

The Effects of Temperature on pH Measurement

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Abstract

Some of the effects of temperature on pH measurement have been described or alluded to in both instrument manufacturers instructions and independent scientific literature. Some of these have been presented in a very theoretical manner and thus have been of limited practical value, others have been described adequately from a practical perspective. However a comprehensive classification of the principal effects of temperature on pH with practical remedial actions to correct, reduce or eliminate these errors has never previously been reported. This paper presents for the first time a clear classification of the practical effects of temperature on pH. It provides a definite set of guidelines on how the different errors can be reduced or eliminated thus giving the user greater confidence in the result of their pH measurements.

1 Introduction

Accurate measurement and reporting of pH data has been a long-standing problem due to the effects of temperature. An increase in any solutions' temperature will cause a decrease in its viscosity and an increase in the mobility of its ions in solution. An increase in temperature may also lead to an increase in the number of ions in solution due to the dissociation of molecules (this is particularly true for weak acids and bases). As pH is a measure of the hydrogen ion concentration, a change in the temperature of a solution will be reflected by a subsequent change in pH⁽¹⁾.

In addition, changes in temperature will also have an influence on the measuring sensor used.

Overall, the effects of temperature can be divided into two main categories:

- Temperature effects that diminish the accuracy and speed of response of the Electrode.
- Temperature Coefficient of Variation effects on the material being measured by the sensor, whether it be calibration buffer or sample.

Further sub-classification is necessary for each of these categories in order to understand the cause of the problem and determine the optimal remedial action.

2 Temperature Effects on the Electrode

Temperature has a variety of effects on pH electrodes of both a physical and chemical nature. These will be discussed in detail under the following headings and include recommendations on how to reduce or account for these sources of error.

- Temperature effects on electrode slope
- Calibration Isothermal point
- Thermal equilibrium
- Chemical equilibrium
- Membrane resistance

2.1 Temperature effects on electrode slope

The response of an ideal pH electrode is defined by the Nernst Equation⁽²⁾:

$$E = E^0 - 2.3 (RT/nF) \log a_{H^+}$$

where:

- E = total potential (in mV) developed between the sensing and reference electrode
- E₀ = standard potential of the electrode at a_{H⁺} = 1 mol/l
- R = Gas constant
- T = temperature
- n = valency of ion

Temperature °C	Nernst slope (mV/pH)
0	54.20
10	56.18
20	58.17
25	59.16
30	60.15
40	62.14
50	64.12
60	66.10
70	68.09
80	70.07
90	72.06

Table 1: The variation in Nernst slope with temperature for an ideal electrode

- F = Faraday constant
- a_{H^+} = activity of the hydrogen ion in solution

The term $2.3RT/nF$ is referred to as the Nernst slope. Table 1 shows the changes in Nernstian slope at increasing temperatures for the ideal electrode⁽³⁾. This change in slope with temperature can be compensated for by the meter using Automatic Temperature Compensation (ATC). All modern pH meters allow for the measurement of the sample temperature using a temperature probe placed in the sample. The meter then adjusts the slope to be correct in accordance with the Nernst equation at the measured temperature during calibration. For manual compensated instruments, a potentiostat is built into the instrument, which can be adjusted by the operator to facilitate the correction.

ATC relies on the accurate measurement of the temperature of the solutions. This can be achieved by using an electrode with a built in temperature sensor or a separate temperature sensor. Combined pH/temperature electrodes offer the advantage that only one probe is required to perform measurements. Such sensors can suffer from a sluggish response since the glass, which surrounds such sensors, has a low thermal conductivity. Alternatively, a separate temperature sensor can be used with the pH meter. However, this can be cumbersome for measurement in small vessels.

2.2 Calibration Isothermal Point

The isothermal point of an electrode is defined as the intersection point of calibration lines plotted for different temperatures⁽⁴⁾ and is characterised by both a pH value and a potential. For an ideal electrode this would represent an isothermal intersection at the zero point (0mV at pH 7) for different temperatures⁽²⁾. For real electrodes the individual potentials which contribute to the overall potential output have separate temperature coefficients of variation. Thus the isothermal intersection point hardly ever coincides with the zero point of the electrode (see Figure 1).

Substantial work has been done on bringing the isothermal intersection and the zero point as close as possible so that the resultant error due to temperature effects can be reduced. This error increases as the temperature difference between the calibration buffer and the sample solution widens. The error can be as high as 0.1 of a pH unit⁽⁶⁾. It can only be eliminated when the temperature of the calibration and the sample solutions are identical under controlled conditions, for example by incubating the calibration buffers and samples in a water bath at a constant temperature. It is important to point out that this error cannot be eliminated by ATC.

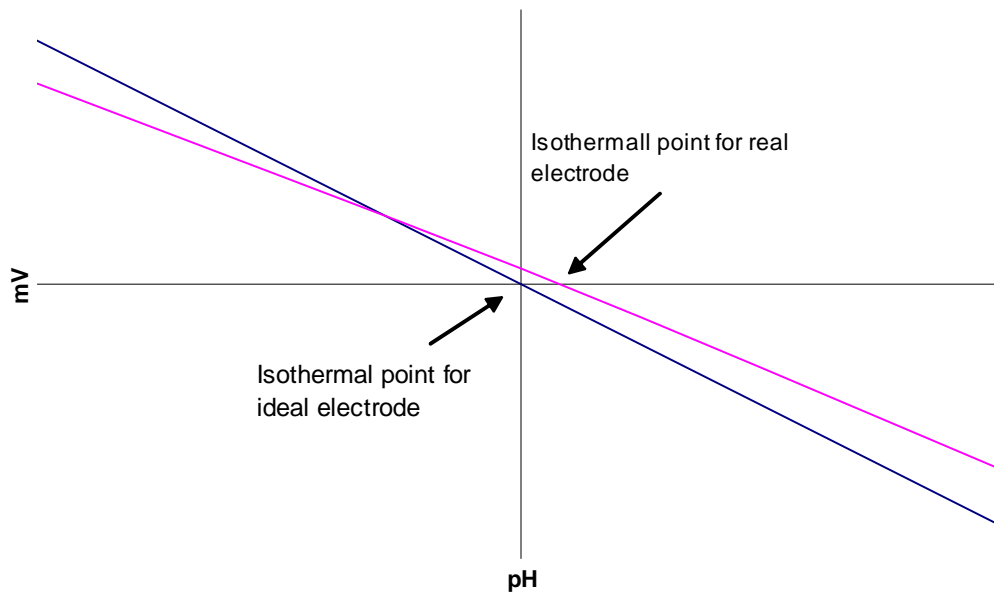


Figure 1: Isopotential points for the ideal and real electrodes at 25°C

2.3 Thermal Equilibrium

Thermal equilibrium effects will be seen when the electrode is transferred between solutions of different temperatures or the temperature of a particular measuring solution changes rapidly during measurement. The resulting slow response of the electrode can manifest itself in drift, which continues until the sample and electrode have reached thermal equilibrium.

A number of researchers have devised solutions to this problem. These solutions include electrode designs with symmetrical warming up or cooling down of the lead-off elements on both the sensing and reference electrodes. An alternative solution developed has been the manufacture of electrodes of different internal chemistry, which are independent of temperature effects⁽⁷⁾. Such dramatic temperature differences are rarely encountered in a laboratory situation and where accurate work is being performed, the remedial action is to perform the calibration and sample measurement at a uniform controlled temperature using a water bath.

2.4 Chemical Equilibrium

Reference electrodes function on the basis of a chemical equilibrium between a metal and a

solution of its ions, which generates a potential. This is affected by temperature because the solubility of the metal salt in the reference electrolyte solution varies with temperature. Changes in this equilibrium will cause the electrode to respond slowly and leads to drift. This error is minimal with modern good quality electrodes and can be overcome if necessary in the same way as thermal equilibrium by incubation of controls and samples in a temperature controlled water bath.

2.5 Membrane Resistance

The resistance of pH membrane glass increases with decreasing temperature. The resulting increase in membrane resistance leads to the electrode having a sluggish response. The degree of change in resistance varies depending on the membrane glass formulation and the membrane shape. This change in resistance may be five-fold for as little as a 15°C drop in temperature. Therefore, a membrane with a resistance of 200 megaohms (mΩ) at 25°C would increase to over 1000 mΩ at 10°C⁽⁸⁾.

The lowest possible operating temperature of a pH electrode is often determined by the resistance increase of the glass membrane at

lower temperatures. The effects of membrane resistance are as follows:

- The electrode may not be useable at all at a particular temperature.
- Even if the electrode is useable, there may be electronic noise from the power cable
- Low resistance at connectors or plugs due to corrosion or moisture may manifest themselves at greatest effect when resistance is very high.

In order to avoid the errors associated with this high resistance, it is important to only use an electrode at low temperatures which has resistance of the order of 100 – 200 mΩ at 25°C.

In practice there is a trade-off between membrane resistance and fitness for purpose. The shape of the spear membrane makes it ideal for use as a stick-in electrode for the measurement of pH in meat or cheese at 4°C and is supplied in this format combined with a low impedance glass membrane⁽⁹⁾.

3 Effects of Temperature coefficient variation on the calibration buffer or sample

The importance of temperature measurement when performing pH measurements has already been mentioned in reference to slope correction. Temperature also has an effect of both pH buffers and solutions, as the hydrogen ion activity will increase with increasing pH.

3.1 Temperature coefficient of variation of pH buffers

Although the temperature coefficient variation

of pH buffers may vary only minimally over a wide span of temperatures in the acid region, it may be quite dramatic in the alkaline region. The consequential error can be substantial in the alkaline region (see Table 2). There are three mechanisms to overcome this temperature coefficient variation:

- The correct pH at a particular temperature may be checked on “lookup” tables on the pH buffer label and the correct value manually inserted into the pH meter at calibration. This approach suffers from the drawback of requiring knowledge of the correct ambient temperature, which can vary quite substantially in a field situation.
- Most modern pH meters have an auto buffer recognition facility, whereby values of pH buffers at various temperatures are stored in memory. Meter standardisation and temperature coefficient of variation correction is therefore automatically done if the correct buffer is used. Meter manufacturers generally specify specific pH buffer types to be used for calibration - for example some pH meters can be calibrated using technical pH buffers or DIN/NIST buffers (values specified at 25°C)⁽¹¹⁾. Use of the incorrect buffer type can lead to inaccurate calibration and hence incorrect pH measurements.
- The measurement of the sample and the buffers can be done under controlled temperature conditions in a water bath, for example at 20°C or 25°C. Such an option is generally only available or feasible for very accurate laboratory work.

Temperature °C	pH 4.00 ± 0.01 @ 25°C ⁽¹⁰⁾	pH 7.00 ± 0.01 @ 25°C ⁽¹⁰⁾	pH 10.00 ± 0.01 @ 25°C ⁽¹⁰⁾
10	4.00	7.07	10.18
15	4.00	7.04	10.14
20	4.00	7.02	10.06
25	4.00	7.00	10.00
30	4.01	6.99	9.95
35	4.02	6.98	9.91
40	4.03	6.97	9.85
50	4.05	6.96	9.78
60	4.08	6.96	9.75

Table 2: Temperature effects on the value of pH buffers

3.2 Temperature coefficient of variation of the sample

Under normal operating conditions this variation may be minimal in the acid region but can be quite dramatic in the alkaline region with significant variation in the neutral area. Table 3 gives an example of pH variation of different solutions with temperature.

The effects of temperature on the pH of the sample can be accommodated as follows:

- It is absolutely imperative for all samples when a pH value is reported that the temperature at which the measurement is

done is also reported. This facilitates comparability and reduces the potential for error or misunderstanding.

- The sample may be placed in a water bath at 20°C or 25°C and measurements taken and reported only at these temperatures.
- In some instances where there is no variation in matrix and the sample is always homogenous, the temperature coefficient variation can be characterised and a “lookup” table established. However, in practice this is rarely done as such a study would be quite laborious. It is also entirely dependent on the make up chemistry of the sample always remaining the same.

pH Range	Temperature		
	0°C	25°C	60°C
Acid	pH 0.99	pH 1.00	pH 1.01
Neutral	pH 7.47	pH 7.00	pH 6.51
Basic	pH 14.94	pH 14.00	pH 13.02

Table 3: Typical changes in pH for solutions due to temperature coefficient of variation effects

4 Conclusion

Temperature has a number of significant effects on pH measurement. Analysts must have an appreciation of these effects so that they can improve and maximise the accuracy of their pH measurements. Automatic Temperature Compensation (ATC) should always be utilised during calibration to correct for the non-Nernstian slope of electrodes. For pH meters that feature automatic buffer recognition, the correct calibration buffers, as specified by the instrument manufacturer, must always be used as the meter has the temperature profile for these buffers stored in memory. Additional sources of error include the calibration isopotential point, thermal or chemical equilibrium effects on the electrode and the temperature coefficient of variation on buffers and samples. To reduce these potential errors, instrument calibration and sample measurement should be performed at the same temperature ideally using a water bath. Also, as the pH of solutions is temperature dependent, the measurement temperature should always be recorded.

Implementation of these simple guidelines will lead to either a reduction or elimination of the problems associated with temperature. This will result in improved accuracy in pH results thus giving the user greater confidence in their pH measurements. Depending on the decisions made based on the pH readings the consequences of inaccurate pH measurement can be more than just a waste of the analysts’ time.

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Biographical Notes:

John J Barron is Managing and Technical Director of Reagecon Diagnostics Limited. The company, which was founded in 1986, is the largest producer worldwide of Conductivity Standards and is also a major producer of other chemical standards. Mr. Barron is an expert in several areas of analytical chemistry, including electrochemical analysis, good laboratory practice (GLP) and chemical metrology. He has written and lectured extensively and is credited with several scientific discoveries including stable low level conductivity standards.

Colin Ashton has worked in the Reagecon group since 1994 and is currently Head of the Chemical Metrology Department. A graduate of the

particular expertise in the development, stabilisation, manufacture and validation of cation, anion and electrochemical standards. He has particular scientific interest in all aspects of on line chemical analysis and has lectured and published on several areas of this field.

Leo Geary has worked for Reagecon Diagnostics Ltd. since 1998 and is currently the Senior Chemist in the Technical Services Department. In this role, he is involved in the provision of technical support for the complete Reagecon product range to customers to enable them to achieve high quality analytical results. This includes the provision of a traceable calibration and requalification service for all electrochemistry instruments.

This paper was presented as a poster at the 57th Annual Meeting of the International Society of Electrochemistry, which was held in Edinburgh in September, 2006. It forms part of a comprehensive series of papers that the authors have written covering all of the practical requirements for accurate electrochemical measurement. These papers are available via Reagecon's website at www.reagecon.com.

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