

Electroanalytical Chemistry: Analytical Applications

2 Main classes of electroanalytical techniques:

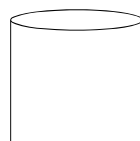
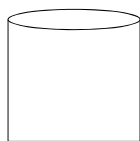
1.) Control current, measure potential: Potentiometry

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?



2

Electrodes for Potentiometry

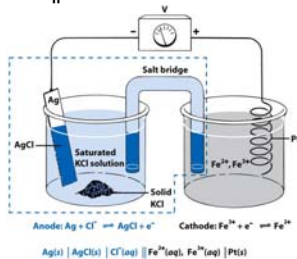
- Reference Electrode
- Indicator Electrode
- Ion Selective Electrodes

Reference Electrodes:

Silver/Silver Chloride:



Saturated Calomel (SCE):



3

Practical Reference Electrodes

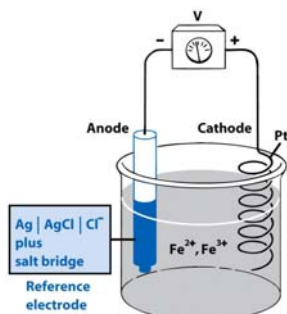


Figure 15-2
Quantitative Chemical Analysis, Seventh Edition
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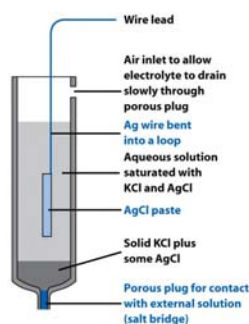
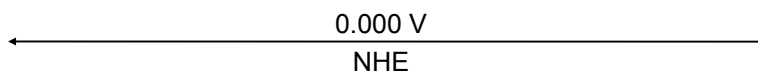


Figure 15-3
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Conversion between Reference Electrodes:



Junction Potentials

4

Ion Selective Electrodes

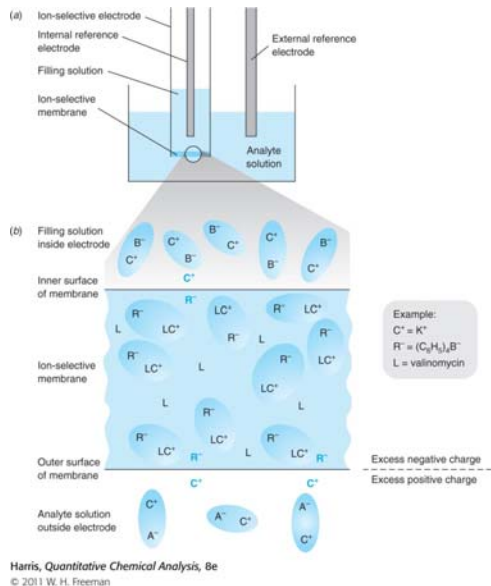
Rely on ion-selective membrane or interface

- 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

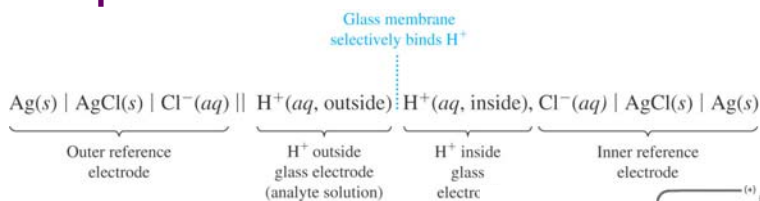
Ultimately leads to Nernstian response

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



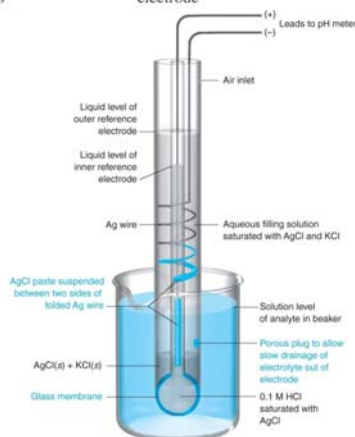
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pH Electrodes: Proton selective



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

General response:



3

pH Electrodes: Practical Considerations

Limitations of pH electrodes:

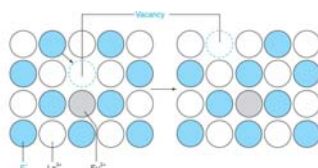
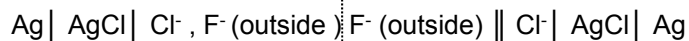
1. Standards
2. Junction Potentials & Drift
3. Alkaline Error
4. Acid Error
5. Response Time
6. Hydration
7. Temperature

Care and Feeding of pH Electrodes

7

Fluoride and other ISEs

Same general concepts, "membrane" is a little different



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 ⁻⁶ -1	AgCl	2-11	CN ⁻ , S ²⁻ , I ⁻ , S ₂ O ₃ ²⁻ , Br ⁻
Br ⁻	10 ⁻⁶ -1	AgBr	2-12	CN ⁻ , S ²⁻ , I ⁻
I ⁻	10 ⁻⁶ -1	AgI	3-12	S ²⁻
SCN ⁻	10 ⁻⁶ -1	AgSCN	2-12	S ²⁻ , I ⁻ , CN ⁻ , Br ⁻ , S ₂ O ₃ ²⁻
CN ⁻	10 ⁻⁶ -10 ⁻²	AgI	11-13	S ²⁻ , I ⁻
S ²⁻	10 ⁻⁵ -1	Ag ₂ S	13-14	

Harris, Quantitative Chemical Analysis, 8e
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