pH Temperature Compensation

There are two types of temperature compensation when discussing pH measurements. Automatic Temperature Compensation (ATC), which compensates for the varying milli-volt output from the electrode due to temperature changes of the process solution and Solution Temperature Compensation (STC), which corrects for a change in the chemistry (change in pH) of the solution as the temperature of the solution changes.

Automatic Temperature Compensation

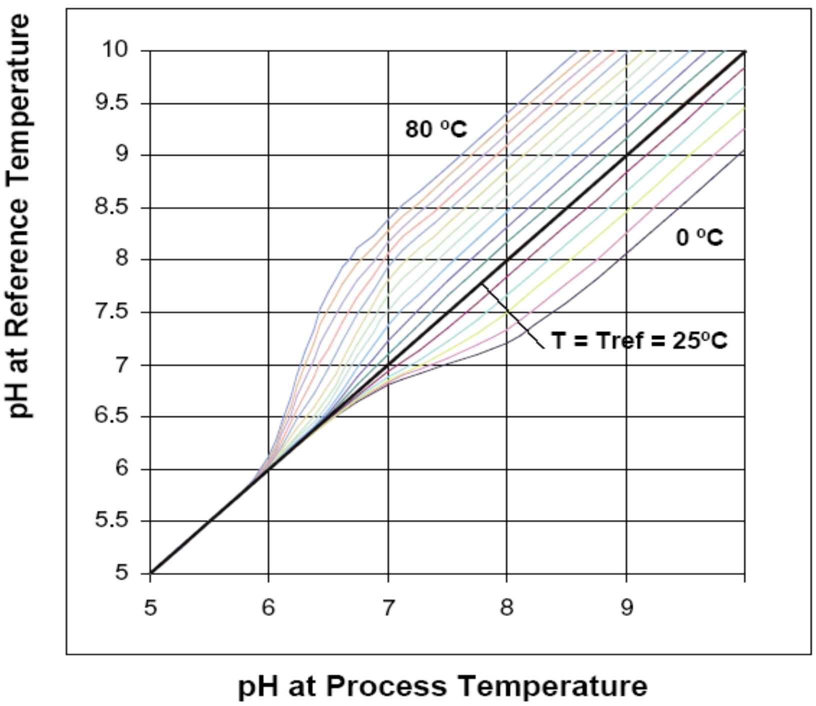
In a pH-measuring loop, there are three main components. The glass (pH) measuring electrode, the reference electrode and the temperature electrode. When the electrodes are placed in a solution, a voltage (mV) is generated depending on the hydrogen *activity* of the solution. The varying voltage (potential) is dependent on the acidity or alkalinity of the solution and varies with the hydrogen ion *activity* in a known manner, the Nernst Equation. The potential (voltage) of the glass electrode is compared to the potential of the reference electrode and the difference between the two potentials is the measured potential. When placed in a pH 7 buffer most electrodes are designed to produce a zero (0) mV potential. As the solution becomes more acidic (lower pH) the potential of the glass electrode becomes more positive (+ mV) in comparison to the reference electrode and as the solution becomes more alkaline (higher pH) the potential of the glass electrode becomes more negative (- mV) in comparison to the reference electrode. The Nernst Equation shows the relationship between temperature and its affect on the activity of the hydrogen ion. At 25°C, each additional pH unit change represents a +/- 59.16 mV change in the potential of the glass electrode from a starting point of pH 7 (0 mV). At 80°C each additional pH unit change represents a +/-70.1 mV change.

		pH/mV Ratio (measured with regard to the saturated calomel electrode)									
pH	**Temp.° C**	**0°**	**10°**	**20°**	**30°**	**40°**	**50°**	**60°**	**70°**	**80°**	**90°**
0.0		379.4	393.3	407.1	421.0	434.9	448.8	462.7	476.6	490.5	504.4
0.5		352.3	365.2	378.1	391.0	403.9	416.8	429.7	442.5	455.5	468.3
1.0		325.2	337.1	349.0	360.9	372.8	384.7	396.6	408.5	420.4	432.3
1.5		298.1	309.0	319.9	330.8	341.7	352.6	363.6	374.5	385.4	396.3
2.0		271.0	280.9	290.8	300.7	310.7	320.6	330.5	340.4	350.3	360.3
2.5		243.9	252.8	261.7	270.7	279.6	288.5	297.5	306.4	315.3	324.2
3.0		216.8	224.7	232.7	240.6	248.5	256.5	264.4	272.3	280.3	288.2
3.5		189.7	196.6	203.6	210.5	217.5	224.4	231.4	238.3	245.2	252.2
4.0		162.6	168.5	174.5	180.4	186.4	192.3	198.3	204.3	210.2	216.2
4.5		135.5	140.5	145.4	150.4	155.3	160.3	165.3	170.2	175.2	180.1
5.0		108.4	112.4	116.3	120.3	124.3	128.2	132.2	136.2	140.1	144.1
5.5		81.3	84.3	87.2	90.2	93.2	96.2	99.2	102.1	105.1	108.1
6.0	**+ mV**	54.2	56.2	58.2	60.1	62.1	64.1	66.1	68.1	70.1	72.1
6.5	⇑	27.1	28.1	29.1	30.1	31.1	32.1	33.1	34.0	35.0	36.0
7.0	╠	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7.5	⇓	27.1	28.1	29.1	31.1	31.1	32.1	33.1	34.0	35.0	36.0
8.0	**- mV**	54.2	56.2	58.2	60.1	62.1	64.1	66.1	68.1	70.1	72.1
8.5		81.3	84.3	87.2	90.2	93.2	96.2	99.2	102.1	105.1	108.1
9.0		108.4	112.4	116.3	120.3	124.3	128.2	132.2	136.2	140.1	144.1
9.5		135.5	140.5	145.4	150.4	155.3	160.3	165.3	170.2	175.2	180.1
10.0		162.6	168.5	174.5	180.4	186.4	192.3	198.3	204.3	210.2	216.2
10.5		189.7	196.6	203.6	210.5	217.5	224.4	231.4	238.3	245.2	252.2
11.0		216.8	224.7	232.7	240.6	248.5	256.5	264.4	272.3	280.3	288.2
11.5		243.9	252.8	261.7	270.7	279.6	288.5	297.5	306.4	315.3	324.2
12.0		271.0	280.8	290.8	300.7	310.7	320.6	330.5	340.4	250.3	360.3
12.5		298.1	309.0	319.9	330.8	341.7	352.6	363.6	374.5	385.4	393.3
13.0		325.2	337.1	349.0	360.9	372.8	384.7	396.6	408.5	420.4	432.3
13.5		352.3	365.2	378.1	391.0	403.9	416.8	429.7	442.5	455.4	468.3
14.0		379.4	393.3	407.1	421.0	434.9	448.8	462.7	276.6	490.5	504.4

When heat is applied to the solution being measured, the hydrogen ions move faster (increased activity) and the measured voltage increases. When the solution is cooled, the hydrogen ions move slower and the measured voltage decreases. The temperature electrode, measures changes in the temperature of the solution and the pH analyzer uses this information (via the Nernst Equation) to correlate the mV input to the correct pH value. Example: In a pH 5 solution at 25°C, the voltage generated is +118.32 mV (59.16 x 2). In the same solution at 100°C the voltage generated is +148.08 mV (74.04 x 2). The pH value has not changed only the voltage output from the electrode because of the increase in the activity of the hydrogen ion.

Solution Temperature Compensation

Solution temperature compensation corrects for changes in the solution chemistry (pH) as the temperature of the solution changes. In certain solutions (ultra-pure water, bleach stock in paper applications and other high alkaline solutions), the pH of the solution will change (typically increase) as the solution cools. Solution temperature compensation is primarily used in power plant and other pure water applications less then 30µS/cm conductivity. When the solution temperature compensation function is active, the displayed reading will be referenced to 25°C regardless of the actual process temperature.



For pure makeup water or boiling water reactor samples, the solution temperature coefficient should be set to –0.016 pH/°C. For ammonia, phosphate and/or amine-treated water, the solution temperature coefficient should be set to –0.033 pH/°C. For other process solutions the correct solution temperature coefficient can be calculated by developing temperature vs. pH data. The negative slope of this data is the solution temperature compensation value.

Below is an example for how to calculate the exact temperature coefficient for a process solution. Usually (but not always) as the process solution cools the pH will rise, so:

$$\frac{pH\,1 - pH\,2}{Temp\,1 - Temp\,2} = \frac{8.93 - 9.10}{30°C - 25°C} = \frac{-0.17}{5°C} = -0.034°C$$

In the Yokogawa pH202 Two-Wire Transmitter, the value you would enter is based on a 10°C change so you would enter -0.34 into the analyzer. In the Model pH450 analyzer, the value is based on a 1°C change so you would enter -0.034 into the analyzer

Because the solution temperature compensation is unique to the process solution and is different from the buffer solutions, it is not active during calibrations. Once the calibration is completed, the solution temperature compensation value is again active, so if the electrodes are placed back into the buffers, they might not read the correct value. To read and verify the exact value of the buffer, the solution temperature compensation value must be temporarily set to 0 or the turned off.