

Theory and Practice of pH Measurement



THEORY AND PRACTICE OF pH MEASUREMENT

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SECTION 1.0 OVERVIEW

- 1.1 INTRODUCTION
- 1.2 OPERATIONAL DEFINITION OF pH
- 1.3 pH MEASUREMENTS IN INDUSTRY

1.0 OVERVIEW

The determination of pH is one of the most common process chemical measurements made today. This booklet explains the principles behind the measurement and discusses ways of avoiding common pitfalls. The booklet also discusses industrial ORP (oxidation-reduction potential) measurements. Although the determination of ORP is not nearly as common as pH, certain industries make valuable use of the measurement.

1.1 INTRODUCTION

pH is a measure of the relative amount of hydrogen and hydroxide ions in an aqueous solution. In any collection of water molecules a very small number will have dissociated to form hydrogen (H^+) and hydroxide (OH^-) ions:



The number of ions formed is small. At 25°C fewer than 2×10^{-7} % of the water molecules have dissociated. In terms of molar concentrations, water at 25°C contains 1×10^{-7} moles per liter of hydrogen ions and the same concentration of hydroxide ions.

In any aqueous solution, the concentration of hydrogen ions multiplied by the concentration of hydroxide ions is constant. Stated in equation form:

$$K_w = [H^+][OH^-] \quad (1)$$

where the brackets signify molar concentrations and K_w is the dissociation constant for water. The value of K_w depends on temperature. For example, at 25°C $K_w = 1.00 \times 10^{-14}$ and at 35°C $K_w = 1.47 \times 10^{-14}$.

Acids and bases, when dissolved in water, simply alter the relative amounts of H^+ and OH^- in solution. Acids increase the hydrogen ion concentration, and, because the product $[H^+][OH^-]$ must remain constant, acids decrease the hydroxide ion concentration. Bases have the opposite effect. They increase hydroxide ion concentration and decrease hydrogen ion concentration. For example, suppose an acid is added to water at 25°C and the acid raises the H^+ concentration to 1.0×10^{-4} moles/liter. Because $[H^+][OH^-]$ must always equal 1.00×10^{-14} , $[OH^-]$ will be 1.0×10^{-10} moles/liter.

pH is another way of expressing the hydrogen ion concentration. pH is defined as follows:

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

Therefore, if the hydrogen ion concentration is 1.0×10^{-4} moles/liter, the pH is 4.00.

The term neutral is often used in discussions about acids, bases, and pH. A neutral solution is one in which the hydrogen ion concentration exactly equals the hydroxide ion concentration. At 25°C, a neutral solution has pH 7.00. At 35°C, a neutral solution has pH 6.92. The common assertion that neutral solutions have pH 7 is not true. The statement is true only if the temperature is 25°C.

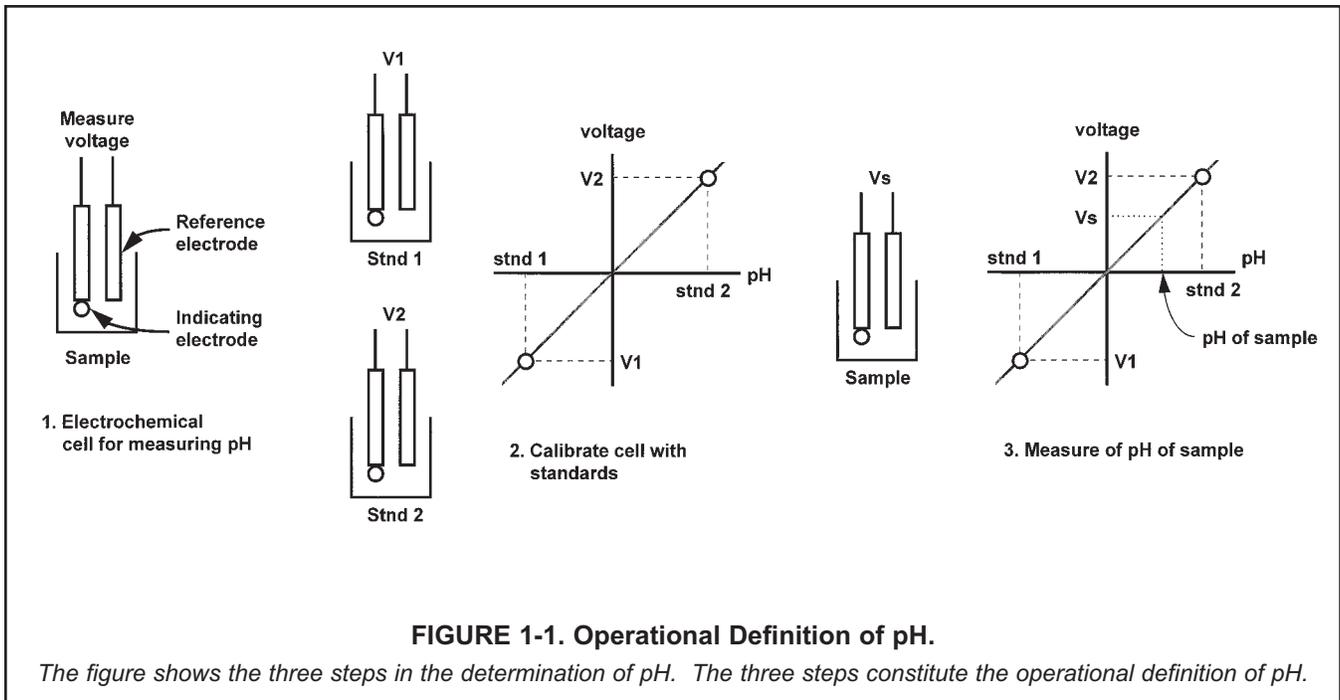
1.2 OPERATIONAL DEFINITION OF pH

Although equation 2 is often given as the definition of pH, it is not a good one. No one determines pH by first measuring the hydrogen ion concentration and then calculating pH. pH is best defined by describing how it is measured.

Figure 1-1 illustrates the operational definition of pH. The starting point is an electrochemical cell. The cell consists of an indicating electrode whose potential is directly proportional to pH, a reference electrode whose potential is independent of pH, and the liquid to be measured. The overall voltage of the cell depends on the pH of the sample. Because different indicating electrodes have slightly different responses to pH, the measuring system must be calibrated before use. The second step in the operational definition of pH is calibration. The system is calibrated by placing the electrodes in solutions of known pH and measuring the voltage of the cell. Cell voltage is a linear function of pH, so only two calibration points are needed. The final step in the operational definition is to place the electrodes in the sample, measure the voltage, and determine the pH from the calibration data.

It is apparent that the practical determination of pH requires standard solutions of known pH. The standard solutions are called buffers, and the pH values assigned to them define the pH scale. The procedure by which pH values are assigned to buffers is beyond the scope of this discussion. There is one important point, though. Determining pH values requires making assumptions concerning the chemical and physical properties of electrolyte solutions. Slightly different assumptions lead to slightly different pH values for the same solution. Therefore, slightly different pH scales can exist.

Finally, it should be noted that equation 2 is somewhat misleading. The equation implies that pH is a measure of concentration. In fact, pH is really a measure of ion activity. Concentration and activity are not the same, but they are related. See Section 3.3 and the Glossary for more information.



1.3 pH MEASUREMENTS IN INDUSTRY

Although pH is a measure of hydrogen ion activity, the fact is of little interest to anyone but a physical chemist. It is certainly of scant importance in industrial pH measurements. The major use of pH in industry is process control. Controlling pH helps ensure product quality, reduces corrosion and scaling in plant equipment, and protects the environment by helping wastewater dischargers meet regulatory limits.

Process pH control limits are often empirical. It is less important to know why a given pH range works than to keep the pH in the desired range. It is, therefore, important that the person making and using pH measurements understand how the measurement is made, how to calibrate the measuring instrument, and how to recognize and avoid common problems.

This booklet has five major sections. The first section discusses the construction and features of the electrochemical cell used for measuring pH. The second section discusses how the pH analyzer converts the measured cell voltage into pH. The third section discusses some fundamental limitations to pH measurements. The fourth section discusses industrial ORP measurements. Because ORP measurement cells have much in common with pH cells, much of the information in the pH cell section applies to ORP measurements. The fifth section deals with installation, maintenance, and troubleshooting of pH systems.

SECTION 2.0

CELLS FOR MEASURING pH

- 2.1 GENERAL
- 2.2 MEASURING ELECTRODE
- 2.3 REFERENCE ELECTRODE
- 2.4 LIQUID JUNCTION POTENTIAL
- 2.5 DOUBLE JUNCTION REFERENCE ELECTRODES

2.1 GENERAL

In nearly every industrial and scientific application, pH is determined by measuring the voltage of an electrochemical cell. Figure 2-1 shows a simplified diagram of a pH cell. The cell consists of a measuring electrode, a reference electrode, a temperature sensing element, and the liquid being measured. The voltage of the cell is directly proportional to the pH of the liquid. The pH meter measures the voltage and uses a temperature-dependent factor to convert the voltage to pH. Because the cell has high internal resistance, the pH meter must have a very high input impedance.

Figure 2-1 shows separate measuring and reference electrodes. In most process sensors, the electrodes and the temperature element are combined into a single body. Such sensors are often called combination electrodes.

The cell voltage is the algebraic sum of the potentials of the measuring electrode, the reference electrode, and the liquid junction. The potential of the measuring electrode depends only on the pH of the solution. The potential of the reference electrode is unaffected by pH, so it provides a stable reference voltage. The liquid junction potential depends in a complex way on the identity and concentration of the ions in the sample. It is always present, but if the sensor is properly designed, the liquid junction potential is usually small and relatively constant. All three potentials depend on temperature.

The construction of the electrodes and the electrical potentials associated with them are discussed in Sections 2.2 and 2.3.

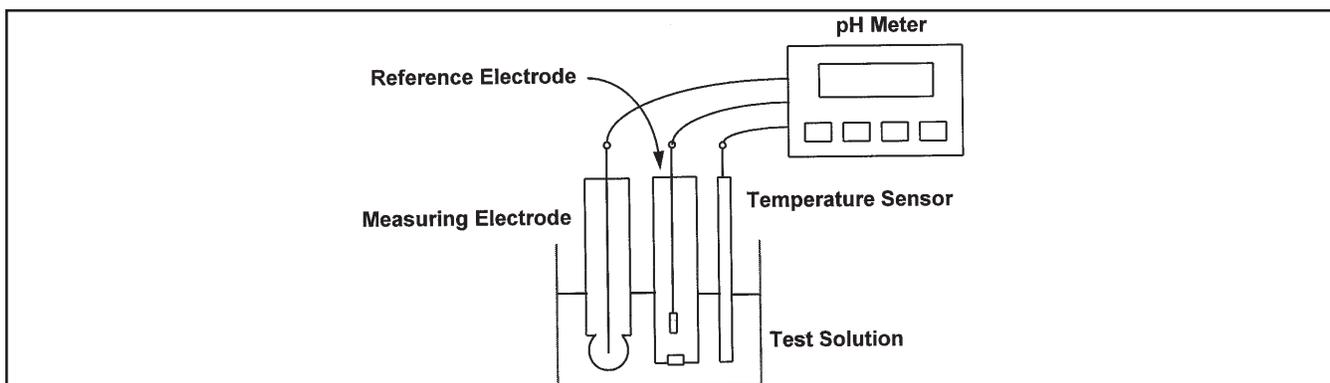


FIGURE 2-1. pH Measurement Cell.

The cell consists of a measuring and reference electrode. The voltage between the electrodes is directly proportional to the pH of the test solution. The proportionality constant depends on temperature, so a temperature sensor is also necessary. A 100 Ω platinum RTD is commonly used, although 1000 Ω platinum RTDs, 3 k Ω Balco RTDs, and thermistors are also used.

2.2 MEASURING ELECTRODE

Figure 2-2 shows the internals of the measuring electrode. The heart of the electrode is a thin piece of pH-sensitive glass, which is blown onto the end of a length of glass tubing. The pH-sensitive glass, usually called a glass membrane, gives the electrode its common name: glass electrode. Sealed inside the electrode is a solution of potassium chloride buffered at pH 7. A piece of silver wire plated with silver chloride contacts the solution.

The silver wire-silver chloride combination in contact with the filling solution constitutes an internal reference electrode. Its potential depends solely on the chloride concentration in the filling solution. Because the chloride concentration is fixed, the electrode potential is constant. See Appendix A for a more detailed discussion of how the chloride concentration determines the electrode potential.

As Figure 2-2 shows, the outside surface of the glass membrane contacts the liquid being measured, and the inside surface contacts the filling solution. Through a complex mechanism, an electrical potential directly proportional to pH develops at each glass-liquid interface. Because the pH of the filling solution is fixed, the potential at the inside surface is constant. The potential at the outside surface, however, depends on the pH of the test solution.

The overall potential of the measuring electrode equals the potential of the internal reference electrode plus the potentials at the glass membrane surfaces. Because the potentials inside the electrode are constant, the overall electrode potential depends solely on the pH of the test solution. The potential of the measuring electrode also depends on temperature. If the pH of the sample remains constant but the temperature changes, the electrode potential will change. Compensating for changes in glass electrode potential with temperature is an important part of the pH measurement.

Figure 2-3 shows a cross-section through the pH glass. pH sensitive glasses absorb water. Although the water does not penetrate more than about 50 nanometers (5×10^{-8} m) into the glass, the hydrated layer must be present for the glass to respond to pH changes. An ion exchange mechanism involving alkali metals and hydrogen ions in the hydrated layer is responsible for the pH response of the glass. The layer of glass between the two hydrated layers remains dry. The dry layer makes the glass a poor conductor of electricity and causes the high internal resistance (several hundred megohms) typical of glass electrodes.

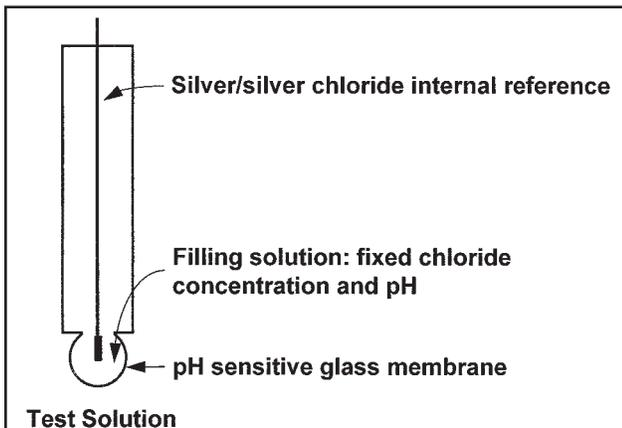


FIGURE 2-2. Measuring Electrode.

The essential element of the glass electrode is a pH-sensitive glass membrane. An electrical potential develops at glass-liquid interfaces. The potential at the outside surface depends on the pH of the test solution. The potential at the inside surface is fixed by the constant pH of the filling solution. Overall, the measuring electrode potential depends solely on the pH of the test solution.

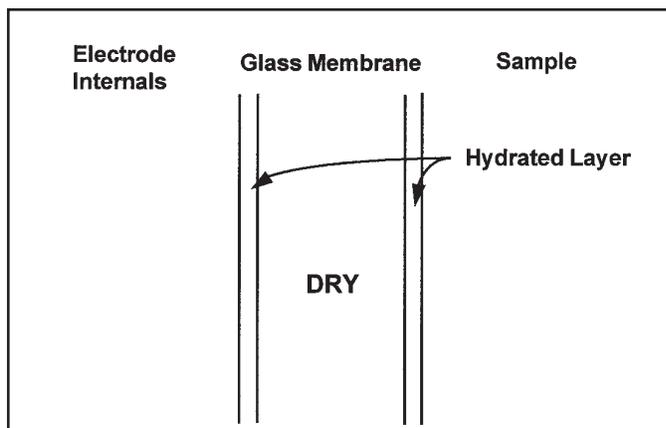


FIGURE 2-3. Cross-Section through the pH Glass.

For the glass electrode to work, the glass must be hydrated. The hydrated layer gradually dissolves and is replaced by a fresh layer. Thus, the surface of the electrode continuously regenerates itself. The rate of dissolution depends on temperature. At 50°C, the loss is about ten times greater than at 25°C. Electrodes wear out faster at high temperatures. To maintain the hydrated layer, the glass bulb must be wet at all times.

2.3 REFERENCE ELECTRODE

As Figure 2-4 shows, the reference electrode is a piece of silver wire plated with silver chloride in contact with a concentrated solution of potassium chloride held in a glass or plastic tube. In many reference electrodes the solution is an aqueous gel, not a liquid. Like the electrode inside the glass electrode, the potential of the external reference is controlled by the concentration of chloride in the filling solution. Because the chloride level is constant, the potential of the reference electrode is fixed. The potential does change if the temperature changes.

Industrial reference electrodes differ from laboratory types in an important way. Laboratory electrodes are available with either gelled or liquid filling solutions. Industrial reference electrodes almost always have gelled filling solutions. Gelled filling solutions allow industrial sensors to be installed in pressurized pipes and tanks. The reference electrode is sealed above the gel. Therefore, very little process liquid can enter the reference electrode and contaminate it. There is a drawback, however. Potassium chloride in the gel ultimately becomes depleted. The gel cannot be replenished, so after a while the sensor fails. Maximum life for a gel-type sensor is about 12 months. The solution in liquid-filled electrodes can be replenished, and these electrodes have fairly long operating lives.

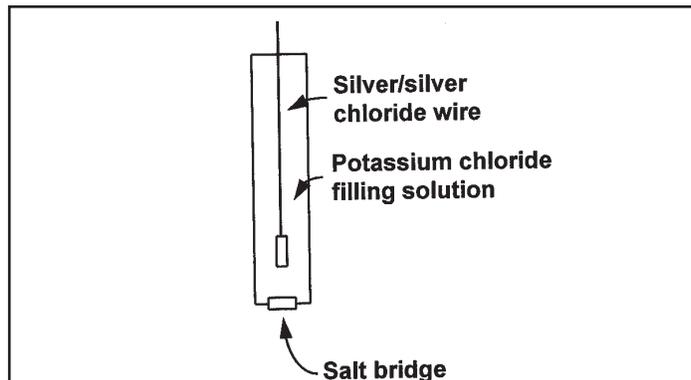


FIGURE 2-4. Reference Electrode.

The fixed concentration of chloride inside the electrode keeps the potential constant. A porous plug salt bridge at the bottom of the electrode permits electrical contact between the reference electrode and the test solution.

2.4 LIQUID JUNCTION POTENTIAL

The salt bridge (see Figure 2-4) is an integral part of the reference electrode. It provides the electrical connection between the reference electrode and the liquid being measured. Salt bridges take a variety of forms, anything from a glass frit to a wooden plug. Salt bridges are highly porous, and the pores are filled with ions. The ions come from the filling solution and the sample. Some bridges—for example, those using gelled filling solutions—permit only diffusion of ions through the junction. In other designs, a slow outflow of filling solution occurs in addition to diffusion. Diffusion of ions generates a voltage, called the liquid junction potential. The liquid junction potential is in series with the measuring and reference electrode potentials and is part of the overall cell voltage.

Figure 2-5 helps illustrate how liquid junction potentials originate. The figure shows a section through a pore in the salt bridge. For simplicity, assume the bridge connects a solution of potassium chloride and hydrochloric acid of equal molar concentration. Ions from the filling solution and ions from the sample diffuse through the pores. Diffusion is driven by concentration differences. Each ion migrates from where its concentration is high to where its concentration is low. Because ions move at different rates, a charge separation develops. As the charge separation increases, electrostatic forces cause the faster moving ions to slow down and the slower moving ions to speed up. Eventually, the migration rates become equal, and the system reaches equilibrium. The amount of charge separation at equilibrium determines the liquid junction potential.

Liquid junction potentials exist whenever dissimilar electrolyte solutions come into contact. The magnitude of the potential depends on the difference between the mobility of the ions. Although liquid junction potentials cannot be eliminated, they can be made small and relatively constant. The liquid junction potential is small when the ions present in greatest concentration have equal (or almost equal) mobilities. The customary way of reducing junction potentials is to fill the reference electrode with concentrated potassium chloride solution. The high concentration ensures that potassium chloride is the major contributor to the junction potential, and the nearly equal mobilities of potassium and chloride ions make the potential small.

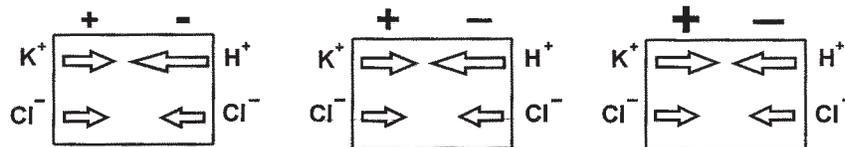


FIGURE 2-5. The Origin of Liquid Junction Potentials.

The figure shows a thin section through a pore in the junction plug. The junction separates a solution of potassium chloride on the left from a solution of hydrochloric acid on the right. The solutions have equal molar concentration. Driven by concentration differences, hydrogen ions and potassium ions diffuse in the directions shown. The length of each arrow indicates relative rates. Because hydrogen ions move faster than potassium ions, positive charge builds up on the left side of the section and negative charge builds up on the right side. The ever-increasing positive charge repels hydrogen and potassium ions. The ever-increasing negative charge attracts the ions. Therefore, the migration rate of hydrogen decreases, and the migration rate of potassium increases. Eventually the rates become equal. Because the chloride concentrations are the same, chloride does not influence the charge separation or the liquid junction potential.

One of the major problems associated with the determination of pH is plugging of the liquid junction. For the junction to work properly, ions must be free to migrate through the junction pores. If the pores become blocked, ions cannot diffuse. The electrical resistance of the junction increases. The pH readings drift and become noisy. Severe fouling can even completely block the junction, breaking the electrical connection between the electrode and the sample, and making the electrode unusable. Plugging can come from two sources: suspended solids in the sample or solids resulting from a chemical reaction involving the electrolyte fill solution. Plugged junctions are difficult to clean.

If the sample contains suspended solids, the reference junction is always in danger of plugging. The greater the amount of suspended solids, the greater the tendency toward fouling. Generally, the smaller the surface area of the junction, the more rapidly fouling occurs. Therefore, one way to combat fouling is to use a junction with a large surface area. Another approach is to make a junction having pores much smaller than the smallest particles likely to be present. As Figure 2-6 shows, if the junction pores are small, the particles cannot get into the pores and instead accumulate on the surface. The pores remain open. Ions can diffuse easily and the junction resistance stays low.

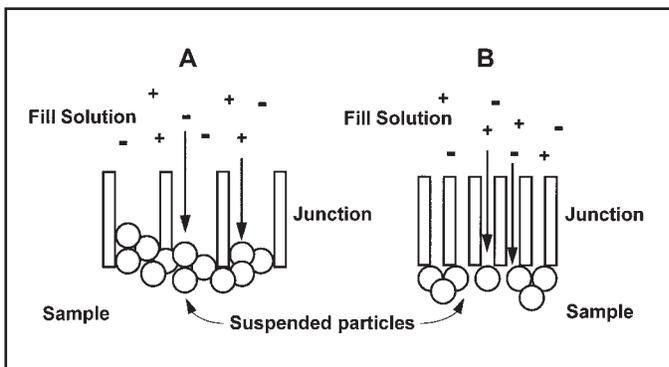


Figure 2-6. Comparison of Large Pore and Small Pore Liquid Junctions.

In **A** the suspended particles are smaller than the pores in the junction plug. The particles get into the pores and eventually plug them. Because ion diffusion, which provides the electrical connection between the electrode and sample, is hindered, the resistance of the junction increases. In **B** the pores are smaller than the suspended particles. The particles accumulate on the surface, and the pores remain open. Even though the particles may pack on the surface, there is usually sufficient space between them to allow ion diffusion.

Reactions between the process liquid and the filling solution can also produce solids that plug the reference junction. Potassium, chloride, and silver ions from the filling solution are always present in the junction. The origin of potassium and chloride is obvious; the source of the silver is discussed later. If the sample contains ions that form insoluble compounds with the filling solution, a precipitate will form in the junction pores. The precipitate ultimately plugs the junction. Examples of ions that foul the junction are lead, silver, and mercury (II), which form insoluble chloride salts, and sulfide, which forms an insoluble silver salt.

Precipitation of solids from the filling solution can also occur. Silver/silver chloride reference electrodes contain a fairly concentrated potassium chloride solution. Although silver chloride is relatively insoluble in water, the solubility increases if a high concentration of chloride is present. The increase in solubility is caused by the formation of a soluble silver chloride complex ion (AgCl_2^-). If the chloride concentration drops, the complex ion decomposes and solid silver chloride forms. The change in solubility with chloride concentration causes junction plugging.

Figure 2-7 shows how insoluble silver chloride forms in the liquid junction. Suppose a silver chloride complex ion finds its way into a junction pore and begins migrating toward the sample. Because the sample is unlikely to contain as much chloride as the filling solution, the chloride concentration decreases along the length of the pore. At some point the chloride concentration is too small to sustain the complex, and silver chloride precipitates. Eventually, enough silver chloride deposits and the pore becomes blocked.

2.5 DOUBLE JUNCTION REFERENCE ELECTRODES

One way to minimize plugging from silver chloride is to use a double junction reference. Figure 2-8 shows a typical arrangement. The concentration of the silver chloride complex in the top chamber—the one containing the reference element—is relatively high. Typically the solution is saturated with the complex ion. However, the concentration in the bottom chamber is substantially lower because the only way the complex ion can get into the lower compartment is to diffuse through the inner bridge. Because the level of silver chloride complex in the second compartment is small, the rate of pluggage in the sample junction is slow.

A double junction can also be used to reduce plugging caused by reaction of the reference electrolyte with the sample. If the lower chamber of Figure 2-8 contains an electrolyte that does not react with the sample, no precipitation will occur in the sample bridge. Typical fill solutions for this application are ammonium nitrate, and sodium and potassium nitrate and sulfate.

A third use of the double junction is to reduce poisoning. Poisoning occurs when an agent in the sample migrates through the bridge and reacts with the reference electrode. Common poisoning agents are sulfide and cyanide. Both react with the silver/silver chloride electrode, converting it into a silver/silver sulfide or silver/silver cyanide complex electrode. Poisoning changes the reference voltage by several hundred millivolts. Poisoning is discussed in more detail in Section 7.2.2.

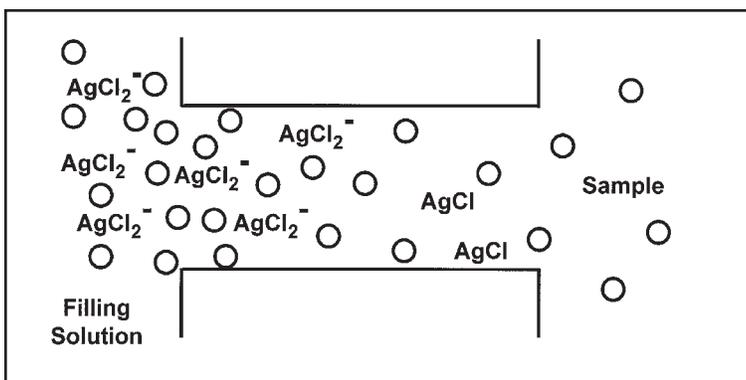


FIGURE 2-7. Junction Plugging Caused by Silver Chloride.

The figure shows a junction pore. The circles represent chloride ions (Cl^-). The silver chloride complex is shown as AgCl_2^- . Note that the concentration of chloride decreases moving toward the sample side of the pore. At some point the chloride concentration becomes too small to hold the silver chloride complex in solution and solid silver chloride (AgCl) precipitates.

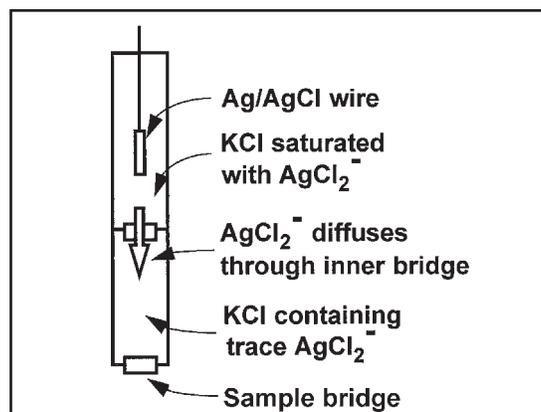


FIGURE 2-8. Double Junction Reference Electrode.

Both chambers contain potassium chloride solution. The top chamber contains the silver/silver chloride reference element. The potassium chloride in this chamber is saturated with the soluble silver chloride complex. The silver chloride complex diffuses through the inner bridge into the second chamber. The concentration of the complex ion in the second chamber remains low, so the rate of pluggage in the sample bridge is slow.

SECTION 3.0

MAKING THE pH MEASUREMENT

- 3.1 CONVERTING VOLTAGE TO pH
- 3.2 GLASS ELECTRODE SLOPE
- 3.3 BUFFERS AND CALIBRATION
- 3.4 PRECAUTIONS USING BUFFERS
- 3.5 ISOPOTENTIAL pH
- 3.6 SOLUTION TEMPERATURE COMPENSATION
- 3.7 SHIELDS, INSULATION, AND PREAMPLIFIERS
- 3.8 SENSOR DIAGNOSTICS

3.1 CONVERTING VOLTAGE TO pH

Equation 1 summarizes the relationship between measured cell voltage (in mV), pH, and temperature (in Kelvin):

$$E(T) = E^{\circ}(T) - 0.1984 T \text{ pH} \quad (1)$$

The cell voltage, $E(T)$ —the notation emphasizes the dependence of cell voltage on temperature—is the sum of five electrical potentials. Four are independent of the pH of the test solution and are combined in the first term, $E^{\circ}(T)$. $E^{\circ}(T)$ is the sum of the following:

1. the potential of the reference electrode inside the glass electrode
2. the potential at the inside surface of the glass membrane
3. the potential of the external reference electrode
4. the liquid junction potential.

The second term, $-0.1984T\text{pH}$, is the potential (in mV) at the outside surface of the pH glass. This potential depends on temperature and on the pH of the sample. Assuming temperature remains constant, any change in cell voltage is caused solely by a change in the pH of the sample. Therefore, the cell voltage is a measure of the sample pH.

Note that a graph of equation 1, $E(T)$ plotted against pH, is a straight line having a y-intercept of $E^{\circ}(T)$ and a slope of $-0.1984T$.

3.2 GLASS ELECTRODE SLOPE

Equation 1 is usually rewritten to remove the temperature dependence in the intercept and to shift the origin of the axes to pH 7. See Appendix B for a more detailed discussion. The result is plotted in Figure 3-1. Two lines appear on the graph. One line shows how cell voltage changes with pH at 25°C, and the other line shows the relationship at 50°C. The lines, which are called isotherms, intersect at the point (pH 7, 0 mV). An entire family of curves, each having a slope determined by the temperature and all passing through the point (pH 7, 0 mV) can be drawn on the graph.

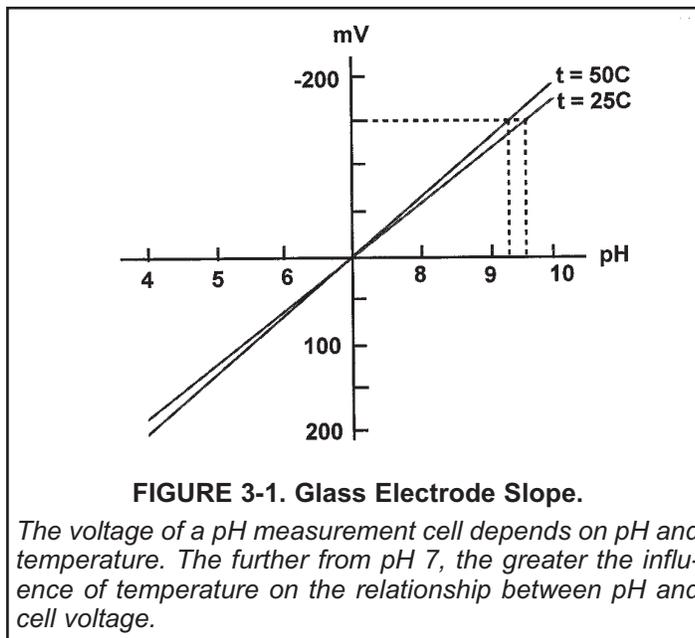
Figure 3-1 shows why temperature is important in pH measurements. When temperature changes, the slope of the isotherm changes. Therefore, a given cell voltage corresponds to a different pH value, depending on the temperature. For example, assume the cell voltage is -150 mV. At 25°C the pH is 9.54, and at 50°C the pH is 9.35. The process of selecting the correct isotherm for converting voltage to pH is called temperature compensation. All modern process pH meters and most laboratory meters have automatic temperature compensation.

The slope of the isotherm is often called the glass electrode or sensor slope. The slope can be calculated from the equation: slope = $-0.1984 (T)$, or converting from Kelvin to Celsius, as slope = $-0.1984 (t + 273.15)$, where t is temperature in °C. The slope has units of mV per unit change in pH. The table lists slopes for different temperatures.

Temp (°C)	Slope (mV/unit pH)
15	-57.2
20	-58.2
25	-59.2
30	-60.1
35	-61.1

The negative slope means that as pH increases, the voltage reading decreases.

As the graph in Figure 3-1 suggests, the closer the pH is to 7, the less important is temperature compensation. For example, if the pH is 8 and the temperature is 30°C, a 10°C error in temperature introduces a pH error of ± 0.03 . At pH 10, the error in the measured pH is ± 0.10 .



3.3 BUFFERS AND CALIBRATION

Figure 3-1 shows the performance of an ideal cell: one in which the voltage is zero when the pH is 7, and the slope is $-0.1984T$ over the entire pH range. In a real cell the voltage at pH 7 is rarely zero, but it is usually between -30 mV and $+30$ mV. The slope is also seldom $-0.1984T$ over the entire range of pH. However, over a range of two or three pH units, the slope is usually close to ideal.

Because pH cells are not ideal, they must be calibrated before use. pH cells are calibrated with solutions having exactly known pH, called buffers. Assigning a pH value to a calibration buffer is not a simple process. The laboratory work is demanding, and extensive theoretical work is needed to support certain assumptions that must be made. The need for assumptions when defining pH values can be traced to the fact that pH depends on hydrogen ion activity, not concentration. Activity is related to concentration and is a way of accounting for the difference between observed and predicted behavior in chemical systems. When physical or chemical measurements are made on real solutions, the results are usually different from the values predicted from the behavior of ideal solutions. The ratio of the true value to the ideal value at a given concentration is called the activity coefficient. The product of the activity coefficient and the concentration is the activity. For reasons well beyond the scope of this discussion, activity coefficients for single ions, for example, the hydrogen ion, cannot be measured. They can be calculated, but the calculation involves making certain assumptions—these are the assumptions that must be made when assigning pH values to buffers.

Normally, establishing pH scales is a task best left to national standards laboratories. pH scales developed by the United States National Institute of Standards and Technology (NIST), the British Standards Institute (BSI), the Japan Standards Institute (JSI), and the German Deutsche Institute für Normung (DIN) are in common use. Although there are some minor differences, for practical purposes the scales are identical. Commercial buffers are usually traceable to a recognized standard scale. Generally, commercial buffers are less accurate than standard buffers. Typical accuracy for commercial buffers is ± 0.01 pH units. Commercial buffers, sometimes called technical buffers, do have greater buffer capacity. They are less susceptible to accidental contamination and dilution than standard buffers.

TABLE 3-1. NIST Standard Buffers

Temp °C	PRIMARY STANDARDS						SECONDARY STANDARDS	
	Tartrate	Phthalate	Phosphate 1:1	Phosphate 1:3:5	Borax	Carbonate/ bicarbonate	Potassium Tetroxalate	Calcium hydroxide
0	-	4.003	6.982	7.534	9.460	10.321	1.666	-
5	-	3.998	6.949	7.501	9.392	10.248	1.668	-
10	-	3.996	6.921	7.472	9.331	10.181	1.670	-
15	-	3.996	6.898	7.449	9.276	10.120	1.672	-
20	-	3.999	6.878	7.430	9.227	10.064	1.675	-
25	3.557	4.004	6.863	7.415	9.183	10.014	1.679	12.454
30	3.552	4.011	6.851	7.403	9.143	9.968	1.683	-
35	3.549	4.020	6.842	7.394	9.107	9.928	1.688	-
37	-	4.024	6.839	7.392	9.093	-	-	-
40	3.547	4.030	6.836	7.388	9.074	9.891	1.694	-
45	3.547	4.042	6.834	7.385	9.044	9.859	1.700	-
50	3.549	4.055	6.831	7.384	9.017	9.831	1.707	-
55	3.554	4.070	-	-	-	-	1.705	-
60	3.560	4.085	-	-	-	-	1.723	-
70	3.580	4.12	-	-	-	-	1.743	-
80	3.609	4.16	-	-	-	-	1.766	-
90	3.650	4.19	-	-	-	-	1.792	-
95	3.674	4.21	-	-	-	-	1.806	-

The table above lists NIST standard buffers. Although NIST provides reagents and instructions for preparing the buffers, NIST or NIST-traceable buffers are readily available commercially. There are six primary standards and two secondary standards. The pH of each buffer depends on temperature, and the range of temperatures over which pH values are defined is not the same for every buffer. Although NIST standard buffers are defined to three digits past the decimal, practical measurements of pH are rarely more accurate than ± 0.05 pH units. See Section 4.0 for more information of fundamental limitations on the accuracy of pH measurements.

Figure 3-2 shows graphically what happens during calibration. Assume the sensor is being calibrated with commercial pH 7 and pH 10 buffer. When the electrodes are placed in pH 7 buffer, the cell voltage is V_7 , and when the electrodes are placed in pH 10 buffer, the cell voltage is V_{10} . Note that V_7 is not 0 mV as would be expected in an ideal sensor, but is slightly different. During calibration, the analyzer also measures the temperature, t .

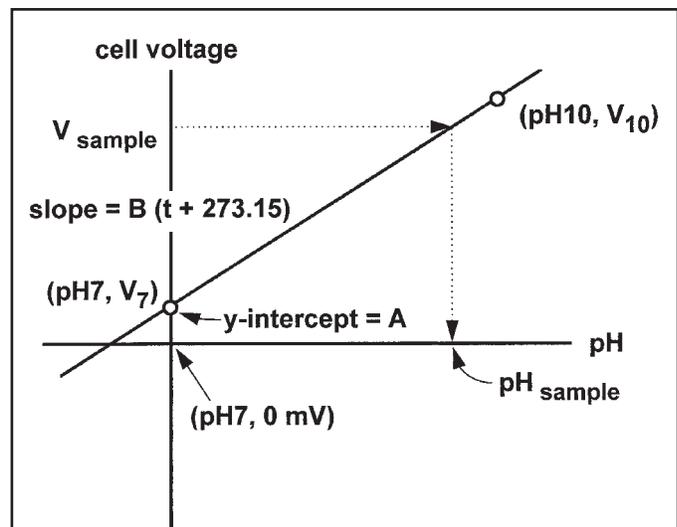


FIGURE 3-2. Two-Point Buffer Calibration.

The graph shows a calibration using pH 7 and pH 10 buffers. The calibration equation is the straight line connecting the two points.

The microprocessor calculates the equation of the straight line connecting the points. The general form of the equation is:

$$E = A - B(t + 273.15)(\text{pH} - 7) \quad (2)$$

The slope of the line is $-B(t + 273.15)$, where t is the temperature in °C, and the y-intercept is A .

Most pH instruments, after calculating the slope and y-intercept from the calibration data, compare the results with reference values programmed into the instrument. If the difference between the calculated slope and intercept and the reference values are too great, the instrument will alert the user that a possible error exists. If the discrepancy is very large, the instrument might also refuse to accept the calibration.

Once the sensor has been calibrated, the analyzer uses the calibration equation to convert subsequent cell voltage readings into pH. The graph in Figure 3-2 illustrates the process.

3.4 PRECAUTIONS USING BUFFERS

It is apparent from the preceding discussion that a pH measurement is no better than the buffers used for calibration. If the buffers are contaminated or used improperly, the calibration will be in error and all subsequent measurements will be wrong. Proper handling, storage, and use of buffers is important.

1. Calibrate with buffers having pH values that bracket the pH of the sample. For example, if the expected pH is between 8 and 9, calibrate with pH 7 and 10 buffers. Commercial buffers for intermediate ranges are readily available. Buffers outside the range pH 3 to pH 10 may not be available and must be prepared by the user.
2. Before starting calibration, be sure the sensor and the buffer are at the same temperature. If the sensor was removed from a process stream having a temperature more than a few degrees different from the buffer, allow at least twenty minutes for temperature equilibration.
3. If possible, calibrate with buffers having the same temperature as the process. If the buffer and process temperature differ by more than about 15°C an error as great as 0.1 pH may result. Using hot buffers can be difficult, and precautions are necessary. Refer to Section 3.5 for more information.
4. As Table 3-1 shows, the pH of a buffer is a function of temperature. For example, NIST pH 10.01 buffer has pH 10.01 only at 25°C. At 20°C the pH is 10.06, and at 30°C the pH is 9.97. Generally, the pH of an alkaline buffer changes more with temperature than the pH of an acidic or neutral buffer. To reduce errors caused by failure to use temperature-corrected buffer values, many process pH meters have an automatic calibration feature. Buffer pH and temperature data are programmed into the instrument. The instrument looks up and uses the correct value in the calibration.
5. Buffers have limited shelf lives. Do not use a buffer if the expiration date has passed. Store buffers at controlled room temperature.
6. Do not return used buffer to the stock bottle. Discard it.
7. Protect buffers from excessive exposure to air. Atmospheric carbon dioxide lowers the pH of alkaline buffers. Other trace gases commonly found in industrial environments, for example, ammonia and hydrogen chloride, also affect the pH of buffers. Molds, from airborne spores, grow readily in neutral and slightly acidic buffers. Mold growth can substantially alter the pH of a buffer.
8. If a calibration involving an alkaline buffer gives suspect results, repeat the calibration using an acidic buffer in place of the alkaline one. For example, suppose a sensor is calibrated using pH 7 and pH 10 buffer, and the slope is 80% of the expected value. The low slope suggests a serious problem with the sensor. However, the calibration was done with pH 10 buffer—a buffer highly susceptible to atmospheric contamination. Therefore, before replacing the sensor, repeat the calibration using pH 7 and pH 4 buffers. If the slope calculated using these buffers is reasonable, then it is likely that the pH 10 buffer used in the first calibration was bad. Obtain fresh pH 10 buffer and repeat the calibration.

- Rinse the sensor with deionized water before placing it in the buffer. Remove excess water from the sensor by gently daubing it with a clean tissue. Do not wipe the sensor. Wiping may generate a static charge, leading to noisy readings. The static charge may take hours to dissipate. The few drops of deionized water carried with the sensor into the buffer will not appreciably alter the pH.

3.5 ISOPOTENTIAL pH

Frequently, the calibration temperature and the process temperature are different. Therefore, the calibration slope, which depends on temperature, is not appropriate for the sample. Figure 3-3 shows what the microprocessor does when buffer and sample temperatures are different. Assume the sensor was calibrated at temperature t_1 and the process temperature is t_2 . To measure the pH of the process, the microprocessor rotates the calibration line about the point (pH 7, A) until the slope equals $B(t_2 + 273.15)$. The microprocessor then uses the new isotherm to convert voltage to pH. The point (pH 7, A) is called the isopotential pH. As Figure 3-3 shows, the isopotential pH is the pH at which the cell voltage does not change when the temperature changes. All modern pH meters assume the cell isopotential pH is 7.00. Some pH meters permit the user to change the isopotential setting. Generally, the isopotential pH should not be changed unless the sensor manufacturer specifically states what the isopotential pH should be.

The microprocessor makes assumptions when the measurement and calibration temperatures are different. It assumes the actual pH cell isotherms rotate about the point (pH 7, A). The assumption may not be correct, causing the measurement to be in error. The size of the error depends on two things: the difference between pH 7 and the cell isopotential pH and the difference between the calibration and measurement temperatures. For a 10°C temperature difference and a difference in isopotential pH of 2, the error is about ± 0.07 pH units. The factors that cause the isopotential pH of a real cell to differ from 7 are beyond the scope of this discussion and to a great extent are out of the control of the user as well. See Appendix B for a more detailed discussion of isopotential pH.

Most pH cells do not have an isopotential pH point. Instead, the cell isopotential pH changes with temperature, and the cell isotherms rotate about a general area. Most process pH sensors have an isopotential area centered reasonably close to pH 7.0.

One way to reduce the error caused by disagreement between the sensor and meter isopotential pH is to calibrate the sensor at the same temperature as the process. However, great care must be exercised when the buffer temperature is significantly greater than ambient temperature. First, the buffer solution must be protected from evaporation. Evaporation changes the concentration of the buffer and its pH. Above 50°C, a reflux condenser may be necessary. Second, the pH of buffers is defined over a limited temperature range. For example, if the buffer pH is defined only to 60°C, the buffer cannot be used for calibration at 70°C. Finally, no matter what the temperature, it is important that the entire measurement cell, sensor and solution, be at constant temperature. This requirement is critical because lack of temperature uniformity in the cell is one reason the cell isopotential point changes when the temperature changes.

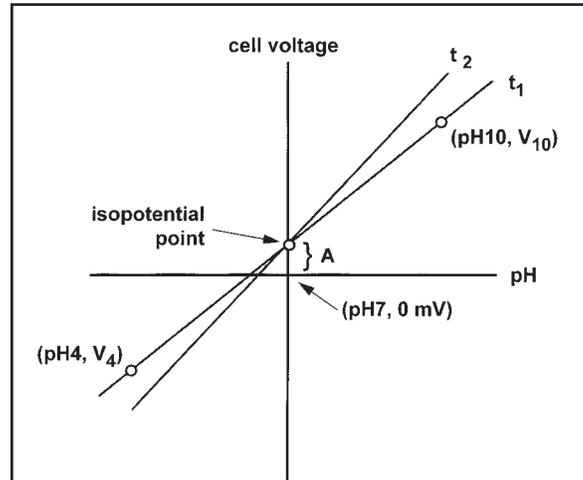


FIGURE 3-3. Isopotential pH.

The graph shows two calibration lines. The original calibration was done with pH 4 and pH 10 buffers at temperature t_1 . Suppose the temperature changes to t_2 . The pH analyzer automatically changes the slope by the ratio $(t_2 + 273.15)/(t_1 + 273.15)$. The calibration equations rotate about the point (pH 7, A).

3.6 SOLUTION TEMPERATURE COMPENSATION

The pH of a solution, particularly an alkaline one, is a function of temperature. If the temperature changes, so does the pH, even though the concentration of the acid or base causing the pH remains constant. Solution temperature compensation is a way of converting the pH at the measurement temperature to the pH at a reference temperature. The reference temperature is almost always 25°C. **Solution temperature compensation is not the same as temperature compensation.** Temperature compensation is the automatic calculation of pH from the measured cell voltage and temperature. Solution temperature compensation is the calculation of pH at a reference temperature from the measured pH.

The change in pH with temperature is called the solution temperature coefficient. It has units of $\Delta\text{pH}/^\circ\text{C}$. For example, ammonia solutions having concentration between 0.1 and 20 ppm have a temperature coefficient of -0.032 pH units/ $^\circ\text{C}$. The pH decreases 0.032 units for every $^\circ\text{C}$ increase in temperature. Therefore, if the pH at 30°C is 9.32, the pH at 25°C is $9.32 + (25 - 30)(-0.032)$ or 9.48. The size of the temperature coefficient depends on the identity of the acid or base and its concentration. Usually the temperature coefficient must be determined empirically. Most industrial pH analyzers have a solution temperature compensation feature.

3.7 SHIELDS, INSULATION, AND PREAMPLIFIERS

pH measurement systems, cell and meter, have high impedance. The high impedance circuit imposes important restrictions on how the systems are designed.

The pH glass membrane causes the internal resistance of the pH cell to be several hundred M Ω . For the pH meter to make an accurate voltage measurement, its input impedance must be substantially greater than the cell resistance. Typical pH meters have an input impedance of about 1,000,000 M Ω . The high input impedance of the meter requires that the insulation between the glass and reference electrode terminals be of high quality. If the insulation is inadequate, the signal may bypass the meter input impedance. The resulting pH measurement will be seriously in error.

Because the lead wire from the glass electrode connects two high resistances, electrostatic charges, which accumulate on the wire from environmental influences, cannot readily drain away. Buildup of charge results in degraded, noisy readings. Shielding the wire with metal braid connected to ground at the instrument is one way to improve the signal. It is also helpful to keep the sensor cable as far away as possible from AC power cables. To provide further protection from environmental interference, the entire sensor cable can be enclosed in conduit.

To avoid the need for expensive cable and cable installations, a preamplifier built into the sensor or installed in a junction box near the sensor can be used. The preamplifier converts the high impedance signal into a low impedance one that can be sent as far as 2000 feet without special cable.

3.8 SENSOR DIAGNOSTICS

Sensor diagnostics alert the user to problems with the sensor or to actual sensor failures. The two sensor diagnostics are reference impedance and glass impedance.

The major contributor to reference impedance is the resistance across the liquid junction plug. In a properly functioning electrode, the resistance of the liquid junction should be less than about 40 k Ω . If the junction is plugged or if the filling solution or gel is depleted, the resistance increases. A high reference impedance may also mean the sensor is not immersed in the process stream.

Glass impedance refers to the impedance of the pH-sensitive glass membrane. The impedance of the glass membrane is a strong function of temperature. As temperature increases, the impedance decreases. For a change in glass impedance to have any meaning, the impedance measurement must be corrected to a reference temperature. The impedance of a typical glass electrode at 25°C is about 100 M Ω . A sharp decrease in the temperature-corrected impedance implies that the glass is cracked. A cracked glass electrode produces erroneous pH readings. The electrode should be replaced immediately. A high (temperature-corrected) glass impedance implies the sensor is nearing the end of its life and should be replaced as soon as possible.

SECTION 4.0

FUNDAMENTAL LIMITATIONS

4.1 JUNCTION POTENTIAL MISMATCH

4.2 SODIUM ERROR

4.1 JUNCTION POTENTIAL MISMATCH

All process and most laboratory pH sensors have a liquid junction. The presence of the liquid junction and the need to calibrate pH sensors with buffers causes a fundamental error in the measurement.

When the glass and reference electrodes are placed in a buffer, a liquid junction potential, E_{lj} , develops at the interface between the buffer and the salt bridge. The liquid junction potential is part of the overall cell voltage and is included in A in equation 2. Equation 2 on page 12 can be modified to show E_{lj} , as a separate term:

$$E = A' + E_{lj} - B (t + 273.15) (\text{pH} - 7) \quad (3)$$

or

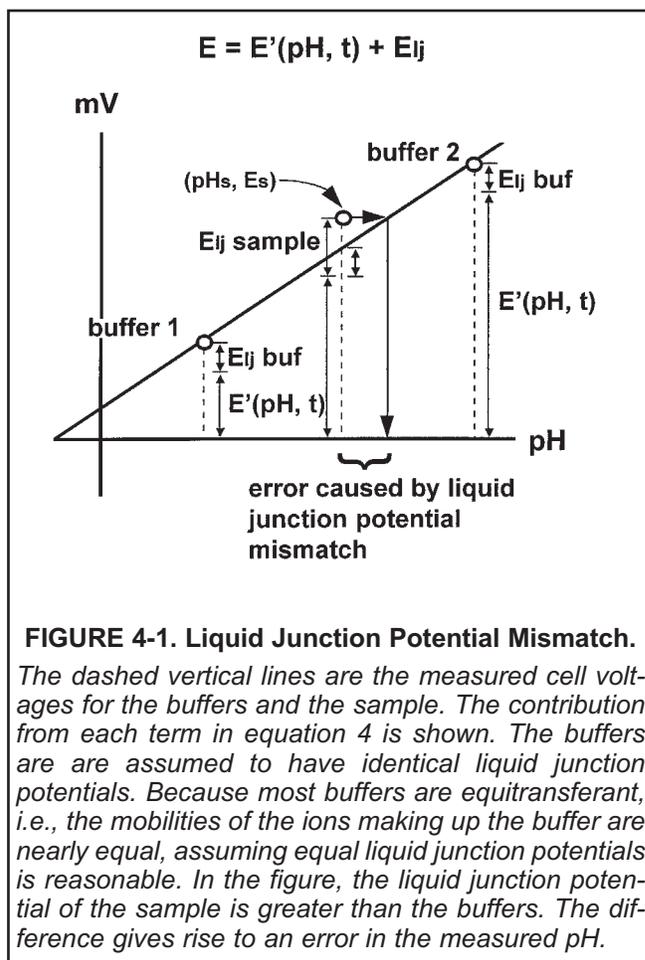
$$E = E'(\text{pH}, t) + E_{lj} \quad (4)$$

where $E'(\text{pH}, t) = A' - B (t + 273.15) (\text{pH} - 7)$.

In Figure 4-1, calibration and measurement data are plotted in terms of equation 4. The cell voltage, E , is represented by the dashed vertical lines. The contribution of each term in equation 4 to the voltage is also shown. The liquid junction potentials in the buffers are assumed to be equal and are exaggerated for clarity.

If the liquid junction potential in the sample differs from the buffers, a measurement error results. Figure 4-1 illustrates how the error comes about. Assume the true pH of the sample is pH_s and the cell voltage is E_s . The point (pH_s, E_s) is shown in the figure. If the liquid junction potential in the sample were equal to the value in the buffers, the point would lie on the line. However, the liquid junction potential in the sample is greater, so the point E_s lies above the calibration line. Therefore, when the cell voltage is converted to pH, the result is greater than the true pH by the amount shown.

A typical mismatch between liquid junction potentials in buffer and sample is 2-3 mV, which is equivalent to an error of about ± 0.02 pH units. If the sample contains a strong acid or base or has a conductivity less than about $1 \mu\text{S}/\text{cm}$, the junction potential mismatch can be on the order of 20-25 mV (± 0.4 pH units). The mismatch produces a fundamental error in pH determinations using a cell with liquid junction.



4.2 SODIUM ERROR

Figure 4-2 is a graphical depiction of sodium error. As the figure shows, sodium errors occur at high pH and cause the measured pH to be less than the true value. Sodium errors come about because the potential of the glass membrane depends not only on the concentration of hydrogen ions but also on the concentration of other metal ions, for example, sodium.

Equation 1 on page 9 gave the relationship between cell voltage and pH.

$$E(T) = E^{\circ}(T) - 0.1984 T \text{ pH} \quad (1)$$

Rewriting pH as $-\log [H^+]$, equation 1 becomes:

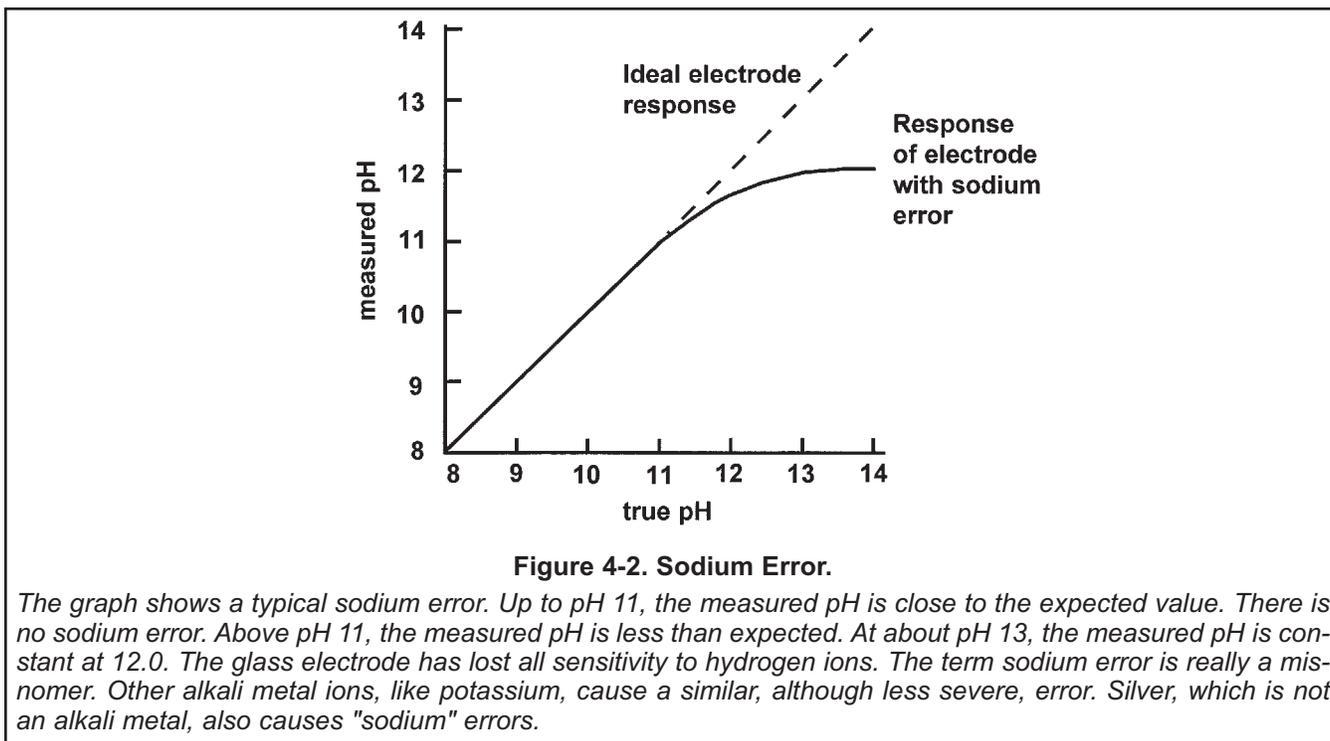
$$E(T) = E^{\circ}(T) + 0.1984 T \log [H^+] \quad (5)$$

Recasting equation 5 to account for the influence of sodium gives:

$$E(T) = E^{\circ}(T) + 0.1984 T \log \{[H^+] + k[Na^+]\} \quad (6)$$

In equation 6, k is a constant that describes the sensitivity of the glass membrane to sodium ions. The smaller k is, the less susceptible the pH glass is to sodium error. As equation 6 shows, when the hydrogen ion concentration is large, it alone determines the cell voltage $E(T)$. However, as pH increases and the hydrogen ion concentration decreases, $k[Na^+]$ starts to become the more important term in the argument of the logarithm. Because $k[Na^+]$ is a constant, the measured voltage does not change as much as it should for a given change in $[H^+]$, so the pH is lower than expected. Eventually, the error becomes so great that changes in the hydrogen ion concentration no longer affect the measured pH. At this point the concentration of sodium determines the cell voltage.

Most general purpose glass electrodes on the market today have almost no sodium error up to about pH 11. Above pH 11 the measured pH can be substantially less than expected. High pH glass electrodes are available which have practically no sodium error at pH 12, an error of about 0.2 pH at pH 13, and an error of about 0.4 pH at pH 14. Sodium error tends to increase as the glass electrode ages.



SECTION 5.0

ORP MEASUREMENTS

5.1 INTRODUCTION

5.2 MEASURING ELECTRODE

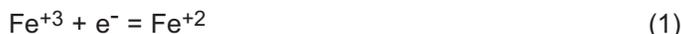
5.3 INTERPRETING ORP MEASUREMENTS

5.4 CALIBRATION

5.1 INTRODUCTION

ORP is oxidation-reduction potential. ORP depends on the ratio of the concentrations of oxidized and reduced substances in the sample. In a typical system, the measuring electrode is an inert metal such as gold or platinum, and the reference electrode is the usual silver/silver chloride electrode.

Figure 5-1 shows a platinum ORP electrode in contact with a solution of iron (II) and iron (III). Iron (II) and iron(III) are a redox couple. A redox couple is simply two compounds that can be converted into one another by gain or loss of electrons. The oxidized form, iron (III), can be converted into the reduced form, iron (II), by the gain of one electron. Similarly iron (II) can be converted to iron (III) by the loss of one electron. The interconversion is summarized by the equation:



If a redox couple is present, a stable electrical potential eventually develops at the interface between the platinum electrode and the sample. The magnitude of the potential is described by the following equation, called the Nernst equation:

$$E = E^{\circ} - \frac{0.1987 (t + 273.15)}{n} \log \frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]} \quad (2)$$

In the Nernst equation, E is the electrode potential and E° is the standard electrode potential, both in millivolts, t is temperature in $^{\circ}\text{C}$, n is the number of electrons transferred ($n = 1$ in the present case), and $[\text{Fe}^{+2}]$ and $[\text{Fe}^{+3}]$ are the concentrations of iron (II) and iron (III) respectively. There are several ways of defining the standard electrode potential, E° . No matter which definition is used, the standard electrode potential is simply the electrode potential when the concentrations of iron (II) and iron (III) have defined standard values.

Equation 2 shows that the electrode potential is determined by the logarithm of the ratio of the concentration of iron (II) to iron (III). Therefore, at 25°C if the ratio changes by a factor of ten, the electrode potential changes by

$$- \frac{0.1987 (25 + 273.15)}{1} \log 10 = - 59.2 \text{ mV}$$

As the expression above shows, the voltage change is also directly proportional to temperature and inversely proportional to the number of electrons transferred.

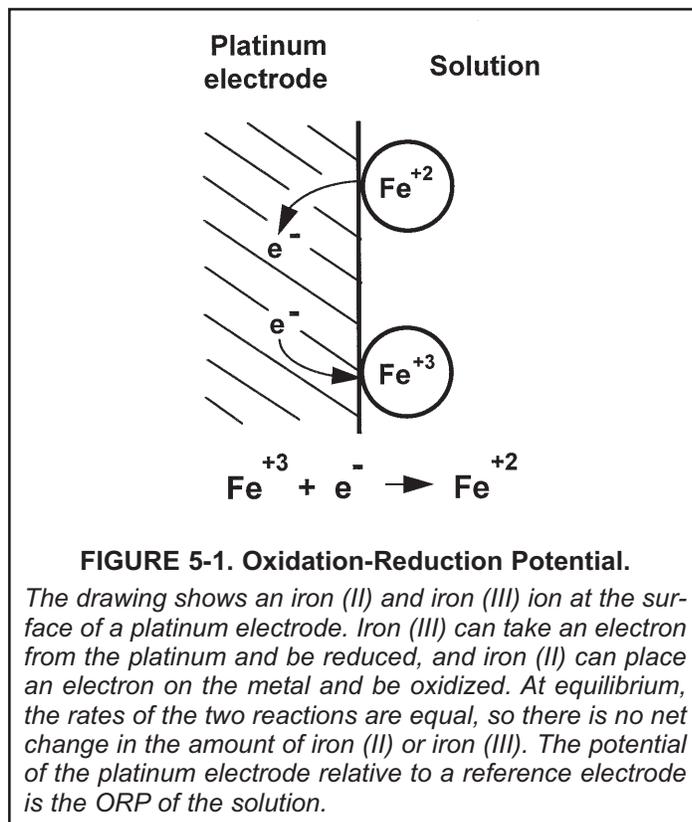


Figure 5-2 shows a simplified diagram of an electrochemical cell that can be used to determine the ORP of a sample. An ORP measurement cell is similar to a pH cell. The major difference is the glass measuring electrode for pH has been replaced with an ORP electrode. The cell voltage is the ORP of the sample. In most industrial and scientific applications, a pH meter is used to measure the voltage. Because a pH meter is nothing more than a high impedance voltmeter, it makes an ideal ORP meter.

The cell voltage is the algebraic sum of the potential of the measuring electrode, the reference electrode, and the liquid junction. As discussed above, the potential of the measuring electrode depends on the ORP of the solution. The potential of the reference electrode is unaffected by ORP, so it provides a stable reference voltage. Unlike the liquid junction potential in a pH cell, which is usually small, the liquid junction potential in an ORP cell can be quite high. Liquid junction potentials depend on the relative mobilities of ions. Hydrogen ions have a much greater mobility than other ions. Because ORP is often measured in highly acidic solutions, liquid junction potentials can be large. All three potentials depend on temperature.

The construction of the ORP electrode is discussed in Section 5.2. For a discussion of the reference electrode and the liquid junction potential, see Sections 2.3 and 2.4.

5.2 MEASURING ELECTRODE

Figure 5-3 shows a typical ORP measuring electrode. The electrode consists of a band or disc of platinum attached to the base of a sealed glass tube. A platinum wire welded to the band connects it to the electrode lead wire. Unlike a glass electrode, there is no fill solution.

5.3 INTERPRETING ORP MEASUREMENTS

Interpreting ORP measurement requires caution. There are several concepts to keep in mind concerning industrial ORP measurements.

- ORP is best used to track changes in concentration or to detect the presence or absence of certain chemicals. For example, in the treatment of wastes from metal finishing plants, chromium (VI) is converted to chromium (III) by treatment with sulfur dioxide. Because chromium (VI) and chromium (III) are a redox couple, ORP can be used to monitor the reaction. As sulfur dioxide converts chromium (VI) to chromium (III), the concentration ratio changes and the ORP drops. Once all the chromium (VI) has been converted to chromium (III) and a slight excess of sulfur dioxide is present, the chromium couple no longer determines ORP. Instead, ORP is controlled by the sulfur dioxide-sulfate couple. Sulfate is involved because it is the product of the reaction between sulfur dioxide and chromium (VI).

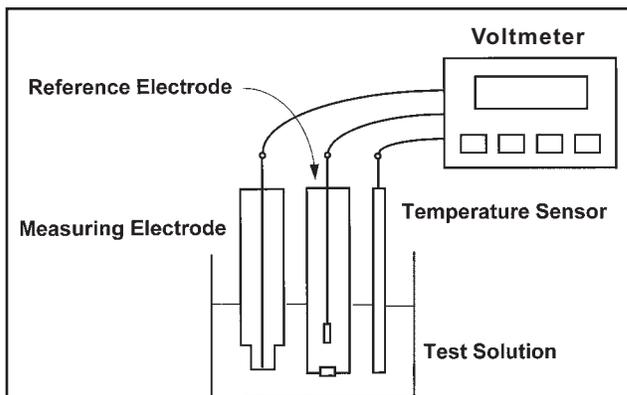


FIGURE 5-2. ORP Measurement Cell.

The cell consists of a measuring and reference electrode. The voltage between the electrodes is the ORP of the test solution. Although the electrodes are shown separate, in most process ORP sensors, the electrodes and the temperature element are combined into a single sensor. Because ORP depends on temperature, the temperature at which the measurement is made must be reported.

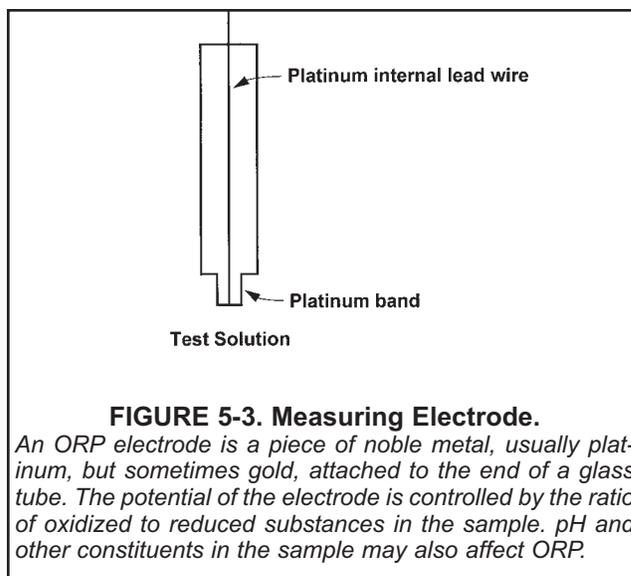


FIGURE 5-3. Measuring Electrode.

An ORP electrode is a piece of noble metal, usually platinum, but sometimes gold, attached to the end of a glass tube. The potential of the electrode is controlled by the ratio of oxidized to reduced substances in the sample. pH and other constituents in the sample may also affect ORP.

Figure 5-4 shows how ORP and the concentration of chromium (VI) change as sulfur dioxide is added. Because the change in ORP at the endpoint is large, monitoring ORP is an efficient way of tracking the process.

- To be strictly correct, ORP is controlled by the ratio of activities, not concentrations. The dependence of ORP on activity has an important consequence. Suppose a salt, like sodium sulfate, is added to a solution containing a redox couple, for example iron (II) and iron (III). The sodium sulfate does not change the concentration of either ion. But, the ORP of the solution does change because the salt alters the ratio of the activity of the ions.
- pH can have a profound influence on ORP. Refer to the earlier example where ORP was used to monitor the conversion of chromium (VI) to chromium (III). The reaction is generally carried out at about pH 2. Because the concentration ratio in the Nernst equation also includes hydrogen ions, the ORP of a mixture of chromium (VI) and chromium (III) is a function of pH.

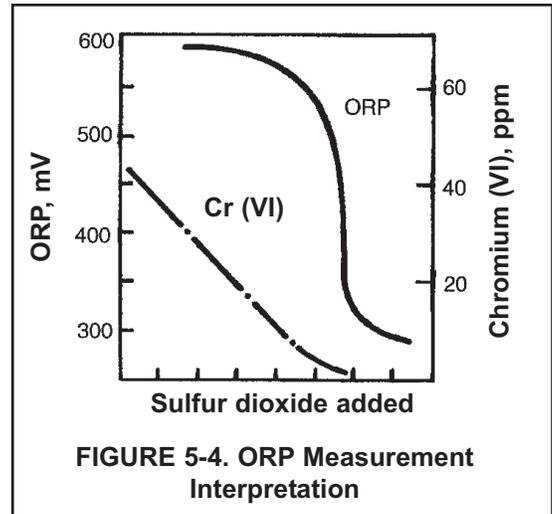
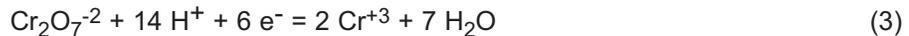


FIGURE 5-4. ORP Measurement Interpretation

In acidic solution the chromium (VI) to chromium (III) half reaction is:



Chromium (VI) exists as dichromate, $\text{Cr}_2\text{O}_7^{2-}$, in acidic solution.

The Nernst equation for reaction 3 is:

$$E = E^\circ - \frac{0.1987 (t + 273.15)}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}] [\text{H}^+]^{14}} \quad (4)$$

Note that the hydrogen ion factor in the concentration ratio is raised to the fourteenth power. The table shows the expected effect of changing pH on the measured ORP at 25°C.

pH changes	ORP changes by
from 2.0 to 2.2	7 mV
from 2.0 to 2.4	35 mV
from 2.0 to 1.8	47 mV
from 2.0 to 1.6	75 mV

The Nernst equation can be written for any half reaction. However, not all half reactions behave exactly as predicted by the Nernst equation. The reasons are beyond the scope of this discussion. The potential of chromium (VI) - chromium (III) couple used as an example above does not perfectly obey the Nernst equation. However, the statement that pH has a strong effect on the electrode potential of the couple is nonetheless true.

- As mentioned earlier, ORP is best suited for measuring changes, not absolute concentrations. Be careful using ORP to determine concentration. An example is the determination of chlorine in water. When water is disinfected by treatment with chlorine gas or sodium hypochlorite, free chlorine forms. Free chlorine is a mixture of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-). The relative amount of each depends on pH. For disinfection control, total free chlorine, the sum of hypochlorous acid and hypochlorite ion, is important. Equation 5 shows the half reaction for hypochlorous acid:



The Nernst equation is

$$E = E^\circ - \frac{0.1987 (t + 273.15)}{2} \log \frac{[\text{Cl}^-]}{[\text{HOCl}] [\text{H}^+]} \quad (6)$$

Only the concentration of hypochlorous acid appears in the Nernst equation. To use ORP to determine total free chlorine, equation 6 must be rewritten in terms of free chlorine. The result is shown in equation 7:

$$E = E^{\circ} - \frac{0.1987 (t + 273.15)}{2} \log \frac{[\text{Cl}^-] \{[\text{H}^+] + K\}}{C_a [\text{H}^+]^2} \quad (7)$$

where K is the acid dissociation constant for hypochlorous acid (2.3×10^{-8}) and C_a is the total free chlorine concentration. As equation 7 shows the measured ORP depends on the hydrogen ion concentration (i.e., pH), the chloride concentration, the free chlorine concentration, and temperature. Therefore, for ORP to be a reliable measurement of free chlorine, pH, chloride, and temperature must be reasonably constant.

Assume the free chlorine level is 1.00 ppm and the chloride concentration is 100 ppm. The table shows how slight changes in pH influence the ORP.

pH changes	ORP changes by
from 8.0 to 7.8	10 mV
from 8.0 to 7.6	19 mV
from 8.0 to 8.2	10 mV
from 8.0 to 8.4	19 mV

Around pH 8 and 1.00 ppm chlorine, a change in ORP of 1.4 mV corresponds to a change in chlorine level of about 0.1 ppm. Therefore, if pH changed only 0.2 units and the true chlorine level remained constant at 1.00 ppm, the apparent chlorine level (determined by ORP) would change about 0.7 ppm.

5.4 CALIBRATION

Although there is no internationally recognized ORP calibration standard, the iron (II) - iron (III) couple enjoys some popularity. The standard is a solution of 0.1 M iron (II) ammonium sulfate and 0.1 M iron (III) ammonium sulfate in 1 M sulfuric acid. The solution has good resistance to air oxidation. If stored in a tightly closed container, the shelf life is one year. Because the standard contains equal amounts of iron (II) and iron (III), the ORP does not change appreciably if the solution becomes slightly diluted. In addition, minor variability in actual concentration does not affect the standard ORP.

The ORP of the iron (II) - iron (III) standard when measured with a platinum electrode against a saturated silver-silver chloride reference is 476 ± 20 mV at 25°C. The range of values is caused primarily by the high and variable liquid junction potential generated in solutions containing high acid concentrations.

Quinhydrone - hydroquinone ORP standards are also used. They are prepared by dissolving excess quinhydrone in either pH 4.00 or pH 6.86 buffer. The ORP of the standards at a platinum electrode against a silver - silver chloride reference has been measured at 20°C, 25°C, and 30°C.

Temperature	ORP in pH 4.00 buffer	ORP in pH 6.86 buffer
20°C	268 mV	92 mV
25°C	263 mV	86 mV
30°C	258 mV	79 mV

There are two disadvantages to using quinhydrone standards. First, the shelf life is only about eight hours, so fresh standard must be prepared daily. Second, hydroquinone is highly toxic, so preparing, handling, and disposing of the standards requires care.

Unlike pH calibrations, which are generally done using two calibration buffers, ORP calibrations are almost always single point calibrations.

SECTION 6.0

SENSOR INSTALLATIONS

- 6.1 GENERAL**
- 6.2 SAFETY**
- 6.3 IMMERSION AND INSERTION APPLICATIONS**
- 6.4 ELECTRICAL CONNECTIONS**

6.1 GENERAL

Industrial pH sensors can be installed in the process piping, immersed in a tank or basin, or placed in a sidestream sample. In a sidestream, a portion of the process liquid is continuously removed from the main process and directed to the pH sensor. Sidestream systems are necessary when the temperature and pressure of the process liquid exceed the sensor rating. The sample is cooled and the pressure reduced before the liquid reaches the sensor. In a sidestream, the sample can either be returned to the process or drained to waste. Retractable sensors, which can be removed from the process piping without shutting down the system, are also popular.

6.2 SAFETY

There are safety hazards associated with pH sensors installed in process streams. If the temperature or pressure of the liquid exceeds the rating of the sensor, the sensor may fail, allowing the process liquid to leak out from around the sensor. There are special hazards associated with retractable sensors. To avoid accidents, always follow the manufacturer's instructions for inserting and removing the sensor. Never attempt to remove a retractable sensor unless the process conditions meet the manufacturer's requirements. Also, install retractable sensors only in places where access is easy and the person retracting the sensor has good footing.

6.3 IMMERSION AND INSERTION APPLICATIONS

A bit of thought when designing an in-line pH measurement system can save a lot of headaches later on.

1. If a pH sensor is to be inserted directly into a pipe, choose a location that is always flooded. If that is not possible, pay attention to how far the sensor extends into the pipe. If the liquid level varies, the sensor may become uncovered. It may be not immediately obvious that the sensor is no longer submerged. Most industrial pH electrodes are combination sensors. So long as a liquid film provides a conductive path between the glass membrane and the reference junction, the sensor will produce a reading. The reading, however, is the pH of the film, not the process liquid. If the film dries out, the sensor will appear to have failed. pH analyzers with sensor diagnostic features will indicate a high reference and glass impedance at this point. The high impedance could be caused by either a dry sensor or an actual failure.
2. Always consider the velocity and density of the liquid flowing past the sensor. A dense liquid moving at a high flow rate can deform the sensor, particularly if it extends some distance into the stream. If a retractable sensor becomes bent or distorted, it might no longer be possible to safely remove it. In fact, it might be impossible to retract the sensor at all.
3. Install pH sensors with the bulb down, within 80° from vertical. The potassium chloride and buffer solution inside the glass electrode must completely wet the inside surface of the glass bulb, and there must be a conductive path between the internal reference electrode and the inside glass surface. Installing the electrode bulb pointed up or at an angle too close to horizontal will break the connection.

4. pH sensors need regular calibration and, in some applications, regular cleaning. The ease with which the sensor can be removed from the piping should always be considered. If the sensor is installed in the process pipe or inserted through a vessel wall, the process might have to be shut down and at least a portion of the system drained before the sensor can be removed. In these situations, a retractable sensor can be the solution. For sensors installed in sidestreams or flow-through piping, isolation is relatively easy. See Figure 6-1.

Removing sensors with screw-in (pipe thread) connections can be a problem. To prevent twisting the cable and breaking wires and shielding, the cable must be disconnected before unscrewing the sensor. Disconnecting the cable, reconnecting it so the sensor can be calibrated, disconnecting the cable after calibration, and finally reconnecting the cable can make calibrations an ordeal. A good alternative to a screw-in sensor is a sensor inserted through a large diameter tubing-to-pipe-thread adapter. A plastic compression fitting seals against the body of the sensor, and the pipe thread screws into the process fitting. To remove the sensor, loosen the compression fitting until the sensor is free. In some designs, a collar around the sensor body prevents the sensor from being removed. In this case, loosen the compression fitting until the sensor turns freely, unscrew the threaded connection, and remove the sensor/fitting assembly.

Retractable sensors can be removed from the process for calibration without having to disconnect wiring. Many manufacturers offer quick disconnect fittings as well.

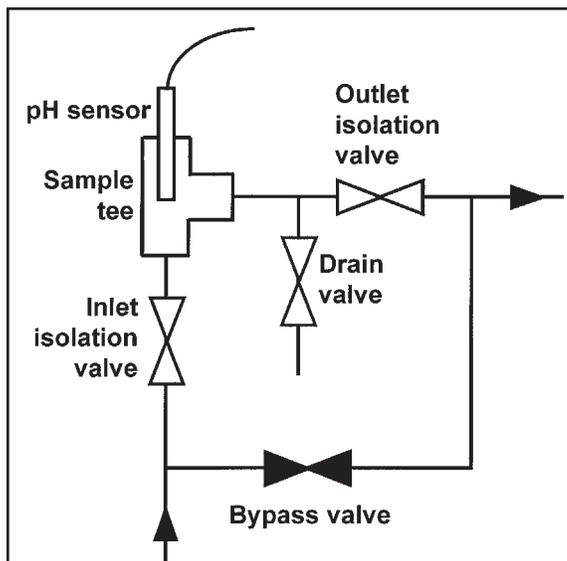


Figure 6-1. pH Sensor Installed in Flow-Through Piping.

The sensor is installed in a pipe tee. Although the sensor is at a high point, the end of the sensor extends well into the process stream. There is little danger that trapped air will interfere with the measurement. Valves in the inlet and outlet of the tee permit the sensor to be isolated. Another valve allows pressure to be bled off before removing the sensor. An optional bypass line is also shown.

For additional information, refer to the Mounting Solutions Handbook from Rosemount Analytical (PN 91-6020).

6.4 ELECTRICAL CONNECTIONS

The following is a list of precautions to observe when wiring the sensor to the analyzer.

1. Always run sensor cable as far away as possible from power conductors. Never run sensor cable (or signal carrying wires) in the same conduit or cable tray with ac power conductors.
2. Avoid twisting the pH sensor cable. Twisting can easily break the shield around the conductor carrying the pH signal. Unless the signal has been preamplified at the sensor, the broken shield will result in noisy, degraded readings.
3. Consider amplifying the pH signal at the sensor. Most manufacturers offer pH sensors with built-in preamplifiers or offer preamplifiers that can be placed in junction boxes mounted on or located near the sensor. Generally, an unamplified pH signal should be run no more than about 15 feet. Preamplified signals can be run several thousand feet.
4. Keep the analyzer as dry as possible. Even a small amount of moisture on the surface of the insulator separating the pH and reference connections can cause a large error in the measurements.

SECTION 7.0 MAINTENANCE

- 7.1 GENERAL**
- 7.2 CLEANING pH SENSORS**
- 7.3 CALIBRATING pH SENSORS**
- 7.4 STORING pH SENSORS**

7.1 GENERAL.

Maintenance of of pH measurement systems involves mostly cleaning and calibrating the pH sensor. The analyzer itself requires almost no maintenance.

7.2 CLEANING pH SENSORS.

The frequency at which a sensor should be inspected and cleaned can be determined only by experience. If the process liquid coats or fouls the sensor, frequent cleaning may be necessary. If the process does not contain a high level of suspended solids, the need for regular cleaning will be less. Sensor diagnostic measurements, if available, can also help indicate when a sensor needs cleaning. Often an increase in glass or reference impedance indicates the electrode is becoming fouled.

7.2.1. Cleaning Methods

Table 7-1 lists suggested cleaning methods.

TABLE 7-1. Cleaning Procedures

PROBLEM	CLEANING SUGGESTIONS
Loose scale or debris tion	Use a stream of water from a wash bottle to rinse away solids from the tip of the sensor. If water does not work, gently wipe the glass bulb and liquid junction with a soft cloth, tissue, cotton-tipped swab, or a soft bristle brush.
Oil and grease	Wash the glass bulb with mild detergent solution and rinse thoroughly with water.
Hard scale (carbonate sulfate scales and corrosion products)	If wiping the sensor tip with a tissue or cotton swab does not remove the scale, soak the glass bulb ONLY in a solution of 5% hydrochloric acid. To prepare the acid solution, add 15 mL of concentrated hydrochloric acid to 85 mL of water with constant stirring. Keep the acid away from the liquid junction and from any stainless steel part of the sensor. Rinse the sensor thoroughly with deionized water. Some scales (for example, calcium sulfate) cannot be removed easily with acid. Soaking the glass bulb in a 2% solution of disodium EDTA for about five minutes may be helpful. Because EDTA solutions attack glass, avoid lengthy soaking periods.

When using acid or alkaline solvents, keep the solvent away from the liquid junction. If the cleaning solvent contacts the junction, hydrogen ions (acid solvent) or hydroxide ions (alkaline solvent) will diffuse into the junction. Because hydrogen and hydroxide ions have much greater mobility than other ions, they produce a large junction potential. When the electrode goes back in service, the hydrogen or hydroxide ions slowly diffuse out of the junction, causing the liquid junction potential and the pH reading to drift. It may take hours or days for the reading to stabilize.

Always recalibrate the sensor after cleaning. If the sensor was cleaned with detergent or acid, soak the sensor in pH 4 buffer for at least an hour before calibrating.

7.2.2 Checking the Reference Electrode

Some processes contain substances, for example, sulfides, that poison the reference electrode. Poisoning alters the reference electrode potential. For example, sulfide poisoning converts the reference electrode from a silver/silver chloride electrode into a silver/silver sulfide electrode, causing a shift in potential of several hundred millivolts. The cell isopotential point changes as well.

A good way to check for poisoning is to compare the voltage of the reference electrode with a silver/silver chloride electrode that is known to be good. The reference electrode from a new sensor is the best choice. To check the suspect electrode, place both sensors in a beaker containing buffer or a solution of potassium chloride. Connect the reference leads to a voltmeter and measure the potential difference. If the suspect electrode is good, the difference should be no more than about 20 mV. Refer to Figure 7-1. A poisoned reference electrode usually requires replacement.

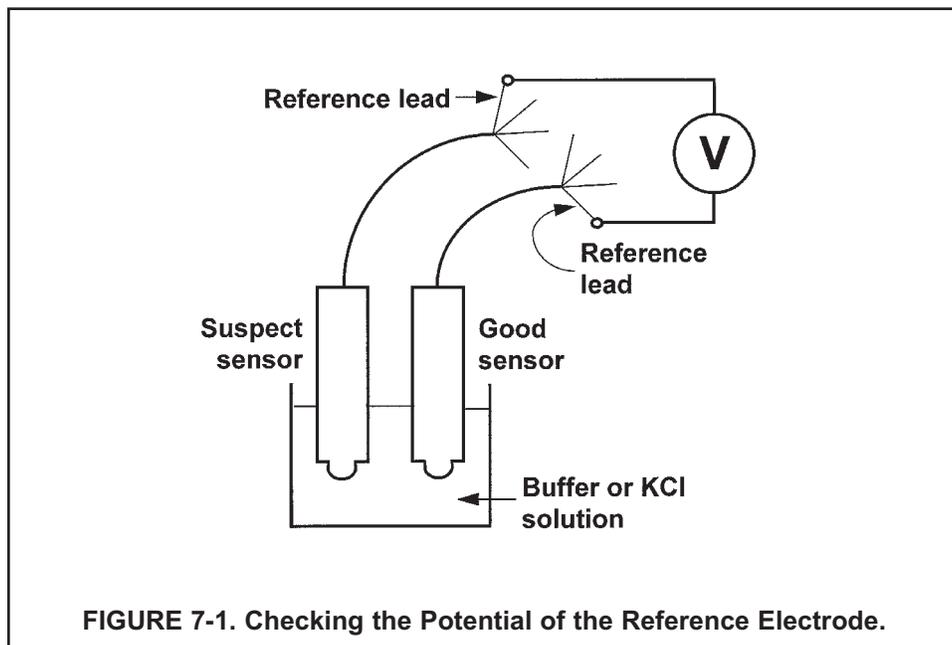


FIGURE 7-1. Checking the Potential of the Reference Electrode.

7.3 CALIBRATING pH SENSORS.

Many users regard calibration as part of routine maintenance. The question that arises is how often should sensors be calibrated.

Like cleaning, the frequency at which sensors should be calibrated can be determined only by experience. Many factors influence calibration frequency. Sensors installed in dirty or corrosive process streams usually require more frequent calibration than sensors used in clean water. Sensors measuring extreme pH values, particularly high pH, also require more frequent calibration than sensors measuring mid-range pH. The width of the pH or ORP control range and the consequences of an out-of-limits condition has a major influence on calibration frequency. The narrower the control range and the greater the sensitivity of the process to control excursions, the more often the sensor should be checked. Finally, if monitoring data are reported to regulatory agencies, the agency itself may dictate the calibration frequency.

Use the following procedure to determine how often a pH sensor should be calibrated.

1. Calibrate the sensor. Record the date of calibration and the sensor response in buffers. That is, after calibrating, place the sensor back in the buffers and record the pH and temperature reading in each buffer. Also note the value of the reference offset and slope.
2. Install the sensor in the process stream.
3. After the appropriate period—two weeks for a clean process, several days for a dirty or aggressive process—remove the sensor and check its performance in buffers. Record the pH and temperature readings. The performance of the sensor in buffer after it has been in service is called the as-found condition. Keeping a good record of as-found data is an important step in determining the calibration frequency.
4. If the as-found data are acceptable, do not recalibrate the sensor. Return it to the process. Continue checking the calibration at the same or slightly longer interval.
5. If the as-found data are not acceptable, recalibrate the sensor. After calibration, check the sensor response in each buffer and record the results. Also note the reference offset and the slope. Return the sensor to service. Check the sensor again after a period shorter than the one originally selected. For example, if the first interval was two weeks, repeat the check after one week.
6. After a while it will become apparent how long the sensor holds calibration. The minimum calibration frequency can then be determined.
7. Check the calibration of the sensor at least several times during the regular calibration interval. Interim checks verify the sensor is still in calibration and validate the process measurements made since the last calibration or calibration check.

7.4 STORING pH SENSORS.

Out of service pH sensors should be stored wet. pH 4 buffer to which a small amount of potassium chloride has been added is the best storage solution. Do not store sensors in deionized water or alkaline buffers. If a sensor dries out during storage, soaking it overnight in pH 4 buffer will usually restore the hydrated glass layer and the reference junction.

SECTION 8.0

TROUBLESHOOTING

- 8.1 INTRODUCTION**
- 8.2 INSTALLATION**
- 8.3 WIRING**
- 8.4 PROBLEMS WITH CALIBRATIONS**
- 8.5 NOISE**
- 8.6 DRIFT**
- 8.7 GROUND LOOPS**

8.1 INTRODUCTION

The first step in troubleshooting a pH system is to determine whether the problem lies with the instrument, the sensor, or the installation. The majority of pH measurement problems can be traced to the sensor or the installation. Comparatively few problems arise from the analyzer.

8.2 INSTALLATION

Section 6.0 gives general information about installation and some of the symptoms of an improperly installed sensor. A sensor may appear to have failed when in fact it has merely been installed incorrectly.

8.3 WIRING

Section 6.4 gives some general information about wiring sensors. Improperly wired sensors usually give noisy or drifting readings or no reading at all. Occasionally, the output signal cable or alarm connections may be the cause of erroneous pH readings. Therefore, when troubleshooting, it is always a good idea to disconnect output signal wires and alarm wires one at a time to see if they are the problem.

8.4 PROBLEMS WITH CALIBRATIONS

At room temperature, the slope of a properly operating pH measurement cell is about 59 mV per unit pH. In other words, a unit change in pH causes the cell voltage to change 59 mV. Many industrial pH analyzers automatically compare the slope calculated during calibration with reference values. If the slope is too high or too low, the instrument displays a warning message, or possibly refuses to accept the calibration. If the analyzer does not have such a feature, the user should check the raw voltage readings in buffer and calculate the slope manually.

8.4.1 Slope too low.

1. Inaccurate buffers can cause a low slope. Alkaline buffers, pH 10 or greater, are the major problem. These buffers absorb carbon dioxide from the air, which depresses the pH. Thus, the true pH is less than the expected value, and the calibration slope is low. If the calibration slope is low, repeat the calibration using fresh buffers. If using a high pH buffer continues to give a low slope, repeat the calibration using a lower pH buffer. For example, use pH 4 and 7 buffer instead of pH 7 and 10 buffer.
2. Allow adequate time for readings in the buffer to become constant. If the sensor was in a process appreciably colder or hotter than the buffer, allow at least 20 minutes for stabilization. Alternatively, place the sensor in a container of tap water at ambient temperature for 20 minutes before starting the calibration.

3. If buffer problems have been eliminated as the source of the problem, verify that the sensor is properly wired to the analyzer.
4. If sensor is properly wired to the analyzer, check the sensor for cleanliness. If the sensor is dirty or fouled, clean it. See Section 7.2.
5. If after cleaning the sensor, the calibration is still bad, the sensor may be faulty. The best way to check for a faulty sensor is to repeat the calibration using a new sensor. If the new sensor can be calibrated, the old sensor has failed.
6. If a new sensor cannot be calibrated, check the analyzer. The best way to check analyzer performance is to calibrate it using simulated pH and temperature values. If the analyzer accepts the simulated calibration, it is probably functioning properly. Commercial pH simulators are available, including ones that produce a high impedance voltage signal. Table 8-1 gives resistance as a function of temperature for typical RTDs used in pH sensors. Table 8-2 gives voltages for different pH values at three temperatures.

TABLE 8-1. RTD Resistance Values

Temperature	Pt 100 Resistance	Pt 1000 Resistance	3K Balco Resistance
0°C	100.0 ohms	1000 ohms	2670 ohms
10°C	103.9 ohms	1039 ohms	2802 ohms
20°C	107.8 ohms	1078 ohms	2934 ohms
25°C	109.6 ohms	1096 ohms	3000 ohms
30°C	111.7 ohms	1117 ohms	3067 ohms
40°C	115.5 ohms	1155 ohms	3198 ohms
50°C	119.4 ohms	1194 ohms	3330 ohms
60°C	123.2 ohms	1232 ohms	3472 ohms
70°C	127.1 ohms	1271 ohms	3594 ohms
80°C	130.9 ohms	1309 ohms	3726 ohms
90°C	134.7 ohms	1347 ohms	3858 ohms
100°C	138.5 ohms	1385 ohms	3990 ohms

TABLE 8-2. Input Signals for Simulated Buffer Calibration.

pH	Temperature		
	20°C	25°C	30°C
2	290.8 mV	295.8 mV	300.8 mV
4	174.5 mV	177.5 mV	180.4 mV
7	0.0 mV	0.0 mV	0.0 mV
10	-174.5 mV	-177.5 mV	-180.4 mV
12	-290.8 mV	-295.8 mV	-300.8 mV

8.4.2 Slope too high.

A too high slope is relatively unusual. If the calibration slope is too high, the problem is most likely spoiled buffers or failure to wait long enough for temperatures to become constant. See steps 1 and 2 in Section 8.4.1.

8.5 NOISE.

Noise is a rapid, random fluctuation in a signal. Noisy pH readings can have many causes.

1. The pH signal is high impedance, so it is susceptible to environmental noise. See Section 3.6 for additional information. Problems with environmental noise can also be minimized by preamplifying the signal at the sensor.
2. The impedance of the glass electrode increases as temperature decreases. An increase in impedance caused by a cold sample might be contributing to noise.
3. A plugged or depleted liquid junction can also be a source of noise.
4. Noisy readings, particularly if accompanied by offsets that disappear when the sample is electrically isolated from the process piping, can be a symptom of ground loops. See Section 8.7.
5. Noise can be a severe problem when measuring the pH of high purity water. pH readings in high purity water are also flow sensitive. High flow can produce very noisy readings as well as offsets as great as 0.5 pH units. The problem is likely caused by variations in the electrical potential at the surface of the junction plug. The fluctuating potentials are related to the flow of filling solution through the junction pores. Several manufacturers offer pH electrodes specifically designed for measuring high purity water.

8.6 DRIFT.

Drift is a gradual increase or decrease in a signal not caused by an actual change in the process liquid. Drift, like noise, has many causes.

1. Temperature changes can cause drift. The problem is often seen following calibration. If the temperature of the buffers was significantly different from the process liquid, the pH reading, once the sensor is returned to the process, will drift as the temperature of the sensor approaches the temperature of the process. Because industrial pH sensors often have plastic bodies, which are poor heat conductors, it may take 10 to 20 minutes for the sensor to equilibrate. While equilibration is occurring, the pH reading will drift.
2. Dirty sensors often produce pH readings that drift. The sensor voltage depends on the pH of the liquid at the surface of the pH sensitive glass. If the bulb is dirty or fouled, it may take some time for the liquid to diffuse through the coating and reach the membrane. The response of the sensor to step changes will be slow, and readings will drift to the final values.
3. Memory of past junction potentials can also lead to drift. When a pH sensor is transferred from one sample to another, liquid that has diffused into the reference junction is carried with the sensor. When the sensor is first placed in the new solution, both the old and new solutions determine the junction potential. As the new solution diffuses into the junction and the old solution diffuses out, the liquid junction potential gradually changes. The changing junction potential causes the pH reading to drift. The effect is most severe when the ions involved have substantially different mobilities. If the solutions are more or less equitransferent, the memory effect will be relatively small. The type of junction also influences the amount of drift. In flowing junctions, the filling solution washes out the previous sample, so the time for the memory to disappear is a few minutes to an hour. In gel type sensors, diffusion alone is responsible for movement of ions through the junction. Therefore, the time required for the memory to dissipate can be quite long.

8.7 GROUND LOOPS

A ground loop exists when a circuit is connected to earth ground at two or more points. Because the potential of the earth varies from point to point, two or more connections to ground cause currents to flow. If the current flows through a signal carrying wire, the result is a noisy, offset signal. The classic symptom of a ground loop is a sensor that reads correctly in buffers, but gives a reading grossly in error when placed in the process liquid.

In a typical process measurement, the pH sensor is connected through the process liquid and piping to earth ground. If the circuitry in the pH analyzer becomes connected to a second earth ground, current will flow through the reference electrode. A voltage proportional to the current and the electrode resistance develops across the reference electrode. Because the voltage is in series with the other cell voltages, the ground loop current causes the pH reading to be substantially different from the expected value. The currents created by ground loops are often unstable, so pH readings affected by ground loops are often noisy.

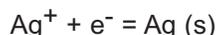
Use the following procedure to check for ground loops.

1. Remove the pH sensor from the process liquid.
2. Calibrate the sensor in buffers. Be sure there is no direct electrical connection between the container holding the buffer and the process liquid or piping.
3. Strip back the ends of a heavy gauge wire. Connect one end of the wire to the process piping or, better, place it in the process liquid. Place the other end of the wire in the container with the buffer and sensor. The wire makes an electrical connection between the process and sensor.
4. If the pH reading changes or becomes noisy after making the connection, a ground loop exists. If no symptoms develop a ground loop probably does not exist.

APPENDIX A

SILVER/SILVER CHLORIDE ELECTRODE POTENTIALS

Consider a piece of silver wire in contact with a solution of silver ions, the ions coming from a soluble silver salt like silver nitrate. The half reaction is:



The electrode potential E is given by the Nernst equation:

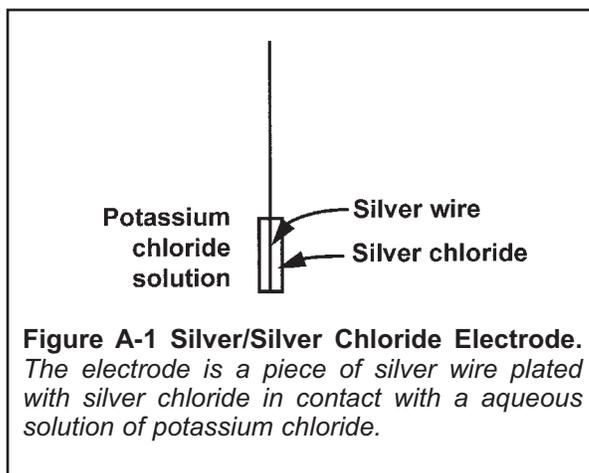
$$E = E^\circ - \frac{2.303RT}{n\mathfrak{F}} \log \frac{1}{[\text{Ag}^+]} \quad (1)$$

E° is the standard state electrode potential, R is the universal gas constant, T is temperature in Kelvin, n is the number of moles of electrons transferred, \mathfrak{F} is Faraday's constant, and $[\text{Ag}^+]$ is the concentration of silver ions. Technically, the Nernst equation should be written in terms of activity, but for simplicity, concentration will be used instead. Using concentration in place of activity in no way affects the conclusions. Equation 1 shows clearly that the potential of the silver electrode depends on the concentration of silver ions.

Now consider the system pictured in Figure A-1. The silver wire is in contact with a quantity of solid silver chloride, and the wire and the silver chloride are in contact with a concentrated solution of potassium chloride. The concentration of chloride is $[\text{Cl}^-]$.

As before, the electrode potential depends on $[\text{Ag}^+]$. However, $[\text{Ag}^+]$ cannot have any arbitrary value. As long as solid silver chloride is present, the chloride concentration controls the silver ion concentration.

In aqueous potassium chloride solution, silver chloride dissolves to produce a mixture of free silver ions (Ag^+), molecular silver chloride (AgCl), and a silver chloride complex ion (AgCl_2^-). The concentration of each species depends on the equilibrium constant for its formation and on the chloride concentration. The concentration of Ag^+ is controlled by the ionic solubility product for silver chloride, K_{sp} : $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$



(2)

Solving equation 2 for $[\text{Ag}^+]$ and substituting into equation 1 gives:

$$E = E^\circ - \frac{2.303RT}{n\mathfrak{F}} \log \frac{[\text{Cl}^-]}{K_{\text{sp}}} \quad (3)$$

Equation 3 shows that if silver chloride and potassium chloride are present, the chloride concentration controls the electrode potential. Therefore, if the chloride concentration is fixed, as it is inside the glass electrode and as it is (more or less) inside the reference electrode, the silver/silver chloride electrode potential will be constant. Because temperature appears in the coefficient of the logarithmic term in equation 3 and because it affects the magnitude of K_{sp} , temperature will also affect the electrode potential.

APPENDIX B

ISOPOTENTIAL pH

The voltage of a pH measuring cell as a function of temperature and pH is given by equation 1:

$$E(T) = E^\circ(T) - 0.1984T\text{pH} \quad (1)$$

As the notation emphasizes, $E^\circ(T)$ is a function of temperature. In modern pH methodology, the way in which $E^\circ(T)$ changes with temperature is usually expressed in terms of an isopotential pH. The isopotential pH is the pH at which the cell voltage is independent of temperature.

Assume $E^\circ(T)$ can be expressed as a polynomial function of temperature, then:

$$E^\circ(T) = a + bT + cT^2 + \dots \quad (2)$$

Ignore the quadratic and higher terms, and write $E^\circ(T)$ as a linear function of temperature:

$$E^\circ(T) = a + bT \quad (3)$$

Substituting equation 3 into equation 1 gives:

$$E(T) = a + bT - 0.1984T\text{pH} \quad (4)$$

Let pH_{iso} be the isopotential pH. By definition, when the pH is pH_{iso} , the cell voltage, $E(T)$, is independent of temperature. In other words, at the isopotential pH,

$$\frac{\partial E(T)}{\partial T} = 0 \quad (5)$$

Differentiating equation 4 with respect to T gives:

$$\frac{\partial E(T)}{\partial T} = b - 0.1984\text{pH} \quad (6)$$

If the pH is pH_{iso} , then equation 6 becomes:

$$0 = b - 0.1984\text{pH}_{\text{iso}} \quad (7)$$

Solving equation 7 for b and substituting into equation 4, gives after rearranging:

$$E(T) = a - 0.1984T(\text{pH} - \text{pH}_{\text{iso}}) \quad (8)$$

pH measuring cells are usually designed to have an isopotential pH of 7, so equation 8 can be rewritten as:

$$E(T) = a - 0.1984T(\text{pH} - 7) \quad (9)$$

As shown in Figure B-1, a plot of $E(T)$ against $(\text{pH} - 7)$ is a straight line with a y-intercept of a and a slope of $-0.1984T$. In an ideal cell the slope is $-0.1984T$, where 0.1984 is a collection of constants. In a real cell, the slope might be slightly different, so for the most general case, equation 9 can be written as:

$$E(T) = a - BT(\text{pH} - 7) \quad (10)$$

The important feature of equation 10 is that it was derived assuming $E^\circ(T)$ was a linear function of temperature. If $E^\circ(T)$ is not linear with respect to temperature, the isotherms will not pass through a single point. Instead, they will intersect in a general area. Real pH cells do not have a true isopotential point. The lack of a true isopotential point leads to errors when the measurement cell is calibrated at one temperature and measurements are made at a different temperature.

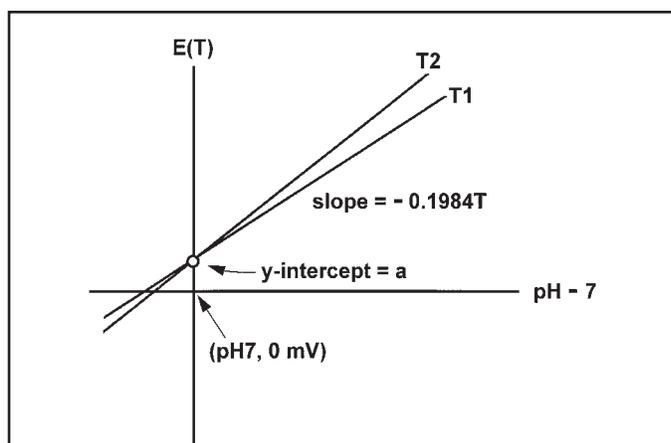


FIGURE B-1. Cell Voltage as a Function of pH.

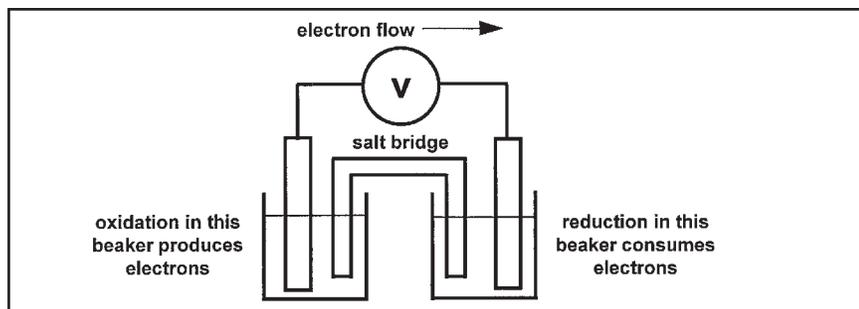
The graph shows cell voltage as a function of pH at two temperatures T1 and T2. Both lines, which are called isotherms, pass through the point (pH7, a). The point (pH7, a) is the isopotential point of the pH cell.

APPENDIX C GLOSSARY

TERM	DEFINITION
Acid	When dissolved in water acids increase the hydrogen ion concentration. Pure water at 25°C contains 1×10^{-7} moles per liter of hydrogen ions (H^+) and an equal concentration of hydroxide ions (OH^-). An acid increases the hydrogen ion concentration above the value found in pure water and decreases the hydroxide ion concentration. However, the product of the hydroxide and hydrogen concentrations remains constant.
Activity	Physical and chemical measurements made in real solutions are usually different from the values predicted from the behavior in ideal solutions. Activity is a way of accounting for the discrepancy. For ions in solution ideal behavior occurs at infinite dilution. Infinite dilution means the solution contains so few ions that they behave independently of one another. As the concentration of the ions increase, they start to interact and the properties of the solution begin to deviate from the ideal. The ratio of the true value to the ideal value at a given concentration is the activity coefficient. The product of the activity coefficient and the concentration is the activity.
Alkali metal	The alkali metals are lithium, sodium, potassium, and cesium. They form ions having unit positive charge. Ion exchange reactions involving alkali metal ions cause certain types of glass to develop electrical potentials in the presence of hydrogen ions.
Balco RTD	The sensing element in a Balco RTD is an alloy containing 70% nickel and 30% iron. Balco RTDs are identified by their resistance at 25°C. The resistance changes about +0.45% per °C.
Base	When dissolved in water, bases decrease the hydrogen ion concentration. Pure water at 25°C contains 1×10^{-7} moles per liter of hydrogen ions (H^+) and an equal concentration of hydroxide ions (OH^-). A base decreases the hydrogen ion concentration below the value found in pure water and increases the hydroxide ion concentration. However, the product of the hydroxide and hydrogen concentrations remains constant. Alkali is another word for base.
Buffer (calibration)	A calibration buffer is a solution having accurately known pH. Calibration buffers have a nominal pH, which is the pH at 25°C. Changing the temperature changes the pH value of a buffer. Buffers define the pH scale and are used to calibrate the response of pH measurement cells.
Buffer	The term buffer generally refers to a solution that resists changes in pH upon dilution or the addition of small amount of a strong acid or base.
Calibration	Chemical sensors are transducers. They produce a signal related to concentration or to a physical property. Calibration is the process of assigning known concentrations or known physical values to the sensor signal. Because the relationship between sensor output and physical or chemical property is often linear, only one or two calibration points is needed.
Combination electrode	In a combination electrode, the measuring electrode and reference electrode are combined in a single body. Often the temperature element is included in the body as well.
Common	A point in a circuit against which voltages are measured.
Electrode potential	Electrode potential is a measure of the tendency of a half reaction to occur as written. Electrode potentials are stated relative to a reference electrode, which by convention is the normal hydrogen electrode. The normal hydrogen electrode is assigned a potential of zero volts.

Electrochemical cell

An electrochemical cell consists of two half reactions occurring in separate containers connected electrically by a salt bridge. The electrons produced by the oxidation half reaction are consumed by the reduction half reaction. Because the electrons must pass through an external circuit, they can be made to do useful work. The drawing below shows a simple electrochemical cell.



The voltage of the electrochemical cell (measured without drawing current from the cell) is the algebraic sum of the potentials of the two electrodes.

Electrode

Electrochemistry is the study of charge transfer across boundaries. The charge being transferred can be ions or electrons. An electrode is a two-phase system where the charge transfer across the interface involves electrons. A real physical electrode may incorporate several boundaries.

Electrolyte

An electrolyte is a substance that when dissolved in water produces an appreciable concentration of ions. Most salts, mineral acids (sulfuric acid, hydrochloric acid, phosphoric acid, and nitric acid), and most bases are electrolytes.

Equitransferent

A solution is equitransferent if the ions have the same mobilities. Potassium chloride is almost equitransferent. The mobility of potassium and chloride differ by only 2%.

Filling solution

The electrolyte solution inside an electrode is called the filling solution. The buffered electrolyte solution inside a glass electrode is usually called the internal filling solution. The solution inside the reference electrode is usually called the external filling solution, or, simply, the filling solution. In many industrial reference electrodes, the filling solution is not a liquid but is a semi-solid gel.

Glass impedance

The overall resistance of the glass membrane to the flow of current. Glass impedance is a strong function of temperature. Impedance increases as temperature decreases. Temperature corrected glass impedance is a valuable diagnostic tool. Abnormally low impedance implies a cracked or broken glass membrane. High impedance suggests that the electrode is nearing the end of its life.

Glass electrode

pH measuring electrodes are often called glass electrodes. The electrode is a piece of glass tubing that has a pH-sensitive glass membrane blown onto the end. The tube is filled with a buffered solution of potassium chloride. A silver wire coated with silver chloride contacts the fill solution, and the silver wire is connected to the electrode lead wire. The entire electrode is sealed. "Glass" refers to the pH-sensitive glass membrane in the sensor.

Glass membrane

The glass membrane is the pH-sensitive glass piece blown onto the bottom of the glass tube that forms the body of the glass electrode. The pH sensitive glass is usually a bulb, but it can be flat.

Ground

Ground usually refers to either earth ground or a common. Earth ground is the earth or a conducting body serving in place of the earth. A common is a point in a circuit to which other voltages are compared. The meaning intended is usually clear from the context.

Ground loop	<p>A ground loop exists when a circuit is connected to earth ground at two or more points. The potential of the earth varies from point to point, so multiple connections to ground cause currents to flow. If the current flows through a signal carrying wire, the result is a noisy, offset signal. In a typical process measurement, the pH sensor is connected through the process liquid to earth ground. If the circuitry in the pH transmitter becomes connected to a second earth ground, current will flow through the reference electrode. A voltage, proportional to the current and the electrode resistance, develops across the reference electrode. Because the voltage is in series with the other potentials in the cell, the ground loop current causes the pH reading to be substantially different from the expected value. pH readings affected by ground loops are often noisy as well.</p>
Half reaction	<p>A half reaction shows the gain or loss of electrons by a chemical species. The half reaction for a silver-silver chloride reference electrode is</p> $\text{AgCl (s)} + \text{e}^- = \text{Ag (s)} + \text{Cl}^-$ <p>In the half reaction, a silver ion in the silver chloride crystal gains an electron and becomes a silver atom. The electron consumed by the silver ion comes from a second half reaction occurring elsewhere in the system.</p>
Isopotential pH	<p>The isopotential pH is the pH at which voltage is independent of temperature. The transmitter isopotential pH is 7.00. The isopotential pH of the measuring cell may be different from 7.00. The greater the difference between the transmitter and cell isopotential pH, the greater the error when the calibration and measurement temperatures are different.</p>
Isotherm	<p>A plot of cell voltage against pH is a straight line. The line is called an isotherm. When temperature changes, the slope of the isotherm changes. Therefore, the pH to which a given cell voltage corresponds depends on temperature. Meter isotherms intersect at the meter isopotential point. Isotherms for pH measurement cells rarely intersect at a single point, but they usually cross in a fairly small area.</p>
Junction box	<p>Signal carrying wires are conveniently joined together in a junction box. Usually the box contains two terminal strips connected internally point to point. The wires in one cable are terminated on one strip, and the wires in the other cable are terminated on the second strip. The point to point connection between the terminal strips produces a point to point connection between the wires.</p>
Liquid junction potential	<p>A liquid junction potential exists when two dissimilar electrolyte solutions come into contact but are not allowed to mix. The potential arises from the different mobilities of the ions in the contacting solutions. Generally the solution of greatest concentration has the greatest influence on the size of the liquid junction potential. Although liquid junction potentials cannot be eliminated, they can be made small and relatively constant if the concentrated solution contains ions of equal or nearly equal mobilities.</p>
Measuring electrode	<p>A measuring electrode is an electrode for which the potential is proportional to the concentration or activity of the substance of interest.</p>
Molar concentration	<p>Molar concentration is the number of moles of substance dissolved in one liter of solution. A mole is a measure of the quantity of ions, molecules, or atoms in a substance.</p>
Nernst equation	<p>The Nernst equation relates the potential of an electrode to the concentration or activity of the chemical substances that appear in the half reaction occurring at the electrode.</p>
ORP	<p>ORP is oxidation-reduction potential. It is the tendency of a chemical species to gain or lose electrons at a noble metal electrode. ORP is usually measured in millivolts. The type of measuring electrode, the type of reference electrode and the temperature must be identified when stating the ORP of a sample.</p>
Oxidation	<p>Oxidation is the loss of electrons. For example, when an iron (II) ion becomes an iron (III) ion, it loses an electron: $\text{Fe}^{+2} = \text{Fe}^{+3} + \text{e}^-$.</p>

pH	Although pH is often defined as the negative common logarithm of the hydrogen ion activity, pH is best defined by describing how it is measured. The measurement requires three steps. Assemble an electrochemical cell consisting of a glass electrode, a reference electrode, and the solution. Calibrate the cell by measuring the voltage of two standard buffer solutions. Finally, measure the cell voltage with sample present. Because voltage is directly proportional to pH, the pH of the sample can be calculated from the calibration data. The operational definition places the pH of the sample on the pH scale defined by the buffers.
Platinum electrode	A platinum electrode is a noble metal electrode commonly used for measuring ORP. The potential developed at the electrode is directly proportional to the ratio of the concentrations of oxidized and reduced substances present in the sample. pH influences the ORP.
Platinum RTD	As the name implies, platinum is the sensing element in a platinum RTD. Platinum RTDs are usually identified in terms of their resistance at 0°C. The resistance of a platinum RTD changes +0.39% per °C.
Preamplifier (remote)	A remote preamplifier, located in either the sensor or in a nearby junction box, boosts the sensor voltage and converts it from high impedance to low impedance before sending it to the analyzer. Generally, if the pH signal is to be sent more than about 15 feet, it should be preamplified.
Reduction	Reduction is the gain of electrons. For example, when an iron (III) ion becomes an iron (II) ion, it gains an electron: $\text{Fe}^{+3} + \text{e}^{-} = \text{Fe}^{+2}$.
Reference electrode	A reference electrode maintains a stable potential independent of the pH or ORP of the sample. The reference electrode also contains a reference junction that electrically connects the electrode with the sample. The silver-silver chloride electrode is the most common reference electrode in industrial and laboratory applications. The electrode consists of a piece of silver wire plated with silver chloride in contact with a solution of concentrated potassium chloride.
Reference impedance	The reference impedance is the overall resistance of the reference electrode to the flow of current through it. Generally, as the reference junction becomes coated and plugged, the reference impedance increases.
Reference offset	When the transmitter reading is forced to match the reading from a second pH meter, the transmitter calculates the difference between its reading and the second meter and converts the difference to voltage. The difference is the reference offset. If the reference offset exceeds the programmed limit, the transmitter will not adjust the pH reading.
RTD	RTD is an acronym for resistance temperature detector.
Salt bridge	A salt bridge provides an electrical connection between two electrolyte solutions without permitting the solutions to mix. The classic salt bridge is a U-shaped tube filled with gelled potassium chloride and plugged at both ends with a porous material. When the ends are inserted in separate beakers an electrical connection is formed between the beakers. See also Electrochemical Cell.
Shield	A shield is a metal braid that encloses the insulated signal carrying wire. The shield protects the signal wire from extraneous signals.
Solution temperature compensation	The pH of many solutions, particularly alkaline ones, is a function of temperature. Therefore, although the concentration of the chemical causing the pH remains constant, pH will change if the temperature changes. Solution temperature compensation is a technique for converting pH measured at any temperature to the pH at a reference temperature. The almost universal reference temperature is 25°C. Different solutions require different solution temperature compensation.
Temperature compensation	A plot of voltage against pH is a straight line, called an isotherm. The slope of the isotherm is a function of temperature, so a measured cell voltage corresponds to a different pH, depending on temperature. Temperature compensation is the process of selecting the correct isotherm.



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