Chapter 1
Electrochemical methods of Analysis-Potentiometry
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Electroanalytical Chemistry

- Electroanalytical chemistry is a group of methods based upon the electrical properties of a solution of the analyte.
- Electroanalytical techniques are capable of producing very low detection limits.
- Electroanalytical techniques are often specific for a particular oxidation state of an element, where other techniques are only capable of revealing total concentrations of an element.
- Electroanalytical techniques require relatively inexpensive equipment.
- Electroanalytical techniques provide information about activities rather than concentrations.
  - Ordinarily, it’s the activities of ions that are significant in “how things work”.
Recall from Freshman Chemistry:

- **Oxidation**: Loss of electrons or increase in the oxidation number
  - \( \text{Fe}^{2+} + e^- \rightarrow \text{Fe}^{3+} \)

- **Reduction**: Gain of electrons or decreases in the oxidation state
  - \( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \)

- **Redox reaction**
  - \( \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \)

- **Oxidizing agent**: Species that is being reduced and causes an oxidation

- **Reducing agent**: Species that is being oxidized and cause a reduction
Half-Cells = Half-cell reaction

\[
\text{Cu(s)} + 2\text{Ag}^+ \leftrightarrow \text{Cu}^{2+} + 2\text{Ag(s)}
\]

\[
\text{Cu} \mid \text{Cu}^{2+} (0.0200 \text{ M}) \parallel \text{Ag}^+ (0.0200 \text{ M}) \mid \text{Ag}
\]

\[
E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}
\]

\[
E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}
\]

**E_{\text{cathode}}**

\[
\text{Ag}^+ + e^- \leftrightarrow \text{Ag(s)}
\]

\[
\text{Ag}^+ (0.0200 \text{ M}) \mid \text{Ag}
\]

**E_{\text{anode}}**

\[
\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu(s)}
\]

\[
\text{Cu}^{2+} (0.0200 \text{ M}) \mid \text{Cu}
\]

By convention, all Half-Cell reactions are written as reduction half-reactions.
Galvanic Cells

- A galvanic cell uses a *spontaneous* chemical reaction to generate electricity.
  - One reagent (Cd) is oxidized at the **anode**.
  - Another reagent (AgCl) is reduced at the **cathode**.

- The process:
  1. Cd metal is oxidized at the anode.
  2. The electrons flow through the circuit to the Ag electrode.
  3. At the surface of the electrode, Ag$^+$ (from AgCl) is reduced to Ag(s).
     - The chloride goes into solution.

- A galvanic cell results in a **positive voltage** because the chemical reaction is *spontaneous*.

\[
\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd} \\
\text{AgCl} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^- 
\]
Galvanic Cells

- The charge actually flows because the sum of the two *half-cell* reactions is NOT in equilibrium (cell potential is not zero V).
  - The magnitude of the potential is related to the tendency for the reaction to proceed toward equilibrium.
  - The potential will become smaller and smaller as the reaction proceeds and will be 0.00V once equilibrium is reached.
Galvanic Cell = Battery

\[ \text{Ag}^+ + e^- \leftrightarrow \text{Ag(s)} \]
\[ \text{Cu(s)} \leftrightarrow \text{Cu}^{2+} + 2e^- \]

\[ 2\text{Ag}^+ + \text{Cu(s)} \leftrightarrow 2\text{Ag(s)} + \text{Cu}^{2+} \]
Electrolytic Cells

\[ \text{Ag(s)} \leftrightarrow \text{Ag}^+ + e^- \]
\[ \text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu(s)} \]

\[ 2\text{Ag(s)} + \text{Cu}^{2+} \leftrightarrow 2\text{Ag}^+ + \text{Cu(s)} \]
Anodes and Cathodes

**Anode** - Oxidation takes place

- \( \text{Cu(s)} \leftrightarrow \text{Cu}^{2+} + 2e^- \)
- \( 2\text{Cl}^- \leftrightarrow \text{Cl}_2(g) + 2e^- \)
- \( \text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^- \)

**Cathode** - Reduction takes place

- \( \text{Ag}^+ + e^- \leftrightarrow \text{Ag(s)} \)
- \( \text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \)
- \( \text{NO}_3^- + 10\text{H}^+ + 8e^- \leftrightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \)
Cu(s) + 2Ag⁺ ↔ Cu²⁺ + 2Ag(s)

Cu | Cu²⁺(0.0200 M) || Ag⁺(0.0200 M) | Ag
Electrode Potentials

- It is the driving force for either reduction or oxidation half reaction, when by convention, they are both written as reductions.

- $\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}$
- $\text{Ag}^{+} + e^- \leftrightarrow \text{Ag}$
Controlling and measuring Potential

- **Electrochemical Cell Consists of**: Two or more electrodes, Electrolyte, Electronics for controlling and measuring the potential
  - **Indicator (Working) Electrode**: One whose potential is sensitive to the analyte’s concentration
  - **Counter (Reference) Electrode**: It completes the electric circuit and provides a reference potential against which the working electrode potential is measured. *Its potential remains constant*
Reference Electrodes

• One of the half-cells provides a known reference potential, and the potential of the other half-cell indicates the analyte's concentration.

• By convention, \( E_{cell} = E_{ind} - E_{ref} \)

• The ideal reference electrode must provide a stable potential so that any change in \( E_{cell} \) is attributed to the indicator electrode, and, therefore, to a change in the analyte's concentration.
H₂ gas
1.000 atm

Reference Electrode, SHE

Glass envelope

Platinum wire

Platinum foil covered with platinum black

1 M HCl

E = 0.000000 V
**Calomel Electrode**

- **saturated calomel Electrode- S.C.E**
- **$E^0 = +0.241 \text{ V}$**

A small hole connects the two tubes, and an asbestos fiber serves as a salt bridge to the solution in which the SCE is immersed. The stopper in the outer tube may be removed when additional saturated KCl is needed.
If the KCl solution is saturated then
\[ E_0(\text{saturated KCl}) = 0.197 \, \text{V} \]
The potential of the indicator electrode in a potentiometric electrochemical cell is proportional to the concentration of analyte.

Two classes of indicator electrodes are used in potentiometry: **metallic electrodes**, and **membrane ion-selective electrodes**.
Membrane Ion-Selective Electrodes

- The discovery, that a thin glass membrane develops a potential, called a membrane potential, when opposite sides of this membrane are in contact with solutions of different pH led to the eventual development of a whole new class of indicator electrodes called ion-selective electrodes (ISEs).
Using Ion-Selective Electrodes

Advantages of ion-selective electrodes
• Linear response to log A over a wide range.
• Don’t consume unknown.
• Don’t contaminate unknown.
• Have short response time.
• Color and turbidity do not hinder the electrode.

Disadvantages
• Respond to the activity (not concentration).
• Only responds to uncomplexed analyte ions.
• Precision is rarely better than 1%.
• Certain ions interfere with or poison particular electrodes which leads to sluggish, drifting response.
• Some are fragile and have limited shelf life.
Practical Applications of Potentiometry with Ion-Selective Electrodes

ISE are unique in determining:
- Free ions (good for toxicity).
- Determination of anions.
- Monitoring toxic gases e.g., $\text{SO}_2$, $\text{H}_2\text{S}$, $\text{NH}_3$, CN.
- Accessible to automated continues.

Scope of Applications:
- Water analysis:
  - Surface, Sea, ground, potable, and waste water.
- Atmospheric analysis:
- Gases are absorbed in solutions aerosol is deposited on filters.
- Sediment dust and soil are tedious to prepare.
- Analysis of foodstuffs.
- Clinical analysis.
Advantages of Ion-selective electrodes

1) When compared to many other analytical techniques, Ion-Selective Electrodes are relatively inexpensive and simple to use and have an extremely wide range of applications and wide concentration range.

2) The most recent plastic-bodied all-solid-state or gel filled models are very robust and durable and ideal for use in either field or laboratory environments.

3) Under the most favorable conditions, when measuring ions in relatively dilute aqueous solutions and where interfering ions are not a problem, they can be used very rapidly and easily (e.g. simply dipping in lakes or rivers, dangling from a bridge or dragging behind a boat).

4) They are particularly useful in applications where only an order of magnitude concentration is required, or it is only necessary to know that a particular ion is below a certain concentration level.
5) They are invaluable for the continuous monitoring of changes in concentration: e.g. in potentiometric titrations or monitoring the uptake of nutrients, or the consumption of reagents.

6) They are particularly useful in biological and medical applications because they measure the activity of the ion directly, rather than the concentration.

7) In applications where interfering ions, pH levels, or high concentrations are a problem, then many manufacturers can supply a library of specialized experimental methods and special reagents to overcome many of these difficulties.
8) With careful use, frequent calibration, and an awareness of the limitations, they can achieve accuracy and precision levels of 2 or 3% for some elements and thus compare favorably with analytical techniques which require far more complex and expensive instrumentation.

9) ISEs are one of the few techniques which can measure both positive and negative ions.

10) ISEs can be used in aqueous solutions over a wide temperature range. Crystal membranes can operate in the range 0°C to 80°C and plastic membranes from 0°C to 50°C.
Types of Ion-selective Electrodes

There’s four classes of ion-selective electrodes:

1. Glass membranes
   - These are selective to $\text{H}^+$ and certain monovalent cations.

2. Solid-state electrodes
   - These are made of inorganic salt crystals.
   - The inorganic salt is made such to have vacancies in its lattice structure.
   - The vacancies allow the ion (needed to fill the vacancy) to migrate through the salt.
3. **Liquid-based electrodes**

   - A mobile carrier transports the selected ion across a membrane impregnated with a liquid solution of the carrier.

4. **Molecular Electrodes**

   1. These contain a conventional electrode surrounded by a membrane that isolates (or generates) the analyte to which the electrode responds.

   2. For example, a $\text{CO}_2$ electrode responds the change in pH due to the presence of the $\text{CO}_2$. 
Combined Glass Electrodes for measuring pH

- These consists of a thin glass bulb at the bottom that is selective to H+.
- Two reference electrodes (usually Ag/AgCl) measure the potential difference across the membrane.

\[
E_{\text{cell}} = K + \frac{0.0592}{z} \log[H^+] 
\]
Membrane Potentials

• ISE, such as the glass pH electrode, function by using a membrane that reacts selectively with a single ion.

\[ E_{cell} = K + \left( \frac{0.0591}{z} \right) \log [A] \text{ sample} \]

• This equation applies to all types of ISE’s.

• For the glass electrode:

\[ E_{cell} = K + \left( \frac{0.0591}{1} \right) \log [H^+] \text{ sample} \]

\[ E_{cell} = K - (0.0591 \text{pH}) \]
Example

A glass electrode–SCE pair is calibrated at 25°C with a pH standard buffer, the measured voltage being 0.814 V. What voltage would be measured in a 1.00 \times 10^{-3} \text{ M} acetic acid solution? Assume \( a_{H^+} = [H^+] \).

**Solution**
From Example 6.7 in Chapter 6, the pH of a 1.00 \times 10^{-3} \text{ M} acetic solution is 3.88,

\[
\therefore 3.88 = 4.01 + \frac{0.814 - E_{\text{cell unk}}}{0.0592}
\]

\( E_{\text{cell unk}} = 0.822 \text{ V} \)
Potentiometric Methods

a) Direct Potentiometry

• Measure the electrode response in an unknown solution and read the concentration directly from the calibration graph (either manually or using special computer graphics and calculations) or from the meter display on a self-calibrating ion meter.
Electrochemical cell for potentiometry with an ion selective membrane electrode
Schematic of an ISE measurement
Potential measuring device

• The indicator electrode produces a voltage that is proportional to the concentration of the $M\pm$ concentration, and the measurement is made by a pH meter.
• The indicator electrode is attached to control electronics which convert the voltage to a pH (in case of a pH electrode) reading and displays it on a meter.
EXAMPLE: Response of an Ion-Selective Electrode

When an $F^-$ electrode was immersed in standard $F^-$ solutions (maintained at a constant ionic strength of 0.1 M with NaNO₃), the following potentials (versus S.C.E.) were observed:

<table>
<thead>
<tr>
<th>$[F^-]$ (M)</th>
<th>$E$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.00 \times 10^{-5}$</td>
<td>100.0</td>
</tr>
<tr>
<td>$1.00 \times 10^{-4}$</td>
<td>41.5</td>
</tr>
<tr>
<td>$1.00 \times 10^{-3}$</td>
<td>$-17.0$</td>
</tr>
</tbody>
</table>

Since the ionic strength was held constant, the response should depend upon the logarithm of the $F^-$ concentration. What potential is expected if $[F^-] = 5.00 \times 10^{-5}$ M? What concentration of $F^-$ will give a potential of 0.0 V?

We seek to fit the calibration data with an equation in the form of Equation 15-26:

$$E = m \log[F^-] + b$$

Plotting $E$ versus $\log[F^-]$ gives a straight line with a slope of $-58.5$ mV and a $y$-intercept of $-192.5$ mV. Setting $[F^-] = 5.00 \times 10^{-5}$ M gives

$$E = (-58.5) \log [5.00 \times 10^{-5}] - 192.5 = 59.1$$ mV

If $E = 0.0$ mV, we can solve for the concentration of $[F^-]$: 

$$0.0 = (-58.5) \log[F^-] - 192.5 \quad \Rightarrow \quad [F^-] = 5.1 \times 10^{-4}$$ M
Potentiometric Titrations

• Potentiometry is generally valuable as a technique for detecting the end-point of titrations where there is often a drastic change in the concentrations of the reactants and thus a big shift in the electrode potential.

• These end point determinations can often be made more precisely than other ISE methods because they depend on the accuracy of the volumetric measurements rather than the measurement of the electrode potential.

• For example, when a calcium solution is titrated against the complexing reagent EDTA there is a gradual decrease in the Ca concentration as more EDTA is added until the end point when all the Ca disappears from solution.

• The progress of this titration can be monitored using a calcium electrode.
Potentiometric Titration

Diagram:
- pH vs. volume of titrant
- Point of inflection
- Bisector line
- End-point volume
- Line from point of inflection intersecting volume axis and perpendicular to it
First derivative plot of a potentiometric titration curve
Second derivative plot of potentiometric titration curve