# Voltammetric methods

Voltammetric methods: Measurement of current as a function of applied potential between two electrodes.

- At the E^o potential where the redox reaction occurs, a current takes place due to the passage of electrons.

- In the electrochemical cell, a concentration gradient is created (polarization of electrodes).
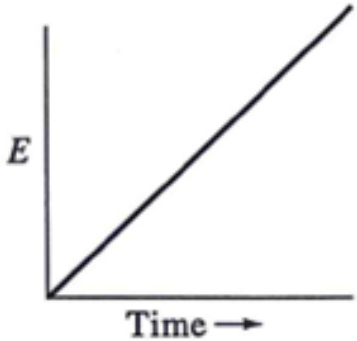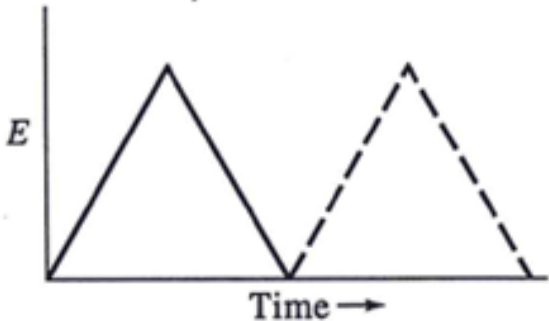
- A linear relationship should exist between cell voltage and current (V = RI).

- If not: cell is polarized.

- An electrode completely surrounded by ions is called **_passive_** and cannot accept or donate more electrons than at a limited rate.

A polarized electrode
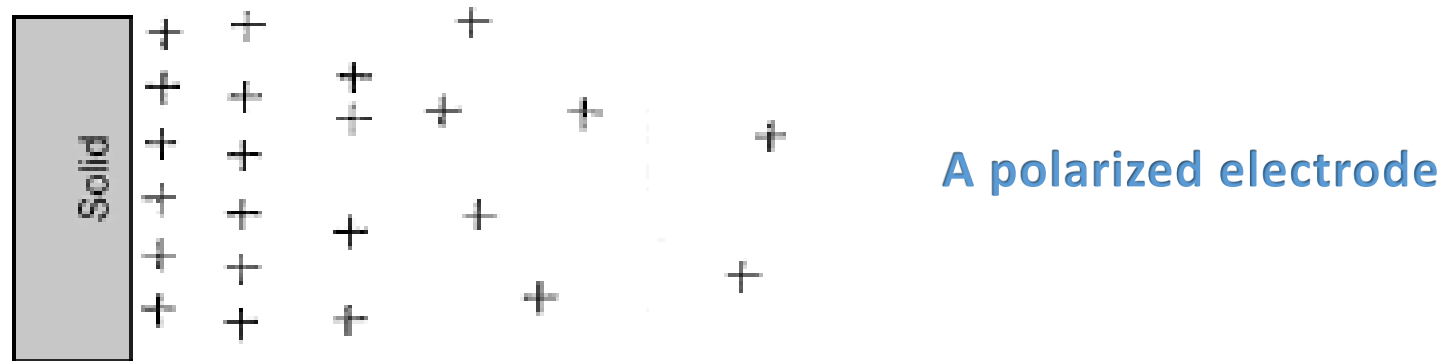
- Limiting currents are proportional to analyte concentration, and used for quantitative analysis.

Voltammetric experiments

- A variable potential called *excitation signal* is forced on an electrochemical cell.
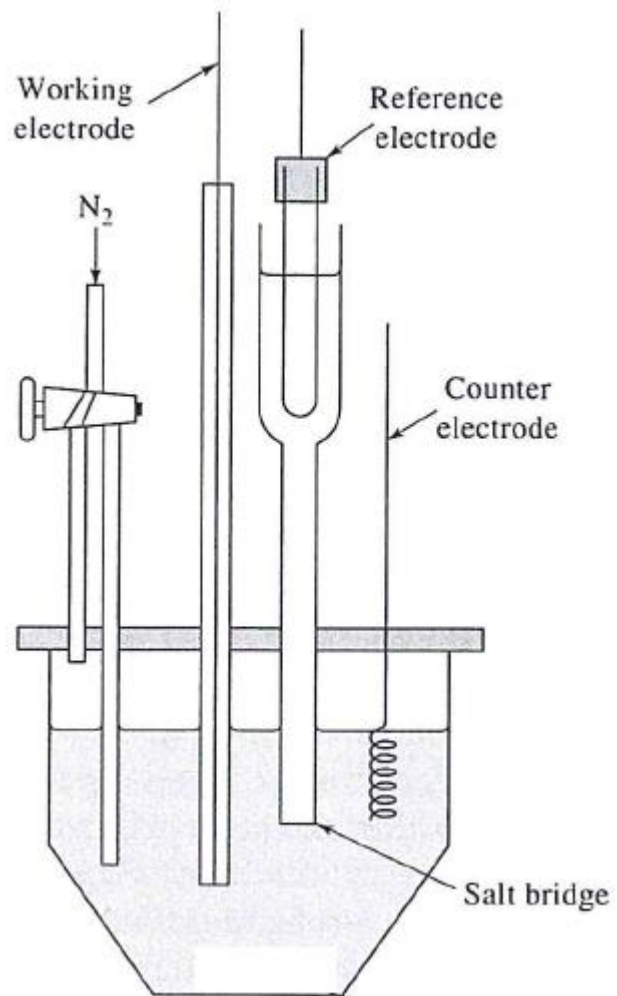- This signal triggers a characteristic polarized current response.

Name	Waveform	voltammetry
Linear scan	E ↗ / Time →	Polarography Linear-scan voltammetry
Triangular	E △△ / Time →	Cyclic voltammetry

method	potential ramp	polarogram
classical (linear sweep)	E	I
triangular wave	E	I

Instrumentation

Cell: Three electrodes in sample solution + support electrolyte

1. Working electrode (μ electrode): the potential of this electrode varies with time. Electrode is small, to enhance polarization. For analytical half-reaction.

2. Reference electrode (Ag/AgCl or SCE). Potential remains constant throughout the experiment.

3. Counter electrode (Pt). Serves to conduct electricity through the solution.

Different working electrodes

Wire

Teflon

Conducting disk

Hg

Hg drop

Wire

Hg

Tygon tubing

HMDE

Capillary

Hg drop
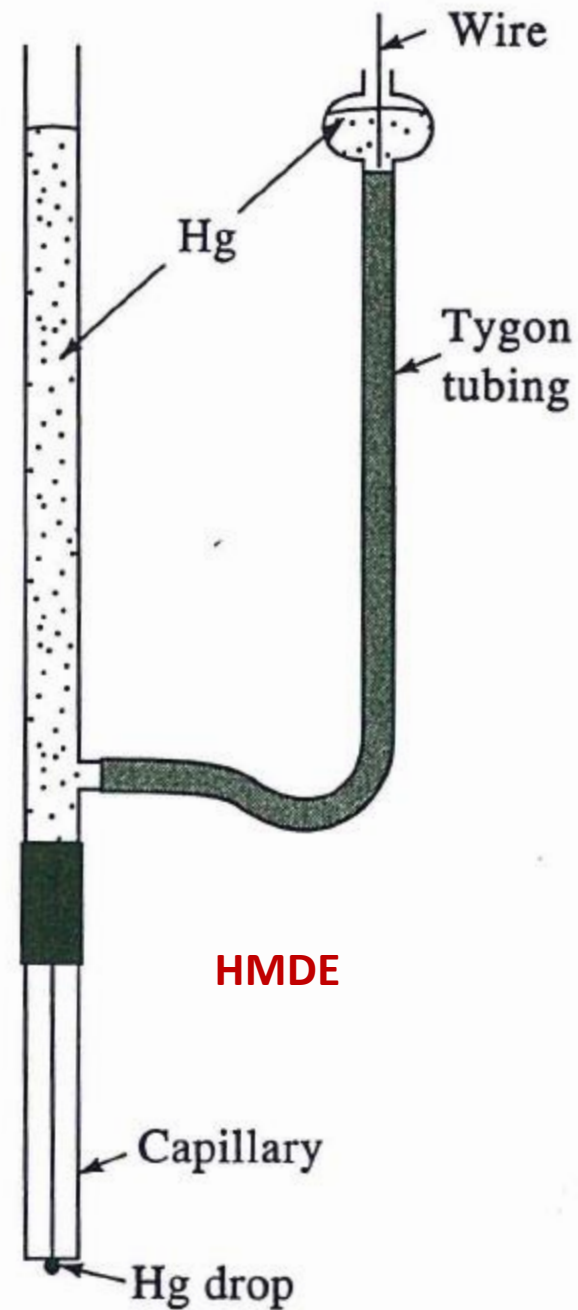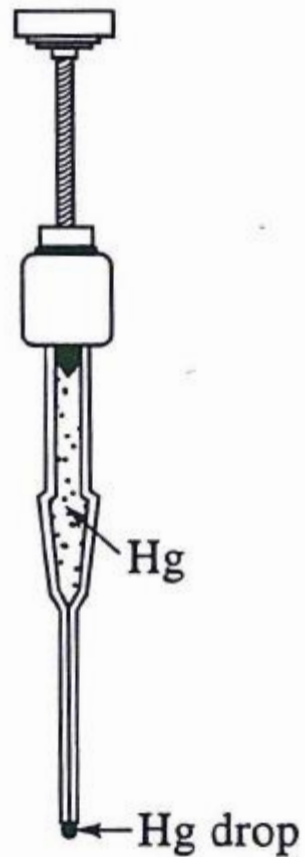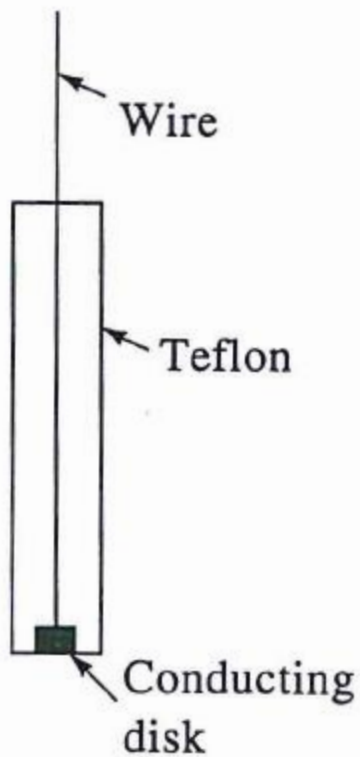
Why use Hg μ electrodes:

- A fresh metallic surface is readily formed by production of a new drop

- Currents measured are very sensitive to impurities

HMDE: Hanging mercury dropping electrode

- 10 cm of a 50 μm i.d. capillary tube

- A new drop forms and breaks every 2-6 s.

- Drop diameter: 0.5-1 mm

- Mechanical knocker

Polarography

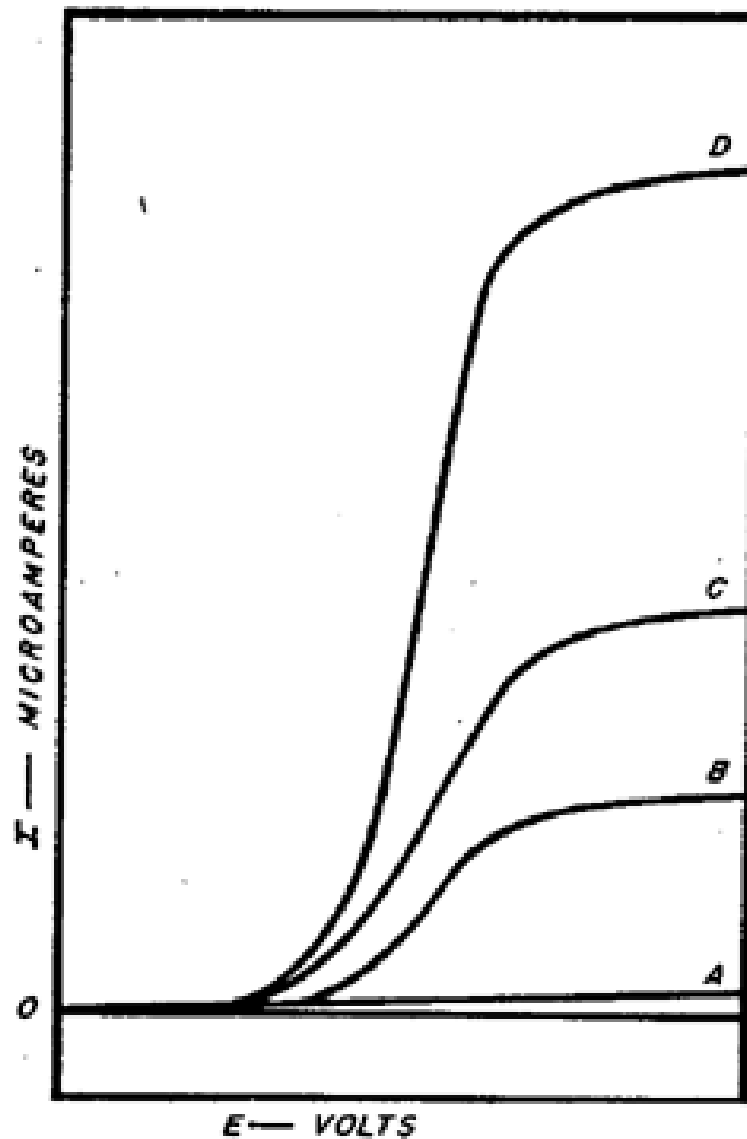- First type of voltammetry developped.

- Uses a dropping Hg electrode

Limiting currents are proportional to analyte concentration.

$$i_l = kCA$$ **(Ilkovic equation)**

Effect of concentration

$$i_d = kCA$$

Cd²⁺ + 2e + Hg → Cd(Hg) — $Cd^{2+} + 2e + Hg \rightarrow Cd(Hg)$

A

1 M HCl + 5 x 10⁻⁴ M Cd²⁺ — $1\ M\ HCl + 5 \times 10^{-4}\ M\ Cd^{2+}$

Limiting current

i_{max}

i_{avg}

Half-wave potential

Diffusion current, i_d

$i_d/2$

B

Residual current

1 M HCl

20

15

10

5

0

0   −0.3   −0.6   −0.9   −1.2

Applied potential, V vs. SCE

Wire

Hg

Tygon tubing

Capillary

Hg drop
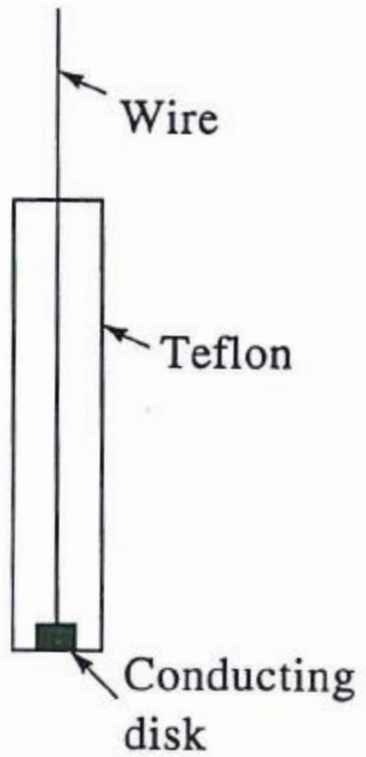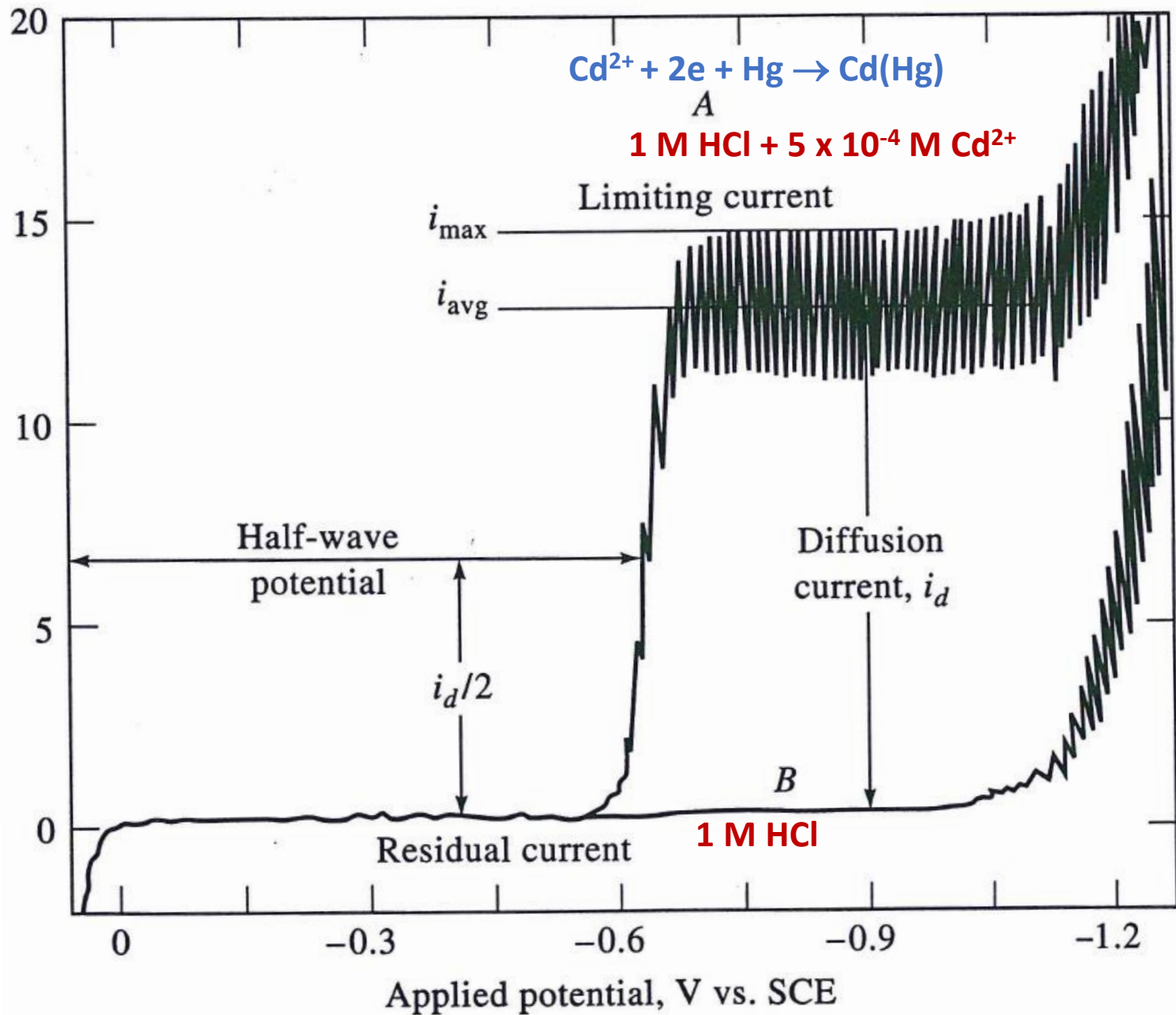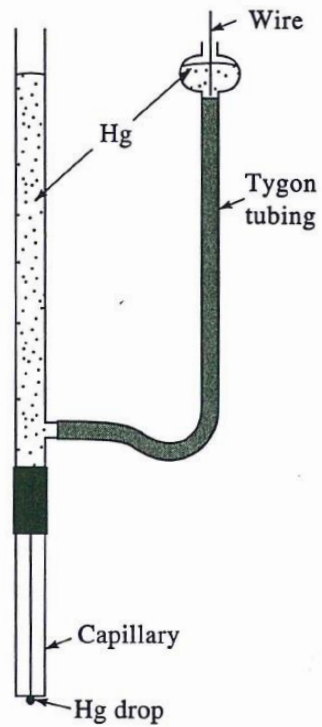
Standard electrode potentials in aqueous solution at 25°C

Cathode (Reduction) Half-Reaction	Standard Potential $E°$ (volts)
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04
$K^+(aq) + e^- \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.76
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	-0.04
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 (ref)
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.16
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.17
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.199 (ref)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_2^-(aq) + 2OH^-(aq)$	0.35

Cathode (Reduction) Half-Reaction	Standard Potential $E°$ (volts)
$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.52
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightarrow ClO^-(aq) + 2OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.44
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87

The Ilkovic equation relates the diffusion current (I_d) and the concentration of the analyte (C_A).

$$I_{d,avg} = 607 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot C_A$$

$$I_{d,max} = 708 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot C_A$$

D: diffusion constant of the analyte (cm^2/s)

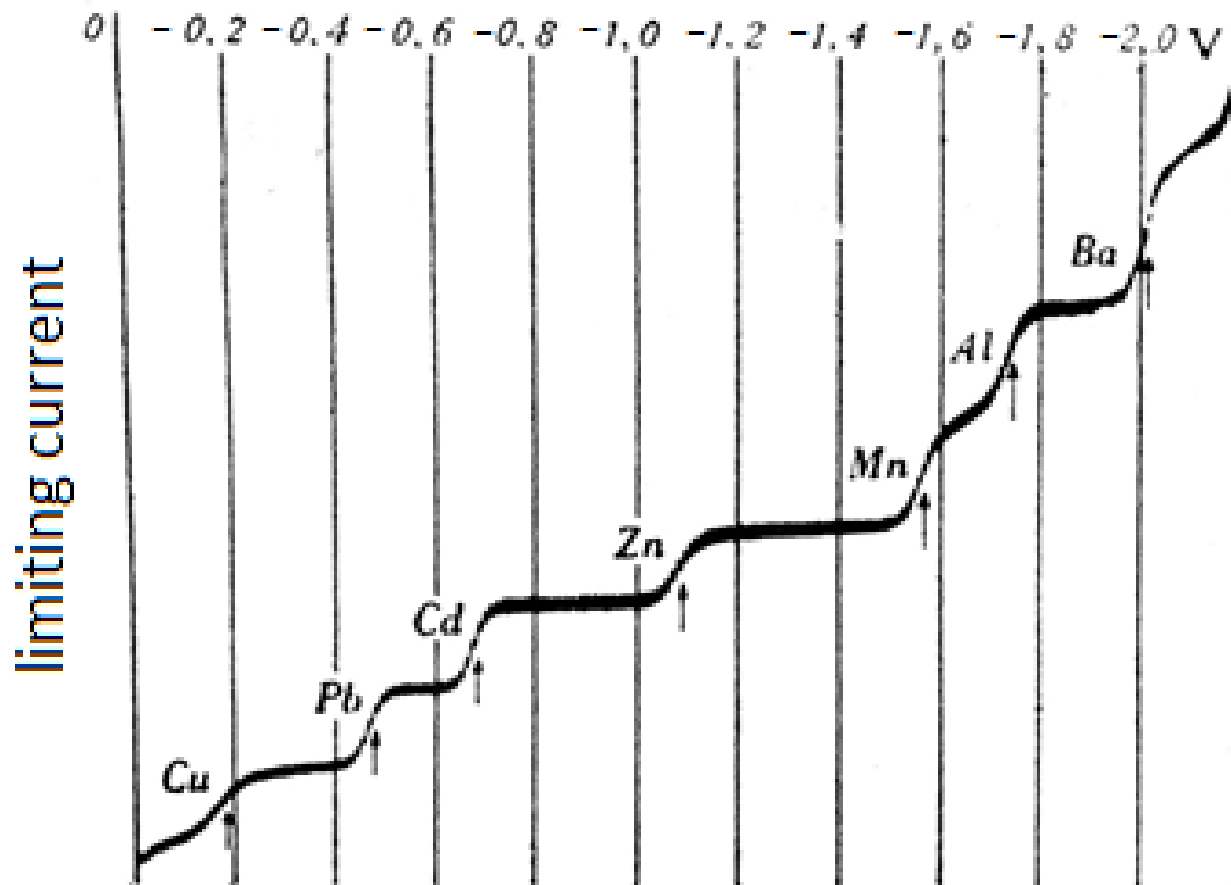n: number of electrons exchanged in the electrode reaction

m: mass flow rate of Hg through the capillary (mg/sec)

t: drop lifetime in seconds
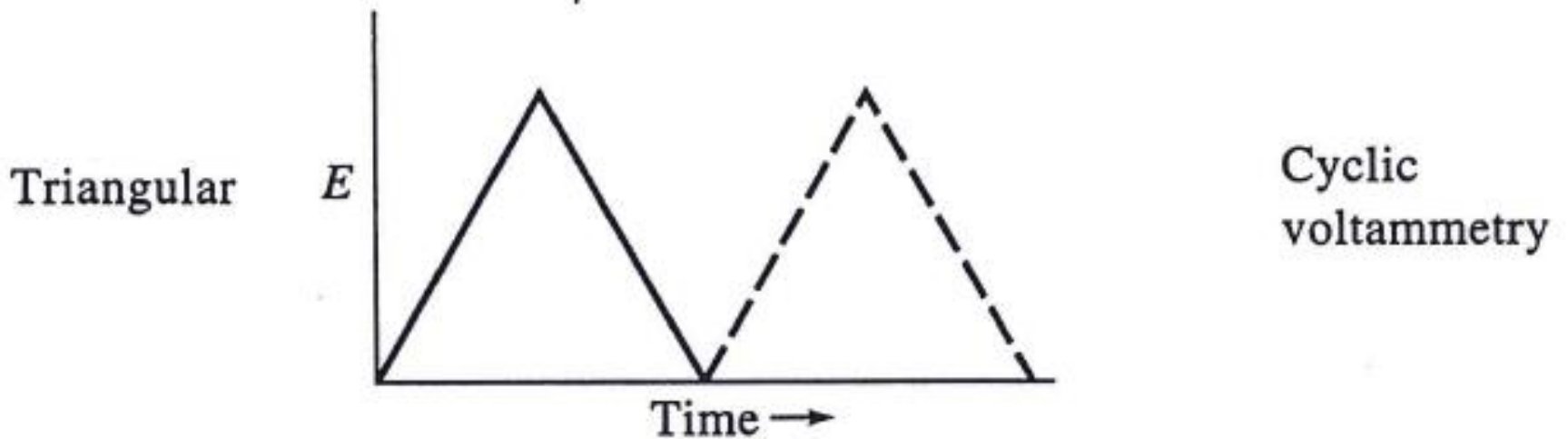
C_A: concentration in mol/mL

(named after the Slovak chemist, Dionýz Ilkovič (1907-1980)).

Multi element analysis

Cyclic voltammetry

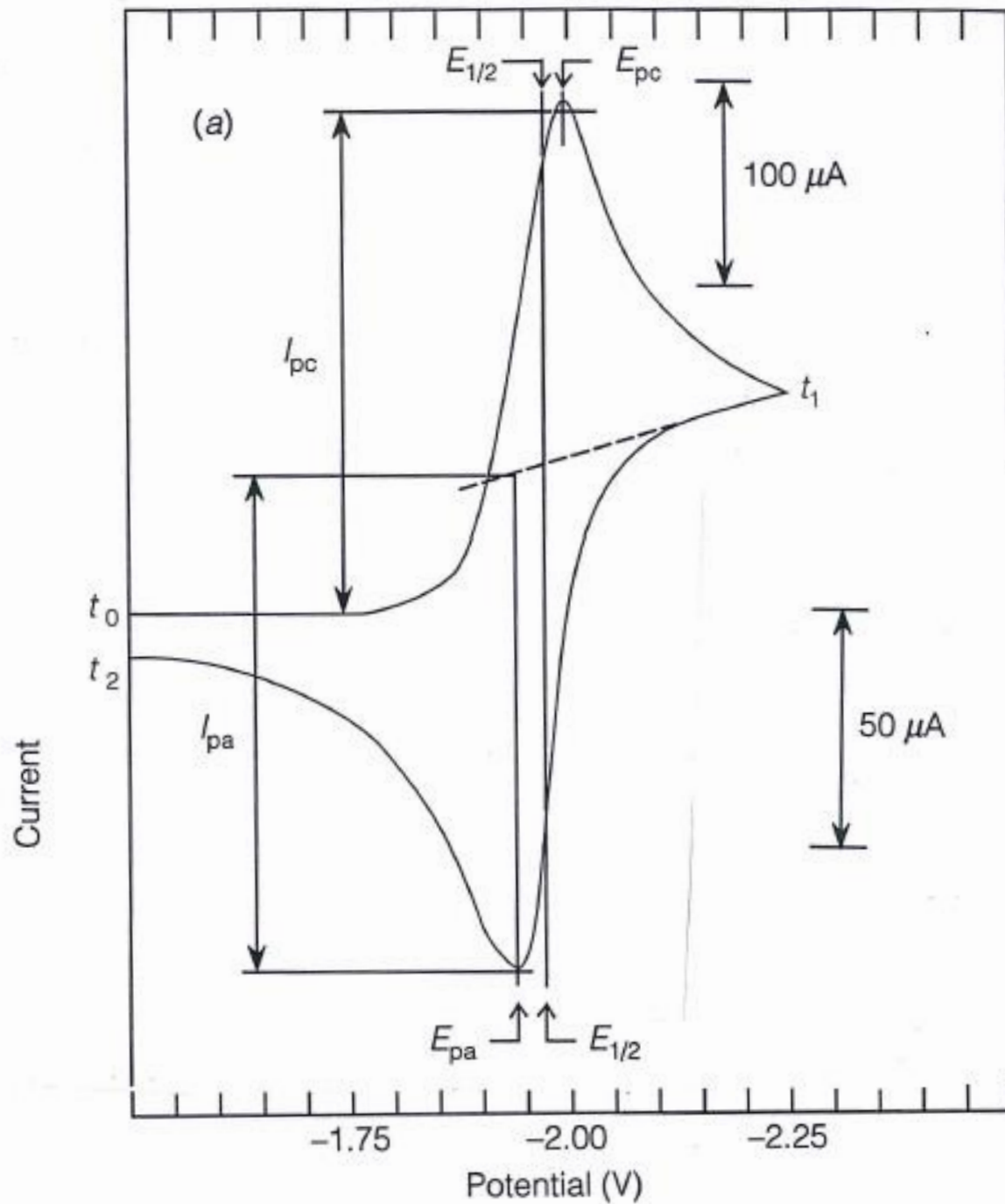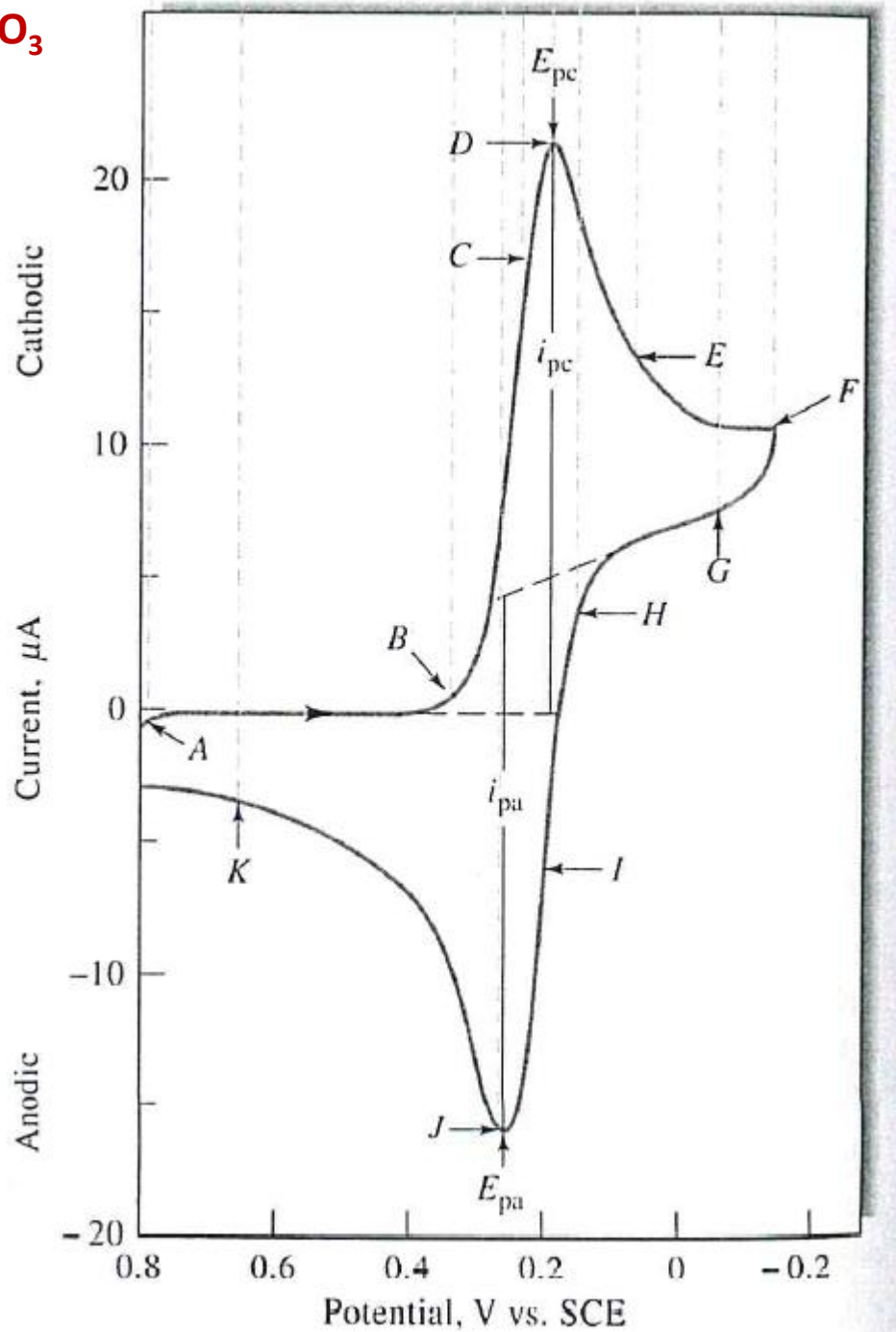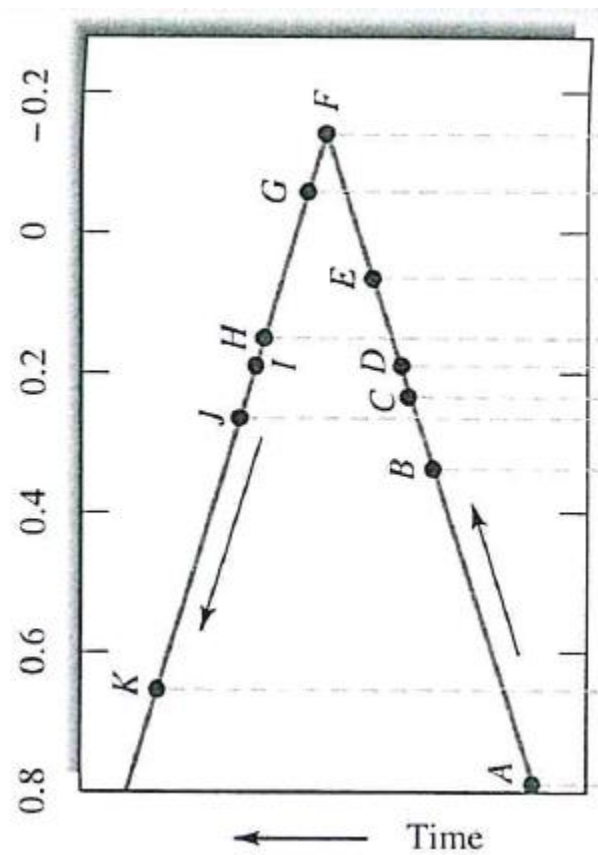Current response of a small stationary electrode excited by a triangular wave in an unstirred solution.

Triangular E Cyclic voltammetry

Time ⟶

Figure 25-20: 6 mM K₃Fe(CN)₆ in 1 M KNO₃

SCE. Pt

A: Oxidation of water to give oxygen (negative current).

B: start of reduction of hexaferrocyanate (III) into hexaferrocyanate (II).

From B to D: current from diffusion plus surge to attain Nernst equation equilibrium concentrations. At E_{pc}, there is no more Nernst pair and the diffusion current starts to decrease as the diffusion layer is going away from the electrode.

F: Change of scan direction.

Important parameters:

Cathodic peak potential E_{pc}
Anodic peak potential E_{pa}
Cathodic peak current i_{pc}
Anodic peak current i_{pa}

For a reversible reaction: i_{pc} and i_{pa} are equal in absolute value.
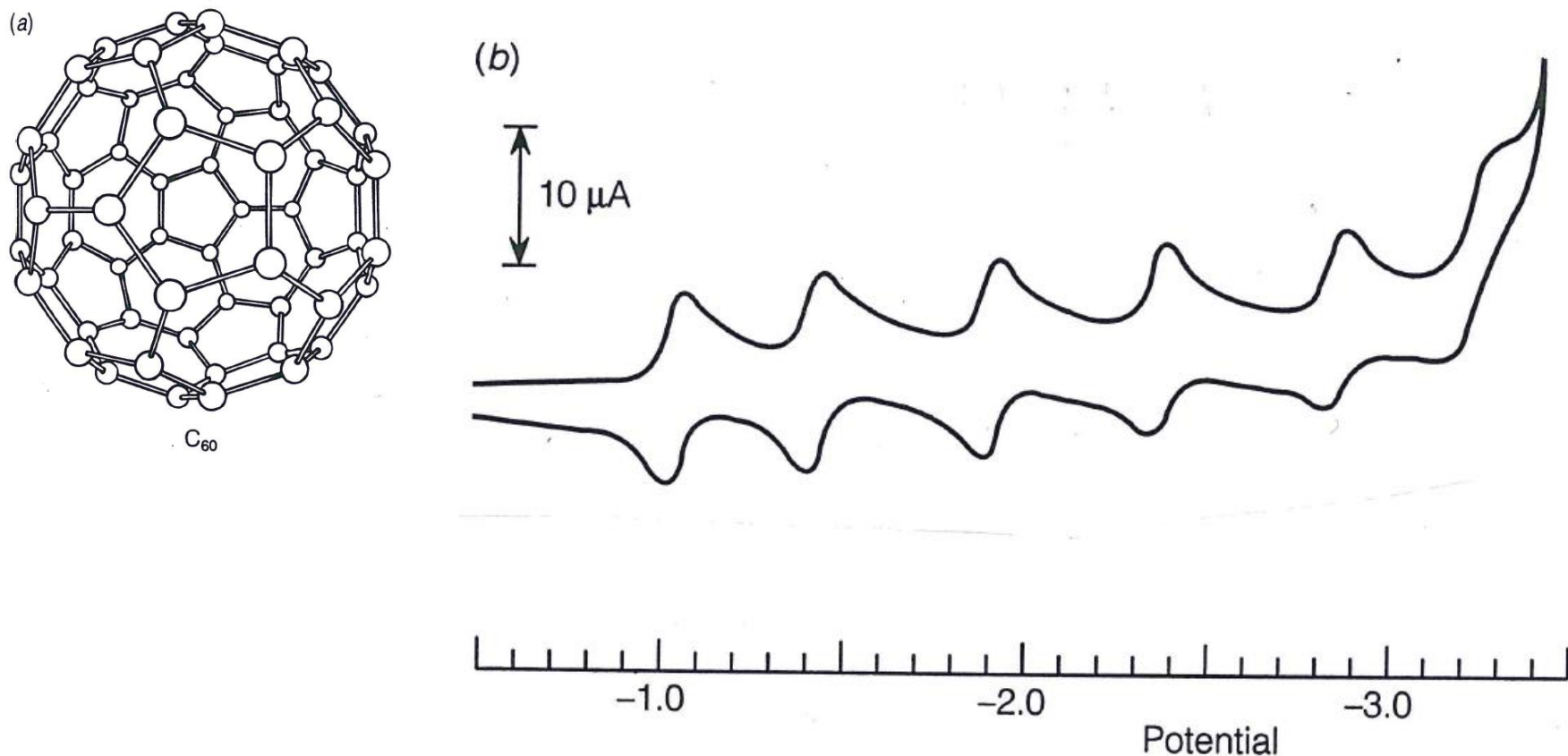
$E_{pc}-E_{pa} = 0.0592/n$

Figure 18-21 (a) Structure of C_{60} (buckminsterfullerene). (b) Cyclic voltammetry and (c) differential pulse polarography of 0.8 mM C_{60} showing six waves for reduction to C_{60}^-, $C_{60}^{2-} \cdots C_{60}^{6-}$. The acetonitrile/toluene solution was at $-10°C$ with $(n-C_4H_9)_4N^+PF_6^-$ supporting electrolyte. The reference electrode contains the ferrocene|ferricinium redox couple (Section 17-5). [From Q. Xie, E. Pérez-Cordero, and L. Echegoyen, *J. Am. Chem. Soc.* **1992,** *114,* 3978.]

Questions

1.
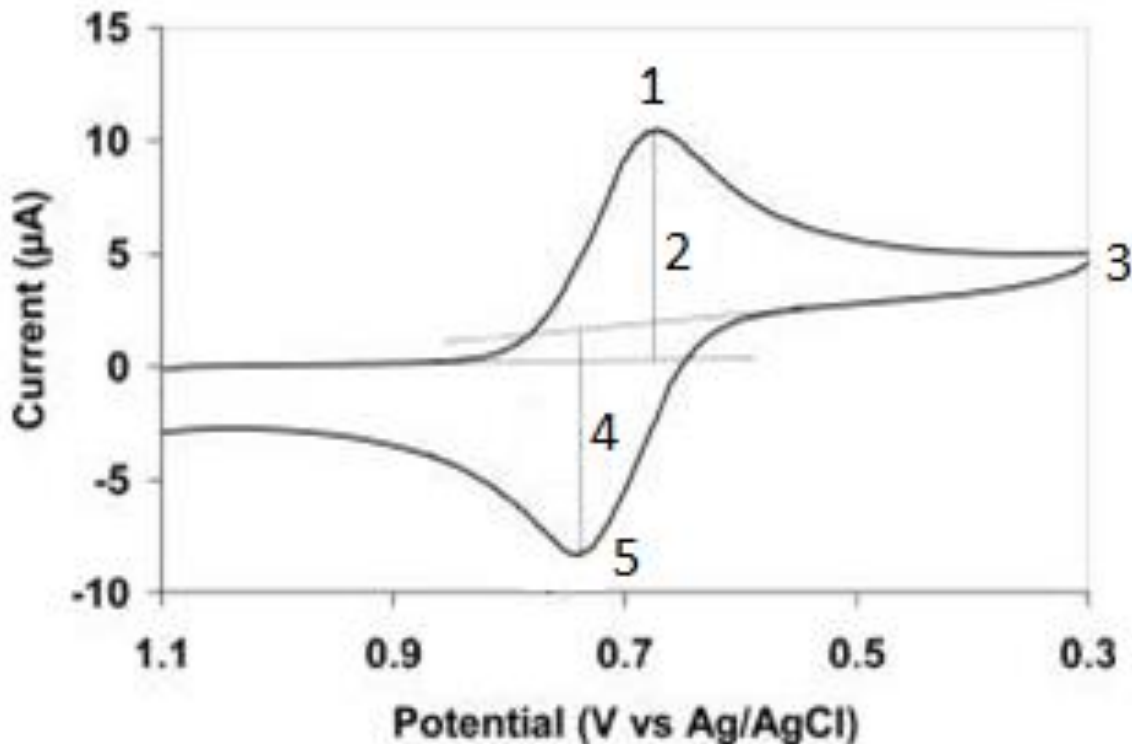
$E^o_{Ag,AgCl}$ = +0.199 V

According to this voltammogram:
a)   The analyte is first oxidized, then reduced and its reduction potential is 0.67 V
b)   The analyte is neither reduced nor oxidized as the reaction is reversible.
c)   The analyte is first reduced, then oxidized and its reduction potential is 0.90 V
d)   Ag(s) in the reference electrode is oxidized at an oxidation potential of 0.72 V
e)   None of these answers

2.

Describe what you are seeing in the voltammogram shown below at points 1, 2, 3, 4, 5.