

## The pH Electrode: A Neutralization Reaction Tracking Device

Acid-base titration curves are tracked by measuring the potential difference across a combination glass pH electrode as the neutralization reaction proceeds. At 25°C, pH electrodes are known to adhere to the following equation given below:

$$E = E' - 0.0591\text{pH}$$

It is derived from the Nernst equation.  $E$  is the voltage measured for a specific pH of a buffer.  $E'$  depends on the internal reference and the glass membrane behavior. The internal reference remains constant; however, the glass membrane potential changes with time. Hence, calibration of the pH electrode is required. On a short time scale,  $E'$  is constant.

What type of function does this equation represent? Sketch a graph of  $E$  as a function of pH and label the axes and any other important information. Use the language of mathematics!

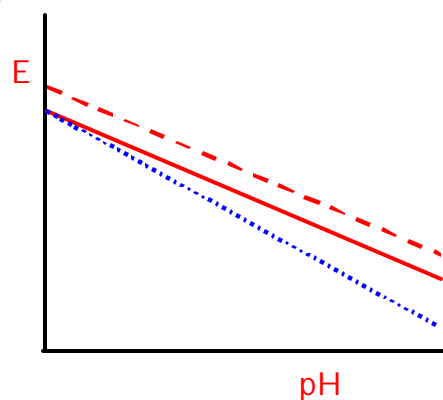
As pH increases,  $E$  decreases (slope is "-ve")

It is a linear equation:  $E = -0.0591\text{pH} + E'$

$$y = m x + b$$

How is the function influenced by a change in  $E'$ ?

$E'$  is the intercept, if it changes the line shifts parallel to line on graph.



For calibration, the electrode is placed into a buffer of known pH and the potential developed across the membrane is measured as the voltage produced,  $E$ . This is a typical single-point calibration. If a pH = 5.00 buffer gave a voltage of  $E = 0.912\text{v}$ , what is the value of  $E'$ ?

$$E' = E + 0.0591\text{pH} = 0.912 + 0.0591(5.00) = 1.208 \text{ v}$$

What is the pH of another solution if the voltage,  $E$ , is 0.671v for the calibrated electrode above?

$$\text{pH} = (E' - E)/0.0591 = (1.208 - 0.671)/0.0591 = 9.09$$

If an electrode sits for a long period of time, the glass membrane will age and its behavior changes. How will this influence the calibration equation? How will the graph of E as a function of pH change? Sketch and label on your graph above.

The intercept of the line will shift. See dashed line (----) on graph.

Temperature is another variable that influences pH. Let's examine the equation modified for influence of a temperature change compared to 25°C (298K).

$$E = E' - 0.0591(T/298)pH$$

In the equation, T is temperature in Kelvin and E' is also a weak function of temperature (We will assume it is constant). If the temperature changes, how will this influence the graph of E as a function of pH? Sketch and label on your graph above. A change in temperature will influence the slope of the line. If T increases, the slope becomes more negative and if T decreases, slope becomes less negative. See blue dotted (.....) line on graph which shows a temperature increase.

A two-point calibration, using two differing buffers as in the laboratory with the Vernier pH probe, automatically compensates for any temperature differences. This assumes all your solutions to be measured and buffers are at a constant laboratory temperature. Explain why this works. (Think about the mathematics of two points. What do they define?)

Two points define a straight line, with a fixed slope and intercept.

Now how critical is temperature compensation in normal laboratory measurements. Calculate the slope correction factor, T/298, for a 25°C ± 5°C range in temperature (20-30°C). 293 - 303 K put range in T/298 and evaluate

293/298 = 0.98 (2%)                      303/298 = 1.02 (2%)  
relatively small changes in slope

If you were analyzing near-boiling hot springs water at 370 K, such as from Yellowstone National Park, would temperature correction be required? Explain why or why not.

370/298 = 1.24 (24%)                      large error in slope!