Electroanalytical Chemistry: Analytical Applications

2 Main classes of electroanalytical techniques:

1.) Control current, measure potential: **Potentiometry**

2.) Controlled potential, measure current (or charge): **Amperometry** (or **coulometry**)

Potentiometry

We’ll focus on potentiometry. What do we need to conduct a potentiometry experiment?
Electrodes for Potentiometry

Reference Electrode
Indicator Electrode
Ion Selective Electrodes

Reference Electrodes:

Silver/Silver Chloride:
\[ \text{Ag} \, || \, \text{AgCl} \, || \, \text{Cl}^- \, || \, \text{cathode} \quad E^0 = +0.197 \text{V (sat'd KCl)} \]

Saturated Calomel (SCE):
\[ \text{Pt} \, || \, \text{Hg} \, || \, \text{Hg}_2\text{Cl}_2 \, || \, \text{Cl}^- \, || \, \text{cathode} \quad E^0 = +0.241 \text{V (sat'd KCl)} \]

Practical Reference Electrodes

Conversion between Reference Electrodes:

0.000 V
NHE

Junction Potentials
Ion Selective Electrodes

Rely on ion-selective membrane or interface
- Responds (ideally) to a single ion
- System would like to equalize activities on opposite sides of membrane
  - But it can't, leading to free energy difference

Differences in activity across membrane leads to difference in potential

Ultimately leads to Nernstian response

\[ E = \text{const.} + \frac{RT}{nF} \ln \frac{A_{\text{outside}}}{A_{\text{inside}}} \]

pH Electrodes: Proton selective

Glass membrane selectively binds H⁺

\[
\begin{align*}
\text{Ag(s)} & | \text{AgCl(s)} | \text{Cl}^- (aq) | | \text{H}^+ (aq, \text{outside}) | \text{H}^+ (aq, \text{inside}), \text{Cl}^- (aq) | \text{AgCl(s)} | \text{Ag(s)}
\end{align*}
\]

Glass Electrode: “membrane” is glass bulb
Surface of glass is weakly acidic.

General response:
pH Electrodes: Practical Considerations

Limitations of pH electrodes:
1. Standards
2. Junction Potentials & Drift
3. Alkaline Error
4. Acid Error
5. Response Time
6. Hydration
7. Temperature

Care and Feeding of pH Electrodes

Fluoride and other ISEs

Same general concepts, "membrane" is a little different

Ag | AgCl | Cl⁻, F⁻ (outside) || Cl⁻ | AgCl | Ag

Many other types of ISE's each with same basic operation
- Solid state, liquid-based, compound electrodes

Electrodes respond to Activities, not just concentration!