

PRINCIPLES AND GUIDELINES

of pH measurement

By Steve Rupert

The measurement of pH is common to all industries that use water. The proper pH of a solution can assure product quality, optimize the yield, increase the rate of reaction, or in general terms, just improve the process. While you can measure pH several ways—litmus paper, pH electrodes, colorimetric dyes, or titrations—pH glass electrodes are the preferred method.

pH is a measure of the hydrogen ion activity of a solution, which defines the degree of acidity or alkalinity of the solution. Therefore, pH is the unit of measure for acidity, as pounds are for weight. Acidity is a chemical parameter; it's a concentration. But due to chemical notation's wide measurement range and unwieldy nature, P.L. Sorensen, a Danish chemist who developed the pH scale in 1909, defined pH as the negative logarithm of the hydrogen ion concentration, which he later changed to hydrogen ion activity.

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

This allows you to write concentrations like 0.0000001 molar hydrogen ion as pH 7.

Measure the pH of a solution with a potentiometric cell consisting of a pH-sensitive glass electrode, a reference electrode and a high-input impedance volt meter. The output of the cell is temperature sensitive in accordance with the Nernst Equation, so a temperature electrode is also included in most systems. Walther Nernst first elucidated the theory of galvanic cells in 1889, which related the voltage of a cell to its physical and chemical properties. For pH, it is: $E = E_0 + 2.3RT/F \log a_{\text{H}^+}$.

Where E equals the voltage of the cell, E_0 equals the standard voltage of the cell, R equals the Universal Gas Constant, F equals the Faraday Constant, and T is the temperature in degrees Kelvin. The $2.3RT/F$ is the Nernst number or slope, and at 25, C equals 59.16 mV/pH.

In 1906, M. Cremer, who invented the glass electrode in collaboration with Fritz Haber, reported the glass plates isolating the electrochemical cells in his experiments developed a potential proportional to the acidity of the solutions. When in an aqueous solution, a pH glass electrode develops a potential of 59 mV for each pH unit. The diffusion of lithium ions out of the glass generates the potential preferentially with respect to the hydrogen ions in solution. Generation occurs with zero mV at pH 7, with positive values from 0-7 pH and negative values from 7-14 pH.

The reference electrode must produce a potential independent of the measured solution and provide a stable electrical contact to the solution to complete the measurement circuit. You accomplish this by constructing a battery that is silver metal coated with silver chloride placed in a potassium chloride electrolyte that

contacts the solution through a salt bridge, the liquid junction. A liquid junction is a porous plug that restricts the flow of electrolyte out of the reference, keeping the battery at a constant potential while providing electrical contact through its salt-filled pores.

Most industrial reference electrodes use diffusion of potassium chloride out of the sensor to make the electrical contact. Diffusion is the force where a high concentration moves to a lower concentration. An equivalent of pressure, diffusion drives ions from one region to another. The larger the difference in ionic strengths, the stronger the diffusion force. Potassium ions and

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chloride ions have slightly different mobility, so when they diffuse through a liquid junction a charge separation occurs. The charge separation is proportional to the diffusion rate and inversely proportional to the pore size of the liquid junction (i.e., it forms a large potential with small pores and high diffusion rates). By definition, a charge separation is a potential, and in this case, the liquid junction potential.

Calibrating an electrode in standard pH buffers forms a junction potential. If you then use the electrode in a solution of the same ionic strength, 0.1M, the reference potential will be the same as in the calibration solution. This results in a highly accurate reading. However, if the ionic strength is different, it will introduce an error. In some solutions, such as high purity water or salt brines, the error can be 0.5-2 pH units.

Reference electrodes with very porous junctions or aperture style junctions are good at minimizing diffusion related potentials as well as drift caused by fouling. However, the high porosity tends to deplete the potassium chloride in the reference, and the electrode dies.

The best way to monitor the reference electrode is with the Reference Impedance Diagnostic on the pH meter. While not all meters have this capability, it is worth seeking out when selecting an instrument. The proper measurement of pH will improve the quality and efficiency of most processes; these benefits can be lost, or more serious consequences can ensue with the improper measurement of pH. ▶

▶ Behind the Byline

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