Electroanalytical – Voltammetric Methods
Ch 23, 7th e, WMDS)

Hmwk – Chapter 23

– due Monday, May 1

Problems 1, 5, 6

INSTRUMENTAL METHODS OF ANALYSIS
Seventh Edition
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Voltammetry is the name given to a wide range of methods that study the composition of a solution by looking at current – potential relationships. The variety of techniques are shown in Table 23.1, p 697.

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Polarography (one of several voltammetric methods) is the measurement of current in an electrolysis cell as a function of the potential applied to the working electrode. (The name comes from the fact that the method biases the electrode, ie, puts an electrical charge on it.) This is not classified as an electrolysis method because only a few small amount of the sample is electrolyzed. The basis of this method is the *diffusion current* which is related to the concentration of the analyte.

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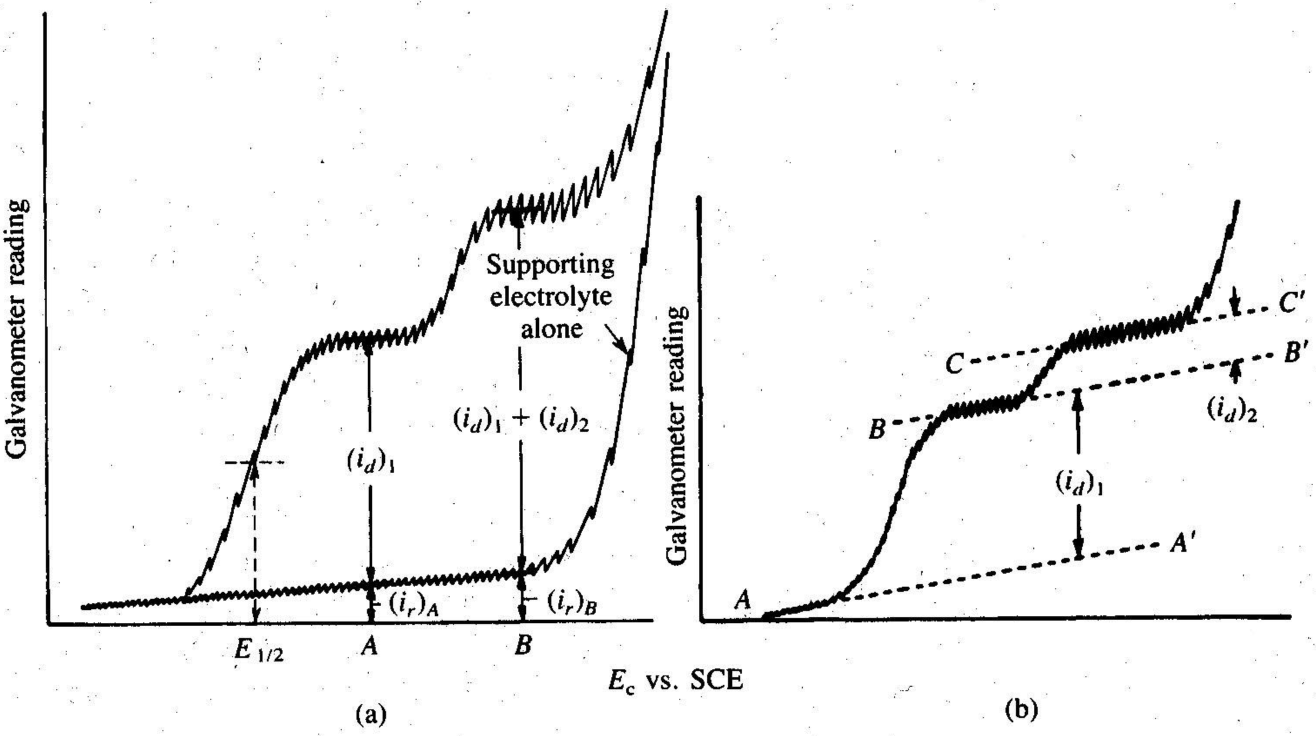
FIGURE 23.7 Polarographic current-potential curves. Measurement of the faradaic current: (a) subtraction of the signal from the supporting electrolyte and (b) extrapolation of the residual current.



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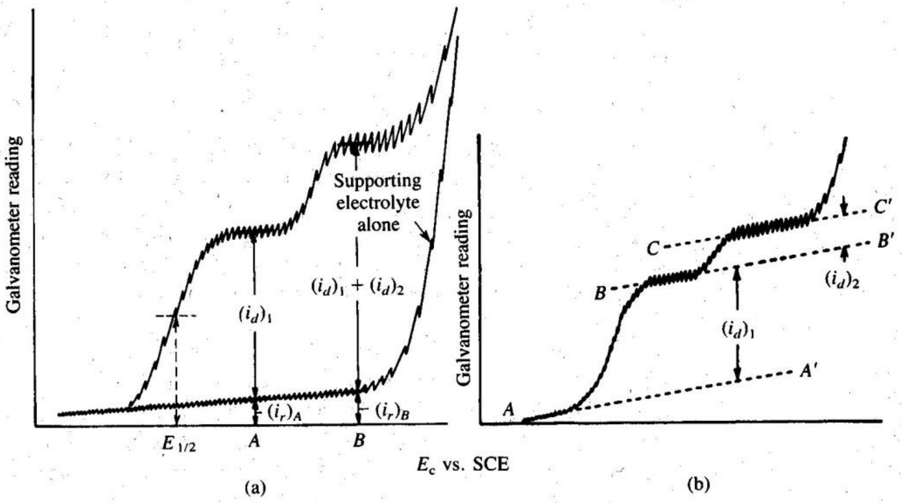

FIGURE 23.7 Polarographic current-potential curves. Measurement of the faradaic current: (a) subtraction of the signal from the supporting electrolyte and (b) extrapolation of the residual current.

Important terms

- polarogram
- residual current
- limiting current
- diffusion current, I_d
- polarographic wave
- supporting electrolyte
- half-wave potential - related to $E_{1/2}$ for that half-cell reaction for reversible process. (If reversible, plot of E vs log $I/(I_d - I)$ has slope of 0.0592/n

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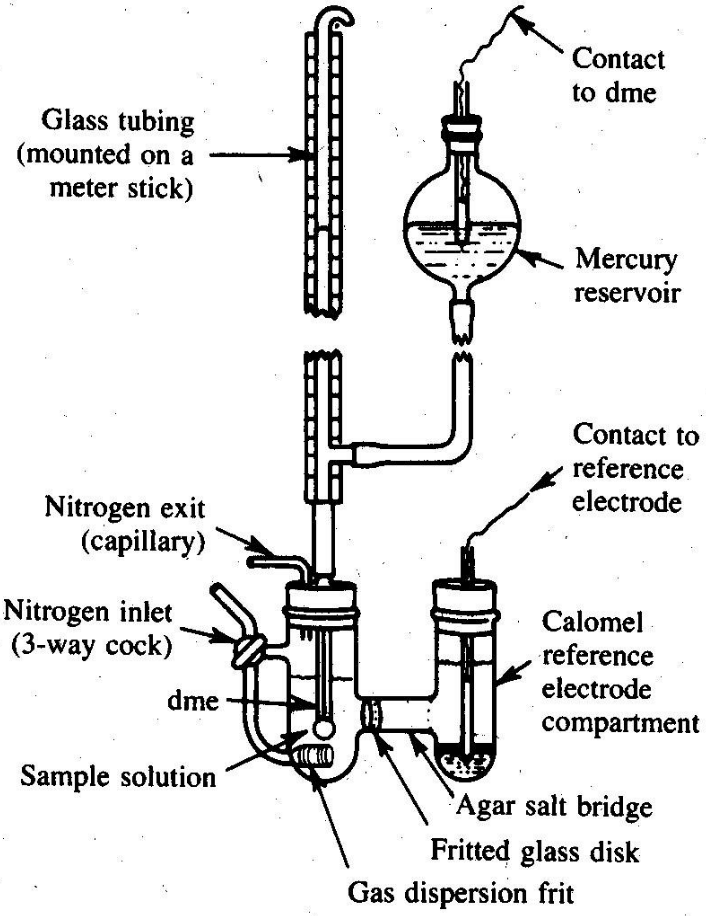
Ch 23, 7th e, WMDS)

FIGURE 23.1
Dropping mercury microelectrode and reservoir arrangement for polarographic cell.



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In classical polarography the working electrode is the dropping mercury electrode (dme) as shown on the proceeding slide. There are several distinct advantages to using the dme over other electrodes:

1) its surface is reproductible for a given capillary.
2) the electrode is renewed with a new drop, eliminating any poisoning effects of what has already been electrolyzed.
3) large cathodic overpotential for H_2 on Hg surface allows measurements of several metals otherwise not possible.
4) mercury forms amalgams with most metals
5) the diffusion current has a steady state value and is reproducibile.

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Ch 23, 7th e, WMDS)

Relationship between I_d and C is given by

the Ilkovic equation: $I_d = 708nCD^{1/2}m^{2/3}t^{1/6}$

where I_d is current in μA, D is the diffusion constant in cm^2/s, C is concnetration is mM, m is drop rate of the Hg in mg/s and t is time in s.

What is generally done is to keep all of the variables constant and note $I_d = f(C)$; Construct plot of C vs I_d . Alternately, the standard addition method may also be used.

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Variations of Voltammetry

A. Different electrodes

- 1 – Static Mercury Drop (HDME) – experiment performed on a single Hg drop
- 2 – Thin-Film Hg Electrode
- 3 – Solid electrodes, including Pt, Au, C, Ni, Ti
- 4 – Rotating Disk or Ring disk Electrodes

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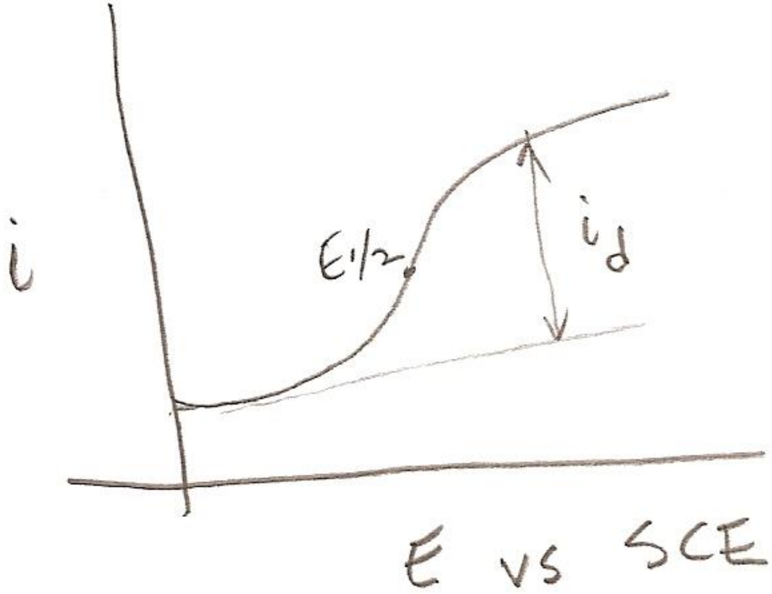
Ch 23, 7th e, WMDS)



The voltammogram with solid electrodes is similar to that of those produced by polarography except they do not have the waves caused by the dme.

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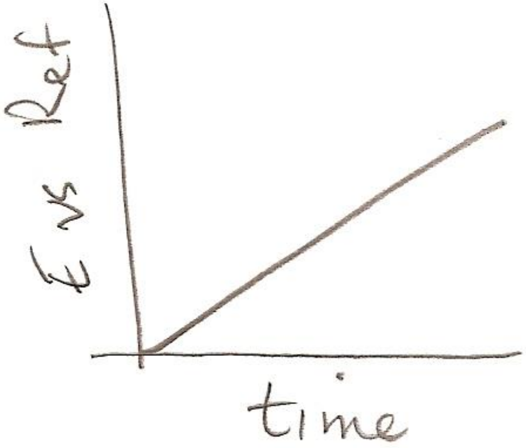
Applied signal

In all voltammetry the voltage on the working electrode is changed in some way as a *f*(time). Different methods arise from the differences in that applied voltage.



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Ch 23, 7th e, WMDS)

<u>Applied signal</u>

Different methods arise from the differences in that applied voltage.

- Traditional polarography – applies a ramp voltage, increasing cathodic or anodic.
- Pulse voltammetry – applies a square wave signal superimposed on the ramp voltage; reason is to reduce the charging current.
- Square wave voltammetry
- AC polarography – superimposed AC signal on the ramp voltage.

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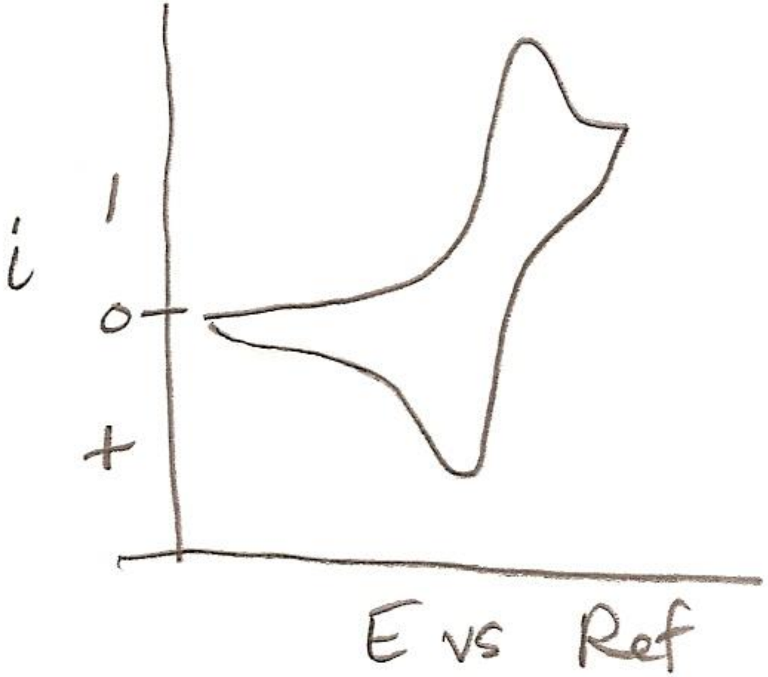
Ch 23, 7th e, WMDS)

Applied signal

- Cyclic Voltammetry – saw tooth signal applied; polarity of the working electrode changes.



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Stripping Analysis - chronoamperometry

1. The analyte is electrochemical deposited on the working electrode.
2. The polarity of the working electrode is reversed and the analyte ‘stripped’ from the electrode. During this step the current is monitored, The more easily oxidized substances are removed first – see Figure 23.15. The integrated areas under each peak is proportional to the amount of that species present.

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<u>Applications of Voltammetry</u>

1 – Organic compounds – bonds reduced at the dme shown in Table 23.2
2 – Inorganic compounds
  Metal ions
  Ammonia
  Cyanide
3 – Determination of oxygen
4 – Combination with spectroscopy