Orion pH, ORP and ISE Theory

Why is pH Important?
pH is one of the most common laboratory measurements because many chemical processes are dependent on pH. The speed or rate of chemical reactions can often be significantly altered by changing the pH of the solution. The solubility of many chemicals in solution, and their bio-availability is dependent on pH. The physiological chemistry of living organisms usually has very specific pH boundaries. In our modern lives, virtually everything we use has been tested for pH at one time: from the tap water we brush our teeth with, the paper we write on, the food we eat, to the medicines we take, at some point a pH measurement was performed.

Basic pH Theory
The term pH derives from a combination of "p" for the word power and "H" for the symbol of the element Hydrogen. Together the meaning is the power or exponent of hydrogen.

The Chemical Equation for pH
pH is defined as the negative log of hydrogen ion activity, where the activity, a_{H+}, describes the free hydrogen ion, or the "effective concentration", in the presence of other ions:

$pH = -\log a_{H+}$ or $H+ = 10^{-pH}$

Thus, a pH of 3 is equivalent to a hydrogen ion activity of 10^{-3} Molar (M), a pH of 11 is an activity of 10^{-11} M, and a pH of 11.5 would be a hydrogen ion activity of $10^{-11.5}$ or 3.2×10^{-12} M. Water (H_2O) dissociates into hydrogen ions (H^+) and hydroxide ions (OH^-) in an aqueous solution. The following equilibrium reaction is used to describe pH:

$2H_2O = H_3O^+ + OH^-$ or simply $H_2O = H^+ + OH^-$

The dissociation constant, K_w, is the product of the hydrogen and hydroxide ion concentrations:

$K_w = [H^+] [OH^-] = 1.0 \times 10^{-14}$ M at 25 °C

At 25 °C, K_w remains constant at 1×10^{-14} M. Therefore, the concentration of hydrogen or hydroxide ions can be calculated if the other concentration is known. A pH of 7 is considered to be neutral at 25 °C because the activity of the hydrogen and hydroxide ions are both equal to 10^{-7} M. The activity range for the hydrogen ion, as defined by the dissociation product, is 100 to 10^{-14} M. The activity range of hydrogen ion relates to a pH scale of 0 to 14. Each unit on the pH scale represents a ten-fold change in the activity. For more information, see notes (1) and (2).

Practical Application of pH
pH serves as a convenient way to compare the relative acidity or alkalinity of a solution at a given temperature. As discussed, a pH of 7 describes a neutral solution because the activities of hydrogen and hydroxide ions are equal. When the pH is below 7, the solution is described as acidic because the activity of hydrogen ion is greater than that of hydroxide ion. A solution is more acidic as the hydrogen ion activity increases, therefore the pH decreases. Conversely, as the hydroxide ion activity increases, the solution becomes more alkaline, also referred to as basic, and the pH will increase. In practice, pH electrode measurements are made by comparing readings in a sample with readings in standards whose pH has been defined "buffers". These measurements are relative rather than exact thermodynamic determinations of activity. pH electrode measurements can be used to detect a titration endpoint, which will give the acidity or alkalinity in terms of total concentration, rather than activity.

Basic pH Electrode Theory
pH electrodes measure the pH of a solution potentiometrically. A potentiometric measurement relies on an electrical signal. When a pH sensing electrode comes in contact with a sample, a potential develops across the sensing membrane surface. The membrane potential varies with the pH. Making a measurement requires a second unvarying potential to quantitatively compare the changes of the sensing membrane potential. A reference electrode provides this function. Electrode behavior is described by the Nernst equation:

$E_{measured} = E_o + (2.3\ RT/nF) \log a_{H+}$

$E_{measured}$ is the measured potential from the sensing electrode, E_o is related to the potential of the reference electrode, (2.3 RT/nF) is the Nernst factor, and $\log a_{H+}$ is the pH. The Nernst factor, 2.3 RT/nF, includes the Gas Law constant (R), Faraday's constant (F), the temperature in degrees Kelvin (T) and the charge of the ion (n). For pH, where n = 1, the Nernst factor is 2.3 RT/F. Since R and F are constants, the factor and therefore electrode behavior is dependent on temperature. pH and temperature effects are discussed on page 62. The electrode slope is a measure of the electrode response to the ion being detected and is equivalent to the Nernst factor. When the temperature is equal to 25 °C, the Nernst factor or slope is 59.16 mV/pH unit. Most Orion pH meters display the slope as a percentage of the theoretical value. For example, a 98.5% slope is equivalent to a slope of 58.27 mV/pH unit for a two-point calibration. When a pH meter detects the sensing membrane signal, reference signal and the temperature, the meter software calculates the pH using the Nernst equation. Microprocessor controlled Orion pH meters contain pH versus temperature values for commonly used buffers. This allows the meter to recognize a particular pH buffer and calibrate with the correct value.

Notes

(1) "Uses and Abuse of pH Measurements," Feldman, Issac, Analytical Chemistry, 28, 1861 (1956)

(2) "Determination of pH: pH Theory and Practice," Bates, Roger, John Wiley and Sons, New York, 1973

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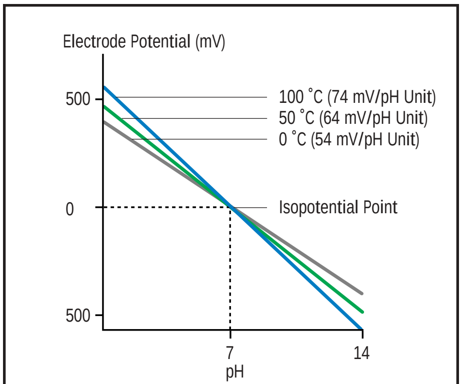

Change of pH Slope with Temperature

pH Values versus Temperature

25 °C	1.68	3.78	4.01	6.86	7.00[1]	7.41	9.18	10.01	12.46
0 °C	1.67	3.86	4.00	6.98	7.11	7.53	9.46	10.32	13.42
5 °C	1.67	3.84	4.00	6.95	7.08	7.50	9.40	10.25	13.21
10 °C	1.67	3.82	4.00	6.92	7.06	7.47	9.33	10.18	13.01
20 °C	1.67	3.79	4.00	6.87	7.01	7.43	9.23	10.06	12.64
30 °C	1.68	3.77	4.02	6.85	6.98	7.40	9.14	9.97	12.30
40 °C	1.69	3.75	4.03	6.84	6.97	7.38	9.07	9.89	11.99
50 °C	1.71	3.75	4.06	6.83	6.97	7.37	9.01	9.83	11.71
60 °C	1.72	–	4.08	6.84	–	–	8.96	–	–
70 °C	1.74	–	4.13	6.85	–	–	8.92	–	–
80 °C	1.77	–	4.16	6.86	–	–	8.89	–	–
90 °C	1.79	–	4.21	6.88	–	–	8.85	–	–

Key

(1) Non-NIST phosphate buffer

pH and Temperature

The most common cause of error in pH measurements is temperature. There are at least five ways that temperature variations can affect pH:

- Electrode Slope
- pH Buffers
- Samples
- Reference Element Drift
- Temperature Sensor Errors

Electrode Slope Changes

The electrode slope will change with variations in temperature. Slope changes may be compensated for manually, automatically with an automatic temperature compensation probe (ATC) or with digital LogR™ technology on PerpHecT® pH meters. Orion meters calculate the slope value based on the temperature input and automatically adjust the measured pH values. The illustration on this page shows the change in electrode slope with temperature.

Buffer and Sample pH Changes

Buffer and sample pH values vary with temperature because of their temperature dependent chemical equilibria. The problem of differing pH values is easily solved by calibrating the electrode with characterized standard buffers whose true pH values versus temperature are known. pH buffer values at different temperatures are given on this page. Orion meters calibrate with the correct pH buffer values based on the manual, ATC or digital LogR temperature value. The problem of the sample equilibrium varying with temperature in an uncharacterizable manner will always remain. Therefore, calibration and measurement should be performed at the same temperature and pH values should be reported along with temperature. For best results, an ATC probe should be used.

Reference Element Drift

Drift can occur when the internal reference elements inside the pH and reference portions of the electrode are reaching thermal equilibrium after a temperature change. Long term drift or slow response can last until the sample and electrode are at the same temperature. Orion ROSS Ultra™, ROSS™ and PerpHecT ROSS pH electrodes use a patented internal reference that minimizes equilibration time. The new ROSS Ultra electrodes are virtually drift-free over time.

Temperature Sensor Errors

When a pH and temperature probe are placed into a sample that varies significantly in temperature, the readings can drift for two reasons. First, the temperature response of the electrode and temperature probe may not be similar which prolongs equilibration and drift. Second, a sample may not have a uniform temperature, therefore the pH electrode and temperature probe are responding to different environments. Using digital LogR technology, Orion PerpHecT meters sense not only pH but also temperature directly from the PerpHecT or PerpHecT ROSS pH electrode. Only PerpHecT pH meters allow for direct temperature measurement and compensation from the pH electrode. Patented LogR technology makes it all possible; this system is based on using the electrical resistance of the glass-sensing bulb of the electrode as the temperature indicator. The logarithm of the resistance varies almost linearly with the temperature. As the temperature increases the resistance decreases. The algorithm that delivers this relationship is built into the PerpHecT meters. With the combination of the PerpHecT meters and PerpHecT electrodes temperature compensated measurements are made easier. Although other Orion electrodes may be used with the LogR feature, the algorithm is optimized for the PerpHecT series electrode temperature response. Alternatively, pHuture™ probes contain an on-chip temperature sensor. The pH and temperature response is identical since measurements occur at the sensing surface. Therefore, drift is minimized and errors due to environmental differences are eliminated.