Technical Note 147

The Effect of Temperature on pH

Effect of temperature on pH measurement

At the heart of any electrochemical process are oxidation and reduction processes. In half-cell reactions, as used in electrochemical sensors (including pH), the response of an electrode is defined by the Nernst equation where:

$$E = E^o + \frac{RT}{nF} \ln a_i$$

E = cell potential

E^o = standard cell potential

R = molar gas constant

T = temperature (in Kelvin)

n = charge of ion

F = Faraday Constant

a_i = activity of the species being measured

And given that pH is a measure of H^+ activity:

$$pH = -\log a_{H+}$$

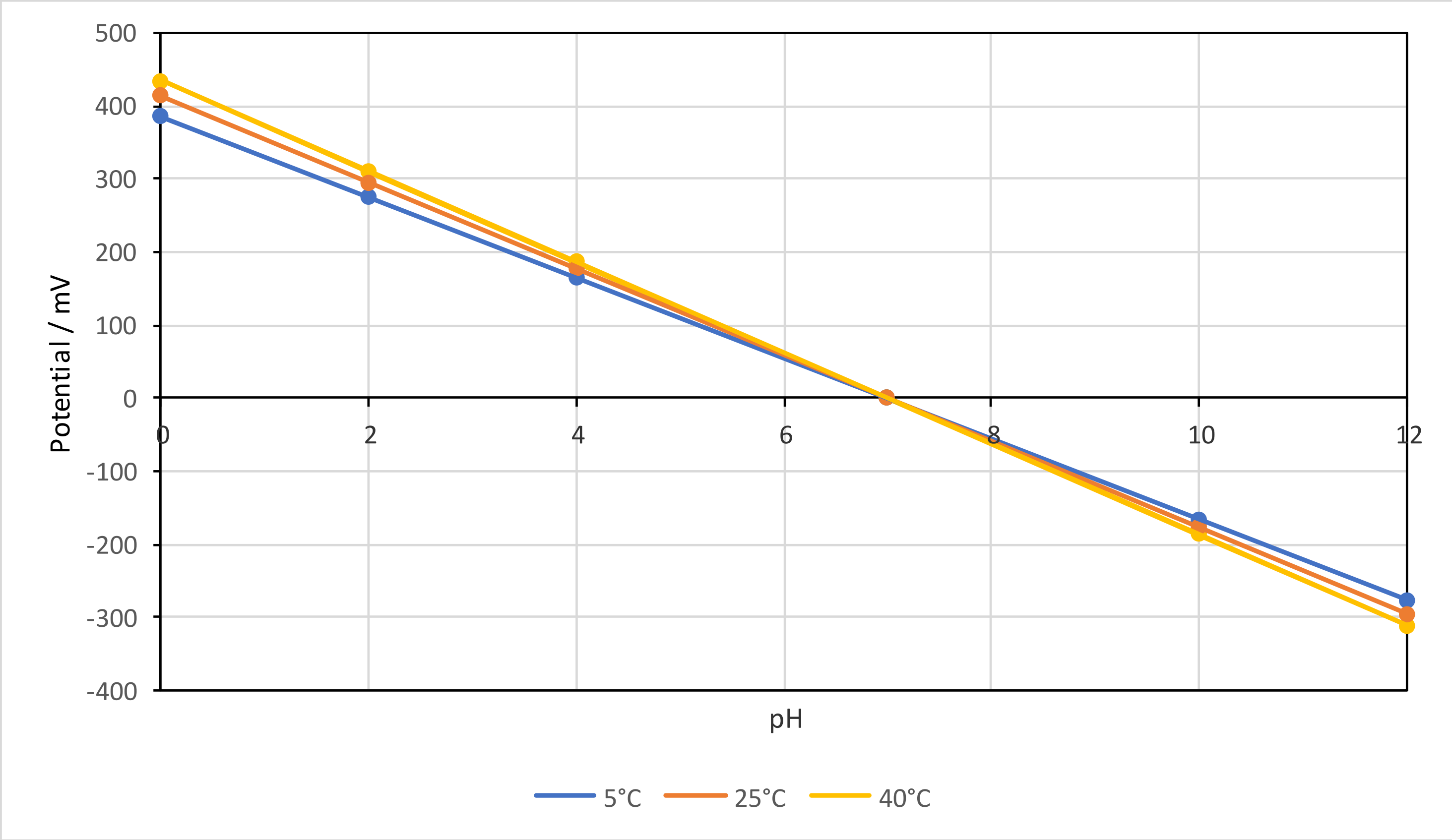
Replacing terms in the Nernst equation with terms from the second equation means that it can be re-written (at 25°C) as:

$$E = E^o - 0.05916\, pH$$

This shows that, at 25˚C, an ideal pH sensor would register a -59.16mV drop in electrode potential for each increase of a pH unit. This is well known, but it is often forgotten that the -59mV per increase in one pH unit only applies at 25˚C. Given that many online pH sensors operate at a different temperature, or even in environments with variable temperatures, it is important to understand the effect of temperature on a pH sensor.

From the above it can be seen that the Nernst equation has a temperature component (T), and therefore the ideal slope of a sensor changes with temperature. A rough 'rule of thumb' for the effect of temperature upon pH measurement in potable water is *"every 5 degree increase in temperature makes the slope 1mV more negative".* This means that at different temperatures the slopes of the sensor response are different, as shown below.

It is important when calibrating and evaluating a pH sensor response to understand this deviation from -59.16mV per pH unit. The colder the water, the more positive the slope will become. It also highlights the need to allow pH sensors to equilibrate fully in a calibration solution before using that solution to calibrate a pH sensor.



The graph above and the table below shows the pH sensor response slopes at different temperatures.

Temperature (°C)	Slope (mV / pH unit)
5	-55.18
10	-56.18
15	-57.17
20	-58.16
25	-59.16
30	-60.15

Calibration and Automatic Temperature Compensation (ATC) in Pi's CRONOS® and CRIUS®4.0

pH sensor calibrations are calculated as an ideal slope gain error and offset error of the isopotential point against the ideal response. The isopotential point is the point at which the electromotive force of the sensor is independent of temperature. This is nominally at pH7, where the sensor measures a potential difference with the reference of 0mV.

ATC operates by calculating the ideal slope at a given or measured temperature. As shown in the table above, at 5°C this would be -55.18mV. The sensor reading is used with this ideal slope and the current calibration to determine a pH value.

What Does This Mean To The Operator?

When looking at the slope under the maintenance menu it is important not to make the assumption that the ideal slope is -59.16mV. It is possible to forget the effect of temperature, and to assume that a reported slope is "no good" if it is significantly above -59.16mV. Pi recommends that the operator refers to the "Health" reported by the analyser, which takes into consideration the temperature of the sample. As long as the health remains above 85% then the sensor is operating correctly. If the health drops below 85% then the sensor should be cleaned. If cleaning the sensor doesn't restore the health to >85% then consider replacing it.

When calibrating a pH sensor it is very important to allow the sensor to equilibrate with regard to temperature of the calibration solution. This takes longer than many operators recognize given that the sensor body is normally plastic. This is especially true when there is a large temperature difference, such as when the calibrants have come out of a warm car or office on a winters day and the water is close to 0°C.