Electroanalytical Chemistry: Analytical Applications

2 Main classes of electroanalytical techniques:

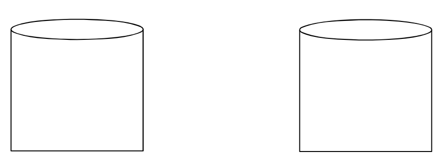
1.) Control current, measure potential: **Potentiometry**

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

1

Potentiometry

We'll focus on potentiometry. What do we need to conduct a potentiometry experiment?



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Electrodes for Potentiometry

Reference Electrode
Indicator Electrode
Ion Selective Electrodes

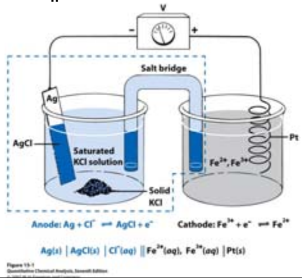
Reference Electrodes:

Silver/Silver Chloride:

Ag│ AgCl│ Cl^- ║*cathode* E^o = +0.197V (sat'd KCl)

Saturated Calomel (SCE):

Pt│ Hg│Hg_2Cl_2│ Cl^- ║*cathode* E^o = +0.241V (sat'd KCl)



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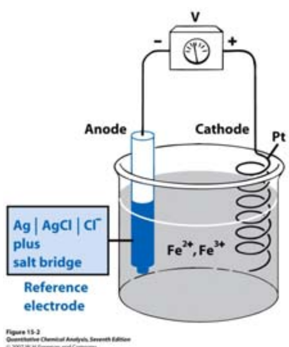
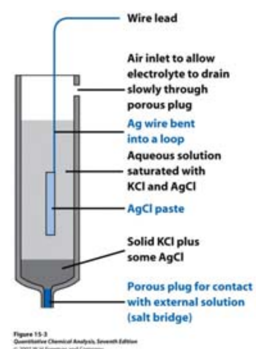
Practical Reference Electrodes





Conversion between Reference Electrodes:

0.000 V

NHE

Junction Potentials

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Ion Selective Electrodes

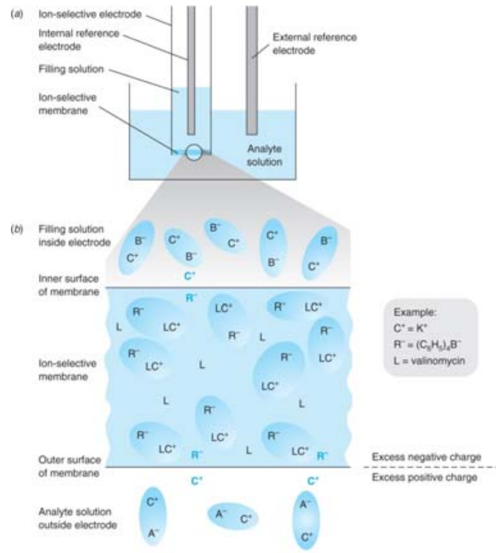
Rely on ion-selective membrane or interface

- 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

$$E = \text{const.} + \frac{RT}{nF} \ln A_{\text{outside}}$$



Harris, *Quantitative Chemical Analysis*, 8e

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pH Electrodes: Proton selective

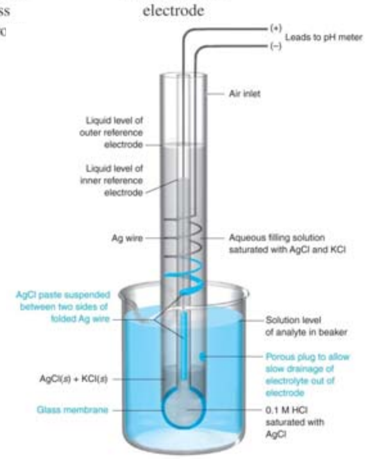
Glass membrane selectively binds H^+

$$\underbrace{Ag(s)\,|\,AgCl(s)\,|\,Cl^-(aq)}_{\text{Outer reference electrode}}\,||\,\underbrace{H^+(aq,\text{ outside})}_{\text{H}^+\text{ outside glass electrode (analyte solution)}}\,\vdots\,\underbrace{H^+(aq,\text{ inside})}_{\text{H}^+\text{ inside glass electrc}},\,\underbrace{Cl^-(aq)\,|\,AgCl(s)\,|\,Ag(s)}_{\text{Inner reference electrode}}$$

Glass Electrode: "membrane" is glass bulb

Surface of glass is weakly acidic.

General response:



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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

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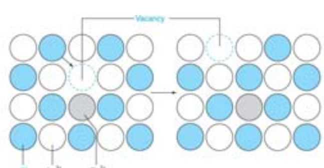
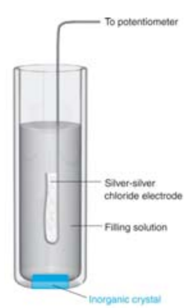
Fluoride and other ISEs

Same general concepts, “membrane” is a little different

Ag│ AgCl│ Cl^- , F^- (outside) ⋮ 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!

TABLE 14-5 Properties of solid-state ion-selective electrodes

Ion	Concentration range (M)	Membrane material	pH range	Interfering species
F^-	10^{-6}–1	LaF_3	5–8	OH^- (0.1 M)
Cl^-	10^{-4}–1	AgCl	2–11	CN^-, S^{2-}, I^-, $S_2O_3^{2-}$, Br^-
Br^-	10^{-5}–1	AgBr	2–12	CN^-, S^{2-}, I^-
I^-	10^{-6}–1	AgI	3–12	S^{2-}
SCN^-	10^{-5}–1	AgSCN	2–12	S^{2-}, I^-, CN^-, Br^-, $S_2O_3^{2-}$
CN^-	10^{-6}–10^{-2}	AgI	11–13	S^{2-}, I^-
S^{2-}	10^{-5}–1	Ag_2S	13–14	

Harris, *Quantitative Chemical Analysis*, 8e

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