Introduction to pH sensors

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Introduction

In modern day research and industrial applications knowing the exact pH at the exact time is of paramount importance. This need is answered by various pH measurement devices which this article will later on discuss. Before going into the pH meters themselves, it is important to specify what the pH actually is.

What is measured as pH is logarithm taken from hydrogen ion concentration in moles per liter, mathematically often expressed as following:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

It describes the acidity or alkalinity of a solution, for example used in an industrial process. Lower case letter p stands for negative base ten logarithm ad the upper case letter H stands for element hydrogen.

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Common pH scale runs from 0 to 14 with 0 being strongly acidic and 14 being strongly alkaline. In the middle of the scale there is neutral 7 which represents ideally pure water.

Principles of work
There are many ways to measure pH from a solution. One very common way is the color changes in chemical powders, like litmus strips used in elementary chemistry. In modern industrial applications, a pH probe is often used. This kind of probe contains two electrodes that generate voltage, which is proportional to pH of the solution in question.

One of the two electrodes is a measurement electrode constructed out of special glass in order to create ion selective barrier. This barrier hen screens out hydrogen ions from the large flock of ions otherwise present in the solution [1]. Reference electrode is designed in a way that it maintains a constant potential at any given temperature. When reference potential is compared to the potential of the pH electrode, a millivolt signal proportional to pH is created allowing for the measurement. [2]

Reference electrode is made using chemical solution that is neutral pH buffer solution that is allowed to exchange ions with the process solution through a porous separator, forming low resistance connection to the test liquid. This electrode creates a reference that it both tries to maintain and that on which to compare potential readings from the measurement electrode. Reason for usage of wet chemical interface is that they produce less voltage across the interface of contact, allowing for more accurate measurements [1].

Almost all pH sensors are designed to produce a 0 mV signal at neutral pH of 7 with slope of 59.16 mV /pH at 25 °C. This theoretically ideal slope represents sensitivity and the point usually represents what is called an isopotential point, where potential is constant with temperature changes. When isopotential point is known, it can be used together with theoretical knowledge of electrodes behavior, allowing correction of the pH measurement at any temperature by comparing it to the reference temperature. [2]
Actual pH measurement loop consists of three different components, the pH sensor with parts discussed above including temperature sensor, a preamplifier and either analyser or transmitter. This loop can be considered a battery in terms of electrical calculations with positive terminal being the measuring electrode and negative the reference electrode. Once the measuring electrode produces potential out of hydrogen ions it is compared to stable potential of the measuring electrode’s liquid [1].

Factors affecting accuracy and performance of glass pH electrodes
Millivolt output of the sensor tends to change as the fill solution with known pH interacts with the process solution. Not even new electrodes always have the ideal sensitivity of 59.16 mV/pH, as the glass electrode ages it’s sensitivity (slope) decreases. In addition to the changes in millivolt output, temperature also affects the electrodes measurement. Very high temperatures can boil the solution inside or very low temperature can make it freeze, both resulting in cracking of the tip [2].

A very high pH can cause a “sodium error”, meaning a state where hydrogen ion concentration is very low compared to sodium ion concentration. This state effectively can lead into the electrode reacting to the sodium ions, giving false readings of lower than actual pH. Solutions that reach pH in excess of 14 can destroy a pH electrode in hours. Conductivity measurement is recommended instead for situations of this high pH.

Hydrofluoric acid can dissolve pH glass quickly unless it is of special HF resistive type which lasts longer and can be used for certain amounts of time. Since hydrofluoric acid (HF) damages the glass but is considered weak acid there is possibility of the solution to contain fairly large amounts of fluoride ions (F⁻). This means that at high pH solution might not damage the glass at all, but when pH drops and Fluoride (F⁻) and hydrogen ion (H⁺) combine it forms more damaging hydrofluoric acid (HF).

Depending on the pH sensor, most of them shouldn’t be stored in de-ionized or demineralized water because of it shortening the lifespan of the sensor [4].

Factors affecting accuracy and performance of reference electrodes

Common way of building reference electron is constructing it from silver wire with silver chloride coating and a fill solution of potassium chloride. This fill solution maintains reproducible voltage on the wire and must be uncontaminated in order to give accurate results.

One reason for inaccuracy is called “reference poisoning” meaning a conversion of the electrode into another silver compound. Typical compounds that can cause reference poisoning are bromide, iodide and sulfide ions, all of which can form insoluble precipitates together with silver into the solution. This change doesn’t happen instantly because of protective silver chloride coating replenish the silver ions in the solution as long as it exists. When the effect occurs, however, there is significant change in the potential and temperature behavior of the reference electrode. Other reason for this to happen might be reducing agents such as bisulfite that reduce silver ion concentrations into silver metals [2].

Reference electrode side of the pH sensors can fail to measure correctly because of plugged liquid junction. Measurement cannot be taken if electrical contact between the reference and pH electrodes is not maintained, for example because of insoluble precipitate within the liquid junction. Such precipitates may be caused by heavy metal ions, like lead and mercury forming insoluble salt with chloride ions. Some sensor types use multiple junction reference electrodes to slow down the effect of both “poisoning” and plugging [2].

Cleaning of the pH sensor
Sensors measuring pH must be cleaned in order to avoid performance and accuracy issues caused by abovementioned reasons. In addition to the failures and accuracy problems, uncleansed sensor can have drastically reduced response time, making measurements much more time consuming.

Cleansing in laboratories is usually done with mild but still effective solutions to avoid causing problems of similar nature to those that want to be avoided. Alkaline depositions coating the pH sensor can be removed with weakly acidic solutions such as 5% HCL or vinegar. Acidic deposits can usually be removed with 1 % caustic soda or other mildly caustic solutions. Use of solvents or detergent solutions is recommended for organic deposits such as oil and grease [2]. Distilled or de-ionized water helps when applied right after the measurement to wipe off most contaminants that have begun to buildup [3].

**Calibrating pH sensors**

Electrodes in pH sensor are usually calibrated by a two point method with appropriate buffer standards [4]. Single point methods also exist, but some failure modes might escape these checks. In two point calibration, there are two buffer solutions based according to the measurement range of the sensor. Buffer solution of pH 7 is used along with solution of different pH of interest. Probe is dipped into pH 7 solution and then into another solution with careful rinsing in between. Modern sensors have automated calibration functions that require each buffer solution to be used only once [5].

When pH sensor ages its slope and offset will change, dictating calibration frequency and need for completely new sensor. If offset is more than 30 mV or more than 2 minutes are needed for the probe to stabilize in buffer solution it can be considered to have reached the end of its useful life [4].

Sensors measuring pH should be on for at least 30 minutes, depending on the sensor, to ensure that all components are at thermal equilibrium and the calibration solution used should be immersed for atleast a minute to ensure equilibrium [5].
The length of time between cleaning and calibration depends on process conditions and the user's accuracy and stability expectations [1].

### Industrial pH sensors

Industrial-grade pH sensors are typically mounted on special mounts to allow wider range of use in different applications [3]. Different mounts give option for installing the sensor submerged, so that liquid flows through it or so that they are inserted into the liquid when needed. Instruction manuals on this kind of sensors provide various different values and specifications to help determine operability in process conditions. Typically at least measuring range, sensitivity, stability, temperature range, pressure range and weight are quickly and easily obtainable from manuals. Sometimes industrial sensors contain preamplifiers that are installed as close to the sensor unit itself for easier calibration work and also cables of these industrial type sensors are well protected with signal shielding, chemical protection etc. [3].
Picture 3 Cable of industrial pH sensor

References


Images

Picture 1:
http://www2.emersonprocess.com/siteadmincenter/PM%20Rosemount%20Analytical%20Documents/Liq_ADS_43-002.pdf

Picture 2:
http://www.phadjustment.com/TArticles/pH_Probe_Service.html

Picture 3: