1. Introduction to pH Measurements

A pH measurement is a determination of the activity of hydrogen ions in an aqueous solution. Many important properties of a solution can be determined from an accurate measurement of pH, including the acidity of a solution and the extent of a reaction in the solution. Many chemical processes and properties, such as the speed of a reaction and the solubility of a compound, can also depend greatly on the pH of a solution. In applications ranging from industrial operations to biological processes, it is important to have an accurate and precise measurement of pH.

2. pH Theory

pH is mathematically defined as the negative log of hydrogen ion activity (Equation 1). In most cases, the activity of hydrogen ions in solution can be approximated by the Molar concentration of hydrogen ions (\([H^+]\)) in a solution (Equation 2).

\[
pH = -\log aH^+ \quad (1)
\]

Hence,

\[
pH = -\log [H^+] \quad (2)
\]

Using Equation 2, it can be calculated that a pH of 4 corresponds to a hydrogen ion concentration of \(10^{-4}\) Molar.

The benchmark for pH is actually the concentration of hydrogen ions in water at 25° C. At any temperature, water dissociates into hydrogen ions and hydroxide ions as shown in the following equilibrium reaction.

\[
H_2O \leftrightarrow H^+ + OH^-
\]

The rate of the equilibrium reaction above is described by an equilibrium constant \(K_W\), which varies with temperature but is equal to \(1.01 \times 10^{-14}\) at 25° C. This constant is determined using Equation 3.

\[
K_W = [H^+][OH^-] \quad (3)
\]

It is important to note that the value of \(K_W\) varies with temperature, and therefore so does the pH of a solution. For example, given the enthalpy of a reaction and the temperature at which the reaction occurs, the value of \(K_W\) for the reaction can be determined using the van’t Hoff equation (Equation 4).

\[
\ln K_W(T) = \ln K_W(T_1) + (\Delta H^R / RT_1) (T_1^{-1} - T^{-1})
\]

From calculated \(K_W\) values, the actual pH of water can be calculated at different temperatures. The pH of water at temperatures of 0° C, 25° C, and 100° C are shown in Table 2.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(K_W)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0° C</td>
<td>0.114 \times 10^{-14}</td>
<td>7.46</td>
</tr>
<tr>
<td>25° C</td>
<td>1.01 \times 10^{-14}</td>
<td>7</td>
</tr>
<tr>
<td>100° C</td>
<td>49 \times 10^{-14}</td>
<td>6.15</td>
</tr>
</tbody>
</table>

3. pH Measurement

A solution’s pH is commonly measured in a number of ways. Qualitative pH estimates are commonly performed using Litmus paper or an indicator in solution. Quantitative pH measurements are reliably taken using potentiometric electrodes. These electrodes simply monitor changes in voltage caused by changes in the activity of hydrogen ions in a solution. A simple
A potentiometric electrode of this type is shown in Figure 1.

![Figure 1. Simple pH Electrode](image)

Most modern pH electrodes consist of a single combination reference and sensing electrode instead of separate electrodes. This type of pH electrode is much easier to use and less expensive than the electrode pair in Figure 1. A combination electrode is functionally the same as an electrode pair.

Any pH electrode requires both a sensing electrode and a reference electrode. The sensing electrode consists of a thin hydrogen permeable membrane containing a solution and an electrode. The membrane of the sensing electrode allows hydrogen ions to slowly pass, creating a positive voltage across the membrane. The voltage created in this electrode is then compared to the voltage in the reference electrode. The voltage difference between the two electrodes is then used to determine the pH of the unknown solution using the Nernst equation (Equation 5).

\[ E_{(PH)} = E_{(constant)} + (2.3 \times \frac{RT}{nF}) \times \log [H^+] \]  

Where:
- \( E_{(PH)} \) = Voltage difference between sensing electrode and Reference electrode (V)
- \( E_{(constant)} \) = Voltage difference in a solution with pH = 7 (V)
- \( R \) = Gas Constant (8.314 J/K*mole)
- \( T \) = Temperature in Kelvin (K)
- \( n \) = Number of Valence Electrons per Mole (1 for H\(^+\))
- \( F \) = Faraday’s Constant (96500 J/V*mole e\(^-\))

This equation simplifies to Equation 6 after all the constants are introduced.

\[ E_{(PH)} = E_{(constant)} - 1.98158 \times 10^{-4} \text{ Volts/Kelvin} \times T \times pH \]  

4. Electrode Calibration

The only two independent variables in Equation 5 are the temperature and the pH. Because both of these will affect the voltage output of the electrode, temperature compensation in the calibration is very important for pH measurements.

Although \( E_{(constant)} \) is a constant, its value varies between individual electrodes and with temperature. To compensate for this variation, we introduce the variable \( E' \), which is less dependent upon temperature. Most pH electrodes also have sensitivities to pH
that deviate slightly from the ideal Nernst equation. To compensate for slight deviations from the Nernst ideal, we introduce variable s. The value of s corresponds to how well the electrode correlates with the Nernst ideal, with a value of 1 meaning that the electrode does not deviate from the ideal. The introduction of these two variables is shown in Equation 7.

\[ E_{(pH)} = E' + T - 1.98158 \times 10^{-4} \cdot s \cdot T \cdot pH \] (7)

By placing the electrode in two different calibration buffers and recording the voltages produced by the electrode, we can use two simultaneous equations to determine the values of \( E' \) and s. This new equation is then used to determine the pH from any voltage and temperature reading. It is recommended that pH readings always be taken at a temperature near the temperature where calibration was performed. Equation 8 is the final equation used to determine the pH from a calibrated pH electrode.

\[ pH = \frac{(E' + T - E_{(pH)})}{s \cdot 1.98158 \times 10^{-4} \cdot T} \] (8)

5. Important Considerations

After proper calibration, pH electrodes can take extremely accurate and precise measurements.

One important consideration when using pH electrodes is the extremely high impedance signal coming from the pH electrode itself. Most data acquisition devices have high impedance inputs, but the impedance of the pH electrode is so great that a unity gain in-line amplifier is still necessary to lower the source impedance and improve voltage readings.

See Also: