Membrane Electrodes

- Several types – Glass membrane electrode
  - Solid State
  - Liquid Junction
  - Permeable

- Most important is glass electrode for pH

\[
\begin{align*}
[H^+] &= a_1 \\
solution 1
\end{align*}
\]

\[
\begin{align*}
[H^+] &= a_2 \\
solution 2
\end{align*}
\]

potential develops across membrane
Glass pH Electrode

- \[ E = K' - 0.0591 \, \text{pH} \]
- Combine with reference electrode and meter
- Half cell voltage proportional to pH
- Nernstian slope
- Intercept is \( K' \), no \( E^o \)
- Calibrate with buffers
Proper pH Calibration

- \( E = K' - 0.0591 \ \text{pH} \)
- Meter measures \( E \) vs \( \text{pH} \) – must calibrate both slope & intercept on meter with buffers
- Meter has two controls – calibrate & slope
- 1\(^{st}\) use pH 7.00 buffer to adjust calibrate knob

Calibrate knob raises and lowers the line without changing slope
Proper pH Calibration (cont.)

- 2nd step is to use any other pH buffer
- Adjust slope/temp control to correct pH value
- This will pivot the calibration line around the isopotential which is set to 7.00 in all meters

![Graph showing mV vs pH with isopotential at pH 7.00](image)

Slope/temp control pivots line around isopotential without changing it
• Slope comes from RT/nF in Nernst Equation
• Slope is temperature sensitive
• Other factors influence slope including
  – Impurities in glass membrane
  – Overall quality of electrode construction
• Many electrodes exhibit “full Nernstian response” while others may give only 90%

Cell for pH measurement (shorthand notation)

\[
\text{Ag}_\text{(s)} \mid \text{AgCl}_\text{(s)} \mid \text{Cl}^- \text{(aq)} \mid \text{H}^+ \text{unk} \mid \text{HCl(0.1 M)} \mid \text{AgCl}_{\text{sat'd}} \mid \text{Ag}_\text{(s)}
\]

- reference electrode
- test soln
- glass electrode
Errors in pH Measurement 1

- pH measurements are only as good as the buffers used to calibrate
  - Accuracy good to ±0.01 units*
  - Precision may be good to ±0.001 units
- Junction potential dependent on ionic strength of solution – $E_j$ may be a significant error if test solution has different ionic strength than buffers

* Unless using special buffers, temp. control & a Faraday cage
Errors in pH Measurement 2

- Asymmetry potential is another non-ideal potential that arises possibly from strain in the glass. When both internal & external H\(^+\) solutions are the same activity, potential should be 0 but it’s not

\[
E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_j + E_a
\]

- Temperature of electrodes, calibration buffers and sample solutions must be the same primarily because of T in Nernst Eq. ATC probes are available for many meters
Errors in pH Measurement 3

- Alkaline Error or Sodium Error occurs when pH is very high (e.g., 12) because Na⁺ concentration is high (from NaOH used to raise pH) and H⁺ is very low. Electrode responds slightly to Na⁺ & gives a lower reading than actual pH. This is related to the concept of selectivity coefficients where the electrode responds to many ions but is most selective for H⁺. Problem occurs because Na⁺ is 10 orders of magnitude higher than H⁺ in the solution.
Acid and Alkaline error of Some electrodes

A. Corning 015, H₂SO₄  
B. Corning 015, HCl  
C. Corning 015, 1-M Na⁺  
D. Beckman-GP, 1-M Na⁺  
E. L & N Black Dot, 1-M Na⁺  
F. Beckman Type E, 1-M Na⁺
Errors in pH Measurement 4

- Acid Error – electrode reads slightly higher than the actual pH in very acidic solutions (not well understood)
- Response Time – related to activity for all potentiometric electrodes & is fast at high activity (concentration) & slow at low conc.
- Hydration of Glass Surface – glass electrodes must be kept hydrated for good measurement & must be rehydrated for 24 hrs if it dries out – will cause noisy readings
Glass Electrode Summary

- Glass membrane electrodes are very good indicator electrodes in potentiometry.
- Must exercise care in calibration and in maintaining integrity of glass membrane.
- Some errors exist & are unavoidable.
- Glass electrodes available for Na\(^+\), K\(^+\), NH\(_4\)\(^+\), Rb\(^+\), Cs\(^+\), Li\(^+\), Ag\(^+\) (cations only) by varying glass composition.
- Combination electrodes combine pH & ref.
Combination pH Electrode

Air Inlet

Liquid level of outer reference solution

AgCl paste with Ag wire

Aqueous outer solution saturated with AgCl and KCl

Porous plug to allow slow drainage of electrolyte out of electrode

Glass Membrane

Inner solution
0.1 M HCl, saturated with KCl

Leads to pH Meter
Liquid Membrane Electrodes

- Calcium Electrode is good example
- Liquid ion exchanger – water immiscible organic compound with phosphate groups selective for $\text{Ca}^{2+}$ in a hydrophobic membrane
Liquid Membrane Electrodes

- Principle of Ca\(^{2+}\) electrode is the same as for glass electrode, however, since Ca\(^{2+}\) is divalent \(n = 2\) → Nernstian slope = 29.5 mV per 10 fold change in concentration
- Detection limit for Ca\(^{2+}\) is approx. 10\(^{-5}\) M
- Selectivity is:
  - Independent of pH from 5.5 to 11
  - 50 times better for Ca\(^{2+}\) than for Mg\(^{2+}\)
  - 1000 times better for Ca\(^{2+}\) than Na\(^+\) or K\(^+\)
- Other liquid membrane electrodes available
Response of calcium ion liquid membrane electrode

Potential vs. activity

Electrode potential, mV

29.58 mV

Tenfold change

Activity or concentration of Ca$^{2+}$, mol/L
### Table of liquid membrane electrodes

<table>
<thead>
<tr>
<th>Analyte Ion</th>
<th>Concentration Range, M</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>10(^0) to 5 \times 10^{-7}</td>
<td>10(^{-5}) Pb(^{2+}); 4 \times 10(^{-3}) Hg(^{2+}), H(^{+}); 6 \times 10(^{-3}) Sr(^{2+}); 2 \times 10(^{-2}) Fe(^{2+}); 4 \times 10(^{-2}) Cu(^{2+}); 5 \times 10(^{-2}) Ni(^{2+}); 0.2 NH(_3); 0.2 Na(^{+}); 0.3 Tris(^{+}); 0.3 Li(^{+}); 0.4 K(^{+}); 0.7 Ba(^{2+}); 1.0 Zn(^{2+}); 1.0 Mg(^{2+})</td>
</tr>
<tr>
<td>BF(^{-})</td>
<td>10(^0) to 7 \times 10^{-6}</td>
<td>5 \times 10(^{-7}) ClO({}_4^-); 5 \times 10(^{-6}) I(^-); 5 \times 10(^{-5}) ClO(_3^-); 5 \times 10(^{-4}) CN(^-); 10(^{-3}) Br(^-); 10(^{-3}) NO(_2^-); 5 \times 10(^{-3}) NO(_3^-); 3 \times 10(^{-3}) HCO(_3^-); 5 \times 10(^{-2}) Cl(^-); 8 \times 10(^{-2}) H(_2)PO(_4^-); HPO(_4^{2-}); PO(_4^{3-}); 0.2 OAc(^-); 0.6 F(^-); 1.0 SO(_4^{2-})</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>10(^0) to 7 \times 10^{-6}</td>
<td>10(^{-7}) ClO(_4^-); 5 \times 10(^{-6}) I(^-); 5 \times 10(^{-5}) ClO(_3^-); 10(^{-4}) CN(^-); 7 \times 10(^{-4}) Br(^-); 10(^{-3}) HS(^-); 10(^{-2}) HCO(_3^-); 2 \times 10(^{-2}) CO(_3^{2-}); 3 \times 10(^{-2}) Cl(^-); 5 \times 10(^{-2}) H(_2)PO(_4^-); HPO(_4^{2-}); PO(_4^{3-}); 0.2 OAc(^-); 0.6 F(^-); 1.0 SO(_4^{2-})</td>
</tr>
<tr>
<td>ClO(_4^-)</td>
<td>10(^0) to 7 \times 10^{-6}</td>
<td>2 \times 10(^{-3}) I(^-); 2 \times 10(^{-2}) ClO(_3^-); 4 \times 10(^{-2}) CN(^-); Br(^-); 5 \times 10(^{-2}) NO(_2^-); NO(_3^-); 2 HCO(_3^-); CO(_3^{2-}); Cl(^-); H(_2)PO(_4^-); HPO(_4^{2-}); PO(_4^{3-}); OAc(^-); F(^-); SO(_4^{2-})</td>
</tr>
<tr>
<td>K(^+)</td>
<td>10(^0) to 10(^{-6})</td>
<td>3 \times 10(^{-4}) Cs(^+); 6 \times 10(^{-3}) NH(_4^+); Tl(^+); 10(^{-2}) H(^+); 1.0 Ag(^+); Tris(^+); 2.0 Li(^+); Na(^+)</td>
</tr>
<tr>
<td>Water Hardness</td>
<td>10(^{-3}) to 6 \times 10^{-6}</td>
<td>3 \times 10(^{-5}) Cu(^{2+}), Zn(^{2+}); 10(^{-4}) Ni(^{2+}); 4 \times 10(^{-4}) Sr(^{2+}); 6 \times 10(^{-5}) Fe(^{2+}); 6 \times 10(^{-4}) Ba(^{2+}); 3 \times 10(^{-2}) Na(^+); 0.1 K(^+)</td>
</tr>
</tbody>
</table>
Solid State Membrane Electrodes

Ag wire

Filling solution with fixed [Cl⁻] and cation that electrode responds to

Ag/AgCl

Solid state membrane (must be ionic conductor)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ion Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaF₃</td>
<td>F⁻, La³⁺</td>
</tr>
<tr>
<td>AgCl</td>
<td>Ag⁺, Cl⁻</td>
</tr>
<tr>
<td>AgBr</td>
<td>Ag⁺, Br⁻</td>
</tr>
<tr>
<td>AgI</td>
<td>Ag⁺, I⁻</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>Ag⁺, S²⁻</td>
</tr>
<tr>
<td>Ag₂S + CuS</td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Ag₂S + CdS</td>
<td>Cd²⁺</td>
</tr>
<tr>
<td>Ag₂S + PbS</td>
<td>Pb²⁺</td>
</tr>
</tbody>
</table>
Solid State Membrane Electrodes

- Detection limits depend on solubility of the solid state membrane
- $K_{sp}$ for AgCl = approx. $10^{-10}$
- Therefore solubility is $10^{-5}$ M or membrane starts to produce ions of interest in solution
- Mixed crystals improve this somewhat but it is still a limitation
- Interferences or poisoning by high affinity ions
- Can polish electrodes to remove fouling
- Selectivity coefficient = electrode response ratio
# Commercially Available Solid State Ion Selective Electrodes (ISEs)

<table>
<thead>
<tr>
<th>Analyte Ion</th>
<th>Concentration Range, M</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br⁻</td>
<td>10⁰ to 5 × 10⁻⁶</td>
<td>mr: 8 × 10⁻⁵ CN⁻; 2 × 10⁻⁴ I⁻; 2 NH₃; 400 Cl⁻; 3 × 10⁴ OH⁻. mba: S²⁻</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>10⁻¹ to 10⁻⁷</td>
<td>Fe²⁺ + Pb²⁺ may interfere. mba: Hg²⁺, Ag⁺, Cu²⁺</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>10⁰ to 5 × 10⁻⁵</td>
<td>mr: 2 × 10⁻⁷ CN⁻; 5 × 10⁻⁷ I⁻; 3 × 10⁻³ Br⁻; 10⁻² S₂O₃²⁻; 0.12 NH₃; 80 OH⁻. mba: S²⁻</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>10⁻¹ to 10⁻⁸</td>
<td>high levels Fe²⁺, Cd²⁺, Br⁻, Cl⁻. mba: Hg²⁺, Ag⁺, Cu⁺</td>
</tr>
<tr>
<td>CN⁻</td>
<td>10⁻² to 10⁻⁶</td>
<td>mr: 10⁻¹ I⁻; 5 × 10³ Br⁻; 10⁶ Cl⁻. mba: S²⁻</td>
</tr>
<tr>
<td>F⁻</td>
<td>sat'd to 10⁻⁶</td>
<td>0.1 M OH⁻ gives &lt;10% interference when [F⁻] = 10⁻³ M</td>
</tr>
<tr>
<td>I⁻</td>
<td>10⁰ to 5 × 10⁻⁸</td>
<td>mr: 0.4 CN⁻; 5 × 10³ Br⁻; 10⁵ S₂O₃²⁻; 10⁶ Cl⁻</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>10⁻¹ to 10⁻⁶</td>
<td>mba: Hg²⁺, Ag⁺, Cu²⁺</td>
</tr>
<tr>
<td>Ag⁺/S²⁻</td>
<td>10⁰ to 10⁻⁷ Ag⁺</td>
<td>Hg²⁺ must be less than 10⁻⁷ M</td>
</tr>
<tr>
<td></td>
<td>10⁰ to 10⁻⁷ S²⁻</td>
<td></td>
</tr>
<tr>
<td>SCN⁻</td>
<td>10⁰ to 5 × 10⁻⁶</td>
<td>mr: 10⁻⁶ I⁻; 3 × 10⁻³ Br⁻; 7 × 10⁻³ CN⁻; 0.13 S₂O₃²⁻; 20 Cl⁻; 100 OH⁻. mba: S²⁻</td>
</tr>
</tbody>
</table>

mr = maximum ratio of interferent to analyte  
mba = must be absent
Permeable Membrane Electrodes
Gas Permeable Membrane Electrodes
Gas Sensing Electrodes

- Membrane that is permeable to a gas (e.g., \( \text{NH}_3 \)) is the key component of electrode
- Membrane is part of a small chamber which encloses a filling solution with a pH electrode housed inside
- Filling solution has “fixed” \([\text{NH}_4^+]\) which responds to changes in [\(\text{NH}_3\)] passing membrane according to

\[
\text{NH}_3 + \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{NH}_4^+ + \text{OH}^-
\]
pH Electrode Bulb Styles
Gas Permeable Membrane Electrodes

- Electrode immersed in test solution
- $\text{NH}_3$ diffuses through membrane
- $\text{NH}_3$ in test solution equilibrates with $\text{NH}_3$ in filling solution

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$[\text{OH}^-] = \frac{K_b}{[\text{NH}_4^+]} [\text{NH}_3]$$

$$\text{pH} = 14 - \text{pOH} = \text{pNH}_3$$