CYCLIC VOLTAMETRY

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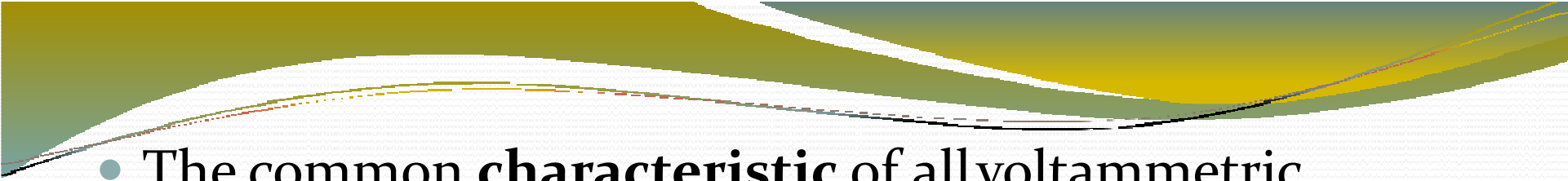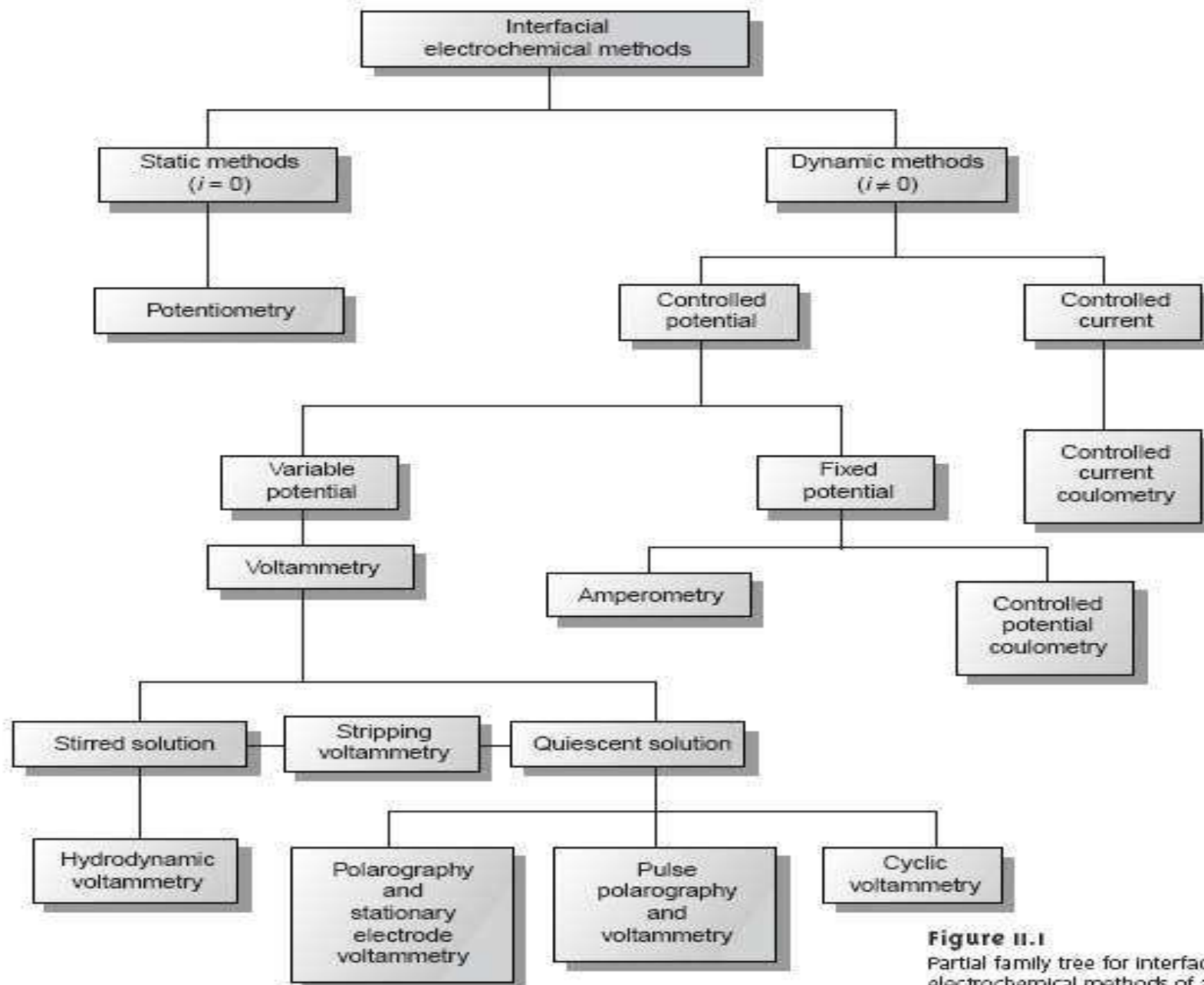**S.S. in Chemistry & Biochemistry**
VIKRAM UNIVERSITY, UJJAIN

Figure II.I
Partial family tree for interfadal electrochemical methods of analysis.

INTRODUCTION

- Voltammetry - from the discovery of polarography in 1922 by the chemist Jaroslav Heyrovsky, received the 1959 Nobel Prize in chemistry.

- The earlier voltammetric methods experienced a number of difficulties, but after in the 1960s and 1970s significant advances were made in all areas of voltammetry (theory, methodology, and instrumentation), which enhanced the sensitivity of analytical methods.

- The common **characteristic** of all voltammetric techniques is that they involve:

- the application of a potential (E) to an electrode

- the monitoring of the resulting current (i) flowing through the electrochemical cell.

- In many cases, the applied potential is varied or the current is monitored over a period of time (t).

- Thus, all voltammetric techniques can be described as some function of E, i, and t.

Governing law: Ohm's law E = ir

WORKING

- A voltammetric cell consistsof the three micro electrodes. They are
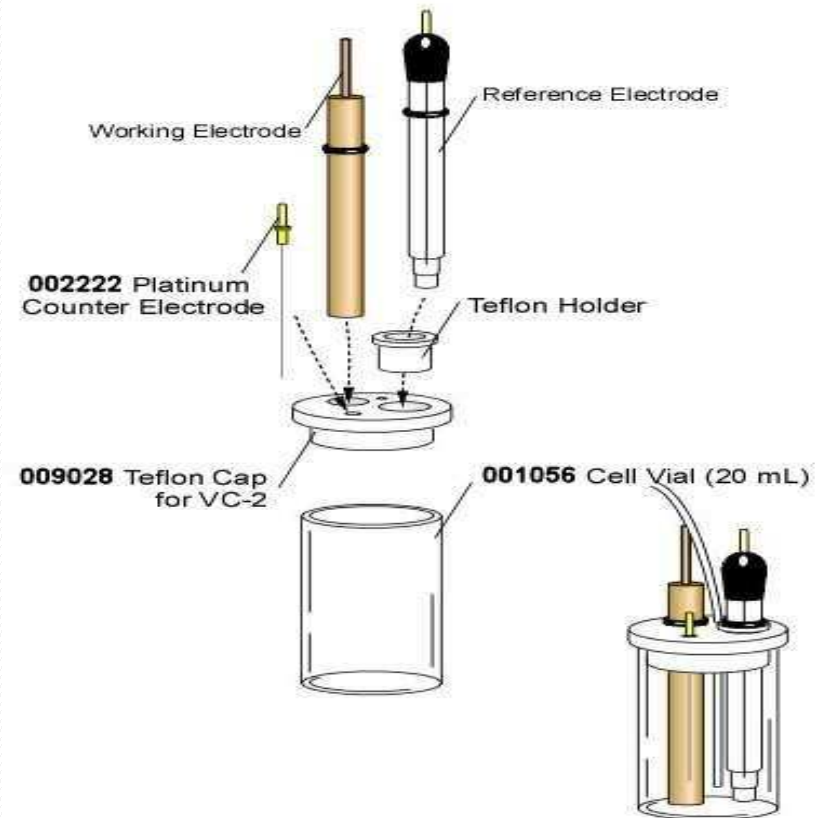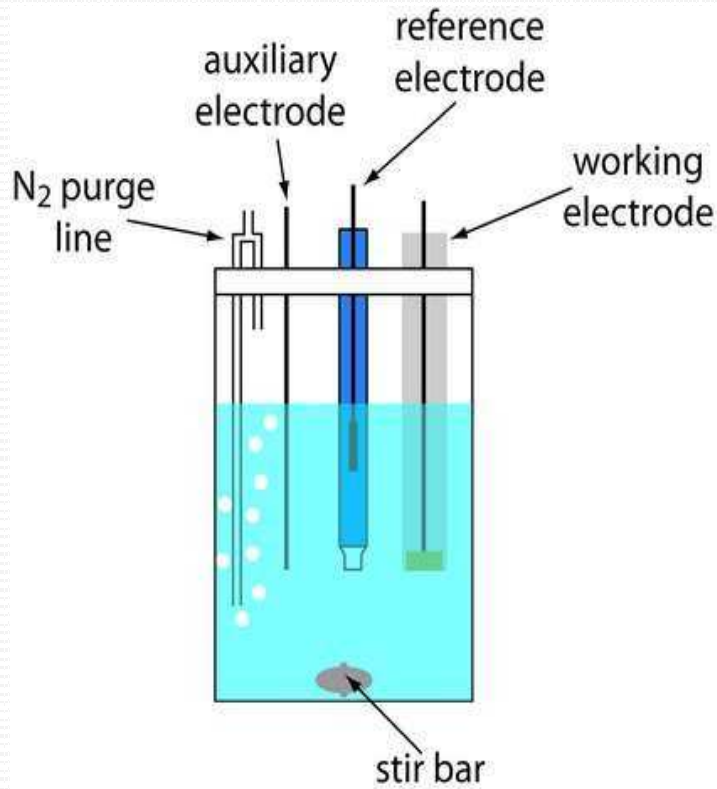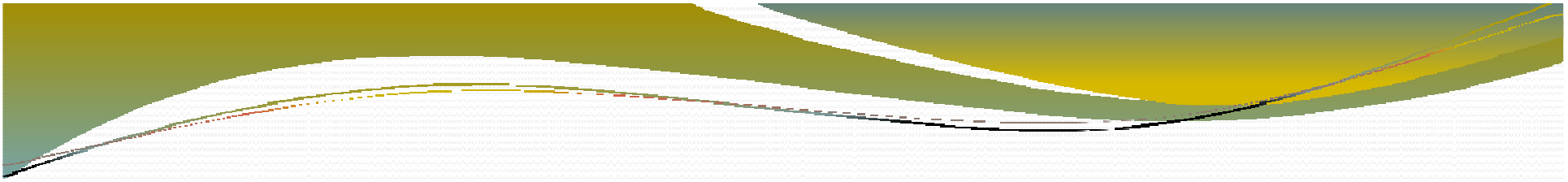
- ***The working electrode***, The working electrodes are of various geometries and materials, ranging from small Hg drops to flat Pt disks.

Mercury - it displays a wide negative potential range (because it is difficult to reduce hydrogen ion or water at the mercury surface), its surface is readily regenerated by producing a new drop or film, and many metal ions can be reversibly reduced into it.

Other commonly used electrode materials are gold, platinum, and glassy carbon.

- **_The auxiliary electrode(counter):_** passes all the current needed to balance the current observed at the working electrode.

- **_The reference electrode_**-The reference electrode should provide a reversible half-reaction with Nernstian behaviour. Its only role is to act as reference in measuring and controlling the working electrode's potential.

- The most commonly used reference electrodes for aqueous solutions are the calomel electrode

INSTRUMENTATION

- The basic components of a modern electroanalytical system for voltammetry are a potentiostat, computer, and the electrochemical cell

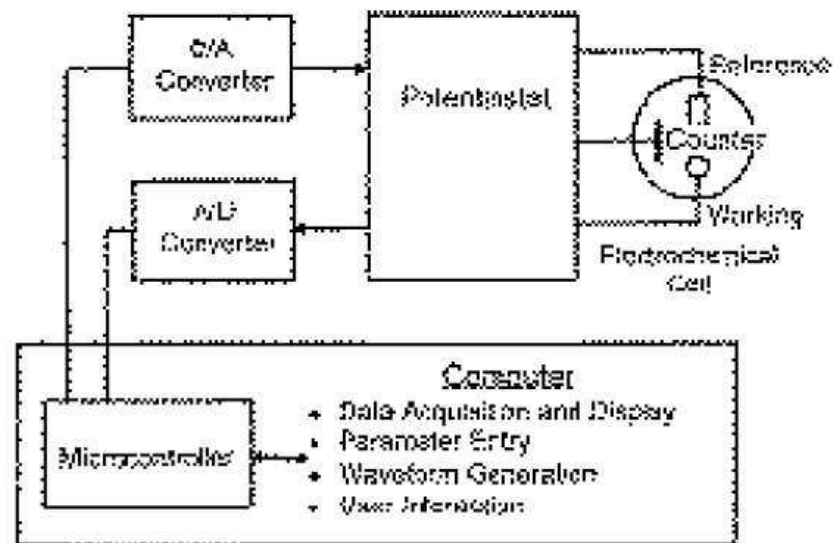Figure 37.1 Block diagram of the major components of an electroanalytical system for performing voltammetric analysis.
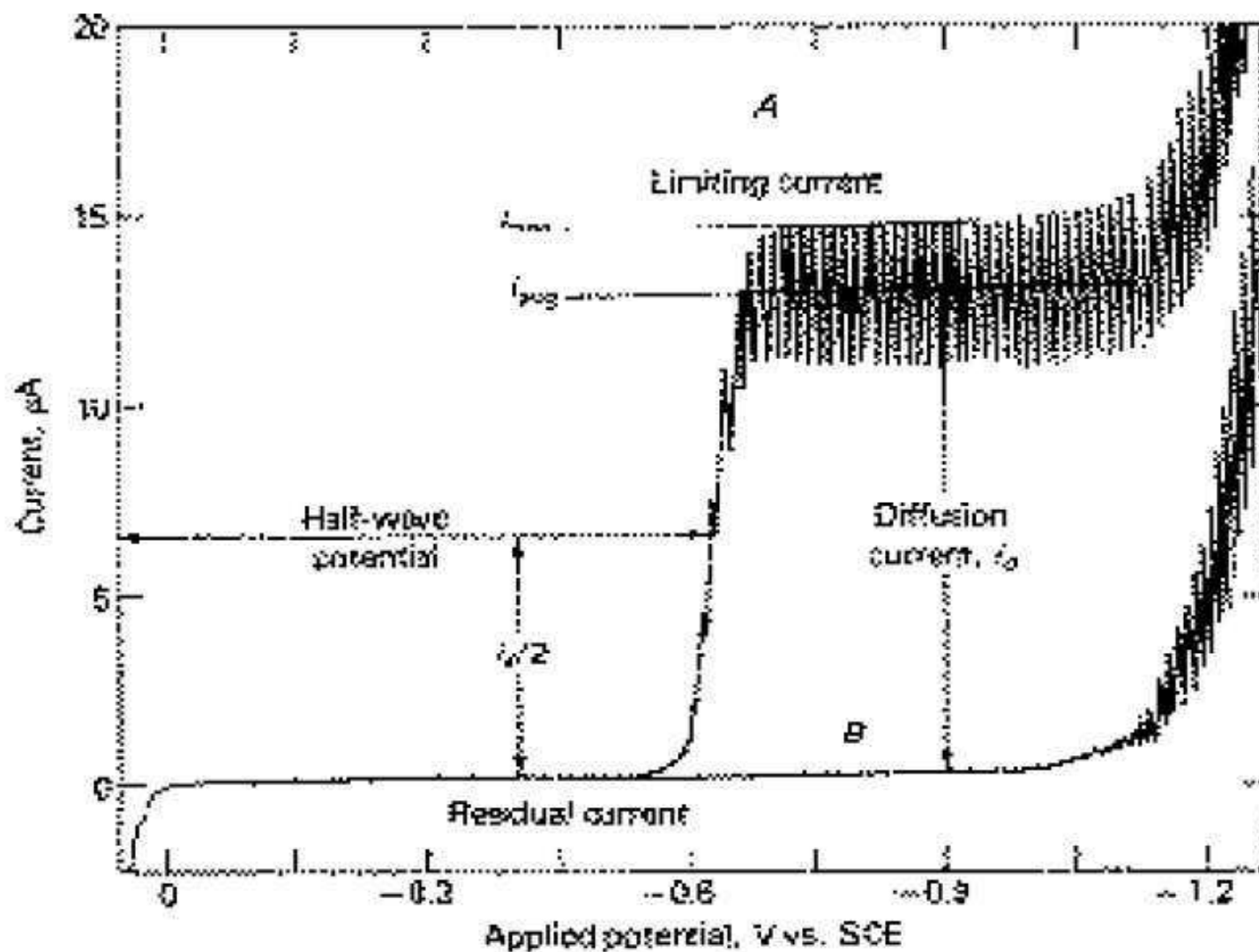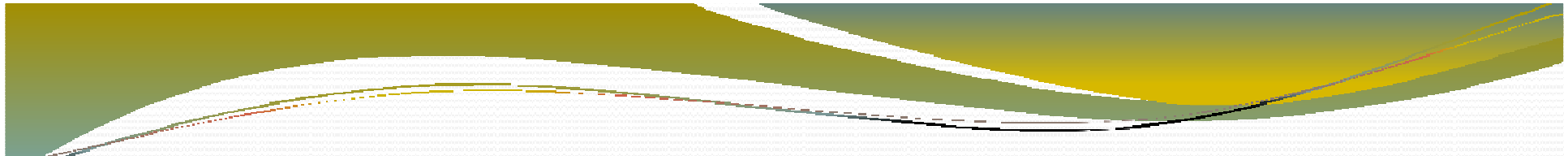
Figure 37.3 Classic polarogram taken at a DME showing background taken in 1 M HCl (line A) and 1 M HCl + 0.5 mM Cd(II) (line B). *(From D. T. Sawyer and J. L. Roberts, Experimental Electrochemistry for Chemists, copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)*

- The minimum potential required to initiate the electrolysis process is called the **decomposition potential.**

- The **faradaic current** is the **current** generated by the reduction or oxidation of some chemical substance at an electrode.

- **Capacitive current**, also called "**non-faradaic**" or "double-layer" **current**, does not involve any chemical reactions (charge transfer), it only causes accumulation (or removal) of electrical charges on the electrode and in the electrolyte solution near the electrode

- The **limiting current**, in electrochemistry, is the **limiting** value of a faradaic **current** that is approached as the rate of charge-transfer to an electrode is increased The **limiting current** can be approached, for example, by increasing the electric potential or decreasing the rate of mass transfer to the electrode.
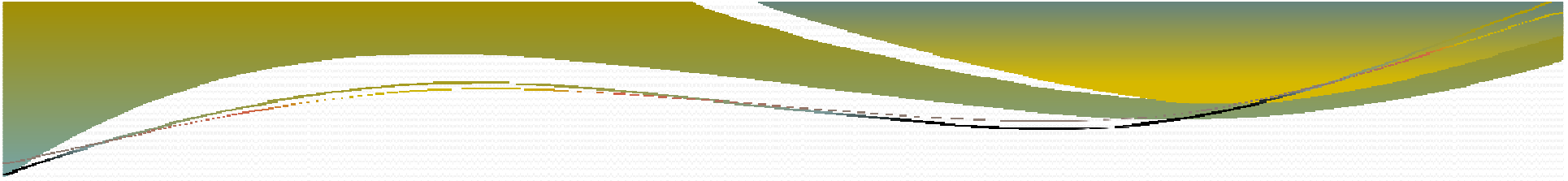
- The potential at which the current is one half the limiting current is called **half-wave potential $E_{1/2}$**

- **Diffusion current** is a **current** in a semiconductor caused by the **diffusion** of charge carriers (holes and/or electrons).

- A **residual-current** device (RCD), or **residual-current** circuit breaker (RCCB), is a device to quickly disconnect **current** to prevent serious harm from an ongoing electric shock

CYCLIC VOLTAMMETRY

- An electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is applied

- CV is performed by cycling the potential of a working electrode, and measuring the resulting current.

- **Governing law: Ohm's law E = ir**
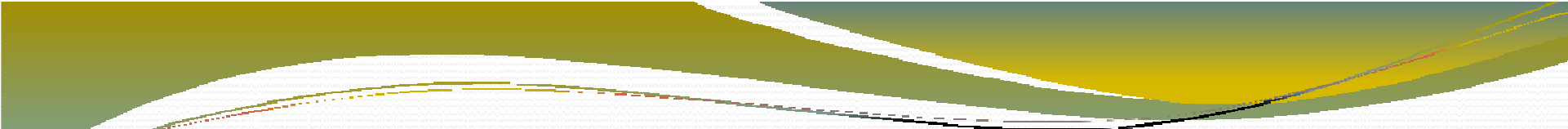
Cyclic Voltammogram
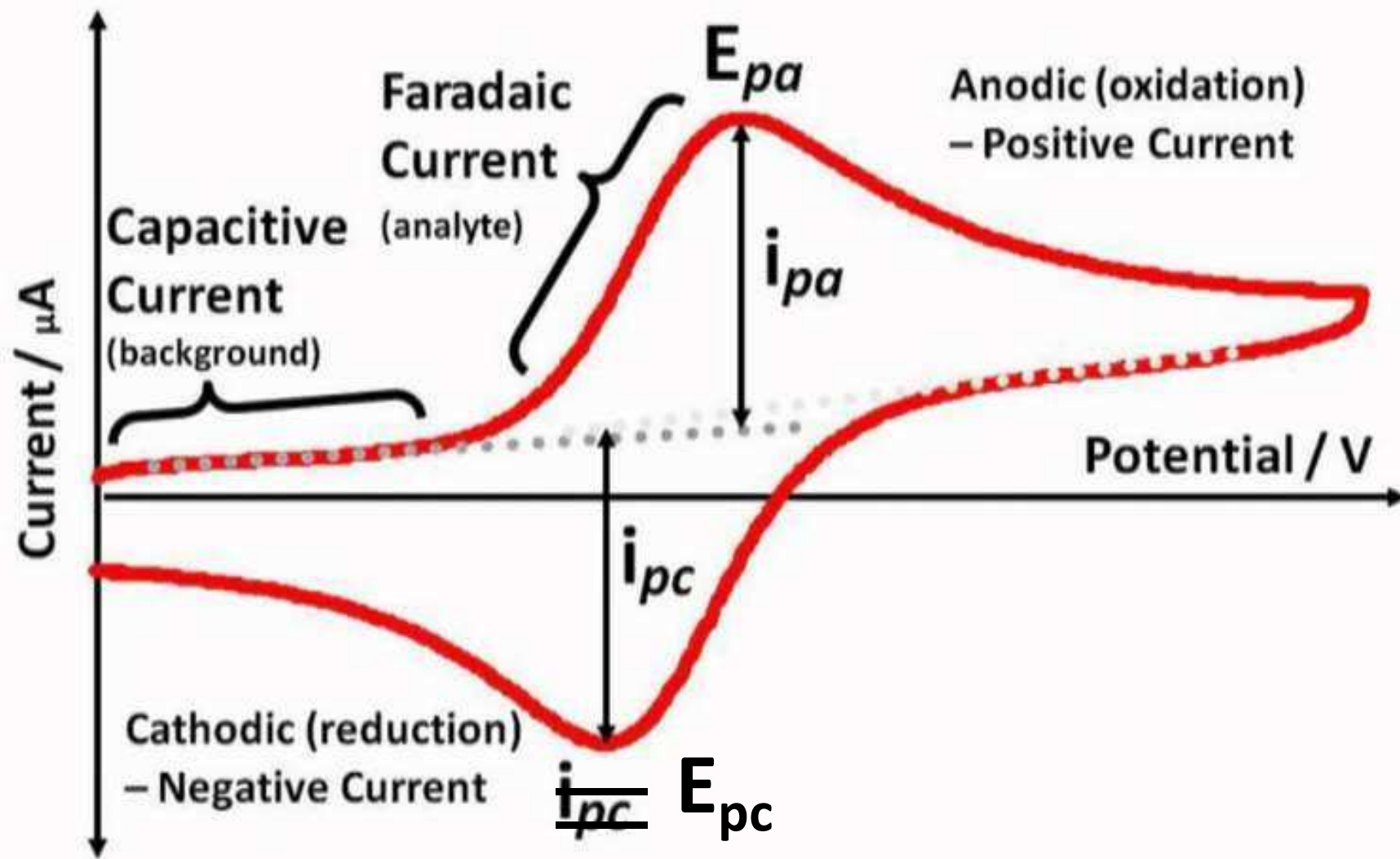
THEORY

- The applied potential controls the concentrations of the redox species at the electrode surface (CO_0 and CR_0), as described by the Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{c_R^0}{c_O^0}$$

where R is the molar gas constant ($8.3144\ J\ mol^{-1}K^{-1}$),
T is the absolute temperature (K), n is the number of electrons transferred,
F = Faraday constant ($96,485\ C/equiv$), and
E_0 is the standard reduction potential for the redox couple

The important parameters in a cyclic voltammogram are the peak potentials (Epc , Epa) and peak currents ($i$pc , $i$pa) of the cathodic and anodic peaks, respectively.

If the electron transfer process is fast compared with other processes (such as diffusion), the reaction is said to be electrochemically reversible, and the peak separation is

$$\Delta E_{\mathrm{p}} = |E_{\mathrm{pa}} - E_{\mathrm{pc}}| = 2.303\ RT/nF$$

- Thus, for a reversibleredox reaction (25 °C)

    DEp =0.0592/n V or about 60 mV for one electron. In practice this value is difficult to attain because of such factors as cell resistance.

- Irreversibility due to a slow electron transfer rate results in DEp > 0.0592/n V, greater, say, than 70 mV for a one-electron reaction.

- The **formal reduction potential (Eo)** for a reversible couple is given by

$$E^o = \frac{E_{pc} + E_{pa}}{2}$$

- For a reversible reaction, the concentration is related to peak current by **the Randles–Sevcik expression(at 25 °C):**

$$i_p = 2.686 \times 10^5 n^{3/2} A c^0 D^{1/2} v^{1/2}$$

- where ip -the peak current inamps,
- A is the electrode area(cm²),
- D is the diffusion coefficient(cm²s⁻¹),
- co is the concentration in mol cm⁻³,and
- n is the scan rate in V s⁻¹

Figure 37.5 Cyclic voltammograms of 5 mM Fe(CN)$_6^{-3}$ in 1 M KCl with ν = 500 mV/s.
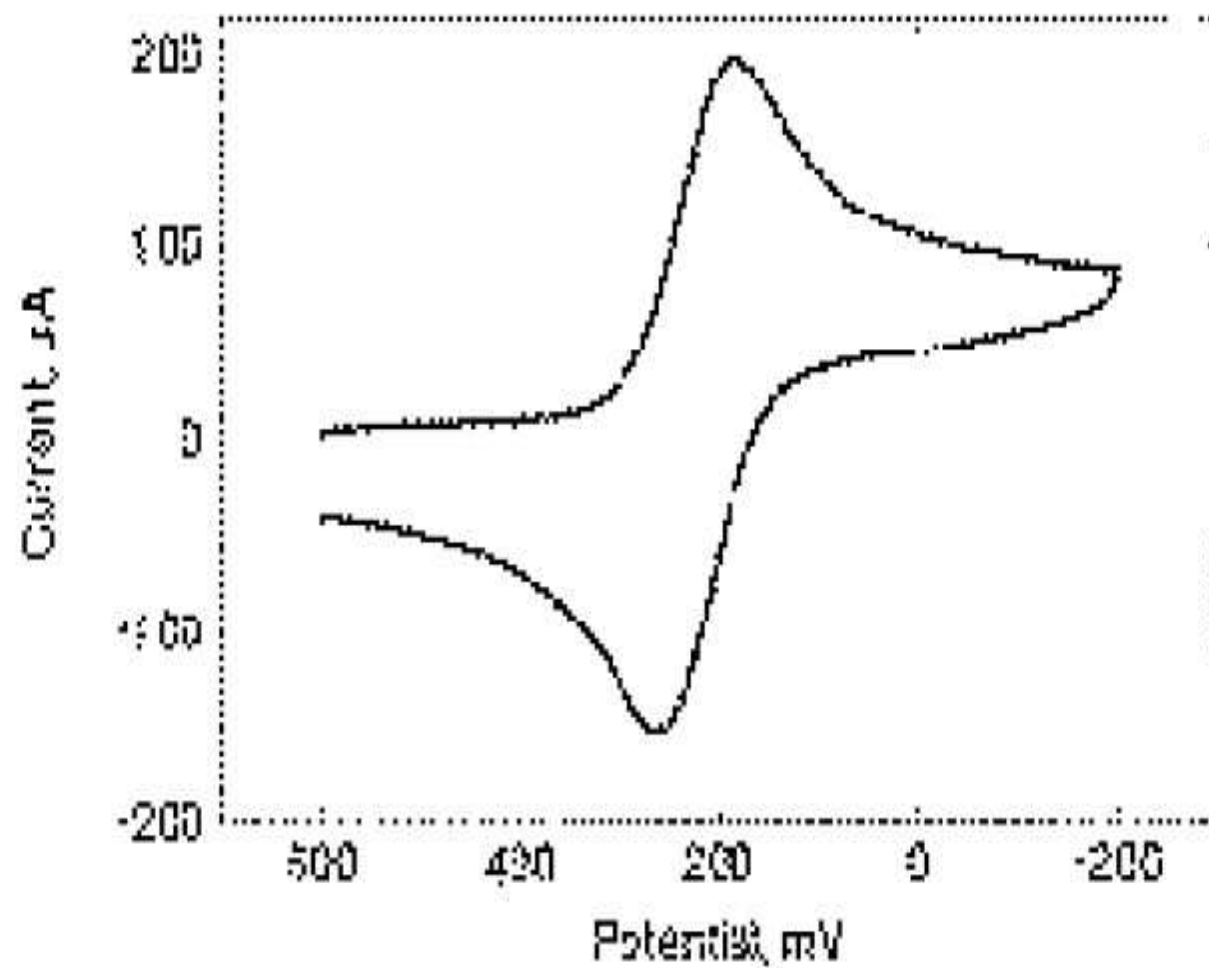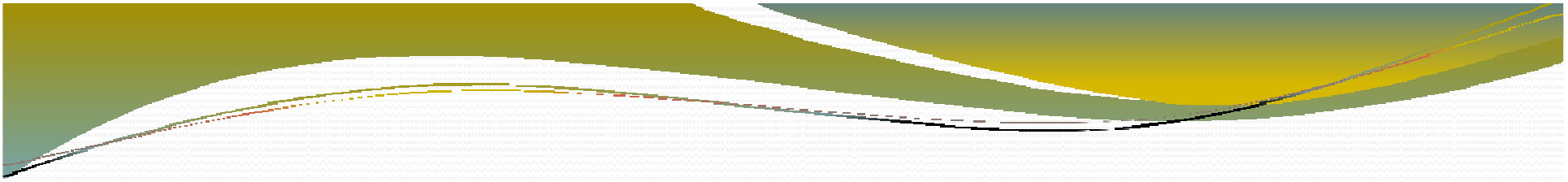
- Irreversible oxidation or reduction-Activated over potential (Extra energy applying to the electrode in the form of increasing potentia).
- Reversibility depends on the relative values of electron transfer rate constant(k_s) and the rate of change of potential-scan rate(n).
- If the ratio of k_s/n is small then nernstian concentration cannot be maintained then the process is called quasi-reversible.
- A quasi-reversible process is characterized by $DE_p > 59.2$/n mV, with the value increasing with increasing n.

APPLICATIONS

- CV is rarely used for quantitative determinations, but it is widely used for
- the study of redox processes,
- for understanding reaction intermediates, and
- for obtaining stability of reaction