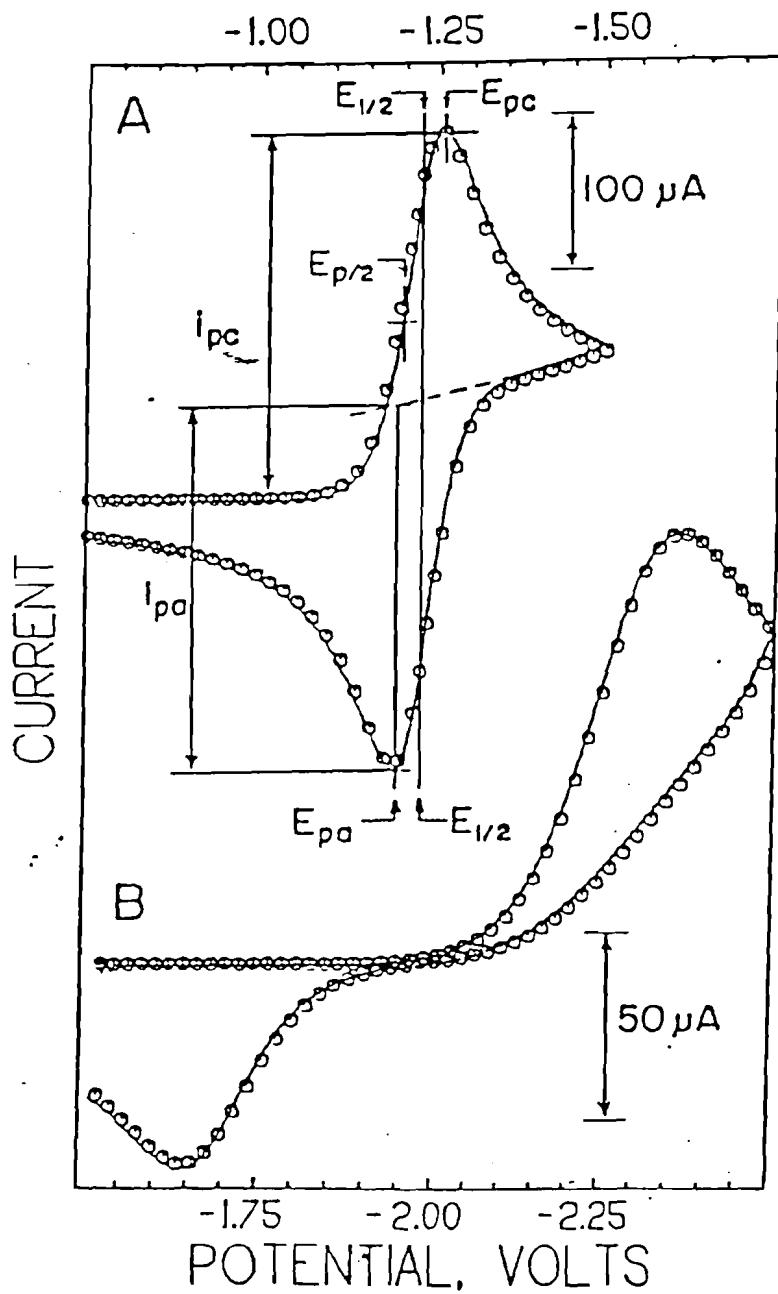
Initially the electrode is poised positive of the bulk solution potential:  $E_{\text{surf}} > E_{\text{soln}}$ . Since we know that electrons flow toward positive potential, we would expect electrons to flow out

5.1

of solution toward the electrode. However, the solution is already rich in oxidized species and poor in reduced species which could lose electrons. Therefore no current flows.

Next we sweep the electrode potential negative with a scan rate,  $\nu$  (V/s). As the electrode or surface solution potential moves negative of the bulk solution potential, electrons begin to flow into solution (electrons move to more positive potential). When the electrode (surface) potential moves very negative of the formal potential of the redox couple, the surface concentration departs radically from the bulk solution concentrations. Eventually, the entire surface region is depleted in oxidized compounds and a diffusion layer forms, causing the currents to tail off, forming a peak shape (Figure 1.2) (1).

The process can be repeated by reversing the direction of the potential scan. At this point the region immediately near the electrode surface is rich in reduced species and low in oxidized species. A potential scan positive will result in the oxidation of the reduced species. The total current potential trace during the potential cycle is a "duck-shaped" cyclic voltammogram (CV). The CV has several distinguishing characteristics. For a simple, reversible, redox reaction, the potential of the reduction peak ( $E_{pc}$ , where "c" stands for cathodic (reduction = **cathode** or "red cat")) differs from the potential of the oxidation peak in the reverse scan ( $E_{pa}$ , where "a" stands for anodic (anodic = **oxidation** or "an ox")) by  $59/n$  mV. The formal potential,  $E^\circ$  (see equation 1.10), lies midway between  $E_{pc}$  and  $E_{pa}$ .



1.2 Cyclic voltammograms at a mercury electrode in acetonitrile.  
 Scan rate: 100V/s. Temperature: 20.0°C. Reference electrode:  
 $\text{Ag}/0.01 \text{ M } \text{AgNO}_3/0.10 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4$  in acetonitrile. Curves:  
 experimental. Symbols: theoretical (digital simulation). A)  
 - 1 mM O<sub>2</sub>; 0.10 M  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  electrolyte; electrode area: 0.016  
 $\text{cm}^2$ ; B) 0.60 mM 2-nitropropane; 0.10 M  $(n\text{-C}_7\text{H}_{15})_4\text{NClO}_4$   
 electrolyte; electrode area: 0.025 cm<sup>2</sup>. (From Ref. 1.)

The peak current for a reversible CV is (2):

$$i_{pc} = 2.69 \times 10^5 n^{3/2} A D_{ox}^{1/2} \nu^{1/2} C_{ox,bulk} \quad [1.14]$$

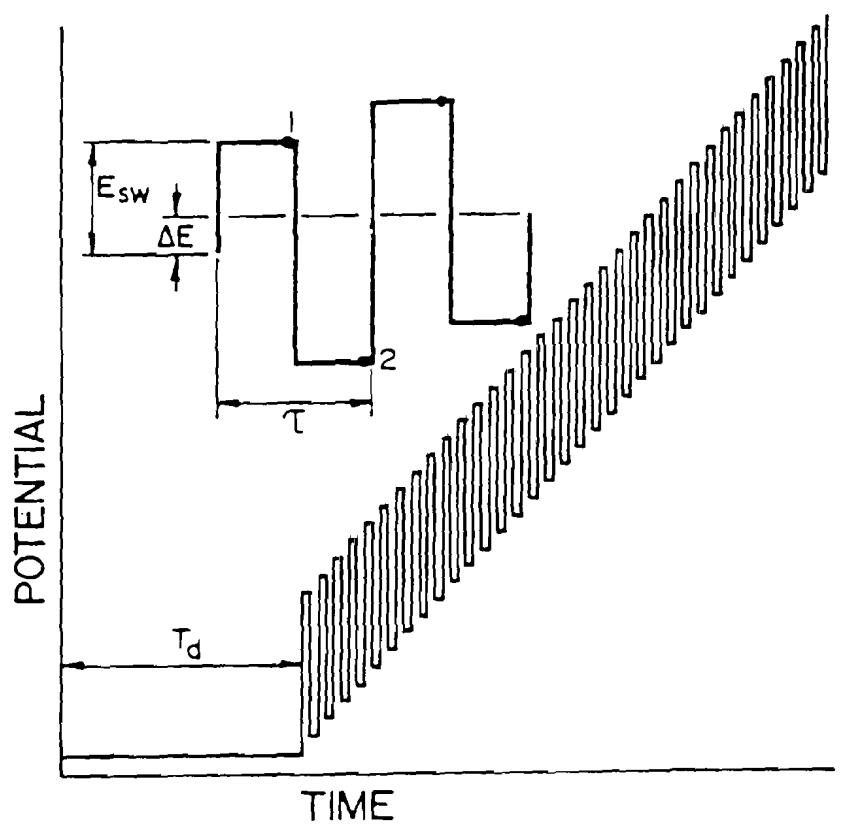
where  $i_{pc}$  is the current measured in amperes, A is the area of the electrode in  $\text{cm}^2$ ,  $D_{ox}$  is the diffusion constant for the oxidized species in  $\text{cm}^2/\text{s}$ ,  $\nu$  is the scan rate in  $\text{V/s}$ ,  $C_{ox,bulk}$  is the bulk solution concentration of the oxidized species in  $\text{mol}/\text{cm}^3$ .

### C. PULSED POTENTIAL TECHNIQUES

Generally CV is used for kinetic studies because minute perturbations in the rate of electron transfer or in coupled chemical reactions show up nicely in the "duck-shaped" current voltage curves. (See Figure 1.2B for an example of such perturbations.) For analytical applications, other techniques give enhanced sensitivity. For example, square wave voltammetry (SWV) or differential pulse voltammetry (DPV), apply a rapid train of potential pulses to the electrode surface, which results in thin diffusion layers, ultimately allowing higher currents to be measured. Figures 1.3-1.6 (3) show examples of SWV and DPV. The peak current for DPV is described by (4):

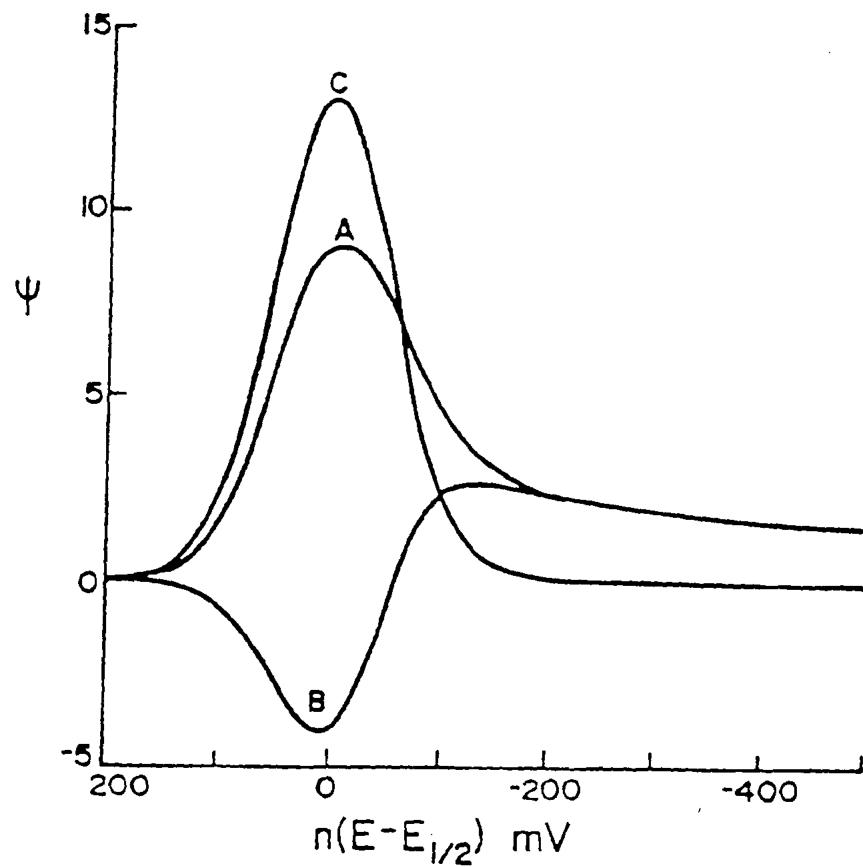
$$\Delta I_p = n^2 F^2 A D_{ox}^{1/2} C_{ox,bulk} \Delta E / 4 R T \pi^{1/2} t^{1/2} \quad [1.15]$$

where the terms have the same significance as in equation [1.14]. Time,  $t$ , is the time elapsed between pulse application and measurement.  $\Delta E$  is the pulse width applied (Figure 1.5). In general, the pulse train in SWV occurs at a much higher frequency than the pulse sequence applied on the linear ramp in DPV. Both SWV and DPV have detection limits significantly lower than CV. Typical values are  $0.1 \mu\text{M}$ . The peak potential in these techniques,

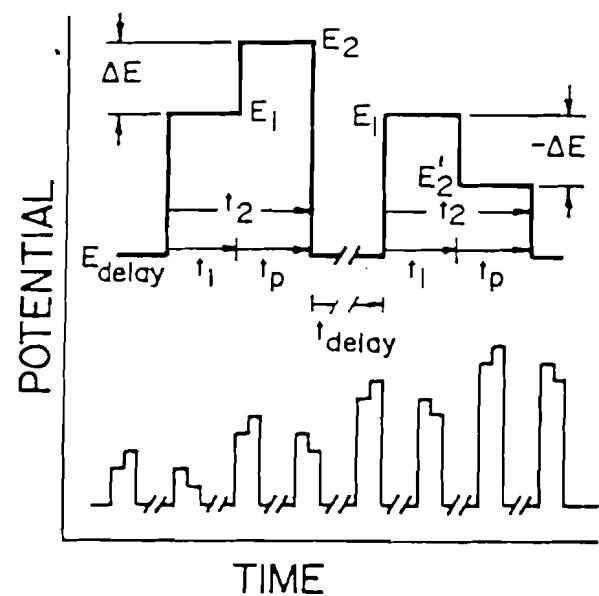


1.3 Excitation signal for square wave voltammetry. (From Ref. 4).

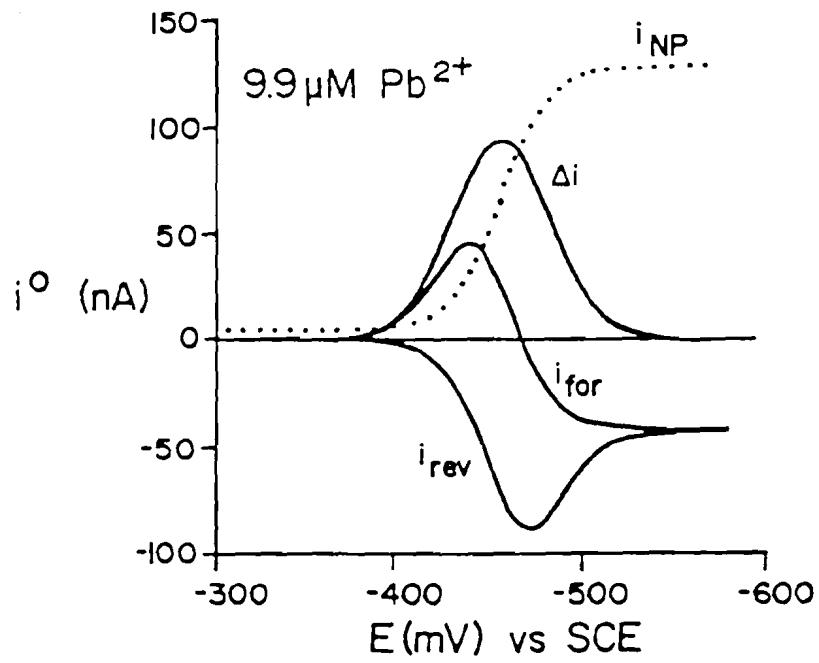
Fig 1.3



1.4 Calculated square wave voltammograms for reversible electron transfer: (A) forward current, (B) reverse current, and (C) net current, dimensionless units. (From Ref. 4).



1.5 Excitation signal for differential "normal pulse voltammetry"  
(From Ref. 4.)



1.6 Forward, reverse and difference current differential normal pulse voltammograms of  $9.9 \mu\text{M}$  ( $2.05 \text{ ppm}$ )  $\text{Pb}^{2+}$  in  $0.5 \text{ M}$   $\text{CH}_3\text{COOH}/0.5 \text{ M} \text{CH}_3\text{COONa}$ . Conventional normal pulse voltammogram is also shown (dotted line). (From Ref. 4.)

for a reversible system, is centered at (5):

$$E_p = E^\circ + \Delta E/2. \quad [1.16]$$

#### D. POLAROGRAPHY

Older literature, where much of the information for physical organic chemists resides, is based on the analysis of polarographic curves. Polarography is the same as voltammetry, except that the electrode is a dropping mercury electrode. Because the fall of the mercury drop disturbs the growing diffusion layer, peaks in the current/potential plots do not develop. The diffusion limited wave (Figure 1.7) has the magnitude (2):

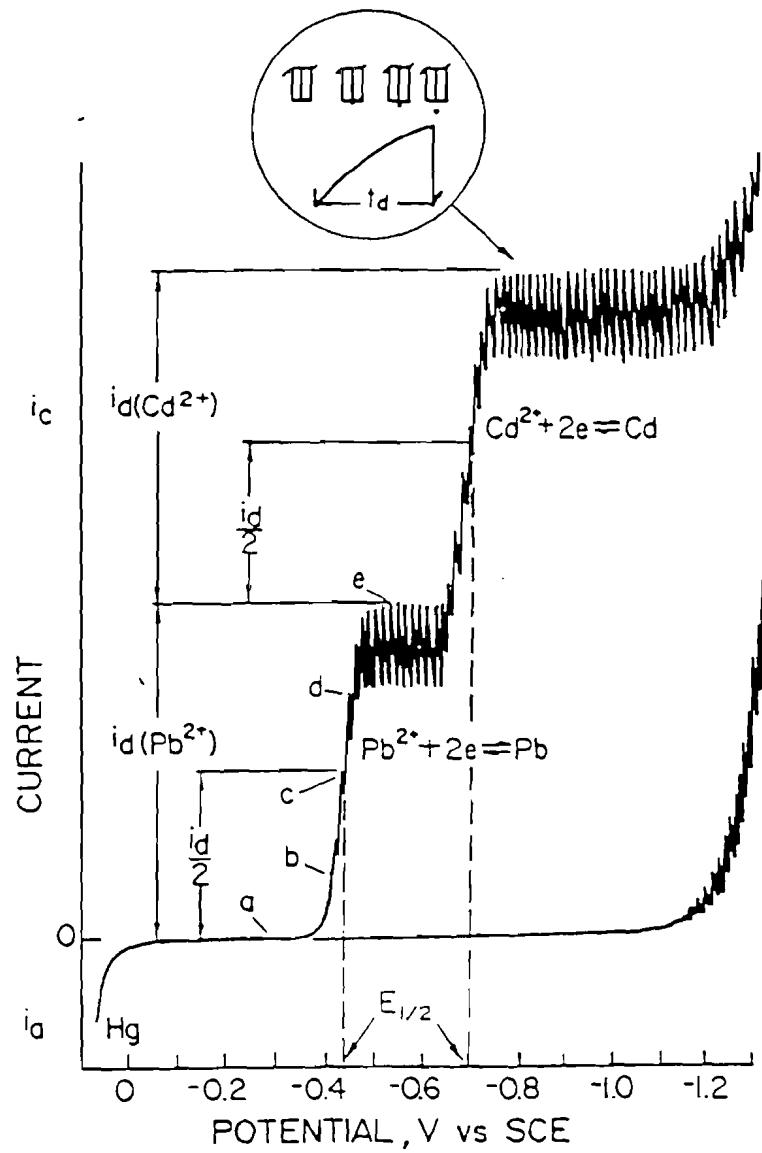
$$i_o = 607nD_{ox}^{1/2}C_{ox,bulk}m^{2/3}t_{max}^{-1/6} \quad [1.17]$$

where  $m$  is the mass flow rate of the mercury and  $t_{max}$  is the maximum life time of the mercury drop. The potential at half wave height is  $E_{1/2}$ :

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{D_{eq}^{1/2}}{D_{ox}^{1/2}} \quad [1.18]$$

#### E. SUMMARY

All that one needs to remember, at this point, is that a plot of current vs potential yields information about the formal potential for the reduction reaction (useful for photo-organic chemists), the bulk solution concentration (useful for analytical techniques), information about chemical reactions coupled to the electron transfer event (useful for physical chemists) and, inevitably, information about diffusion.



1.7 Polarogram of 1.0 mM  $Pb^{2+}$ , 1.0 mM  $Cd^{2+}$ , and 0.1 M KCl.  $O_2$  removed.  
(From Ref. 2.)

## CHAPTER 1: PROBLEMS

- 1.1 a) What is the ratio of reduced and oxidized species ( $E^\circ = 0.200$  V vs SCE) in a solution at equilibrium whose potential is +0.290 V vs SCE?
- b) Suppose two electrodes are inserted into the solution in problem 1.1a and a potential is applied between electrodes. Further suppose that the potential applied shifts the working electrode (electrode of interest) potential to +0.125 V vs SCE. What is the equilibrium ratio of reduced and oxidized species near the electrode?
- c) From your answers in questions 1.1a and 1.1b draw a sketch of concentration as a function of distance from your working electrode. Comment on your sketch.
- 1.2 Calculate the peak current for a CV in which the bulk solution concentration of an oxidized species is 4mM, its diffusion coefficient is  $2 \times 10^2$ /s, the area of the electrode is 0.05 cm<sup>2</sup> and the scan rate is 50 mV/s. Assume a one electron transfer reaction.
- 1.3 Using the same solution and electrode as in 1.2, compute the  $\Delta I_p$  obtained by DPV where  $\Delta E$  pulse width is 5 mV and t is 200 ms.
- 1.4 Compute the magnitude of the diffusion limited wave for the same conditions as in problem 1.2 for polarography where the mass flow rate of the mercury is 1 mL/min and the drop life is 10 s.

#### LITERATURE CITED

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