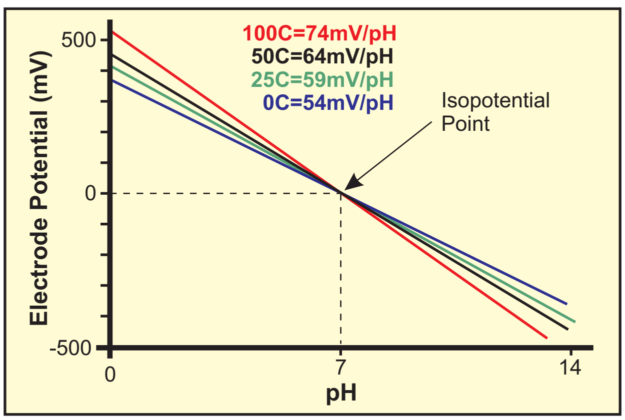
electronics & automation

Basic pH Electrode Theory

Introduction

A pH probe (electrode) outputs a fixed mV value for a given pH solution at a fixed temperature. At 25C the ideal probe output is 59.16mV/pH. At pH = 7 the ideal probe output is 0mV independent of temperature. This is called the isopotential point (i.e. when pH = 7). The probe output "slope" is negative, therefore, the ideal output at pH = 4 is +177.48mV and at pH = 10 the output is -177.48mV. Also, since a pH probe is a very high impedance type sensor, it is not possible to directly measure the output signal with a multimeter. A high input impedance type amplifier is required (standard Op Amps do not have a high enough input impedance for use with pH probes). In addition, the probe output slope will vary in direct proportion to temperature (in Kelvin). This is shown in the graph below.

Figure 1: Ideal Electrode Potential Over Temperature



Two Point Calibration Using Buffer Solutions

At 25C real (as opposed to ideal) probe outputs can vary from 56mV/pH to 62mV/pH. In addition, the probe input amplifier circuit and the Analog-to-Digital converter circuit of the instrument will have a real world gain/offset which will be slightly different than the ideal design values. Therefore, real probes need to be calibrated- while connected to the instrument- using known pH buffer solutions and at a known temperature.

The procedure is to place the pH probe and the temperature probe in the first buffer solution (typically with pH = 4.00) and measure the mV value. Then place the probes in the second buffered solution (typically with pH = 10.00) and measure the new mV value. Both buffered solutions should be at the same temperature. From these two "cal points" the equation for the mV output at the calibration temperature can be calculated as:

Y = A0 * X + B0 where:
Y = mV value
X = pH value
A0 = slope at cal temperature
B0 = Y intercept at cal temp

Next, using the equation above, the isopotential mV value can be calculated by setting X = 7.0. During normal operation a new slope (A) and Y intercept (B) must be continuously calculated based on the live temperature.

The equation for the "live temperature" slope is:

A = A0 * T / T0

where:
A = slope at live temperature
A0 = slope at cal temperature
T = live temperature (Kelvin)
T0 = cal temperature (Kelvin)

Since the isopotential value is independent of temperature, the live temperature Y intercept (B) can be calculated by solving the equation:

Y = A * X + B

using X = 7.0, Y = the isopotential value, and A = the live slope. Once the live temperature A and B values are known any pH value can be calculated for a given probe mV output.

One Point Calibration Using Known pH

Since it is not possible to determine the slope of a line given only one point on the line, the single point calibration method is not as accurate as the two point calibration method. For this method it is assumed that the probe output follows the ideal slope value of 59.16mV/pH at 25C. The live temperature slope is calculated the same as above, i.e. A = A0 * T / T0. The single calibration point is the know pH of the solution and the probe mV output at the calibration temperature. The isopotential at the calibration temperature can be calculated the same as above. The isopotential can then be used to calculate the live B value as above. Essentially, this method takes the ideal slope lines (as shown in figure 1) and shifts them vertically so that the calibrated data point lies on the line with the temperature equal to the calibration temperature.

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