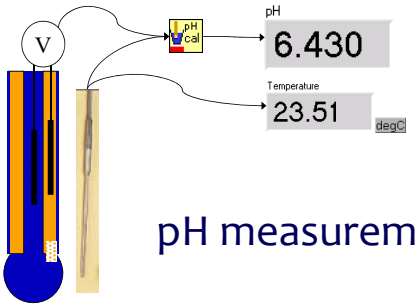
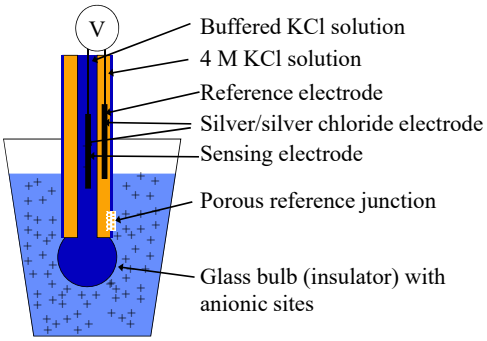


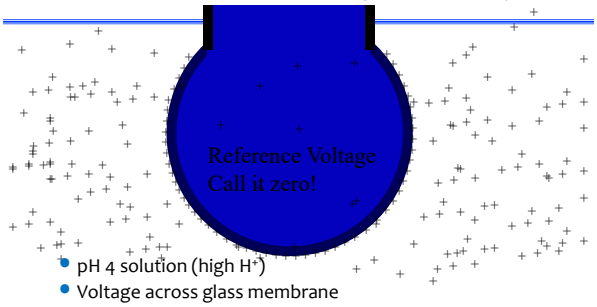
pH measurements

The probe, from chemistry to voltage to a number

pH probe

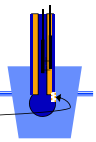


Glass membrane (Insulator)



- pH 4 solution (high H^+)
- Voltage across glass membrane
- Solution voltage is 180 mV higher than reference!
- We need a way to measure the solution voltage

pH Measurements



- The porous frit provides electrical contact between the solution and the electrolyte
  - Must be in contact with the sample solution
  - Probe won't work well if frit is clogged (fouled)
- The voltage measurement requires a very high impedance circuit (high resistance) because a pH probe can't produce much current
- Gentle stirring keeps the solution next to the glass bulb from being depleted of protons

Difficult Measurements?

- pH is difficult to measure in poorly buffered solutions
  - Distilled water
  - Rain
  - Between pKs of dilute buffers

Nernst Equation: Voltage = f(pH)

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{[H^+]}{[H^{+0}]}\right)$$

$$E = E^0 + \frac{RT\ln(10)}{nF}\log\left(\frac{[H^+]}{[H^{+0}]}\right)$$

$$E = E^0 + \frac{RT\ln(10)}{nF}\left[pH^0 - pH\right]$$

$$pH = pH^0 - \frac{(E-E^0)nF}{RT\ln(10)}$$

$[H^{+0}]$ Reference (known) [H+]

E^0 Voltage at $[H^{+0}]$

F Faraday constant

R Gas constant

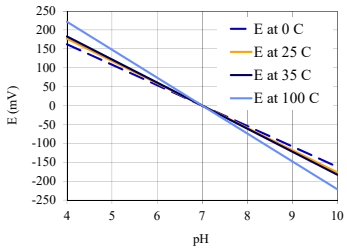
$R = 8.314\frac{J}{mol\cdot K}$

$F = 96500\frac{Coulombs}{mol\ e^-}$

$n = 1\ mol\ e^-$

Nernst Equation

$$pH = pH^0 - \frac{(E-E^0)nF}{RT\ln(10)} \qquad pH = pH^0 + \left(\frac{E^0}{T^0} - \frac{E}{T}\right)\frac{nF}{R\ln(10)}$$



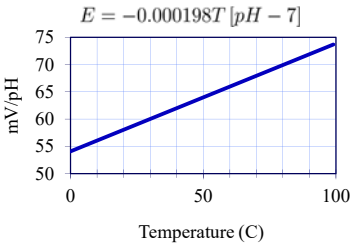
$$R = 8.314\frac{J}{mol \cdot K}$$

$$F = 96500\frac{Coulombs}{mol \quad e^-}$$

$$n = 1\ mol \quad e^-$$

Slope vs. Temperature

$$E = -0.000198T\,[pH - 7]$$



- Temperature compensation is important when temperature changes between samples!

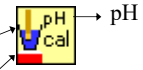
pH Calibration

- It would be possible to make a pH measurement without any calibration
  - Based on theoretical values
  - This is how the software recognizes buffers!
- Calibration accounts for non-ideal probe behavior (fouling) as well as electronic measurement errors
- It is important that buffers be used covering the range of pH measurements

The Challenge

0 to 3 known buffers used as standards
Temperature compensation optional

E	T	Buffer pH

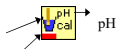


Current measurement (E, T)

Multiple Point Calibrations w/ Temperature Compensation

- How would you use this information to calculate pH?

E (mV)	T (C)	Buffer pH
8	23	7
185	24	4
-170	20	10



Current measurement (E, T)

Calculate E/T

Piecewise linear fit

$$pH = pH^0 + \left(\frac{E^0}{T^0} - \frac{E}{T}\right)\frac{nF}{R\ln(10)}$$