Chronoamperometry

- Stationary electrode
- Unstirred = mass transport by diffusion
- Constant potential
- Measure current vs time

**Theory**

assume $\text{Ox} + n \text{e}^- \leftrightarrow \text{Red}$

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential set so reduction goes to completion at the electrode surface
Components of output signal in Chronoamperometry

$I_{Far}$ decreases because Ox used up at electrode surface and Ox is only replenished by diffusion.

- Faradaic current ($I_{Far}$) follows Cottrell equation.
- Capacitive current ($I_{cap}$) decays exponentially for a constant applied potential.

$I_{cap}$ is high as electrode capacitive layer charges up, then drops off.
Processes perturbing system can cause data to differ from Cottrell Equation

1) Capacitive Current – charging current is exponential as shown

\[ I_{cap} = e^{-kt} \]

Note: Capacitive current decreases more rapidly than Faradaic current so at longer times the ratio \( I_{Far}/I_{cap} \) is larger

2) Occurrence of coupled chemical reactions e.g. Ox + n e\(-\) \(\rightarrow\) Red

\[ 2 \text{Red} \rightarrow A \]
\[ A + n e^- \leftrightarrow B \]

Affects the shape of the current-time curve
Chronoamperometry Applications

• Can measure concentration by measuring I vs conc. at any fixed time
• Can analyze the shape of the current-time curve in order to study coupled chemical reactions
• There are better ways to do both of these with more modern techniques
• Chronoamperometry is important because it is a fundamental method on which other techniques are based
Chronopotentiometry

- Stationary electrode
- Unstirred = mass transport by diffusion
- Constant current applied between electrodes
- Measure potential vs time

Theory

assume \[ \text{Ox} + n \, e^- \rightleftharpoons \text{Red} \]

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- apply current and use up Ox at electrode surface producing Red

Galvanostat
$\text{Ox} + n \text{e}^- \leftrightarrow \text{Red}$

Apply current & use up \text{Ox} at electrode surface while producing \text{Red}
Theory of Chronopotentiometry

\[ E = E^o - \frac{0.059}{n} \log \frac{[\text{Red}]}{[\text{Ox}]} \]

A gradual change in \( E \) occurs as [Red] goes up and [Ox] goes down (transition region).

Ultimately the surface concentration of Ox goes to zero & to sustain the constant current applied, electrode potential makes a rapid change to the value required to make a new process go.
At start no Red is present so E is not defined

Point at which Ox is used up

\[ \tau^{1/2} = \frac{\pi^{1/2} nFAD^{1/2} C_{Ox}}{2i} \]

Sand Equation
Summary of Chronopotentiometry

• In principle quantitative analysis can be done by relating $\tau^{1/2}$ to $C_{ox}$
• In reality it is better done by other methods
• Chronopotentiometry illustrates constant current situation in electrochemistry
• Chronopotentiometry is very poor at handling capacitive current
Coulometry

Methods based on counting coulombs (C), the basic unit of electrical charge (Q)

Faraday’s Law

\[ W = \frac{Q \cdot M}{n \cdot F} \]

Where: 
- \( M \) = molecular weight (g/mole)
- \( W \) = weight (g)
- \( n \) = number of electrons (unitless)
- \( F \) = Faraday’s constant (96,500 C/mol)
Fundamental assumption is that reaction is 100% current efficient i.e., all coulombs go to oxidizing or reducing species of interest.

Kinds of coulometry

1) Controlled Potential Coulometry

\[ Q = \int_{0}^{t} i \, dt \]

Nothing more than integrating area under the curve in chronoamperometry.

Can be referred to as chronocoulometry.

2) Constant Current Coulometry

\[ Q = i \, t \]

Care must be taken so that there is enough stuff to carry the current at electrode surface.

Rarely used anymore.
Major application is coulometric titrations where titrant is prepared electrochemically and standardized by counting coulombs e.g. bromine Br₂ as titrant

\[ 2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^- \]

1) Useful for titrants that can’t be stored as stable solutions

2) Small currents can be measured accurately so even very dilute titrants can be used

3) In theory can count coulombs for any method where current is measured by integrating
Coulometric cell

2 Br\(^-\) → Br\(_2\) + 2 e\(^-\)

Br\(_2\) + C\(_6\)H\(_{10}\) → C\(_6\)H\(_{10}\)Br\(_2\)

Apparatus for coulometric titration of cyclohexene with Br\(_2\). The solution contains cyclohexene, 0.15 M KBr, and 3 mM mercuric acetate in a mixed solvent of acetic acid, methanol, and water. Mercuric acetate catalyzes the addition of Br\(_2\) to the olefin. [Adapted from D. H. Evans, J. Chem. Ed. 1968, 45, 88.]
<table>
<thead>
<tr>
<th>Oplen addition (redox)</th>
<th>KBr (pH &gt; 5)</th>
<th>HCl</th>
<th>Ag⁺ anode</th>
<th>Fe⁺⁺</th>
<th>( Ca^{++} )</th>
<th>( Zn^{++} )</th>
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<tr>
<td>Complexometric</td>
<td>H₄N⁺ edge</td>
<td>HCl</td>
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<td>Neutriization</td>
<td>H₂O</td>
<td>+ H⁺</td>
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<tr>
<td>Neutriization</td>
<td>H₂O</td>
<td>-OH</td>
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<td>Karl Fischer reagent</td>
<td>(pH &gt; 9)</td>
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<tr>
<td>Redox</td>
<td>Ag⁺</td>
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</tbody>
</table>

**Type**

- Precipitation
- Generalized
- Assayed

**Examples of Coulometric Titrations**
Voltammetry

• Stationary electrode
• Stirred = mass transport by convection
• Vary potential linearly with time
• Measure current vs time

Theory

assume \( \text{Ox} + n \text{e}^- \leftrightarrow \text{Red} \)

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential varies
Define - Limiting Current as steady state current when \([\text{Ox}] = 0\) at electrode surface i.e., applied potential is sufficiently cathodic such that all \text{Ox} is reduced at electrode

\[
I = \frac{nFADC_{\text{bulk}}}{\delta}
\]

Gives quantitative information

\[E = E^o - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]}\]
Linear-scan voltammogram for stirred solution