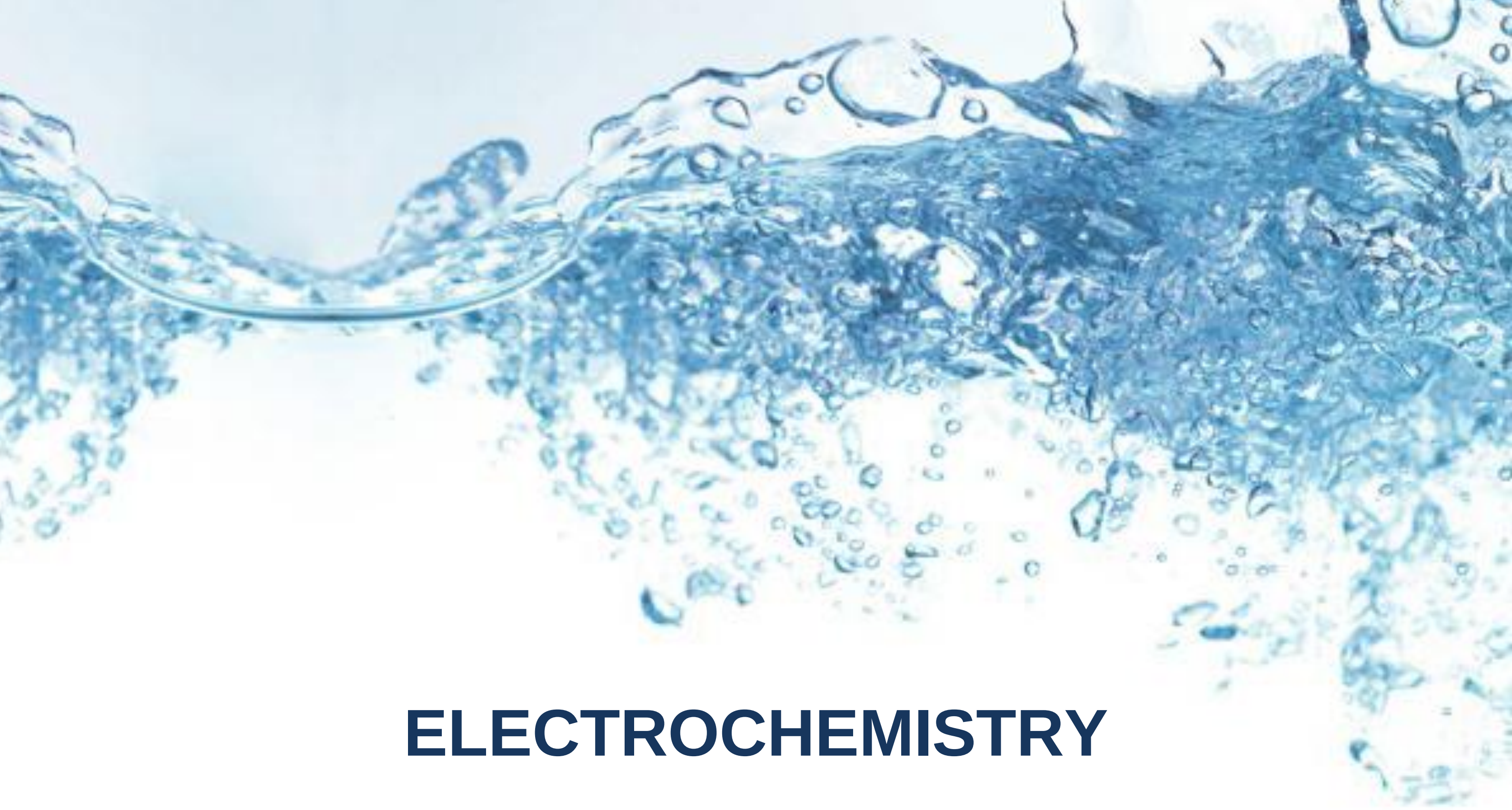


ELECTROCHEMISTRY

Theory and Practice

Dr. Axel Bier
Lab Product Application Manager - Electrochemistry
For more information, please visit: www.hach.com/smartprobes

CONTENT

Hach Company
PO Box 389
Loveland, CO 80539

1.1 INTRODUCTION

pH in an aqueous solutions is a measure of hydrogen and hydroxide ions. Water molecules dissociate in hydrogen (H^+) and hydroxide (OH^-) ions,

$$H_2O \Leftrightarrow H^+ + OH^-$$

but the number of ions formed is very small. Water at 25°C contains 1 x10-7 mol/l of hydrogen ions and the same concentration of hydroxide ions, where the concentration (mol/l) of hydrogen ions $[H^+]$ multiplied by the concentration (mol/l) of hydroxide ions $[OH^-]$ is constant:

$$K_w = [H^+]\,[OH^-] \qquad \text{<1>}$$

K_w is the dissociation constant for water and it depends on temperature.

Temperature °C	K_w
10	$0{,}2920 * 10^{-14}$
15	$0{,}4505 * 10^{-14}$
20	$0{,}6809 * 10^{-14}$
25	$1{,}008 * 10^{-14}$
30	$1{,}469 * 10^{-14}$

Acids in water increase the $[H^+]$ and, because the product $[H^+]\,[OH^-]$ must be constant, acids decrease the $[OH^-]$. Bases increase $[OH^-]$ and decrease $[H^+]$. For example, suppose an acid is added to water at 25°C and the acid raises the $[H^+]$ to 1.0×10^{-3} mol/l. Because $[H^+]\,[OH^-]$ must always equal 1.00×10^{-14}, $[OH^-]$ will be 1.0×10^{-11} mol/l.
pH is the common way of expressing the hydrogen ion concentration $[H^+]$. pH is defined as:

$$pH = -\log\,[H^+] \qquad \text{<2>}$$

In the example above, the hydrogen ion concentration is 1.0×10^{-3} mol/l and the pH is 3.00. Alternatively, if adding base changes the $[H^+]$ to 1.0×10^{-11} then the pH is 11.0.

In fact equation <2> is valid for highly diluted solutions only. If concentrated solutions of acids or bases or even salts are used, the hydrogen concentration must be replaced by the ion activity a_{H+} and the hydroxide concentration by a_{OH-}. The relation between concentration and activity of an ion is

$$a_{ion} = f_{ion} * [ion] \qquad \text{<3>}$$

where f is the activity coefficient for that ion. The reason for the difference of activity and concentration is that in higher concentrated solutions the ions interact with each other and therefore show a different behaviour than in diluted solutions. That means in higher concentrated solutions the amount of “real” active ions is lower than expected. This leads to the pH definition

$$pH = -\log a_{H+} \qquad \text{<4>}$$

1.2 HOW TO MEASURE pH

An electrochemical cell for pH measurement always consists of an indicating electrode whose potential is directly proportional to pH, a reference electrode whose potential is independent of pH, and the aqueous sample to be measured. If all three parts are in contact with each other, a potential can be measured between the indicating electrode and the reference electrode, which depends on the pH of the sample and its temperature.
Because of the complexity of a pH measurement, the combination of indicating and reference electrode must be calibrated in advance, to compensate for slight changes over time. See chapter “calibration”.

The relation between measured potential E (mV), pH and temperature (K) is the Nernst equation.

$$E(T) = E^\circ(T) + \frac{R \bullet T}{M \bullet F} \bullet \log a_{H+} \qquad \text{<5>}$$

$$E(T) = E^\circ(T) - \frac{R \bullet T}{M \bullet F} \bullet pH \qquad \text{<6>}$$

E(T) : measured potential mV at temperature T (Kelvin)
E°(T) : constant, standard potential mV at temperature T (Kelvin)
R : molar gas constant (8.3144 J mol^{-1} K^{-1})
M : factor to convert Ln to Log (2.303)
F : Faraday constant 96485 C mol^{-1}
T : temperature (Kelvin)

Therefore at a given (constant) temperature the potential of a solution depends on the pH only. Equation <6> can be seen as the standard formula for straight lines Y = a + b X, where a is the offset and b is the slope of the line. In case of equation <6> the offset is E°(T) and the slope is the temperature dependent factor $-T \bullet \frac{R}{M \bullet F}$ = -T • 0.1985

At 25°C the slope gives (273.15 + 25) • 0.1985 = -59.18 mV/pH.

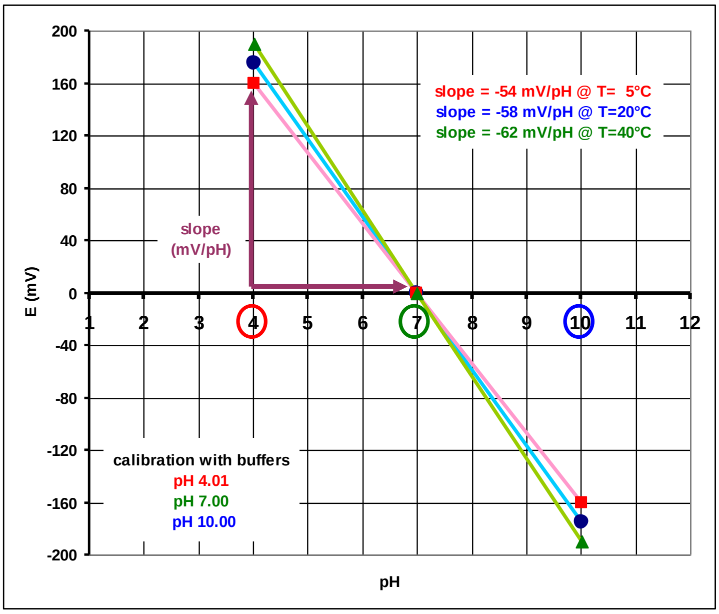


Figure (1): Influence of temperature changes on the Nernst slope of a pH calibration.

1,3 CALIBRATION

The system of pH indicating electrode, reference electrode, pH-meter and lab conditions (stirring / no stirring, thermostated / not thermostated, ambient air humidity / pressure, and so on) is calibrated by placing the electrodes in solutions of known pH (buffers) and measuring the voltage of the cell. Because the cell potential is a linear function of pH (usually in the range of pH 2-11), two calibration points (2 pH buffers) are needed. Most common is the calibration with the IUPAC buffers pH 4.005 and pH 10.012 (@ 25°C).

If the pH measurements are done in extreme areas of pH < 2 or pH > 11 we recommend to calibrate specifically in the low pH range (buffer pH 1.09 + pH 4.01) or in the high pH range (buffer pH 10.012 + pH 12.45).

The calibration parameters are offset (or zero pH) and the slope. Many pH meters calculate the slope as a percentage of the theoretical value, which at 25°C is -59.18 mV/pH. For example, if the calibration slope is determined to be -58.78 at 25^{o}C it would equal 99.3% theoretical.

The following table lists theoretical slopes for different temperatures.

Temperature °C	Slope mV/ pH
15.0	-57.2
20.0	-58.2
25.0	-59.2
30.0	-60.1
35.0	-61.1

2.1 GENERAL

In nearly every industrial and scientific application, pH is determined by measuring the potential of an electrochemical cell. Figure 2 shows a simplified diagram of a pH cell.

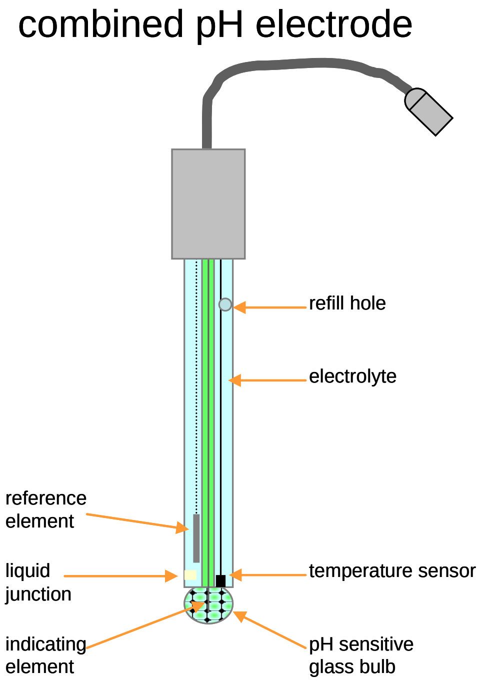


Figure (2): combined pH glass electrode

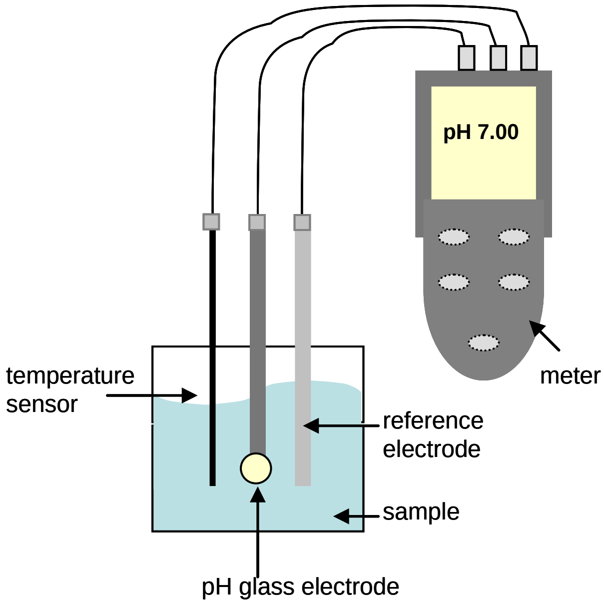


Figure (3): pH measurement system

A pH measurement system (figure (3) consists of a pH probe, reference probe, temperature sensor, pH meter and the sample to be measured. In most cases the three probes are combined in one electrode (figure (2). When the pH probe is in contact with a solution a potential forms between the pH probe and the reference probe (figure (4). The meter measures the potential and converts it, using the calibration curve parameters, into a pH value.

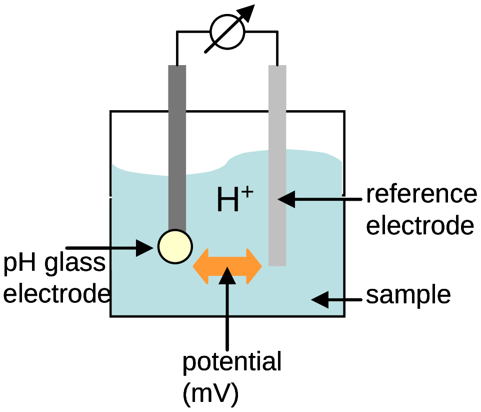


Figure (4): development of a potential (mV) between pH probe and reference probe: “pH cell”

The pH system (pH cell) has a high internal resistance, therefore the pH meter must have a very high input impedance. Never use a conventional volt meter to measure the potential of a pH electrode.

As long as the reference electrode is stable, the pH/potential measurement will vary only with temperature and sample. However, in certain samples the liquid junction plays a role. Based on the type and concentration of ions on both sides of the junction, the liquid junction can add some mV to the measurement potential.

2.2 COMBINED pH ELECTRODE

Figure (2) shows the internal components of the pH electrode. The heart of the electrode is a thin bulb of pH-sensitive glass, which is blown onto the end of a length of glass tubing. The pH-sensitive glass (glass membrane) is sealed to the electrode and contains a solution of potassium chloride at pH 7. A silver wire plated with silver chloride contacts the solution. The Ag/AgCl combination in contact with the filling solution sets an internal reference potential. This potential depends on the chloride concentration in the filling solution and as long as this electrolyte concentration is maintained, the electrode potential is constant.

Electrolyte	Concentration mol/l
KCl	saturated
KCl	3,5
KCl	3
KCl	3 saturated with AgCl
NH4Cl	3

Figure (5): most common electrolyte filling solutions for combined pH glass and reference electrodes.

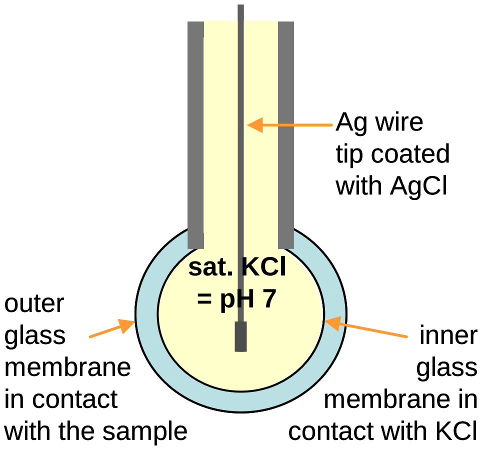


Figure (6): working principle of a pH glass membrane

As Figure 6 shows, the outside surface of the glass membrane is in contact with the sample being measured, and the inside surface contacts the filling solution. A complex mechanism at each glass-liquid interface defines the potential the pH glass electrode. While the inner pH glass / filling solution potential is constant, the outside potentials varies based on the $[H^+]$ in the sample. This equilibrium depends also on temperature.

2.3 REFERENCE ELECTRODE

As figure 7 shows, the reference electrode is a silver wire coated with silver chloride in contact with a defined electrolyte solution, see figure (5). In many reference electrodes a gel is used instead of a liquid as the internal filling. These gels also contain KCl to maintain the reference potential and add sufficient conductivity. As described in 2.2 the reference potential is constant as long as the internal electrolyte is constant. The reference potential also varies slightly with temperature.

The tube containing all the reference elements and solutions/gel is in contact with the sample to measure through a junction (diaphragm). It is essential to maintain a free flow of ions through the junction. Otherwise the reference electrode will not respond properly to pH changes in the sample.

Electrolyte filling

Saturated KCl: a saturated solution of KCl, where additional KCl crystals are added, allow the reference system to work in a wide temperature range. At higher temperatures the additional crystals can dissolve and still maintain a saturated solution. At low temperatures more crystals form, but since the solution is already saturated, the KCl concentration is still saturated. In addition if the electrode has to measure over a longer period of time in an aqueous solution, sample liquid can go through the diaphragm inside the probe and dilute the electrolyte. A saturated solution has therefore a higher “buffer capacity” against dilution.

3 molar KCl: this is the most common electrode filling and available almost everywhere.

3 molar KCl saturated with AgCl: this is a way to longer maintain the Ag/AgCl reference electrode. The additional AgCl slows down the dissolution of the Ag/AgCl element.

Gel: the viscosity of the gel filling helps the probe to work under higher pressure conditions than with liquid fillings. In addition the gel usually does not require a refilling or other maintenance from the user. However, because the gel usually cannot be refilled, the lifetime of a gel-filled probe is much shorter than those with liquid filling, approx. 12 months only.

2.4 LIQUID JUNCTION (salt bridge, diaphragm)

The salt bridge or diaphragm or liquid junction (see figure (2) and (7) is an integral part of the reference electrode. It provides the electrical connection between the reference electrode and the sample being measured. Salt bridges have a variety of forms. Some are highly porous, where the pores are filled with ions from the filling solution and from the sample. Depending on the mechanical design of the diaphragms, the movement of material from inside the reference half cell into the porous material, and from the sample into the porous material is different. For example using a gel-filled salt bridge only ions are permitted to flow across the porous material and the liquid level of the reference compartment remains constant. Other materials allow liquid to flow out of the reference compartment, requiring periodic refilling. These types of diaphragms minimize contamination of the reference half cell, since ions do not flow back from the sample.

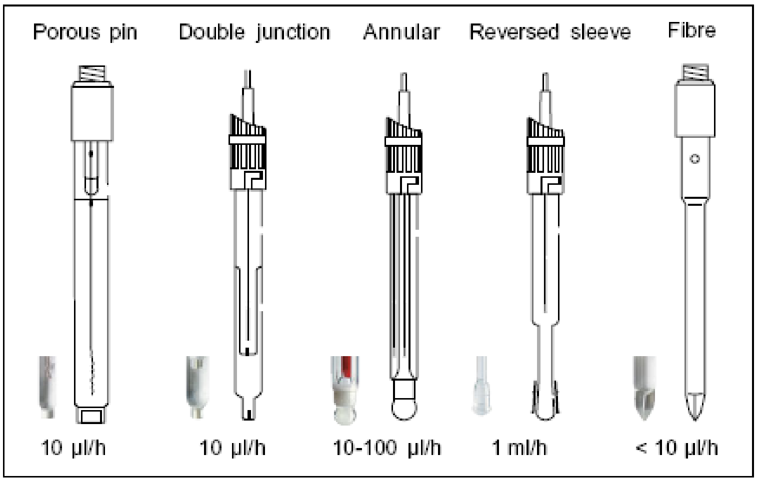


Figure (7): variety of diaphragms and there flow behaviour

The liquid junction is the most problematic part of the probe. If it clogs due to sample particles going into the porous area or because crystals of the filling solution forming inside the junction, the final reading is false or takes much too long to stabilize.

If the electrolyte level inside the reference compartment is low, then another problem can arise where sample solution enters the reference compartment. This dilutes the electrolyte with sample solution and the reference potential is no longer constant.

In certain cases there is blockage due to precipitates forming inside the junction. This can occur if Ag^+ ions come together with S^{2-} ions to form Ag_2S precipitate. In samples with S^{2-} ion, or with biological or medical samples, it is recommended to use a reference probe with double junction, where the outer electrolyte is absolutely free of Ag^+ ions.

3.0 BUFFERS AND CALIBRATION

Figure (1) shows the ideal pH measurement system, where the potential is zero when the pH is 7, and the slope is -0.1984● T over the entire pH range. A real pH system rarely has at pH 7 a potential of zero, but it is usually between -20 mV and +20 mV. The slope is also not -0.1984● T over the entire range of pH and normally changes at pH < 2 or pH > 11.

Because pH systems are not ideal, they must be calibrated before use with pH buffers. These pH buffers have a known pH at different temperatures and cover the whole pH scale. International cooperating institutes (e.g. IUPAC = International Union of Pure and Applied Chemistry, NIST = National Institute of Standards and Technology, DIN = Deutsches Institut für Normung, JSI = Japan Standards Institute) provide the definition of the buffer solutions used for references for pH measurements. All pH measurements are referred to traceable buffer solutions so that those values can be compared worldwide.

How are the calibration parameters calculated during a pH calibration?

Usually two pH buffers are selected to check the pH probe performance, pH 4.01 and pH 7.00. The ratio of the measured potentials (E2 - E1) to the difference of pH (7.000 – 4.01, gives the slope of the straight line.

$$\text{Slope S} = \frac{E_2 - E_1}{pH_2 - pH_1} \text{ [mV/pH]} \qquad <7>$$

Equation <7> is valid at the specific temperature of the buffer solutions.

Example: pH buffer pH 4.01 and pH 7.00 are used for calibration. In buffer pH 4.01 the pH system measures a potential of 170 mV and in buffer pH 7.0 it measures a potential of -3.1 mV.

$$\text{Slope S} = \frac{173-(-3.1)}{7.00-4.01} = \frac{176.1}{2.99} = 58.89 \text{ [mV/pH]}$$

3.1 pH VALUES OF BUFFER SOLUTIONS AT DIFFERENT TEMPERATURES

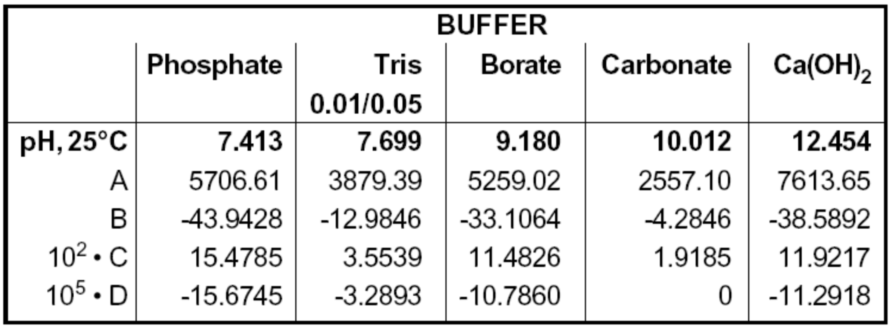
The tables below list the coefficients describing the temperature dependency for several standard buffers .The coefficients A, B, C and D refer to the formula:

$$pH = A / T + B + C \bullet T + D \bullet T^2 \qquad <8>$$

where T is the temperature in Kelvin.

	BUFFER			
	HCl 0.1 M	**Oxalate**	**Saturated Tartrate**	**Citrate 0.05 m**
pH, 25°C	**1.094**	**1.679**	**3.557**	**3.776**
A	0	-362.76	-1727.96	1280.40
B	1.0148	6.1765	23.7406	-4.1650
$10^2 \bullet C$	0.0062	-1.8710	-7.5947	1.2230
$10^5 \bullet D$	0.0678	2.5847	9.2873	0

	BUFFER			
	Phthalate	**Acetate 0.1 M**	**Phosphate**	**Phosphate**
pH, 25°C	**4.005**	**4.650**	**6.865**	**7.000**
A	0	0	3459.39	1722.78
B	6.6146	7.4245	-21.0574	-3.6787
$10^2 \bullet C$	-1.8509	-1.8746	7.3301	1.6436
$10^5 \bullet D$	3.2721	3.1665	-6.2266	0



	BUFFER				
	Phosphate	**Tris 0.01/0.05**	**Borate**	**Carbonate**	**$Ca(OH)_2$**
pH, 25°C	**7.413**	**7.699**	**9.180**	**10.012**	**12.454**
A	5706.61	3879.39	5259.02	2557.10	7613.65
B	-43.9428	-12.9846	-33.1064	-4.2846	-38.5892
$10^2 \cdot C$	15.4785	3.5539	11.4826	1.9185	11.9217
$10^5 \cdot D$	-15.6745	-3.2893	-10.7860	0	-11.2918

Figure (8): pH buffer solutions and the parameters to calculate the pH value for different temperatures.

3.2 PRECAUTIONS USING BUFFERS

Because pH buffer solutions are always the reference of our pH measurements, the pH result can only be as good as the pH buffers used for calibration. If the buffers are contaminated or used improperly, the calibration will be false and all following measurements will be wrong. Therefore proper handling, storage and use of buffers is important.

1. Always use pH buffers which bracket the pH of your sample. If the sample has a pH of 6 use buffers pH 4 and pH 7. If the sample has a pH of 7, use buffers with pH 4 and pH 10. If an alkaline sample is measured, calibrate with buffer pH 7 and pH 12.45.
2. To shorten the stabilization time and to achieve an accurate calibration, make sure the sensor and the buffer are at the same temperature.
3. For greatest accuracy measure samples at close to the same temperature as your calibration buffers.
4. Buffers have limited shelf lives. Do not use a buffer if the expiration date has passed. Store buffers at controlled room temperature and if possible always at the same place.
5. Never return used buffer to the buffer bottle. Discard it.
6. Do not let the buffer bottle open for a longer time (exposure to air). The atmospheric carbon dioxide lowers the pH of alkaline buffers.
7. If a calibration with alkaline buffer gives suspect results first try changing the alkaline buffer. Alkaline buffers are susceptible to contamination by CO_2.
8. Rinse the sensor with deionised water before placing it in the buffer. Remove excess water from the sensor by gently wiping it with a clean tissue.

3.3 TEMPERATURE CORRECTION OF COMPENSATIONS OF THE SAMPLE?

The pH of a solution is dependent of temperature (Nernst equation). Buffer solution “temperature correction” is not the same as sample “temperature compensation”. Automatic temperature compensation (ATC) is the automatic calculation of pH from the measured potential and temperature, using an adjusted slope to the measured temperature.

The change in pH of a solution with temperature is called the solution temperature coefficient (unit is ΔpH/°C). Most standard pH buffers and some chemicals have known solution temperature coefficients (see Figure 8). The temperature variation of standard pH buffers is often printed on their bottles. As long as the solution temperature coefficient is not known for the sample solution, a solution temperature correction can not be done. If necessary the temperature coefficient can be determined manually/empirically.

In order to achieve best results ATC is done in most meters (for samples with unknown temperature coefficient). In any case it is recommended to do a calibration and a sample measurement at the same temperature.

pH – Frequently asked questions

pH measurement in samples...

QUESTION: What factors need to be taken into account when measuring low ionic strength samples and deionised water?

ANSWER: As a general rule, standard pH probes contain a 3 or 3.5 molar KCl electrolyte solution or a gel. As low ionic strength samples and deionised water contain little or no salt, they try to get ions (salt) out of the electrolyte solution. When conventional pH probes are used (e.g. with gel filling), this phenomenon may lead to poor response and unstable readings.

For applications such as these, Hach offers pH probes specifically designed for low ionic strength samples. These probes have high reference electrolyte flow rates to insure a free flowing reference junction.

When KCl crystals are added, the ionic strength can be increased and the response time improved. It is important to use high purity KCl to avoid influencing the pH.

Closed sample containers (flasks) present the advantage of avoiding CO_2 contamination. Use of scrupulously clean equipment and glassware and thorough rinsing before measurement are essential to avoid contamination from previous samples.

Prior to sample measurement, the probe must be calibrated by using high-precision pH buffer solutions.

QUESTION: What is the best way to measure pH in soil?

ANSWER: It is advisable to use a specific pH probe with a strong glass tip and high electrolyte outflow. Mix a 5 g soil sample with 25 g deionised water while stirring carefully. Then let the mixture stand without stirring for 10 minutes to separate the particles from the liquid. Insert the pH probe in such a way that the glass bulb is totally covered by particles, but the diaphragm is not. Wait for a stable reading.

QUESTION: What is the best way to measure pH in high temperature samples?

ANSWER: Before measuring samples over 80°C, check whether the probe is designed to stand such high temperatures. Gel-filled pH probes can be used up to 80°C but no higher. Hach pH probes have an Ag/AgCl reference system which is ideal for higher temperatures. We recommend pH probes with saturated KCl filling solution. As KCl crystals are soluble at higher temperatures, it is a good idea to ensure excess crystals so that the solution remains saturated. If at all possible lower the temperature of the sample to the temperature of the buffers at calibration.

QUESTION: What is the best way to measure pH in high alkaline samples and samples with high salt content?

ANSWER: We recommend pH probes with saturated KCl filling solution. As KCl crystals are soluble at higher temperatures, it is a good idea to ensure excess crystals so that the solution remains saturated. Samples with high salt content and pH>12 may be subject to “sodium error”. Hach/ offers high alkalinity electrodes that minimize “sodium error”.

QUESTION: What is the best way to measure pH in emulsions or fatty solutions?

ANSWER: When measuring fats and emulsions, it is important to choose an electrode with the right diaphragm and reference electrolyte and a junction that is easy to clean. We therefore recommend open liquid junctions and sleeve junctions. After the measurement, the probe should be cleaned thoroughly, i.e. any remaining fat or oil must be removed with soap or surface-active agent.

Maintenance and storage of the pH electrode

QUESTION: How should pH probes be stored best?

ANSWER: All Hach pH probes are delivered with a plastic protection cap that can also be used for storage. Pour a few drops of saturated KCl solution into the cap to ensure that the glass membrane is kept hydrated and ready to use.

For short-term storage, the pH probe can be placed in a solution of 3.5 molar KCl or pH 4.0 or pH 7.0 pH buffer. Always rinse before use.

As a general rule, pH probes (especially reference probes) should never be stored in deionised water.

Overnight, the probe should be stored in the corresponding electrolyte solution, usually saturated KCl.

For long-term storage (2 weeks or more), the pH probe should be stored with its protection cap filled with storage solution and sealed with Parafilm™.

QUESTION: What is the best way to remove air bubbles from inside a pH probe?

ANSWER: Air bubbles can get trapped in the electrolyte solution of the reference system. This results in unreliable and unstable readings and may make it impossible to achieve a reading. In order to remove air bubbles, hold the probe firmly by the cable and swing around so that the air bubbles move to the upper end of the probe. If air bubbles are trapped inside the solid KCl crystals, heat the electrode tip in warm water (max. 60°C). This will dissolve the crystals and release the air. Afterwards, swing the probe around once more as described above and leave it to cool down. Air bubbles inside the pH glass membrane are normal and cannot be removed. They will not cause problems if they are at the upper end of the probe.

QUESTION: Can a pH probe be used straight out of the box?

ANSWER: Although Hach pH probes come with a protective cap which is wet inside, the glass membrane can dry out.

For best results, we recommend rinsing with deionised water then conditioning the probe in pH 4.0 buffer for at least 2 hours. After further rinsing, it is ready to be calibrated. The normal (quick) response time will be achieved after 24 hours hydration. If measurements are needed before this time, calibrations should be repeated often due to drifting potentials.

QUESTION: Do dirty and wet cables have an influence on the pH reading?

ANSWER: Due to the extremely small currents which pass through the pH electrode, the cable, plug and connector must be kept clean and dry if reliable measurements are to be obtained.

QUESTION: How much electrolyte should the pH probe contain?

ANSWER: The level of electrolyte solution should be 1 cm below the filling hole. This is the only way to ensure that the hydrostatic pressure applied to the diaphragm will be high enough to prevent sample passing through the diaphragm into the probe.

QUESTION: What causes a diaphragm to get blocked and how can this be remedied?

ANSWER: Liquid junctions with fibre or ceramic diaphragms can occasionally get blocked due to KCl crystallisation. Try soaking the electrode in warm tap water to dissolve the KCl crystals that cover the diaphragm. Other types of blockage can occur in the form of a precipitate, for example, silver chloride or silver sulphide. Gentle polishing with abrasive paper and soaking in saturated KCl can help.

pH measurement technique

QUESTION: What is the maximum cable length between the pH meter and pH probe?
ANSWER: All pH electrodes have a high impedance and the mV signal is amplified by the electronics in the pH meter or, with Hach digital electrodes, in the probe head. With analogue electrodes, cable lengths of 3 m can normally be used. Digital probes work with cable lengths of up to 30 m or more, because the digital signal is not impaired by the magnetic fields of motors, e.g. pumps.

QUESTION: How does the temperature influence the impedance of the pH glass membrane?
ANSWER: The lower the temperature, the higher the impedance of pH glass. For every 10°C decrease in temperature, the glass impedance will increase about 2.5 times, resulting in slow response. For example, if the pH glass impedance is 100 MOhm at 25°C it will increase to 250 MOhm at 15°C.

QUESTION: What is the lifetime of a pH probe?
ANSWER: The lifetime of a pH electrode depends on several factors including storage conditions, correct maintenance and the type of sample measured. Under normal laboratory conditions, for aqueous samples, the average lifetime is between 12 and 18 months, supposing of course that the electrode is kept clean and kept hydrated during storage.
If the probe is used with dirty samples (e.g. stirred solutions with particles), is subjected to mechanical abrasion or used at high temperature or high pressure, the lifetime may be only a few weeks. In hot alkaline solutions, pH probes can be damaged after only a few hours.
Regular maintenance helps pH probes keep working efficiently for several years.

QUESTION: What is the difference between pH probes with glass body and an epoxy body?
ANSWER: Both electrodes have a glass membrane, a diaphragm, a reference system and offer the same measuring quality. However, epoxy electrodes have a limited temperature range of maximum +80°C, while glass bodies can withstand temperatures of 100-110°C (with an Ag/AgCl reference system). If you are working in the field or in tough conditions, epoxy bodies have the advantage of being more robust and less liable to crack. Electrodes with glass bodies tend to be used in the lab, because they can be cleaned more easily and, unlike epoxy bodies, can withstand organic solvents. pH probes with epoxy bodies are usually less expensive and therefore represent a cost-effective alternative.

QUESTION: What is the point of automatic temperature compensation (ATC)?
ANSWER: Automatic temperature compensation (ATC) has to do with correcting the pH calibration slope to account for the actual temperature of the sample so the pH electrode gives an accurate reading of the pH of the sample. The pH calibration equation is linear and has a slope value at 25^{o}C. Any deviation of the actual temperature from 25^{o}C is compensated in the slope according to the Nernst equation. The pH of the internal solution of the pH bulb is called the isopotential pH. If the pH of the sample is the same as the isopotential pH there is essentially zero potential across the pH membrane. The isopotential pH of most pH electrodes is around pH 7. Temperature has little effect on sample measurement around the isopotential pH and becomes more important as the sample becomes more acidic or basic. ATC becomes important the further the sample pH is away from pH 7.

QUESTION: Is it always necessary to perform a 2-point calibration or is a 1-point calibration sufficient?
ANSWER: If the last calibration was performed on the same day, a control calibration with one buffer is sufficient. Then only the zero potential is adjusted, the old slope will remain as it was.
Otherwise, a 2-point calibration is recommended, because only then an actual probe status can be determined and taken into account for the measurements to come.

QUESTION: What is the recipe of IUPAC pH buffers?

ANSWER:

HCl (pH1.094): 0.1 M HCl,
Oxalate (pH 1.679): 0.05 mol/kg $KH_3C_4O_8$,
Phthalate (pH 4.005): 0.05 mol/kg $KHC_8H_4O_4$,
Acetate (pH 4.650): 0.1/0.1 mol/kg $C_2H_4O_2/C_2H_30_2Na$,
Phosphate (pH 6.865): 0.025/0.025 mol/kg KH_2PO_4/Na_2HPO_4,
Phosphate (pH 7.000): approx. 0.020/0.0275 mol/kg KH_2PO_4/Na_2HPO_4,
Phosphate (pH 7.413): 0.008695/0.03043 m KH_2PO_4/Na_2HPO_4,
Borate (pH 9.180): 0.01 m $Na_2B_4O_7$,
Carbonate (10.012): 0.025/0.025 mol/kg $NaHCO_3/Na_2CO_3$,
$Ca(OH)_2$ (pH 12.45): saturated (at 25°C) and filtered

pH measurement: troubleshooting

PROBLEM: The pH probe response is slow, tends to drift and results are not reproducible

SOLUTION: This may be caused by one of the following:
- the glass membrane or the diaphragm is dirty, e.g. oil, fat, paint, dirt.
- the pH probe is reaching the end of its lifetime.
- a sample of low ionic strength (< 100 µS/cm) is being measured with a conventional rather than a specially designed pH probe.

PROBLEM: The pH measurement system can no longer be calibrated by auto-buffer-recognition

SOLUTION: Check all parts of the system. First eliminate possible mechanical defects such as loose plugs, damaged cable or probe, too low a level of electrolyte etc.

Ensure that fresh pH buffers were used. Buffers are only detected automatically if the mV signal is within a certain range. Old buffers or buffers not meeting DIN/IUPAC specifications cannot be detected by the meter software (AUTOCAL). For instance, pH 6.86 and pH 7.00 buffers are too close together and cannot be distinguished. In order for auto buffer recognition to work properly, the correct type of buffers has first to be selected. Typical combinations of pH buffers are pH 4, 7, 10 or pH 4.01, 6.86, 9.18. Finally, the pH electrode must be cleaned using special cleaning and conditioning solutions which can be found in the GK Annex Electrode Maintenance Kit from Hach.

If the pH probe still does not react normally and a slope of 95% to 102% cannot be achieved during calibration, it should be replaced.

PROBLEM: The response time of the pH probe keeps increasing.

SOLUTION: If the response time is gradually becoming longer, the diaphragm may be blocked or dirty, or the surface of the pH glass membrane may have fat, oil or paint deposits. In order to clean the diaphragm, use the special RENOVO.N and RENOVO.X cleaning solutions found in the GK Annex Electrode Maintenance Kit. Fat deposits can be cleaned off glass membranes by using surfactant solutions. If the glass membrane does still not react properly, it can gently be etched.

Procedure for etching glass membranes

The glass bulb is lowered for 1 minute into a 20% ammonium fluoride solution and then for 15 seconds into a 6 molar HCl. It should then be rinsed thoroughly with deionised water and stored for 24 hours in a slightly acidic buffer such as pH 4.01.

QUESTION: What is the usual stabilisation time for a pH probe in pH buffers?

ANSWER: At room temperature (20-25°C) and with fresh pH buffer solutions, the stabilisation time should not exceed 1 minute; normally a stable reading should be achieved after 30 seconds. Otherwise the pH electrode should be cleaned and conditioned again.

QUESTION: Is it possible to use a pH probe in alcoholic solutions?

ANSWER: Yes, but short-term only. Longer exposure to high percentage alcoholic solutions leads to dehydration of the glass membrane which then has to be conditioned again.