Ch. 14: Potentiometry

Outline:

- 14-1 Reference Electrodes
- 14-2 Indicator Electrodes
- 14-3 What is a Junction Potential?
- 14-4 How Ion-Selective Electrodes Work
- 14-5 pH Measurement with a Glass Electrode
- 14-6 Ion Selective Electrodes

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Potentiometry

*Potentiometry* is the use of electrodes to measure voltages that provide chemical information.

The analyte must be an *electroactive species* (i.e., must be able to donate or accept electrons at one of the electrodes.

The unknown solution is converted into a half-cell by adding an electrode (e.g., Pt wire) that can accept or donate electrons from or to the analyte. This is the *indicator electrode*.

This half-cell is connected to another half-cell with a constant composition via a salt bridge. This is the *reference electrode*.

The *cell voltage* is the difference between the variable potential of the analyte half-cell and the constant potential of the reference electrode.
Reference Electrodes

Suppose you want to measure the relative amounts of Fe$^{2+}$ and Fe$^{3+}$ in a solution. You can make this solution part of a galvanic cell by inserting a Pt wire and connecting the cell to a constant-potential half-cell by a salt bridge.

The two half-reactions (written as reductions) are:

Right electrode:
$$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$$

Left electrode:
$$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-$$

The electrode potentials are

\[ E_+ = 0.771 \text{ V} \]
\[ E_- = 0.222 \text{ V} \]

Recall that:

\[ E_+ \] is the potential of the electrode attached to the positive input of the potentiometer.

\[ E_- \] is the potential of the electrode attached to the negative input of the potentiometer.
Reference Electrodes, 2

The cell voltage is the difference $E_+ - E_-$:

$$E = \left\{ 0.771 - 0.059 \times 16 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \right\} - \left\{ 0.222 - 0.059 \times 16 \log[\text{Cl}^-] \right\}$$

The cell voltage is dependent only upon the quotient $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$, since the composition of the left half-cell is fixed (saturated solution of KCl); the left half-cell is the reference electrode.

The cell and salt bridge enclosed by the dashed line (in the figure on the previous page) can be thought of as a single unit dipped into the analyte solution where:

- Pt wire is the indicator electrode (potential responds to the quotient $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ on the right hand side of the potentiometer).

- The Ag | AgCl | Cl$^-$ reference electrode completes the redox reaction and provides constant potential to the left hand side of the potentiometer.

The voltage really tells us the quotient of activities; however, we will neglect activity coefficients and write the Nernst equation with concentrations instead of activities.
Ag | AgCl Reference Electrode

The silver - silver chloride electrode can be constructed as a thin tube that is dipped into solution (left) or as a double-junction electrode that minimizes contact between analyte solution and KCl from the electrode (right).

Double-junction reference electrode. The inner electrode is the same as the one as pictured to the left. The solution in the outer compartment is compatible with analyte solution. For example, if you do not want Cl\(^{-}\) to contact the analyte, the outer electrode can be filled with KNO\(_3\) solution. The inner and outer solutions slowly mix, so the outer compartment must be refilled periodically with fresh KNO\(_3\) solution.
Ag | AgCl Reference Electrode, 2

The standard reduction potential for the Ag | AgCl half-cell is +0.222 V at 25°C. This would be the potential of a silver-silver chloride electrode if $A_{\text{Cl}^-}$ were unity. But the activity of Cl$^-$ in a saturated solution of KCl at 25°C is not unity, and the potential of the electrode is +0.197 V with respect to S.H.E. at 25°C.

$$\text{Ag | AgCl electrode:} \quad \text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-$$

$$E^o = +0.222 \text{ V}$$

$$E(\text{saturated KCl}) = +0.197 \text{ V}$$

Pros:

- Convenient to make, assemble and use.
- Relatively cheap.
- Much better as reference electrodes than S.H.E. (Pt/H$_2$), since the latter requires (i) a fresh H$_2$(g) source and (ii) Pt catalysts are easily poisoned.

Cons:

- Porous plugs can become plugged, giving unstable electrical responses.
- Designs are available which force fresh fluid through a free-flowing capillary (instead of the porous plug), but these are more costly.
- [Cl$^-$] can change if water evaporates.
The calomel electrode is based on the reaction

\[
\text{Calomel electrode: } \frac{1}{2} \text{Hg}_2\text{Cl}_2(s) + e^- \rightleftharpoons \text{Hg}(l) + \text{Cl}^- \\
\text{Mercury(I) chloride (Calomel)}
\]

The standard potential for this reaction is +0.268 V. If the cell is saturated with KCl at 25°C, the potential is +0.241 V. A calomel electrode saturated with KCl is called a saturated calomel electrode, abbreviated S.C.E. (and pictured to the right). The advantage in using saturated KCl is that [Cl\(^-\)] does not change if some liquid evaporates.
Voltage Conversions on Different Scales

If an electrode has a potential of $-0.461 \text{ V}$ with respect to a calomel electrode, what is the potential with respect to a silver-silver chloride electrode? What would be the potential with respect to the standard hydrogen electrode?

**Point A:**
- $-0.461 \text{ V from S.C.E.}$
- $-0.417 \text{ V from Ag | AgCl}$
- $-0.220 \text{ V from S.H.E.}$

**Point B:**
- $-0.011 \text{ V from S.C.E.}$
- $+0.033 \text{ V from Ag | AgCl}$
- $+0.230 \text{ V from S.H.E.}$
Indicator Electrodes

There are two broad classes of indicator electrodes:

- **Metal electrodes** develop an electric potential in response to a redox reaction at the metal surface. (We will discuss these first)

- **Ion-selective electrodes** involve selective binding of one type of ion to a membrane that generates an electric potential. (We will talk about these later)

**Metal electrodes - some general comments**

Platinum and gold electrodes are very common, since they are not very reactive; hence, their purpose is to transfer electrons to and from solution (gold is typically more inert than platinum). Such electrodes work best when:

- They have a very large surface area.

- They are very clean (clean the electrodes with hot 8.0 M HNO₃ (in a fume hood - be careful!!) and rinse with distilled water.)
A silver electrode can be used with a reference electrode to measure Ag⁺ concentration. The reaction at the Ag indicator electrode is

\[ \text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(s) \quad E^\circ_+ = 0.799 \text{ V} \]

The calomel reference half-cell reaction is

\[ \text{Hg}_2\text{Cl}_2(s) + 2e^- \rightleftharpoons 2\text{Hg}(l) + 2\text{Cl}^- \quad E^- = 0.241 \text{ V} \]

The reference potential (E−, not E−°) is fixed at 0.241 V because the reference cell is saturated with KCl. The Nernst equation for the entire cell is

\[ E = E^\circ_+ - E^- = \left\{ 0.799 - 0.059 \times 16 \log \left( \frac{1}{[\text{Ag}^+]} \right) \right\} - \left\{ 0.241 \right\} \]

The voltage of this cell provides a measure of [Ag⁺]. Ideally, the voltage changes by 59.16 mV (at 25°C) for each factor-of-10 change in [Ag⁺].
e.g., A 100.0-mL solution containing 0.1000 M NaCl was titrated with 0.1000 M AgNO₃, and the voltage of the cell monitored. The equivalence volume is $V_e = 100.0 \text{ mL}$. Calculate the voltage after the addition of (a) 65.0 and (b) 135.0 mL of AgNO₃.

**Solution** The titration reaction is

$$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)$$

(a) At 65.0 mL, 65.0% of Cl⁻ has precipitated and 35.0% remains in solution:

$$[\text{Cl}^-] = (0.350)(0.1000 \text{ M}) = 0.035 \text{ M}$$

$$\text{Initial volume of Cl}^- = \frac{100.0}{165.0} = 0.0212 \text{ M}$$

To find the cell voltage in Equation 14-1, we need to know $[\text{Ag}^+]$:

$$[\text{Ag}^+] [\text{Cl}^-] = K_{sp} \implies [\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.0212 \text{ M}} = 8.5 \times 10^{-9} \text{ M}$$

The cell voltage is therefore

$$E = 0.558 + 0.05916 \log(8.5 \times 10^{-9}) = 0.081 \text{ V}$$

(b) At 135.0 mL, there is an excess of 35.0 mL of AgNO₃ = 3.50 mmol Ag⁺ in a total volume of 235.0 mL. Therefore, $[\text{Ag}^+] = (3.50 \text{ mmol})/(235.0 \text{ mL}) = 0.0149 \text{ M}$. The cell voltage is

$$E = 0.558 + 0.05916 \log(0.0149) = 0.450 \text{ V}$$
The titration curve for the previous example is reminiscent of a pH titration curve (Ag\(^+\) instead of H\(^+\), and Cl\(^-\) instead of a base).

The silver electrode measures pAg, which you can see by substituting pAg = −log[Ag\(^+\)] into the final Nernst equation:

\[
E = 0.558 - 0.05916 \text{ pAg}
\]

A silver electrode can also act as a halide electrode, if solid silver halide is present. If the solution contains AgCl(s), we substitute [Ag\(^+\)] = \(K_{sp}/[\text{Cl}^-]\) into the Nernst equation, giving an expression relating the cell voltage to [Cl\(^-\)]:

\[
E = 0.558 + 0.05916 \log \left( \frac{K_{sp}}{[\text{Cl}^-]} \right)
\]

Metals including Ag, Cu, Zn, Cd, and Hg can be used as indicator electrodes for their aqueous ions (most metals cannot be used, as necessary equilibria at a metal surface are not established).
Junction Potential

Junction potential: A small voltage difference (a few mV) that develops at the interface of two dissimilar electrolyte solutions are in contact with one another. The junction potential is found at each end of a salt bridge connecting two half-cells, and places a fundamental limitation on the accuracy of direct potentiometric measurements, because we usually do not know the contribution of the junction to the measured voltage.

Why does the junction potential arise? Consider NaCl in distilled H₂O:
- Na⁺ and Cl⁻ ions at the interface dissolve in the H₂O
- Cl⁻ ions have higher mobility than Na⁺ ions (faster diffusion for the Cl⁻ ions)
- A region rich in Cl⁻ develops at the front, and rich in Na⁺ at the back, creating a difference in electrical potential at the junction of the NaCl and H₂O phases
- The junction potential opposes the movement of Cl⁻ and accelerates the movement of Na⁺
- At steady state, there is a balance between the unequal mobilities and the retardation on Cl⁻ movement by the charge imbalance at the junction
Salt bridges are usually constructed from compounds with ions possessing similar mobilities (e.g., K\(^+\) and Cl\(^-\)) and therefore small resulting junction potentials.

Nonetheless, the junction potential of 0.1 M HCl | 3.5 M KCl is 3.1 mV. A pH electrode has a response of 59 mV per pH unit. A pH electrode dipped into 0.1 M HCl will have a junction potential of ca. 3 mV, or an error of 0.05 pH units (12% error in [H\(^+\)]).

### Junction Potential, 2

<table>
<thead>
<tr>
<th>Junction</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl</td>
<td>0.1 M KCl</td>
</tr>
<tr>
<td>0.1 M NaCl</td>
<td>3.5 M KCl</td>
</tr>
<tr>
<td>1 M NaCl</td>
<td>3.5 M KCl</td>
</tr>
<tr>
<td>0.1 M HCl</td>
<td>0.1 M KCl</td>
</tr>
<tr>
<td>0.1 M HCl</td>
<td>3.5 M KCl</td>
</tr>
</tbody>
</table>

**NOTE:** A positive sign means that the right side of the junction becomes positive with respect to the left side.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mobility [m(^2)/s \cdot V](^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>36.30 \times 10^{-8}</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>7.92 \times 10^{-8}</td>
</tr>
<tr>
<td>K(^+)</td>
<td>7.62 \times 10^{-8}</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>7.61 \times 10^{-8}</td>
</tr>
<tr>
<td>La(^{3+})</td>
<td>7.21 \times 10^{-8}</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>6.59 \times 10^{-8}</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>6.42 \times 10^{-8}</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>6.12 \times 10^{-8}</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>5.56 \times 10^{-8}</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>5.19 \times 10^{-8}</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>4.01 \times 10^{-8}</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>20.50 \times 10^{-8}</td>
</tr>
<tr>
<td>Fe(CN)(_6^{4-})</td>
<td>11.45 \times 10^{-8}</td>
</tr>
<tr>
<td>Fe(CN)(_6^{3-})</td>
<td>10.47 \times 10^{-8}</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>8.27 \times 10^{-8}</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>8.13 \times 10^{-8}</td>
</tr>
<tr>
<td>I(^-)</td>
<td>7.96 \times 10^{-8}</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>7.91 \times 10^{-8}</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>7.40 \times 10^{-8}</td>
</tr>
<tr>
<td>ClO(_4^-)</td>
<td>7.05 \times 10^{-8}</td>
</tr>
<tr>
<td>F(^-)</td>
<td>5.70 \times 10^{-8}</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>4.61 \times 10^{-8}</td>
</tr>
<tr>
<td>CH(_3)CO(_2^-)</td>
<td>4.24 \times 10^{-8}</td>
</tr>
</tbody>
</table>

*a.* The mobility of an ion is the terminal velocity that the particle achieves in an electric field of 1 V/m. Mobility = velocity/field. The units of mobility are therefore (m/s)/(V/m) = m\(^2\)/s \cdot V. 
Ion-Selective Electrodes

We focus on ion-selective electrodes that respond selectively to one type of ion. Again, there is no redox process involved; rather, the key feature of an ideal ion-selective electrode is a thin membrane capable of binding only the intended ion.

Consider a *liquid-based ISE*, which has an the ion-selective membrane is a hydrophobic organic polymer impregnated with a viscous organic solution containing an ion exchanger and, sometimes, a ligand that selectively binds the analyte cation, $C^+$. 

**Inside the electrode**: filling solution with the ions $C^+$(aq) and $B^−$(aq)  
**Outside the electrode**: immersed in analyte solution containing $C^+$(aq), $A^−$(aq) and (maybe) others (it does not really matter what types of ions $A^−$ and $B^−$ are)

The voltage across the ion-selective membrane is measured by two reference electrodes, which might be Ag | AgCl. If the concentration (activity) of $C^+$ in the analyte solution changes, the voltage measured between the two reference electrodes also changes. By using a *calibration curve*, the voltage tells us the activity of $C^+$ in the analyte solution.
Ion-Selective Electrodes, 2

When a few $C^+$ ions diffuse from the membrane into the outer aqueous phase, there is excess positive charge in this phase. This imbalance creates an electric potential difference that opposes diffusion of more $C^+$ into the aqueous phase.

L: *ionphore* - ligand chosen to have a high affinity for analyte cation, $C^+$, and low affinity for other ions.

$LC^+$: Complex in eqb. with free $C^+$.

$R^-$: hydrophobic anion that is soluble in the membrane and poorly soluble in water (cannot leave membrane for aqueous solution).

$A^-$: insoluble in organic solvents, does not enter membrane

Membrane made of poly(vinyl chloride) impregnated with the plasticizer dioctyl sebacate, plus excess free L, $R^-$, and $LC^+$
When C\(^+\) ions diffuse from the membrane (region of activity \(A_m\)) to the outer solution (region of activity \(A_o\)), there is a change in Gibbs energy:

\[
\Delta G = \Delta G_{\text{solvation}} - RT \ln \left( \frac{A_m}{A_o} \right)
\]

\(\Delta G\) associated with change in solvation energy on going from organic liquid to the aqueous phase

\(\Delta G\) associated with change when a species diffuses between regions of different activities (concentrations)

The driving force for diffusion of C\(^+\) from the membrane to the aqueous solution is the favourable solvation of the ion by water. As C\(^+\) diffuses, there is a buildup of positive charge in the water immediately adjacent to the membrane.

The charge separation creates an electric potential difference (\(E_{\text{outer}}\)) across the membrane. The difference in Gibbs energy for C\(^+\) in the two phases is \(\Delta G = -nFE_{\text{outer}}\), where \(n\) is the charge of the ion. At equilibrium, for diffusion of C\(^+\), the net change in \(\Delta G = 0\).

\[
\Delta G_{\text{solvation}} - RT \ln \left( \frac{A_m}{A_o} \right) + (-nFE_{\text{outer}}) = 0
\]

\(\Delta G\) due to transfer between phases and activity difference

\(\Delta G\) due to charge imbalance
Solving for $E_{\text{outer}}$, we find that the electric potential difference across the boundary between the membrane and the outer aqueous solution is

$$E_{\text{outer}} = \frac{\Delta G_{\text{solvation}}}{nF} - \left(\frac{RT}{nF}\right) \ln\left(\frac{A_m}{A_o}\right)$$

There is also a potential difference $E_{\text{inner}}$ at the boundary between the inner filling solution and the membrane, with terms analogous to those above.

The potential difference between the outer analyte solution and the inner filling solution is the difference $E = E_{\text{outer}} - E_{\text{inner}}$. $E_{\text{outer}}$ depends on the activities of $C^+$ in the analyte solution and in the membrane near its outer surface. $E_{\text{inner}}$ is constant because the activity of $C^+$ in the filling solution is constant.

Activity of $C^+$ in the membrane is very nearly constant, since the high concentration of $LC^+$ in the membrane is in equilibrium with free $L$ and a small concentration of free $C^+$. $R^-$ is poorly soluble in water and cannot leave the membrane. Very little $C^+$ can diffuse out of the membrane because each $C^+$ that enters the aqueous phase leaves behind one $R^-$ in the membrane (causing the potential difference at the phase boundary). When a tiny fraction of $C^+$ diffuses from the membrane into solution, further diffusion is prevented by excess positive charge in the solution near the membrane.
Ion-Selective Electrodes, 5

The potential difference between the outer and the inner solutions is

\[ E = E_{\text{outer}} - E_{\text{inner}} = \frac{\Delta G_{\text{solvation}}}{nF} - \left(\frac{RT}{nF}\right) \ln \left(\frac{A_m}{A_o}\right) - E_{\text{inner}} \]

or

\[ E = \frac{\Delta G_{\text{solvation}}}{nF} + \left(\frac{RT}{nF}\right) \ln A_o - \left(\frac{RT}{nF}\right) \ln A_m - E_{\text{inner}} \]

If the constant terms are combined, we find that the potential difference across the membrane depends only on the activity of analyte in the outer solution:

\[ E = \text{constant} + \left(\frac{RT}{nF}\right) \ln A_o \]

Converting \( \ln \) into \( \log \) and inserting values of \( R \), \( T \) and \( F \) gives

Electric potential difference for ion-selective electrode:

\[ E = \text{constant} + \frac{0.05916}{n} \log A_o \text{ (volts at 25°C)} \]

which applies to any ion-selective electrode, including a glass pH electrode. If the analyte is an anion, the sign of \( n \) is negative.
pH Measurement with Glass Electrode

The glass electrode used to measure pH is the most common ISE. A typical pH combination electrode has both glass and reference electrodes in one body, and has the line diagram:

The reference electrode at the left of the line diagram is the coiled Ag | AgCl electrode in the combination electrode (see next slide).

The reference electrode at the right side of the line diagram is the straight Ag | AgCl electrode at the centre of the electrode (see next slide).

The salt bridge in the line diagram is the porous plug at the bottom right side of the combination electrode (see next slide).

The two reference electrodes measure the electric potential difference across the glass membrane (see next slide).
pH Measurement with Glass Electrode, 2

(a) Glass-body combination electrode with pH-sensitive glass bulb at the bottom. The porous ceramic plug (the salt bridge) connects analyte solution to the reference electrode. Two silver wires coated with AgCl are visible inside the electrode.

(b) A pH electrode with a platinum diaphragm (a bundle of Pt wires), which is said to be less prone to clogging than a ceramic plug.
Silicate glass has an irregular structure (top left), featuring randomly placed SiO\(_4\) tetrahedra (not planar!). Negatively charged oxygen atoms in glass can bind to cations of suitable size. Monovalent cations, particularly Na\(^+\), can move sluggishly through the silicate lattice.

The two surfaces in a cross section of the glass membrane (top right) swell as they absorb water. Metal ions (e.g., Na\(^+\)) in these hydrated gel regions of the membrane diffuse out of the glass and into solution. H\(^+\) can diffuse into the membrane to replace the metal ions - this is called an ion exchange equilibrium (bottom right). The pH electrode responds very selectively to H\(^+\), since H\(^+\) is the only ion that selectively bonds to the hydrated gel layers.
pH Measurement with Glass Electrode, 4

To perform an electrical measurement, at least some tiny current must flow through the entire circuit—even across the glass pH electrode membrane. Studies with tritium (radioactive $^3\text{H}$) show that $\text{H}^+$ does not cross the glass membrane. However, $\text{Na}^+$ sluggishly crosses the membrane. The $\text{H}^+$-sensitive membrane may be thought of as two surfaces electrically connected by $\text{Na}^+$ transport. The membrane’s resistance is typically 108 $\Omega$, so little current actually flows across it.

The potential difference between the inner and outer silver-silver chloride electrodes depends on the $[\text{Cl}^-]$ in each electrode compartment and on the potential difference across the glass membrane. Because $[\text{Cl}^-]$ is fixed in each compartment and because $[\text{H}^+]$ is fixed on the inside of the glass membrane, the only variable is the pH of analyte solution outside the glass membrane. The voltage of the ideal pH electrode changes by 59.16 mV for every pH-unit change of analyte activity at 25°C (according to our previous equations).

$$E = \text{constant} + \beta(0.05916) \log A_{\text{H}^+}(\text{outside})$$

$$E = \text{constant} - \beta(0.05916) \text{pH(outside)} \quad (\text{at } 25^\circ\text{C})$$

The value of $\beta$, the electromotive efficiency, is close to 1.00 (typically >0.98). We measure the constant and $\beta$ when we calibrate the electrode in solutions of known pH.
Errors in pH measurement

1. **Standards** - cannot be more accurate than standards, typically (±0.01 pH units)

2. **Junction potentials** (exist near porous plug) - If the ionic composition of the analyte solution is different from that of the standard buffer, the junction potential will change even if the pH of the two solutions is the same (±0.01 pH units)

3. **Junction potential drift.** A Ag | AgCl reference electrode containing sat’d KCl solution has 350 mg Ag per L dissolved in the KCl. (i) In the porous plug, KCl is diluted and AgCl can precipitate. (ii) If analyte solution contains a reducing agent, Ag(s) also can precipitate in the plug. *Both* change the junction potential, causing a slow drift in pH reading. Calibrating the pH meter every 2-3 hours takes care of this.

Solid colored circles show the drift in apparent pH of a low-conductivity industrial water supply measured continuously by a single electrode. Individual measurements with a freshly calibrated electrode (black circles) demonstrate that the pH is not drifting. Drift is attributed to slow clogging of the electrode’s porous plug with AgCl(s). When a cation-exchange resin was placed inside the reference electrode near the porous plug, Ag(I) was bound by the resin and did not precipitate. This electrode gave the drift-free, continuous reading shown by open diamonds.
Errors in pH measurement, 2

4. **Sodium error (alkaline error)** - If $[H^+]$ is very low and $[Na^+]$ is high, the electrode responds to $Na^+$, and the apparent pH is lower than the true pH.

5. **Acid error** - In very strong acid, the measured pH is higher than the actual pH, usually because the glass is saturated with $H^+$ and cannot be further protonated.

6. **Equilibration time.** It takes time for an electrode to equilibrate with a solution. A well-buffered solution requires ~30 s with adequate stirring. A poorly buffered solution (such as one near the equivalence point of a titration) needs longer.

7. **Hydration of glass.** A dry electrode requires several hours of soaking before it responds to $H^+$ correctly.

8. **Temperature.** A pH meter should be calibrated at the same temperature at which the measurement will be made.

9. **Cleaning.** If an electrode has been exposed to a hydrophobic liquid, such as oil, it should be cleaned with a solvent that will dissolve the liquid and then conditioned well in aqueous solution. The reading of an improperly cleaned electrode can drift for hours while the electrode re-equilibrates with aqueous solution.